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AN IN-SITU ELECTROLYTICALLY FORMED LITHIUM IODINE BATTERY

By

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and approved by

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ABSTRACT OF THE DISSERTATION

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By WILLIAM M YOUREY

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Today the lithium and lithium-ion batteries represent the premiere high energy density battery. Beyond improving performance, there is a desire to reduce cost of manufacture and enable battery technology to adapt conformally to a variety of operating environments. Recently Rutgers introduced a concept of electrolytically formed batteries (EFBs) as a type of self-assembled approach where the entire anode and cathode is formed in-situ on the atomic level. EFBs have the potential to offer a unique pathway to much lower cost cell manufacture (no electrodes, no lithium metal to handle), a non lithium metal containing reserve cell, and to form batteries in very demanding architectures such as those dictated by advanced 3-D battery designs. This thesis represents the first comprehensive research related to lithium EFBs, specifically one based on LiI. Specific focus on the structure and ionic and electronic transport of in-situ formed
polyiodide networks will be discussed along with the key role of stabilizing interphases.
Dedication

I would like to dedicate this thesis to my parents, Anthony and Jennifer Yourey. My deepest gratitude goes to my parents for their unflinching love and support throughout my life; this dissertation would have been simply impossible without them. I am indebted to them for their care and love. They worked industriously to support our family and spare no effort to provide the best possible environment for me to grow up and attend school. For this I am forever grateful.
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# Table of Contents

ABSTRACT OF THE DISSERTATION ................................................................. ii
Dedication ...................................................................................... iv
Acknowledgements .................................................................... v
Table of Contents .......................................................................... vi
List of Figures ................................................................................ x
List of Tables ................................................................................... xxi

1.0 Introduction .................................................................................. 1
   1.1 Common Electrochemical Terminology ........................................... 1
   1.2 General Lithium and Lithium ion Cell Overview ......................... 5
      1.2.1 Lithium Cell Anode Materials ........................................... 8
         1.2.1.1 Lithium Metal Anode .............................................. 9
         1.2.1.2 Carbon Anodes .................................................. 9
         1.2.1.3 Lithium Alloy Negative Electrodes ......................... 11
         1.2.1.4 Other Anode Materials ....................................... 14
      1.2.2 Cathodes .......................................................................... 14
         1.2.2.1 Intercalation Cathodes ......................................... 17
         1.2.2.2 Conversion Cathodes ........................................... 18
         1.2.2.3 Displacement Cathodes ....................................... 19
   1.3 Lithium / Iodine System .............................................................. 19
      1.3.1 Cathode formation and activation ..................................... 21
      1.3.2 SEI Layer in Lithium/iodine Cells ..................................... 24
   1.4 Solid Electrolyte Interphase - SEI ................................................. 30
1.4.1 Carbon effect on SEI Properties 32
1.4.2 Electrolyte Composition: 33
1.4.3 Other factors Effecting SEI Formation 36

1.5 Properties of Components in an Electrolytically Formed Battery 37

1.5.1 Lithium Iodide – Self Formed Cell Electrolyte Material 37

1.5.1.1 Conductivity of Lithium Iodide 41
1.5.1.2 Effect of Doping on Lithium Iodide Conduction 47
  1.5.1.2.1 Addition of Al₂O₃ to Lithium Iodide 47
  1.5.1.2.2 Metal Halide Doping 49

1.5.2 Polyiodides 52

1.5.2.1 Characterization 53
1.5.2.2 Raman Spectroscopy and Structure of Polyiodides 53
  1.5.2.2.1 Triiodides 53
  1.5.2.2.2 Pentaiodides 56
  1.5.2.2.3 Higher order Polyiodides – Heptaiodide and Nonaiodide 59

1.5.2.3 Factors Affecting Peak Position and Intensity 63
1.5.2.4 Conductivity of Polyiodides 67

1.6 Secondary Electrolytically Formed Lithium Iodide Battery System 70

1.6.1 Background of an Electrolytically Formed Battery 70
1.6.2 Advantages of an Electrolytically Formed Battery System 73

1.7 Organization of Thesis 75

1.8 References 77
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 Experimental</td>
<td>80</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>80</td>
</tr>
<tr>
<td>2.2 Materials</td>
<td>80</td>
</tr>
<tr>
<td>2.3 Fabrication of Materials</td>
<td>81</td>
</tr>
<tr>
<td>2.3.1 High Energy Milling</td>
<td>81</td>
</tr>
<tr>
<td>2.3.2 Current Collector Material</td>
<td>83</td>
</tr>
<tr>
<td>2.4 Cell Fabrication</td>
<td>83</td>
</tr>
<tr>
<td>2.4.1 Swagelok Cell Fabrication</td>
<td>83</td>
</tr>
<tr>
<td>2.4.2 Melt Formed Cells</td>
<td>84</td>
</tr>
<tr>
<td>2.5 Material Characterization</td>
<td>85</td>
</tr>
<tr>
<td>2.5.1 X-ray Diffraction</td>
<td>85</td>
</tr>
<tr>
<td>2.5.2 Raman and FT-IR Spectroscopy</td>
<td>87</td>
</tr>
<tr>
<td>2.5.3 AC Impedance and DC Polarization Conductivity Measurements</td>
<td>90</td>
</tr>
<tr>
<td>2.6 Electrochemical Characterization</td>
<td>95</td>
</tr>
<tr>
<td>2.7 References</td>
<td>96</td>
</tr>
<tr>
<td>3.0 Transport Properties of a Polyiodide Based Cathode for an Electrolytically Formed Battery (EFB)</td>
<td>97</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>97</td>
</tr>
<tr>
<td>3.2 Structural Characterization and Conductivities of a Pure I$_2$: PVP System</td>
<td>98</td>
</tr>
<tr>
<td>3.3 Effect of Adding Lithium Iodide</td>
<td>104</td>
</tr>
<tr>
<td>3.3.1 Electronic Conductivity</td>
<td>105</td>
</tr>
<tr>
<td>3.3.2 Ionic Conductivity</td>
<td>107</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.3.3 Structural effect of Lithium Iodide</td>
<td>108</td>
</tr>
<tr>
<td>3.4 Effect of Hydration on Structure and Conductivity</td>
<td>113</td>
</tr>
<tr>
<td>3.5 Conclusions</td>
<td>118</td>
</tr>
<tr>
<td>3.6 References</td>
<td>119</td>
</tr>
<tr>
<td>4.0 Pathways to Enabling Solid State Electrolytically Formed Batteries; The Solid Electrolyte</td>
<td>120</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>120</td>
</tr>
<tr>
<td>4.2. SEI formation</td>
<td>122</td>
</tr>
<tr>
<td>4.3 Ex-Situ formed SEI characterization</td>
<td>127</td>
</tr>
<tr>
<td>4.4 In-Situ formed SEI characterization</td>
<td>134</td>
</tr>
<tr>
<td>4.5 Enabling Anhydrous Lithium iodide nano-composite</td>
<td>139</td>
</tr>
<tr>
<td>4.5.1 Dual Functionality Current Collector</td>
<td>139</td>
</tr>
<tr>
<td>4.6 Discussion</td>
<td>150</td>
</tr>
<tr>
<td>4.7 Demonstration of EFB Versatility</td>
<td>154</td>
</tr>
<tr>
<td>4.8 Conclusion</td>
<td>159</td>
</tr>
<tr>
<td>4.9 References</td>
<td>161</td>
</tr>
<tr>
<td>5.0 Summary</td>
<td>162</td>
</tr>
<tr>
<td>6.0 Future Work</td>
<td>164</td>
</tr>
<tr>
<td>7.0 Curriculum Vita</td>
<td>166</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1: Cell polarization as a function of operating current. Illustrates different factors which contribute to voltage polarization as discharge current is increased [2]. (Handbook of batteries) .......................................................... 3

Figure 1.2: Comparison of gravimetric and volumetric for standard secondary battery chemistries [4]. ................................................................. 6

Figure 1.3: Schematic showing a lithium ion battery, illustrating the battery’s charge and discharge mechanisms along with the reactions taking place at the positive and negative electrodes [6]. ........................................... 8

Figure 1.4: Illustration of graphene layered structure as negative electrode with lithium intercalation occurring between graphene sheets. Lithium intercalation occurs to a maximum of Li:C ratio of 1:6. .............................. 11

Figure 1.5: alloying potentials as a function of lithium content for different possible anode materials. Also included in figure is voltage profile for lithium intercalation into carbon [8]. ...................................................... 12

Figure 1.6: Schematic showing the difference between intercalation, conversion, and displacement cathode materials [12]. .................................................. 17

Figure 1.7: Layered structure of the intercalation cathode material Li$_x$CoO$_2$, along with the associated voltage profile [5]. ................................................. 18

Figure 1.8: Poly-2-vinylpyridine ........................................................................................................ 21

Figure 1.9: The Iodine/P2VP reaction product from thermal activation method. 23
Figure 1.10: Conductivity of iodine:P2VP composites as the I$_2$:P2VP ratio is increased. Sharp decrease present at 8:1 ratio is from phase diagram moving to one phase region. ................................................................. 24

Figure 1.11: Schematic showing increase of SEI thickness as discharge occurs. Reaction location occurs at SEI/Cathode interface................................. 26

Figure 1.12: Showing effect of discharge rate on polarization voltage. Each cell is capacity limited by the cathode. Increase in current causes large degree of polarization related to lithium ion conductivity through the SEI layer. ..... 27

Figure 1.13: Li-I$_2$ cell discharge voltage profiles for cell formed using coated and uncoated anode materials. ................................................................. 28

Figure 1.14: Sketch of a lithiated graphite electrode showing slid electrolyte interphase formation.......................................................... 33

Figure 1.15: Crystal structure of anhydrous lithium iodide [34].......................... 38

Figure 1.16: Crystal structure of lithium iodide tri-hydrate showing hexagonal structure [30]................................................................................. 39

Figure 1.17: Lithium iodide phase diagram as a function of hydration [33]........... 40

Figure 1.18: Lithium iodide conductivity as a function of hydration. Maximum in conductivity occurs at lithium iodide monohydrate as suggested by crystal structure [36]................................................................................. 42

Figure 1.19: Conductivity as a function of pressure for lithium iodide monohydrate. As the pressure is increased the density increases to near the theoretical value [37]. ................................................................. 43
Figure 1.20: polarization curve for Li/LiI/AgI cell showing ohmic resistance of LiI material [38]...........................................................................................................45

Figure 1.21: Discharge profile for three Li/LiI/PbI$_2$-PbS-Pb cells. A) Fresh Cell, B) Cell stored at 45°C for one year, and C) Cell stored at 60°C for one year. ..................................................................................................................................................46

Figure 1.22: Conductivity of LiI-Al$_2$O$_3$ composites as a function of Al$_2$O$_3$ content. Shows maximum in conductivity occurring between 40-50% Al$_2$O$_3$ [40].....48

Figure 1.23: Conductivity of lithium halide composite as a function of CaI$_2$ concentration A) Initial material conductivity B) Conductivity after storage for 500 hours. ..................................................................................................................................................50

Figure 1.24: Lattice parameter for lithium iodide – calcium iodide composite as a function of CaI$_2$ concentration showing increase in lattice parameter as calcium iodide is added [42]. ..................................................................................................................................................51

Figure 1.25: Demonstration of construction of higher order polyiodide species using iodide ion, iodine molecules, and triiodide species as the building components. ..................................................................................................................................................53

Figure 1.26: Linear triiodide molecule..................................................................................................................................................54

Figure 1.27: Schematic showing infinite linear and T-shaped chain structures for a triiodide system [43]..................................................................................................................................................55

Figure 1.28: Raman spectra of triiodide species which initially contains a symmetric structure but as the potential is increase the materials transforms to an asymmetric system [46]..................................................................................................................................................56
Figure 1.29: Common contact geometries for pentaiodide. A) zigzag shaped chain B) alternating twined and zigzag shaped chain C) meander shaped chain D) displaced chain E) cis-shaped chain F) trans-shaped chain G) twinned chain H and I) square nets [43].................................59

Figure 1.30: Typical heptaiodide structure consisting of two iodine molecules and one triiodide [43].................................................................60

Figure 1.31: One possible nonaiodide structural configuration [43].....................60

Figure 1.32: a. 16:3 PPO:I₂, b. 8:3 PPO:I₂, and c. 4:3 PPO:I₂. Decreasing ratio of polymer to iodine causes more higher order polyiodides to form. At the high 16:3 ratio nearly all polyiodides found in the sample are triiodides [48]. ...........................................................................................................................................63

Figure 1.33: Raman spectra of I₉⁻ species showing breakdown of higher order polyiodide species as a function of exposure time to Raman laser. A) Immediate spectra B) Spectra after 40 minutes of exposure time to laser C) Spectra after exposure time of 60 minutes to laser [47]..................65

Figure 1.34: Raman absorbance spectra for I₇⁻ unit showing the effect of excitation laser wavelength on sample peak position and intensity [47]......66

Figure 1.35: Two schematics showing Grotthus mechanism for ionic conduction in polyiodide species [50,51]. ........................................................................68

Figure 1.36: Formation of an electrochemically self-assembled lithium-iodine battery. The initial LiI-based material electrochemically dissociates into a polyiodide positive electrode, a lithium negative electrode, and a LiI-based residual electrolyte..........................................................73
Figure 1.37: Interdigitated current collector configuration illustrating complicated configurations which self-formed batteries can be fabricated in. 200nm of Ti deposited using vapor deposition through mask depositing material on glass slide. Finger spacing ~250μm.

Figure 2.1: Planetary High Energy Ball Mill. Showing rotation of sample holding vials rotates in opposite direction of large sun disc [2].

Figure 2.2: Expanded view of Swagelok™ cell used in fabrication of experimental cells.

Figure 2.3: Demonstrating theory of X-ray diffraction, where at different angles get either constructive or destructive interference [4].

Figure 2.4: Showing difference infrared and Raman absorbance spectroscopy techniques. IR energy differences directly relates to the energy difference between a ground vibrational energy state and an excited vibrational energy state of bond within the molecule structure. Raman absorbance occurs excited the material to a virtual energy state, which then relaxes giving off light with an energy difference corresponding to the vibrational energies of a bond in the sample [5].

Figure 2.5: Representative Nyquist plot [6].

Figure 2.6: DC polarization of a sample for separation of ionic and electronic conductivity.

Figure 2.7: Conductivity of sample at different bias voltages, measured using AC impedance spectroscopy (20-640mV).

Figure 2.8: Change in resistance as a function of thickness.
Figure 3.1: Raman spectra of samples containing different molar ratios of iodine to PVP.  140-220 cm$^{-1}$ ................................................................. 99

Figure 3.2: FTIR of pure Poly (vinyl-pyrrolidone). 10,000MW.  500 scans in the range of 4000-600 cm$^{-1}$ ........................................................................................................ 101

Figure 3.3: FTIR spectra of samples containing different mole ratios of I$_2$:PVP, 500 scans per sample.  Spectra show peaks in the region of 1800-1500 cm$^{-1}$. .................................................................................................................. 102

Figure 3.4: Conductivity of I$_2$:PVP samples, as a function of the I$_2$ concentration ......................................................................................................................... 103

Figure 3.5: Blue shift in the C-N bands as a result of coordination with LiI. Ratios shown are LiI-I$_2$:PVP ................................................................. 105

Figure 3.6: The ionic (3.6-A) and electronic (3.6-B) conductivities of samples containing a fixed ratio of LiI to I$_2$, varying the I$_2$ to PVP ratio.............. 107

Figure 3.7: Raman Spectra from 60 to 220 cm$^{-1}$ with a fixed LiI-I$_2$ ratio. Changing the ratio of I$_2$:PVP........................................................................................................................................... 109

Figure 3.8: Raman spectra of samples containing samples of fixed I$_2$:PVP ratio altering the LiI content.  Three is little to no shift in spectra as change Li Mole %. ........................................................................................................................................... 110

Figure 3.9: 3-Dimensional plot of electronic conductivity of samples containing different mole percents of LiI (anhydrous), I$_2$ and PVP. Markers represent samples tested.  (Applies to all 3-Dimensional plots) .................................................................................. 112

Figure 3.10: 3-Dimensional plot of the ionic conductivity of samples containing different mole percents of LiI (anhydrous), I$_2$ and PVP................................. 113
Figure 3.11: 3-D plot of electronic conductivity for samples containing LiI-monohydrate. ................................................................. 115

Figure 3.12: 3-D plot of the ionic conductivity of cells containing LiI-monohydrate. ................................................................. 116

Figure 3.13: Comparison of sample conductivities for samples containing the same ratios of LiI:I₂:PVP changing hydration.................................. 117

Figure 4.1: A: Schematic of an uncharged cell. B: representation of ideal anode and cathode development. C and D: Two possible situations where soft shorts form in an electrochemically self-formed cell beginning with an anhydrous LiI starting nanocomposite. ........................................ 121

Figure 4.2-A and 4.2-B: Difference in current evolution profiles for two hydrated (B) and two anhydrous (A) samples during charge at 4V. Anhydrous samples short after short charge period, while hydrated samples show no shorts forming in over 150 hours of charging. ........................................ 125

Figure 4.3: A: AC impedance spectra of a hydrated LiI:PVP nano-composite. R1 corresponds to material resistance using two stainless steel current collectors while R2 shows resistance of cells using one stainless steel and one lithium metal current collector. B: AC impedance spectra of an EFB showing similarities between our ex-situ SEI impedance and impedance from a formed cell. R3 represents the cathode impedance. ..................... 127

Figure 4.4: FTIR spectra showing a comparison of absorbance spectra for; LiI (3H₂O), two ex-situ formed SEI layers and a LiOH standard. .............. 129
Figure 4.5: XRD of lithium metal surface showing formation of both LiOH and LiH as components of the ex-situ formed SEI layer.......................... 130

Figure 4.6: FTIR spectra comparing the ex-situ formed SEI layer with that of a mortar and pestle mixed samples. All samples were 1:1 molar ratio of LiI(xH$_2$O):LiOH, where $x = 0, 1, 3$. Also shown in spectra is hydrated lithium iodide standard.......................................................... 131

Figure 4.7: XRD spectra of the mortar and pestle mixed 1:1 molar ratio of LiI(H$_2$O):LiOH, showing no new crystal phases formed. ..................... 132

Figure 4.8: FTIR spectra of ex-situ formed SEI compared with LiI(H$_2$O) and LiOH mixed at different ratios. .......................................................... 133

Figure 4.9: Voltage profile and applied current for hydrated LiI starting composite showing cell formation and cyclability............................ 135

Figure 4.10: Discharge efficiency for EFBs for cells charged to different percentages of the total available capacity................................. 136

Figure 4.11: Comparison of an Ex-situ and In-situ formed SEI layer vs. material a short distance from the in-situ formed SEI............................................. 137

Figure 4.12: Schematic showing possible SEI composition as a function of distance from the anode .......................................................... 138

Figure 4.13: Schematic of cell passivation for configuration of the ESAB: (A): Using an anhydrous LiI starting composite; lithium and polyiodide dendrite growth occurs resulting in soft shorts. (B): LiI xH$_2$O composites allow for a stable oxide based SEI to form resulting in cell functionality. (C): Using an anhydrous LiI composite with an alloying negative current collector
eliminates lithium dendrites, but shorts still occur through polyiodide dendrite growth. (D): Using a dual function current collector with anhydrous Lil eliminates lithium dendrites through alloying and also reacts with polyiodide dendrites forming an insulating metal iodide product eliminating shorts through electrolytic decomposition of the SEI. .............................. 142

Figure 4.14: Cells polarized at 3.5V vs. Li/Li+ using a Lil -I₂-PVP composite (6-1.5-1) placed against different metal positive current collectors. Presents blocking ability of reactive In, Al, Sn, Pb and Ga current collectors to electrolytic decomposition of their in-situ formed iodides opposed to essentially non-blocking Ti and stainless steel. ............................................. 144

Figure 4.15: Increase in cell impedance from growth of insulating indium iodide layer at indium surface when placed in contact with 1.5:6:1 I₂:Lil:PVP composite. Data is shown relative to lack of growth on SS current collector. (Time interval from zero to ten hours)..................................................... 145

Figure 4.16: XRD of indium metal surface previously placed against anhydrous Lil-I₂-PVP composite, showing formation of insulating indium iodine complex. ................................................................. 146

Figure 4.17: EFB using anhydrous lithium iodide-PVP nanocomposite. with first a stainless steel negative current collector(see formation of soft shorts), and second an indium negative current collector. Demonstrates the enabling ability of a dual functionality current collector. Using indium allows for cell formation and eliminated the formation of soft shorts. .............................. 149
Figure 4.18: XRD of indium negative current collector after cycling has occurred. Shows formation of Li-In alloy and InI consistent with ex-situ studies. ..... 150

Figure 4.19: Schematics showing formation of electronically insulating layers between anode and cathode. A: Initial contact between cathode and alloyed Li$_x$In anode. B: results in formation of both InI and Lil. C: InI layer not stable against lithium metal in anode, reduces InI to In and forms Lil product. D: Newly formed indium metal reacts with cathode forming more InI material, eventually isolating the InI from contact with the negative electrode and further insulating anode from cathode................................. 152

Figure 4.20: Percentage of accumulated discharge capacity compared to total theoretical capacity available in entire starting composite vs. cycle number. ........................................................................................................ 153

Figure 4.21: Interdigitated electrode design showing versatility of EFB chemistry. Cell fabrication using this complicated design demonstrates ability of chemistry to form electrochemical cell in any number of electrode configurations ................................................................. 154

Figure 4.22: Small section of an interdigitated cell design showing both an uncharged IDE EFB with thin film Ti current collectors (A) and a partially formed EFB (B). The latter shows the formation of polyiodide as dark regions from the positive current collector and lithium as bright regions on the negative current collector. ................................................................. 157

Figure 4.23: Voltage profile for lithium iodide EFB using interdigitated electrode configuration. Demonstrates ability of cell to form and function in
complicated electrode geometry. Cell discharged at 50nA and charged
potentiostatically at 4.0V................................................................. 157

Figure 4.24: Bipolar series IDE cell design utilized in high voltage EFB (A), with
associated voltage profile (B). Cell charged potentiostatically at 20.0V and
discharged at -50nA to a cutoff of 9V. ................................................. 159
List of Tables

Table 1.1: Showing the various combinations of anode, electrolyte, and cathode that can be combined to make lithium metal and lithium ion cells [5]. ............ 7

Table 1.2: Comparison of theoretical charge and charge density capacities for lithium metal and lithiated carbon negative electrode materials [8].................. 10

Table 1.3: Illustrating one negative effect of lithium alloyed anodes, showing large volume expansion and contraction that occurs during lithiation. Volumetric and gravimetric densities are given for initial unlithiated material [3] .......................................................................................................................... 13

Table 1.4: Possible organic and inorganic SEI components that can form in lithium and lithium ion cells [29].......................................................... 36

Table 3.1: Demonstrating effect alkali halide salt plays in polyiodide formation and therefore conductivity. Small change in ionic conductivity noticed a change in salt suggests polyiodide species are major ion conductors in composite................................................................. 108

Table 4.1: Possible SEI components that can form in a hydrated EFB with corresponding redox potential. ................................................................. 123
1.0 Introduction

Starting in the early 1940’s, the principal use of batteries was in flash lamps, a few toys, radios, and in vehicles (for starting, lighting, and ignition). Since this time the use of small consumer batteries has expanded exponentially. From household uses such as smoke detectors, to personal hygiene uses like toothbrushes, the average household will have between 40 and 60 consumer batteries around at any given time [1]. Although most of these consumer batteries are of the primary (single use) type, there is an increasing demand for secondary, rechargeable batteries. This need has resulted in increased time and money spent on battery research, and more specifically on state of the art lithium and lithium ion battery research and development.

The next sections of this manuscript will review the common battery terms, principles of battery and electrochemical cell functionality along with details regarding some of newer, state of the art lithium and lithium ion battery materials. Following these sections a more in depth review will be performed discussing factors which are more directly related to our electrolytically formed battery chemistry and the experimental results.

1.1 Common Electrochemical Terminology

**Cell:** A cell is the basic electrochemical unit providing a source of electric energy by direct conversion of chemical energy. This is done by electrochemical
oxidation and reduction reactions. A cell typically consists of an assembly of electrodes, separators, electrolyte, container, and terminals [2].

**Battery:** Consists of one or more electrochemical cells electrically connected in an appropriate series and/or parallel arrangement to provide the required operating voltage and current levels [2].

**Open Circuit Voltage (V_{OC}):** One of the more important intrinsic cell parameters. Given by the difference in chemical potential between the anode and cathode [3]:

\[ V_{OC} = \frac{\mu(c) - \mu(a)}{F} \]  \hspace{1cm} (1.1)

Where \( \mu(c) \) and \( \mu(a) \) are the chemical potential of the cathode and anode respectively and \( F \) is Faraday's constant which is 96485 coulombs /mol. The open circuit potential of a cell is the maximum voltage a cell can be operated at. However, during discharge, various parameters will affect the operating voltage of the cell. Figure 1.1 shows the effect operating current has on a cell operating voltage and the various factors causing increased polarization as the discharge current is increased.
Figure 1.1: Cell polarization as a function of operating current. Illustrates different factors which contribute to voltage polarization as discharge current is increased [2].

**Anode:** The negative or reducing electrode, which gives up electrons to the external circuit and is oxidized during the electrochemical reaction on discharge.

**Cathode:** The positive or oxidizing electrode which accepts electrons from the external circuit and is reduced during the electrochemical reaction on discharge.

**Electrolyte:** The ionic conductor which provides a medium for transfer of charge as ions between the cell anode and cathode. Electrolytes can come as solids, gels, or liquids, but ideally have an electronic transference number equal to zero.
Separator: A porous material permeable to liquid electrolytes, which mechanically and electronically isolates the anode and cathode of the cell eliminating the possibility of shorts forming.

Primary Batteries: Contains cell which cannot easily or effectively be recharged electrically, therefore are one time use cells which are discarded after discharge. These cells are typically inexpensive and lightweight. The general advantages of primary cells are good shelf life, high energy density at low to moderate discharge rates, little to no maintenance, and extremely easy to use [2].

Secondary Batteries: Cells which can be recharged back to their original starting chemistry by passing a current through them in the opposite direction at which discharge occurs. In addition to being able to be recharged, secondary batteries are characterized by high energy density, flat discharge curves, and low temperature performance. Secondary batteries are in general more expensive then primary batteries, but can be used multiple times [2].

Capacity Density: A critical property when measuring the total available charge in a cell or battery. Expressed as either specific/gravimetric capacity, or volumetric capacity, with the more common units for each being Ah/g and Ah/cc
respectively. The theoretical gravimetric capacity of an electrode can be estimated by the following equation.

\[ C = \frac{n \times F}{M} \]  

(1.2)

Where \( C \) is the gravimetric capacity, \( n \) is the number of electrons transferred, \( F \) is Faraday’s constant and \( M \) is the molecular weight of the reactant. The theoretical gravimetric capacity can be converted to volumetric capacity by multiplying the gravimetric capacity by the density of the reactant.

**Energy Density:** A measurement of the total available energy in a cell or battery. Typically expressed as gravimetric or volumetric energy density, with the common units being Wh/g and Wh/cc respectively. The theoretical energy density can be calculated by multiplying the capacity density by the open circuit voltage of the cell.

**1.2 General Lithium and Lithium ion Cell Overview**

Lithium metal and lithium ion batteries are of specific interest to the continued development of batteries with higher volumetric and gravimetric energy densities, because they offer an increase in each category. Figure 1.2 illustrates this by comparing the energy densities of secondary lithium metal and lithium ion batteries to the industry standard commercial cells.
Lithium metal is listed as an unsafe battery material for secondary batteries due to its formation of lithium dendrites at the anode electrolyte interface. After numerous cycles of re-depositing lithium metal on the anode, the dendrites grow to a length where they contact the cathode and cause a short in the cell, resulting in safety issues and a faulty cell [3]. For these initial lithium metal anode cells, many different cathode chemistries were implemented, which can also be used as cathodes in lithium ion cells. Due to the problems of using lithium metal, new anode and negative current collector materials were developed for lithium ion cells. Table 1.1 lists the standard lithium metal and
lithium ion battery anode, electrolyte and cathode chemistries. To obtain a cell with high energy density the cell needs both high operating voltage and high capacity. To achieve high operating voltage a cathode is needed with high voltage and an anode with low voltage with the overall cell potential being the difference of the two. For high energy density, a cathode and anode are needed, each of which possess high capacity.

Table 1.1: Showing the various combinations of anode, electrolyte, and cathode that can be combined to make lithium metal and lithium ion cells [5].

Where lithium alloys, lithiated carbons, and other lithiated materials are used as the negative electrode, the battery term to describe these cells is a “rocking chair” or “shuttle” lithium ion cells, where the lithium ions are transported between the anode and cathode repeatedly from charge to discharge of the cells. In such
cells no lithium metal is formed. The following diagram (fig 1.3) is an example of a lithium ion battery, illustrating the battery’s charge and discharge mechanisms along with the reactions taking place at the positive and negative electrodes. In this example a graphite negative electrode is used in conjunction with a LiCoO$_2$ cathode.

![Diagram of lithium ion battery]

*Figure 1.3: Schematic showing a lithium ion battery, illustrating the battery’s charge and discharge mechanisms along with the reactions taking place at the positive and negative electrodes [6].*

An in depth review will now be performed on the more popular anode and cathode materials used in today’s lithium batteries.

**1.2.1 Lithium Cell Anode Materials**
Some of the newer anode materials which were developed to alleviate the dendrite growth problem with lithium metal anodes are listed in table 1.1, with the most popular anode electrode material to date in lithium ion cells being carbon, specifically highly engineered graphite.

1.2.1.1 Lithium Metal Anode

Lithium metal has the lightest weight, highest voltage, and greatest energy density of all metals [5]. The original published interest in lithium metal batteries began in 1958 with work done by Harris [7] and since has grown into an extremely large area of battery research and development. Lithium metal has a molecular mass of 6.941g/mol and a density of 0.53g/cm$^3$. These material properties result in lithium having an energy density of 3.861Ah/g or 2.046 Ah/cm$^3$. Lithium metal is highly reactive and flammable and must be kept in an inert atmosphere such as a glove box or under mineral oil. Exposure to air or moisture results in almost immediate oxidation of the lithium surface.

1.2.1.2 Carbon Anodes

Carbon is popularly used as the negative electrode material in lithium ion batteries for two reasons,

1. Exhibits higher specific charges and a more negative redox potential than most metal oxides, chalcogenides, and polymers.
2. Improved cycling performance due to their dimensional stability relative to Li alloys.

A negative effect of using a carbon anode is a much lower theoretical capacity when compared to lithium metal and alloys, as can be seen in table 1.2. Another drawback of using a carbon anode is the side reaction with certain electrolytes such as propylene carbonate or PC [3].

<table>
<thead>
<tr>
<th>Negative Electrode Material</th>
<th>Theoretical specific charge Ah/kg</th>
<th>Theoretical charge density Ah/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Metal</td>
<td>3862</td>
<td>2047</td>
</tr>
<tr>
<td>LiC₆ (Graphite)</td>
<td>372</td>
<td>833</td>
</tr>
</tbody>
</table>

*Table 1.2: Comparison of theoretical charge and charge density capacities for lithium metal and lithiated carbon negative electrode materials [8].*

Carbon anode materials typically come in two forms, soft carbon (graphitic and coke carbon) and hard carbon (glassy carbon). Hard carbons are typically obtained through thermal decomposition of organics and typically have a significant amount of open micropores. Hard carbons on average show higher capacity but suffer from higher irreversible loss due to solid electrolyte interphase formation on the first charge and a higher potential vs. Li/Li⁺ than graphite. Hard carbons show a sloping discharge profile between 0-1V vs. Li/Li⁺, while graphite has a nearly linear flat discharge profile between 0-0.3V vs. Li/Li⁺ [3]. Carbon
based negative electrodes intercalate lithium between the graphene sheets (Fig. 1.4) causing little expansion allowing stability over many cycles.

Figure 1.4: Illustration of graphene layered structure as negative electrode with lithium intercalation occurring between graphene sheets. Lithium intercalation occurs to a maximum of Li:C ratio of 1:6.

1.2.1.3 Lithium Alloy Negative Electrodes

Lithium alloy anodes are promising anode materials for future secondary lithium ion batteries due to their ability to inhibit dendrite growth, their higher energy capacity, and improved safety characteristics. However, the commercial use of alloy anodes has been hindered due to their low cycle life and high initial capacity loss [9]. The alloying voltages are higher vs. Li/Li\(^+\) compared to carbons based anodes, but still less then, the now popular Li\(_4\)Ti\(_5\)O\(_{12}\) anode material. Figure 1.5 shows the alloying potential for a selection of lithium alloy materials which can be used as anode materials as a function of lithium content. Also
included in this figure is the lithium concentration vs. potential plot for a carbon electrode for comparison purposes.

![Graph showing alloying potentials as a function of lithium content for different possible anode materials. Also included is the voltage profile for lithium intercalation into carbon.](image)

**Figure 1.5:** alloying potentials as a function of lithium content for different possible anode materials. Also included in figure is voltage profile for lithium intercalation into carbon [8].

Although LiₓMᵧ anode materials can accommodate a large concentration of lithium ions, the negative effect is the large volume expansion and contraction that accompanies the lithiation and de-lithiation of the alloying metal [6]. This large expansion and contraction leads to quick electrode deterioration, limiting the lifetime in early research to only a few charge/discharge cycles. Currently the cycle life of such alloys can exceed 500 cycles with appropriate electrode
chemistry, nanostructure and engineering. Table 1.3 illustrates the volume expansion that occurs for different alloy anodes compared to a carbon electrode.

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>Sn</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithiated Phase</td>
<td>LiC₆</td>
<td>Li₉Al₄</td>
<td>Li₂₁Si₅</td>
<td>Li₁₇Sn₄</td>
<td>Li₃Bi</td>
</tr>
<tr>
<td>Theoretical specific Capacity (Ah/kg)</td>
<td>372</td>
<td>2235</td>
<td>4010</td>
<td>959</td>
<td>385</td>
</tr>
<tr>
<td>Theoretical volumetric capacity (Ah/L)</td>
<td>833</td>
<td>6035</td>
<td>9340</td>
<td>7000</td>
<td>3773</td>
</tr>
<tr>
<td>Volume Change %</td>
<td>12</td>
<td>238</td>
<td>297</td>
<td>257</td>
<td>115</td>
</tr>
</tbody>
</table>

Table 1.3: Illustrating one negative effect of lithium alloyed anodes, showing large volume expansion and contraction that occurs during lithiation. Volumetric and gravimetric densities are given for initial unlithiated material [3].

Another major negative aspect of a LiₓMᵧ alloy anode is the irreversible capacity loss which occurs during the first lithiation. This irreversible loss is attributed to the irreversible absorption of lithium into the alloying metal structure and the formation of increased surface area which results in a subsequent increase of SEI material. In many cases the supply of lithium is from that cathode and therefore requires an extra amount of the positive electrode material to be present in the cell [10].
1.2.1.4 Other Anode Materials

Another classification of anode materials are metal oxides. Metal oxides can be divided into two classes, insertion and displacement materials. These materials are characterized as having a high potential (1.4-1.8V) vs. Li/Li⁺, low lithium capacities and often high reversibility. The mechanisms for the intercalation and displacement anodes are similar to the mechanism in cathode intercalation and conversion materials, therefore, will be covered in the next section (cathodes). Along with the metal oxides, other anode chemistries are available such as nitrides which will not be discussed in detail. Although many of these alternative anodes demonstrate excellent capacities, their relatively high voltage vs. Li/Li⁺ leads to an overall reduction in the cell voltage and energy density.

1.2.2 Cathodes

The key requirements for a material to be successfully used as a cathode material are:

1. The material should be a readily reducible/oxidizable ion, such as most transition metals.
2. The material should react with lithium in a reversible manner.
3. The material should react with lithium at a high energy, producing both high voltage and high capacity which leads to high energy storage.
4. The material should have relatively fast reaction kinetics which results in high power density.

5. The material should be electronically conductive.

6. The material should be thermodynamically stable to eliminate phase changes over time.

7. The material should also be low cost and environmentally friendly.

8. The material should be stable in contact with the electrolyte solution [11].

As mentioned in the anode section, there are different classes of cathode materials, intercalation cathodes, conversion cathodes, and displacement cathodes. Figure 1.6 schematically shows the difference between each type of cathode material.
1.2.2.1 Intercalation Cathodes

Intercalation cathode materials are characterized as having a close packed or almost close packed layered structure in which there are alternate layers between the anion sheets. These layers between the anion sheets are occupied by a redox active transition metal which also allows lithium insertion into the layers, while simultaneously reducing the oxidation state of the transition metal within the cathode structure, during cell discharge. The more popular cathode materials in this category are lithium metal oxides such as LiCoO$_2$, LiNi$_{1-y}$Co$_y$O$_2$, LiNi$_y$Mn$_y$Co$_{1-2y}$O$_2$, along with LiTiS$_2$. Figure 1.7 shows the layered structure of an intercalation compound with the associated voltage profile for lithium intercalation.
Figure 1.7: Layered structure of the intercalation cathode material $Li_xCoO_2$, along with the associated voltage profile [5].

Materials in this group can also have a 3-D insertion pathway spinel type structure where a transition metal is located within every layer of the compound structure. Also, other intercalation phases such as chevrel and rutile do exist, but the overall general characteristic these materials have in common is they all contain vacancies which can accommodate lithium ions without significant structural rearrangement of the host structure. Intercalation compounds typically have a lower energy density than conversion cathode materials but have higher reversibility.

1.2.2.2 Conversion Cathodes
Conversion materials, unlike insertion material do not retain the crystal structure upon the addition of lithium. The more popular metal fluoride conversion materials, \( \text{M}_y\text{F}_x \) (\( \text{M} = \text{Co, Cu, Bi, Fe,} \ldots \)) enables full utilization of all the oxidation state of the transition metal present in the materials. This gives the advantage of a much higher energy density when compared to insertion materials by having more than one electron transfer per transition metal. In the case of the metal fluorides, the resulting discharge product is lithium fluoride and the metal.

1.2.2.3 Displacement Cathodes

Similar to conversion materials, displacement materials do not have to possess a layered type structure. Although with displacement materials, full utilization of all the oxidation states of the active transition metal are utilized, without change in crystal structure during charge/discharge. The important difference is that the structure is preoccupied with another mobile cation which is displaced and reduced with the insertion of the first \( \text{Li}^+ \). Typical examples are silver vanadates used in implanted cardiac defibrillators.

1.3 Lithium / Iodine System

The lithium iodine rechargeable system used in our electrolytically formed batteries uses a similar chemistry to primary lithium-iodine batteries which have been used in pacemakers since 1972 [13]. Due to the similarities in these two systems, a broad overview will be given on the \( \text{Li-}\text{I}_2 \) system and the different
factors affecting cell formation and functionality. These primary lithium iodine cells are characterized as having high energy density, excellent reliability, long life spans (usually greater than 10 years), and low self discharge [14], which are all characteristics that should transfer to our electrolytically formed cells.

The overall reaction for these primary cells is fairly straightforward, an electron from the lithium metal cathode travels through an external circuit to the electronically conductive cathode species where an iodine ion is formed. The lithium ion then travels through the solid electrolyte interphase and electrolyte reacting with the iodide ion forming a LiI product, as can be seen in equation 1.3.

\[ 2\text{Li} + \text{I}_2 \rightarrow 2\text{LiI} \]  

The overall Gibbs free energy for this reaction is 269.7 kJ/Mol LiI and results in an OCV of 2.8V.

The initial work that led to the utilization and implementation of the lithium-iodine battery, as a cell for pacemakers, began in 1967. This work involved using charge transfer complexes in electrochemical cells [15]. Charge transfer complexes are materials where there is a weakly bonded electron donor/acceptor pair, which allows electronic conductivity throughout the material. The initial metal iodine cells used various nitrogen containing polymers in combination with iodine to form the cell cathode, and different metals (Ba, Ca, Mg, Al, Ag) as the cell anodes. In fabrication of these cells it was noticed that no electrolyte or separator is needed as an electronically insulating SEI layer of LiI.
forms in-situ at the lithium-iodine composite interface eliminating the possibility of shorts occurring. Following this work, Schneider and Moser [16,17] invented the lithium metal/iodine P2VP battery, where P2VP is poly-2-vinylpyrrole (Fig 1.8).

![Figure 1.8: Poly-2-vinylpyridine](image)

Using P2VP as an additive to iodine and then processing the composite forms an electronically conductive cathode. To date, two methods are used in cathode processing and formation for Li-I$_2$ cells, one, the pressed pellet method, and two, a thermally activated method, which is more widely used today. Despite the cathode fabrication method used, lithium metal is exclusively used as the Li-I$_2$ cells anode.

**1.3.1 Cathode formation and activation**
At room temperature, a light reaction occurs between iodine and P2VP giving approximately a two order of magnitude increase in conductivity over molecular iodine, $\sim 10^{-7}$ S/cm. For the pressed pellet method, iodine and P2VP are ground together at room temperature and pressed into a pellet which is used as the cathode in a cell. Since the thermally activated method is more widely used, it will be discussed in more detail.

In 1973, Mead [18] noticed a large improvement in cathode conductivity as the sample of iodine and P2VP was thermally activated. Since this initial finding, many studies have been done to explain these results. It was found that above the melting temperature of iodine ($113^\circ$C) a highly exothermic reaction takes place between the polymer and iodine giving the sample an intrinsic electronic conductivity through a mechanism which does not occur with the pressed pellet method. This elevated temperature reaction, Fig. 1.9, involves the replacement of a hydrogen atom off the P2VP backbone with an iodine atom in addition with the bonding of an additional iodine molecule with the nitrogen group located on the pyridine ring [19,20].
When these cathode materials are used in pacemaker cells, the body temperature, and cell temperature is 37°C. At this temperature the phase diagram for an I₂:P2VP mixture is complex with the iodine concentration determining phases present. Through the discharge of the cell and decrease in iodine concentration, the complex passes through three distinct phases which are a determining factor in conductivity. Based off this understanding the iodine concentration has a large effect on composite conductivity as can be seen in Figure 1.10. Initially at a high I₂:P2VP ratio the cathode contains both an excess molecular iodine phase and a liquid I₂-P2VP composite. As the discharge continues the material turns into a single phase liquid I₂-P2VP region. Upon further discharge, and the depletion of iodine, at an I₂:P2VP ratio of 8:1, a eutectic is reached resulting in a second two phase region which is responsible for the large decrease in conductivity. Nonetheless, the electronic conductivity mechanism for the iodine:P2VP composite occurs through the formation of this iodine:P2VP bonded composite through molecular orbitals which allows the material to be an electron conductor. Typically in Li-I₂ pacemaker cells the iodine: P2VP ratio in the cathode composite is between 30:1 and 50:1 to start.
Figure 1.10: Conductivity of iodine:P2VP composites as the I$_2$:P2VP ratio is increased. Sharp decrease present at 8:1 ratio is from phase diagram moving to single phase region.

Form this figure it can be seen that as cell is discharged, or the iodine concentration is decreased, that there is an increase in overall cathode composite conductivity, to a ratio of 8:1 where the overall cathode composite peak conductivity occurs.

1.3.2 SEI Layer in Lithium/iodine Cells
In primary lithium iodine cells, the anode material is lithium metal and the cathode is a polymer-iodine composite whose overall discharge product is lithium iodide. When these cells are fabricated, the anode and cathode are placed against one another and a small self discharge occurs forming a solid electrolyte interphase, or SEI, of lithium iodide. Once fully formed the SEI electronically isolates the cell anode and cathode, greatly reducing any further self discharge.

During discharge the $\text{Li}^+$ ion travels through the LiI SEI layer and reacts with an iodide ion on the cathode side of the SEI. As discharge continues the thickness of the LiI SEI layer increases as can be seen in figure 1.11. At early stages of discharge when the SEI is thinnest, a small degree of continuing self-discharge which does occur from lithium ions diffusing through the SEI layer, but is eliminated as the SEI thickness is increased during discharge [13], or as the cell is stored and the SEI is thickened by this slow self-discharge.
Figure 1.11: Schematic showing increase of SEI thickness as discharge occurs.

Reaction location occurs at SEI/Cathode interface

Through the discharge the thickness of this layer grows to a thickness where the Li\(^+\) ion transport becomes the limiting factor in cell discharge causing a large degree of polarization and affecting discharge rates [13]. Fig. 1.12 shows the effect of polarization for cells using three different discharge rates. It should be noticed that as the rate is increased the polarization effect is so great that very little discharge capacity is useful above an operating voltage of 2V. With pacemaker cells the overall discharge rate is less than 100microamp (usually 5-50microamp), but the cell is still severely limited by the SEI layer ionic conductivity. Therefore, different steps have been taken to either decrease thickness of the formed SEI layer or to increase ionic conductivity of the thickening SEI.
Figure 1.12: Showing effect of discharge rate on polarization voltage. Each cell is capacity limited by the cathode. Increase in current causes large degree of polarization related to lithium ion conductivity through the SEI layer.

One method used to decrease SEI thickness was the implementation of a corrugated lithium metal anode. This shaped anode increased the reaction surface area which results in a thinner SEI layer at a given discharge capacity compared to a standard cell. Although this was a short term solution which only delayed the thickening SEI, it was an improvement over flat anode cells.

A second method was discovered by Greatbatch, Mead and Rudolph [21] which shown that if a thin film of P2VP was coated on the anode surface prior to cell fabrication there was greatly enhanced cell performance, as can be seen in figure 1.13.
Initial coating were done by brushing a solution of P2VP mixed with a volatile solvent on the lithium metal anode and allowed to evaporate. Today more evolved methods are used, such as casting a thin layer of P2VP and lightly pressing the lithium metal onto this layer.

Inspection of the cells after cell formation shown that instead of having a Lil solid electrolyte interphase layer formed at the cathode/anode interface, there is both lithium iodide and a yellow colored liquid. This liquid is believed to be a product of a reaction between the P2VP and the other constituents of the cell [22]. It was concluded that this liquid layer is a medium for lithium ion transport.

Figure 1.13: Li-I$_2$ cell discharge voltage profiles for cell formed using coated and uncoated anode materials.
resulting in higher ionic conductivity, decreased polarization, and greater cell efficiency.

Based off the previous data it can be been that the properties of an SEI layer can have a large effect on cell functionality. The following section is an in-depth look at different SEI materials that form in general lithium and lithium ion batteries.
1.4 Solid Electrolyte Interphase - SEI

A solid electrolyte interphase layer is defined as a protecting layer formed on the negative electrode of a battery as a result of electrolyte decomposition [23]. The SEI plays the critical role of passivating the electrode surface towards further cathodic decomposition of the electrolyte on the highly reducing negative electrode surface. This SEI allows functionality of lithium metal, lithium-alloy, lithium ion, and any other alkali metal and alkali earth metal batteries. In primary batteries it determines the safety, self discharge, power capability, low temperature performance and faradaic efficiency. In secondary batteries, in addition to the previous mentioned characteristics, the SEI also determines the faradaic efficiency on charge, the cycle life, the morphology the lithium metal deposits (in lithium metal cells), and the irreversible capacity loss [24]. A good SEI layer must have the following properties, as a lack in any one property could be detrimental to battery performance;

(1) Electronic transference number equal to zero. The SEI layer must be electronically insulating in order to avoid SEI thickening, self discharge, and an increase in internal resistance.

(2) Cation transference number equal to one. Having a high cation transference number will eliminate concentration polarization and assist in more uniform lithium deposition in secondary cells.

(3) High ionic conductivity to reduce over voltage.

(4) Uniform morphology which will allow for uniform current distribution.
(5) Good adhesion to the anode.

(6) Mechanical strength and flexibility [24].

(7) Electrochemical stability relative to the electrode material

(8) No solubility when liquid electrolytes are used.

Over the past 2-3 decades the development and commercial use of lithium and lithium ion batteries has become increasingly popular. With secondary lithium ion batteries the most common negative electrode material is graphite, although numerous other forms of carbon are used as well [23]. An in-depth summary is presented here covering SEI formation in both lithium metal and lithium-carbon anode batteries, but the theory behind SEI development can be applied to all alkali metal anodes [24].

Lithiated graphite anode material is instable in air, so a lithium ion battery is always assembled in the discharge state using a lithiated cathode. During the first charge of the lithium ion battery the electrolyte undergoes reduction at the negatively polarized graphite surface. The product of the reaction is a combination of inorganic and organic materials which form the SEI layer over the cells anode [23]. Since this SEI layer is a direct product of the cells anode and electrolyte materials, it should be understood that the properties of both have a large effect on the SEI performance and functionality. The newly formed SEI layer should be self passivating and electronically blocking to eliminate any further electrolyte decomposition and also should allow lithium ion transport. The next sections take a look at each component that effects SEI formation (anode and electrolyte) along with other factors that can affect SEI morphology.
1.4.1 Carbon effect on SEI Properties

The type and characteristics of the carbon used have a large effect on the SEI formed during use, some of these characteristics being; particle size and shape, pore size distribution, BET surface area, basal vs. edge-planes (C-C bonding) and pore opening are all of critical importance. These not only affect the SEI layer but also have an influence on reversible and irreversible capacity loss. Different authors have shown that the irreversible capacity loss on the first charge is proportional to the BET specific surface area of the carbon [25]. Also, authors have shown that the crystallographic structure and particle morphology of the carbon is as important as the specific surface area when it comes to irreversible capacity loss [26].

As mentioned earlier, lithium ion batteries using a graphite anode electrode are assembled in the discharged state. The cathode, typically a lithium metal oxide, is fully intercalated with lithium prior to assembly and then once fabricated the battery is charged by removing lithium from the cathode and inserting it into the layered carbon structure as the anode. A fraction of the inserted lithium reacts with the electrolyte material forming the SEI layer. The amount of lithium that reacts with the electrolyte is known as irreversible loss. The following figure is an example of what a graphite electrode SEI layer looks like after the initial battery charge.
Figure 1.14: Sketch of a lithiated graphite electrode showing slid electrolyte interphase formation.

1.4.2 Electrolyte Composition:

The other material that contributes to SEI composition is the electrolyte used in the cell. Non aqueous electrolytes used in lithium ion cells, are not thermodynamically stable vs. lithium metal, therefore the electrolyte salt and solvent used have a direct effect on the SEI layer formed and these formed SEI layer are what enables today’s Li-ion battery to operate. It has been reported and is widely understood that when a lithium metal anode, or lithiated carbonaceous anode are placed in an electrolyte there is an almost
instantaneous formation of an SEI layer (<1 ms) [24], with these SEI components begin dependent on the electrolyte composition. For example, lithium alkoxides appear in the SEI formed in ether electrolytes; semi-carbonates and Li₂CO₃ appear in a SEI formed in carbonate electrolytes (PC and EC), lithium alkyl carbonates, while lithium formate appears in SEI layers formed using methyl formate electrolytes [27,28]. The carbonate concentration in the electrolyte also has an effect on SEI composition and the electrolyte decomposition reactions that form the SEI layer.

Another component present in electrolytes is lithium salt. The lithium salt assists in the formation of the inorganic electrolyte components such as LiF. The following table also illustrates some of the possible reactions and products, both organic and inorganic that can be formed as components of an SEI.
\[
\begin{align*}
\text{LiPF}_6 & \rightarrow \text{LiF} + \text{PF}_5 \\
\text{LiPF}_6 + \text{H}_2\text{O} & \rightarrow \text{LiF} + \text{POF}_3 + 2\text{HF} \\
(\text{CH}_2\text{O})_2\text{C} = \text{O} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow \text{Li}_2\text{CO}_3 + \text{CH}_2 = \text{CH}_2 \\
\text{Li}_2\text{CO}_3 + \text{LiPF}_6 & \rightarrow 3\text{LiF} + \text{POF}_3 + \text{CO}_2 \\
\text{Li}_2\text{CO}_3 + 2\text{HF} & \rightarrow 2\text{LiF} + \text{CO}_2 + \text{H}_2\text{O} \\
2\text{CO}_2 + 2\text{Li}^+ + 2\text{e}^- & \rightarrow \text{Li}_2\text{CO}_3 + \text{CO} \\
\text{H}_2\text{O} + \text{Li}^+ + \text{e}^- & \rightarrow \text{LiOH} + \frac{1}{2}\text{H}_2 \\
\text{LiOH} + \text{Li}^+ + \text{e}^- & \rightarrow \text{Li}_2\text{O} + \frac{1}{2}\text{H}_2 \\
\text{Li}_2\text{CO}_3 + \text{PF}_5 & \rightarrow 2\text{LiF} + \text{POF}_3 + \text{CO}_2 \\
\text{ROCO}_2\text{R} + \text{Li}^+ + \text{e}^- & \rightarrow \text{LiOCO}_2\text{R} + \frac{1}{2}\text{R}_2 \\
2\text{LiOCO}_2\text{R} + \text{H}_2\text{O} & \rightarrow \text{Li}_2\text{CO}_3 + 2\text{ROH} + \text{CO}_2 \\
\text{ROCO}_2\text{R} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow \text{Li}_2\text{CO}_3 + \text{R}_2 \\
\text{LiOCO}_2\text{R} + \text{HF} & \rightarrow \text{LiF} + \text{ROH} + \text{CO}_2 \\
\text{ROCO}_2\text{R} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow 2\text{LiOR} + \text{CO} \\
2(\text{CH}_2\text{O})_2\text{C} = \text{O} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow (\text{CH}_2\text{OCO}_2\text{Li})_2 + \text{CH}_2 = \\
(\text{CH}_2\text{OCO}_2\text{Li})_2 & \rightarrow \text{Li}_2\text{CO}_3 + \text{CH}_2 = \text{CH}_2 + \text{CO}_2 + \frac{1}{2}\text{O}_2 \\
\text{Li}_2\text{CO}_3 & \rightarrow \text{Li}_2\text{O} + \text{CO}_2 \\
\text{O}_2 + 4\text{Li}^+ + 4\text{e}^- & \rightarrow 2\text{Li}_2\text{O} \\
(\text{CH}_2\text{OCO}_2\text{Li})_2 + 2\text{Li}^+ + 2\text{e}^- & \rightarrow (\text{LiCO}_2)_2 + (\text{CH}_2\text{OLi})_2 \\
2\text{CH}_3\text{OCO}_2\text{Li} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow (\text{LiCO}_2)_2 + 2\text{LiOCH}_3
\end{align*}
\]
Table 1.4: Possible organic and inorganic SEI components that can form in lithium and lithium ion cells [29].

1.4.3 Other factors Effecting SEI Formation

In addition to the chemical components that effect SEI composition, the electrochemical charging and discharging conditions also play an important role. It has been shown that mode of polarization, overpotential, along with temperature and battery storage all play an important role in SEI formation [23].
1.5 Properties of Components in an Electrolytically Formed Battery

Ion transport and conduction, both ionic and electronic, play a critical role in battery performance. An in-depth understanding of these mechanisms will give insight into which factors affect battery performance and stability. Also, an understanding of these functions will allow one to solve issues with battery development and troubleshoot different cycling problems that could occur.

Through the following sections the different mechanisms affecting both ionic and electronic conductivities of our electrolytically formed battery materials will be discussed.

1.5.1 Lithium Iodide – Self Formed Cell Electrolyte Material

Crystalline lithium iodide comes in a multitude of different hydrations with different crystal structures which result in different properties, such as ionic conductivity. Any hydrations of lithium iodide are extremely hygroscopic [30] and should be kept in a minimal moisture environment such as a dry room or glove box. This hygroscopic characteristic of lithium iodide makes different characterization techniques extremely difficult and limits which techniques can be used, as any interaction with normal atmosphere causes hydration and changes in the cell chemistry.

At room temperature, lithium iodide exists in four crystalline states, LiI(xH₂O), where x = 0, 1, 2, 3. Early literature suggested the existence of a
hemihydrate and sesquihydrate (LiI(0.5H$_2$O) and LiI(1.5H$_2$O)) phase being present [31,32], although future research shows no existence and either crystalline phase [33].

Anhydrous lithium iodide has a rock salt type structure which can be seen in figure 1.15.

Figure 1.15: Crystal structure of anhydrous lithium iodide [34].

Lithium iodide monohydrate (LiI(1H$_2$O)), has a simple cubic, Pm3m perovskite $\text{ABO}_3$ structure where the iodide ions form the primitive cubic lattice (A-position), the water molecules occupy the center of the iodide cubes (B-position), and the
lithium ions occupy one third of the face centered positions. The structure of lithium iodide monohydrate, having many face centered position vacancies is such a structure that favors lithium ion diffusion [35].

Lithium iodide tri-hydrate, LiI(3H₂O) crystalizes in a hexagonal structure. The water molecules are distorted and form one strong linear OH-I hydrogen bond and one weak non-linear hydrogen bond [33]. The structure of lithium iodide tri-hydrate can be seen in figure 1.16.

![Crystal structure of lithium iodide tri-hydrate showing hexagonal structure](image)

**Figure 1.16:** Crystal structure of lithium iodide tri-hydrate showing hexagonal structure [30].

The XRD pattern for lithium iodide di-hydrate, LiI(2H₂O), shows a large number of lines which indicated that lithium iodide dihydrate possesses low symmetry [33].

LiI(H₂O), LiI(2H₂O), and LiI(3H₂O) melt at 128°C, 80°C and 70°C respectively, while the anhydrous form melts at 469°C [33]. As, can be seen
from the following phase diagram, figure 1.17, eutectics do occur between monohydrate and dihydrate as well as between the dihydrate and trihydrate phases.

Figure 1.17: Lithium iodide phase diagram as a function of hydration [33].
1.5.1.1 Conductivity of Lithium Iodide

As suggested from the crystal structure of the different lithium iodide hydrates, the monohydrate phase should possess the maximum in conductivity due to its vacancies of the face centered positions, which should allow lithium ion diffusion. Figure 1.18 shows the effect hydration has on overall material conductivity.
Figure 1.18: Lithium iodide conductivity as a function of hydration. Maximum in conductivity occurs at lithium iodide monohydrate as suggested by crystal structure [36].

As this conduction mechanism in the monohydrate material is believed to be a lithium conductor through lithium vacancies, it can be thought that the conductivity should increase as the density of the material is moved closer to its theoretical value. As the density is increased the amount of void space is decreased resulting in better contact between Lil crystals. The following figure shows the conductivity of Lil monohydrate material as a function pressure. Initially as the pressure is increased the conductivity of the material is increased. As the material approached its theoretical density the conductivity begins to decrease. The reason for this is the material begins to phase transition to the \( \alpha \)-phase which is stable at high pressure and temperatures below -5°C, and has a higher resistance [37].
Figure 1.19: Conductivity as a function of pressure for lithium iodide monohydrate. As the pressure is increased the density increases to near the theoretical value [37].

The conductivities of the LiI crystals are known to be $2 \times 10^{-7}$, $1.2 \times 10^{-5}$, $2.2 \times 10^{-7}$ s/cm and $2.4 \times 10^{-7}$ for the LiI, LiI(H$_2$O), LiI(2H$_2$O), and LiI(3H$_2$O) phases respectively. Although there are slight differences in the literature values all reports show the monohydrate phase having an approximate two order of magnitude increases over the anhydrous and higher hydrate phases [35,36]. In an attempt to separate the overall LiI conductivity into its electronic and ionic portions different experiments were found in the literature. One method used cells that contained a LiI electrolyte with two blocking stainless steel electrodes
and also cells with non-blocking lithium metal electrodes. A D.C. polarization current of 200 mV was applied and the current was monitored as a function of time. The cells prepared using the blocking electrodes showed a current proportional to the leakage current of the system, 60nA, while the cells prepared using non-blocking lithium electrodes shown a current of 3.0μA [37]. These results show the anhydrous LiI electrolyte is pure lithium ion conductor with negligible electronic conductivity. This experiment using blocking and non-blocking electrodes could not be performed using the hydrate phases due to a reaction occurring between the lithium metal and the hydration in the system which would form a lithium hydroxide product and hydrogen gas. This reaction would alter the results due to the much lower conductivity of the LiOH product of $1 \times 10^{-8} \text{S/cm}$ which forms at the lithium metal/electrolyte interface [35].

Experiments have also been used to show the stability of lithium iodide as a material vs. lithium metal. Lithium metal cells were prepared using lithium metal as the cell anode, LiI as the cell electrolyte, and AgI as the cells cathode. The following reaction shows the cell reaction as it would progress during discharge of the cell:

$$\text{Li} + \text{AgI} \rightarrow \text{LiI} + \text{Ag} \quad (1.3)$$

To confirm no side reactions occurred Li/LiI/AgI cells were discharged at different rates and the polarization of the cell was monitored (Figure 1.20). The polarization showed a purely ohmic resistance which confirmed the only reaction
occurring was the discharge reaction of the cell, and no side reactions which
occurred at higher voltages were present. This also allowed for the material
resistance to be calculated from Ohm’s law [38].

Figure 1.20: polarization curve for Li/LiI/AgI cell showing ohmic resistance of LiI
material [38].

Another method which was used to verify the purely ionic conductivity of
the LiI electrolyte material was to monitor the self-discharge or capacity loss in a
LiI electrolyte cell as a function of time and temperature. Literature results for
this experiment were found where the authors formed cells using a lithium metal
anode, a LiI electrolyte, and a composite cathode which contained PbI\(_2\), PbS and Pb metal [39]. These cells were fabricated and sealed to eliminate any atmospheric influence on the results. One cell was stored at 45°C for one year and one cell at 60°C for one year. These discharge profiles were then compared to that of a fresh cell, Fig 1.21. No difference was seen in discharge capacity showing that very little or no self-discharge occurred pointing to the fact that anhydrous lithium iodide material possesses little to no electronic conductivity.

![Discharge profile for three Li/Li\(_2\)/PbI\(_2\)-PbS-Pb cells.](image)

**Figure 1.21**: Discharge profile for three Li/Li\(_2\)/PbI\(_2\)-PbS-Pb cells. A) Fresh Cell, B) Cell stored at 45°C for one year, and C) Cell stored at 60°C for one year.

The fact that lithium iodide is a purely cationic conductor as can be seen from the previous literature results is one reason why lithium iodide material makes an ideal electrolyte material for lithium batteries. The fact that lithium metal cells
containing a lithium iodide electrolyte material shown the same cell voltage and
same capacity on discharge after storage for up to one year also confirms that
fact that lithium iodide material is stable against lithium metal and no reactions
between the electrolyte and anode material are taking place. Although the
overall cationic conductivity of the LiI is relatively low compared to other solid
electrolyte cation conductors such as RbAg₄I₅, the material is stable over a
greater potential range. At higher potentials RbAg₄I₅ forms lithium silver alloys.

Due to the fact that this material does possess low lithium ion conductivity,
even in the hydrated phase, which has a direct effect on cell rates, different
nano-fillers and dopants can be added to the materials to increase the lithium ion
conductivity

1.5.1.2 Effect of Doping on Lithium Iodide Conduction

1.5.1.2.1 Addition of Al₂O₃ to Lithium Iodide

Liang was the first to show a large increase in conductivity from the
addition of Al₂O₃ to a LiI composite [40]. The conductivity of this system showed
a maximum approximately an order of magnitude greater than that of the initial
starting anhydrous lithium iodide composite, Fig. 1.22.
Figure 1.22: Conductivity of LiI-Al$_2$O$_3$ composites as a function of Al$_2$O$_3$ content. Shows maximum in conductivity occurring between 40-50% Al$_2$O$_3$ [40].

Early literature suggests that the increase in conductivity was from the formation of lithium iodide monohydrate phase due to the extremely hygroscopic nature of the anhydrous lithium iodide material and the ability of the nano alumina dopant to retain moisture. This theory was proven incorrect when results were published where the alumina phase also increased conductivity in the monohydrate LiI material. The mechanism for this increase is still under debate although one author suggests the increase in conductivity can be caused from a microstructure forming along the alumina-LiI interface which allows for fast ionic transport. This is in agreement with other literature results which established that such
microstructures can act as rapid ionic transport regions through the formation of imperfections, additional grain boundaries, and dislocations in the lithium iodide crystals [36]. Through a modeling of the Lil-alumina composite it has been shown that the lithium iodide particle size and the amount of dopant present would greatly affect conductivities, assuming the mechanism for the increased conduction is due to interface conductivity.

Overall the addition of alumina to lithium iodide material shows no effect on the electronic conductivity of the material, and shows no interaction between the materials through the introduction of new Bragg peaks in an XRD of the composites. The addition of alumina to a lithium iodide composite is one possible solution to the problem of having a lithium ion conductor which is stable against lithium metal, while also possessing an increase in cationic conductivity over pure lithium iodide.

1.5.1.2.2 Metal Halide Doping

The addition of different metal halide salts such as MgI and CaI$_2$ to lithium iodide has been proven to increase the ionic conductivity of the lithium iodide material [41,42]. In the following section the mechanism for this increase will be reviewed.

The increase in the ionic conductivity of lithium iodide by the addition of minute quantities of higher valence cations is believed to form crystal defects in lithium iodide crystals which are the cause for the increase in ionic conductivity.
The addition of CaI$_2$ to anhydrous lithium iodide results in a substantial increase in ionic conductivity as can be seen in the following figure.

Figure 1.23: Conductivity of lithium halide composite as a function of CaI$_2$ concentration A) Initial material conductivity  B) Conductivity after storage for 500 hours.

The inclusion of the divalent calcium cation to the lithium iodide material induces crystal defects, specifically cation vacancies, in the lithium iodide crystals. This conclusion is also supported by the XRD spectra of the LiI-CaI$_2$ composites where a solid solution between the two materials exists at low concentrations of CaI$_2$. In figure 1.24, the lattice parameters are shown as a function of calcium
iodide concentration showing an increase in lattice parameter from the incorporation of the large calcium ions into the lithium iodide crystal structure.

Figure 1.24: Lattice parameter for lithium iodide – calcium iodide composite as a function of $\text{CaI}_2$ concentration showing increase in lattice parameter as calcium iodide is added [42].

It has been shown that lithium iodide possesses only ionic conductivity and that the addition of different dopants allow an increase in this ionic conduction. Based off the previous section of crystallography data and literature results, lithium iodide makes a more than adequate electrolyte material.
1.5.2 Polyiodides

Polyiodides are chain of iodine atoms. They come in different lengths and different geometries depending on the molecules or ion associated with the polyiodide chain. The typical polyiodide chains that exist are $I_3^-$, $I_5^-$, $I_7^-$, and $I_9^-$, although many different chains have been structurally characterized from $I_2^-$ to $I_{29}^{3-}$ [43]. For as many different configurations that exist, the polyiodides can generally be described, and with few exceptions, as a number of iodine molecules added to an iodide ion, or as iodine molecules added to a triiodide ion, as is demonstrated in figure 1.25,
Figure 1.25: Demonstration of construction of higher order polyiodide species using iodide ion, iodine molecules, and triiodide species as the building components.

1.5.2.1 Characterization

Throughout the literature, several different characterization techniques have been used to determine polyiodide structures and crystallography such as XRD, NMR, and UV-Vis Spectroscopy [43]. One of the more popular and powerful characterization techniques for polyiodide species is vibrational spectroscopy. The following section will take an in-depth look at the Raman vibrational spectroscopy and structure of the typical polyiodide species. The term general polyiodide structures must be used due to the overwhelming number of different polyiodide species that can be formed. For example, to date more than 500 triiodide species have been catalogued each containing a different electron donor giving rise to slightly different crystal structures and absorbance spectra.

1.5.2.2 Raman Spectroscopy and Structure of Polyiodides

1.5.2.2.1 Triiodides

Structurally the most studied polyiodide is the triiodide. This ion is generally linear or nearly linear with an angle of $180^\circ \pm 6^\circ$ [44].
The triiodide molecule comes in two forms, symmetric and asymmetric. Although the difference between these two structures is the bond length, which is dependent on the electron donor associated with the molecule, the overall molecule length remains essentially constant [43]. Triiodide species associated with a large cation are typically symmetric where asymmetry is induced through coordination with a small cation, although exceptions to this rule do exist. Other factors such as hydrogen bonding, packing effect and electrostatic interaction also play a role in the triiodide structure. Triiodide ions can form stacked or layered structures which results in the formation of infinite chains off triiodide with weak I₃⁻ - I₃⁻ interactions. These infinite chains will form in a linear or T-shaped pattern as shown in the following figure.

![Linear triiodide molecule](image)
Figure 1.27: Schematic showing infinite linear and T-shaped chain structures for a triiodide system [43].

Raman spectroscopy structural characterization of the triiodide system shows three vibrational absorbance bands. A symmetric stretching mode at \( \sim 110\text{cm}^{-1} \), the asymmetric stretching which occurs at \( \sim 140\text{cm}^{-1} \) and a bending mode which occurs at \( 70\text{cm}^{-1} \) [45]. These vibrations are approximate as different factors,
which will be discussed later, affect peak position and intensity. The following spectra are that of typical triiodide species. In this figure a potential is applied to the polyiodide species to induce an effect which causes asymmetry to develop to more easily demonstrate both the symmetric and asymmetric vibrational modes.

![Raman spectra of triiodide species](image)

**Figure 1.28:** Raman spectra of triiodide species which initially contains a symmetric structure but as the potential is increase the materials transforms to an asymmetric system [46].

### 1.5.2.2.2 Pentaiodides

Structurally pentaiodides or $I_5^-$ have been structurally characterized as either V/L shaped or linear geometries [43]. The V-shaped molecule is to be
thought of as containing one iodide ion with two iodine molecules, while the L-shaped contains one triiodide unit and one iodine molecule. The linear pentaiodide unit can be thought of as also being one iodide ion with two iodine molecules or as a pure I$_5^-$ unit. Pentaiodide units are linked together through a variety of strong and weak intermolecular interactions to form different 3D or linear geometries. Figure 1.29 shows some common contact geometries for pentaiodide groups.
Figure 1.29: Common contact geometries for pentaiodide. A) zigzag shaped chain  B) alternating twined and zigzag shaped chain  C) meander shaped chain  D) displaced chain  E) cis-shaped chain  F) trans-shaped chain  G) twinned chain  H and I) square nets [43].

The Raman spectra of different polyiodide species show a multitude of different absorbance bands. The large majority show an absorbance occurring at ~165 cm$^{-1}$. Also depending if the pentaiodide unit contains an $I_3^-$ unit within its structure there will also be vibrational modes in the 145 cm$^{-1}$→160 cm$^{-1}$ region.

1.5.2.2.3 Higher order Polyiodides – Heptaiodide and Nonaiodide

As the length of the polyiodide increase the overall geometries become more complicated. The following two figures show examples of the heptaiodide and nonaiodide structures.
Figure 1.30: Typical heptaiodide structure consisting of two iodine molecules and one triiodide [43].

![Typical heptaiodide structure](image)

Figure 1.31: One possible nonaiodide structural configuration [43].

The Raman spectra of the higher order polyiodides can give a variety of different absorbance bands. One general rule applies for characterizing these materials. As longer polyiodide species are formed there is a decrease in I-I bond distance corresponding to a stronger force constant which results in an absorbance occurring at higher energy, or higher wavenumber [47]. This bond strengthening occurs until molecular iodine is present in the sample giving an absorbance at ~180cm\(^{-1}\) [48]. Figure 1.32 below shows polyiodide formation that
occurs as the polymer to iodine ratio is changed. In this example, as the polymer (poly propylene oxide) to iodine ratio is being decreased, more higher order polyiodides are formed.
Figure 1.32: a. 16:3 PPO:I₂, b. 8:3 PPO:I₂, and c. 4:3 PPO:I₂. Decreasing ratio of polymer to iodine causes more higher order polyiodides to form. At the high 16:3 ratio nearly all polyiodides found in the sample are triiodides [48].

1.5.2.3 Factors Effecting Peak Position and Intensity

When performing Raman spectroscopy on a polyiodide species, the preferred method is to use FT-Raman as opposed to resonance Raman, which typically gives the sample less exposure time to the laser. During exposure to a laser the higher order polyiodide species are known to break down into simpler triiodide specie. Shown in figure 1.33, a sample containing higher order polyiodides has a resonance Raman spectra recorded immediately, after 40 minutes, and then again after one hour. The spectra shows the formation of more triiodide units as exposure time increases.
Figure 1.33: Raman spectra of $I_9^-$ species showing breakdown of higher order polyiodide species as a function of exposure time to Raman laser. A) Immediate spectra  B) Spectra after 40 minutes of exposure time to laser  C) Spectra after exposure time of 60 minutes to laser [47].

Another important factor when performing Raman spectroscopy on polyiodide containing samples is to be consistent with the excitation laser wavelength. Using different energies of excitation will not only slightly alter peak locations within the Raman spectra but also affect peak ratios with respect to one another. Figure 1.34 shows a spectra where the excitation frequency is increased and results in a decrease in the triiodide absorbance peak and an increase in the higher order polyiodide intensities.
Figure 1.34: Raman absorbance spectra for $I_\gamma$ unit showing the effect of excitation laser wavelength on sample peak position and intensity [47].
1.5.2.4 Conductivity of Polyiodides

For polyiodide species to be considered a useful cathode material in an electrochemical cell there is a need for the material to be a mixed conductor, meaning it possesses both ionic and electronic conductivity. Similar to adding carbon to a lithium ion cell cathode to incorporate electronic conductivity, polyiodide species should provide pathways for electron mobility, as well as allow for the diffusion of iodide ions.

It has been shown in literature that as iodine is added to electron donors, polymers, or alkali halide salts there is the development of electronic conductivity. It has also been noted that as the electronic conductivity of samples containing polyiodides increased the ionic conductivity also increased [49]. This relationship between the electronic and ionic conductivity in these samples suggest a coupling or mechanism for conductivity that supports both ionic and electronic conduction.

In examining the ionic conductivity of polyiodide-polymer species, which is the most popular way to characterize the conductivity mechanism, it was noted that at high polyiodide concentrations, charge transport is dominated by a process that is much faster than the diffusion of simple ions in polymers [50]. A Grotthus type mechanism similar to proton conduction in water [46,50] explains the ionic conductivity of polyiodide species. In this mechanism there is a rearrangement of long and short polyiodide bonds along a polyiodide chain to allow iodide ions to move throughout the material. The following figure shows
two schematics which represent what occurs during ionic conduction in polyiodide species.

![Figure 1.35: Two schematics showing Grotthus mechanism for ionic conduction in polyiodide species [50,51].](image)

This conduction mechanism is widely accepted [49-54] over other mechanisms which associate the polymer-polyiodide ionic conduction pathway to a process that only occurs above the polymer glass transition temperature. Due to the complex mechanisms related to the ionic and electronic conductivities of polyiodide species and their relation to one another, absolute values for ionic and electronic conductivities could not be found. Since a large variety of parameters such as cation present, salt present (if any), iodine concentration, and method of fabrication all effect polyiodide formation, the determination of each polyiodide species conductivity is extremely difficult although conductivities up to 3 orders of
magnitude higher than molecular iodine have been reported in polyiodide containing composites.

The electronic conductivity of polyiodide species is suggested to come from a delocalization of electrons allowing electron mobility along simple polyiodide chains and along the short contacts between one chain and another [50]. Based off this theory and calculated band gap values infinite triiodide chains would be expected to have the highest electronic conductivity of all polyiodide species [50]. In general polyiodide species are predicted to be semiconductors, and electron delocalization and conductivity should be the most extensive for infinite I$_3^-$ chains. The bandgap energy for polyiodide species is predicted to decrease in the following order: Isolated I$_2$ > Isolated I$_3^-$ > Infinite chains of I$_5^-$ > infinite chains of I$_3^-$ . Asymmetry of the standard polyiodides is expected to have a large effect on band gap energy [50].
1.6 Secondary Electrolytically Formed Lithium Iodide Battery System

1.6.1 Background of an Electrolytically Formed Battery

As technologies develop, devices requiring power continue to decrease in dimensions, as does the need for the power sources for these devices. Scaling down battery fabrication using conventional fabrication methods to create cells with an acceptable energy density and overall volume increases in difficulty as overall cell dimensions decrease. As the cell is “miniaturized” a larger portion of overall cell volume is dedicated to non-energy producing components such as electrolyte, separator, and packaging. Different pathways have been taken to offer solutions to this problem, such as thin film batteries [55]. Our group has shown that using an electrolytically formed battery chemistry [56] we can form a lithium cell where cell shape and dimension are highly flexible. These cells offer one pathway as a power supply, by both easing battery fabrication and eliminating the need of non-energy producing components from the fabrication process. Although certain components are not present during battery fabrication (anode, cathode, separator) they are still required for battery performance as are all components of a functioning lithium cell.

These cells start with a lithium iodide/polyvinylpyrrolidone (PVP) nano-composite and under potential form the cell anode and cathode in-situ, which consequently allows SEI formation. During polarization/electrolytic
decomposition of LiI, lithium metal is plated out as the cells anode and iodide ions coordinate with the PVP polymer additive to form a polypiodide based cathode, comparable to Fig. 1.36.
Figure 1.36: Formation of an electrolytically formed lithium-iodine battery. The initial LiI-based material electrochemically dissociates into a polyiodide positive electrode, a lithium negative electrode, and a LiI-based residual electrolyte.

The chemistry used in these self-formed cells is similar to lithium-iodine primary batteries, although this is the first time lithium iodide has been used in an electrochemically formed cell, and also the first time it has been used as the active material in a secondary cell.

1.6.2 Advantages of an Electrolytically Formed Battery System

The components of a self-formed battery are extremely simple containing just the current collectors and one homogenous nanocomposite. Due to the simplicity of this system the fabrication process is much less complicated when compared to conventional battery systems, and due to the ease of assembly, it allows for the fabrication of cells in sizes and geometries which are not possible in conventional batteries. Figure 1.37 shows one possible current collector geometry which can be used with our electrolytically formed battery chemistry.
Figure 1.37: Interdigitated current collector configuration illustrating complicated configurations which electrolytically formed batteries can be fabricated in. 200nm of Ti deposited using vapor deposition through mask depositing material on glass slide. Finger spacing ~250μm.

Being able to fabricate cells using such a complicated current collector configuration illustrates the versatility of this electrolytically formed battery system. For this particular example, titanium metal was deposited using vapor deposition through a mask onto a glass slide substrate. Finger spacing, and finger width on the interdigitated cell design is approximately 250 micron.

Other advantages of starting with one composite are both the cost of fabrication and the overall volume of a packaged cell/chemistry ratio is lower than
conventional batteries. With fewer cell components, the cost of fabrication for a finished, packaged cell is expected to be much less than conventional lithium batteries. Fewer components also allow a greater volume of a packaged cell to be active, energy producing materials.

Another important advantage of the electrolytically formed battery is life span of the cell. After fabrication and before cell charging/formation the cell is simply an inert material packaged between current collectors and hermetically sealed. The lifespan is essentially infinite as no self-discharge or decomposition can occur because the anode and cathode are not present in the uncharged state. Essentially, in an uncharged state this chemistry acts as a reserve cell where it can be stored until needed, charged and used as a power source.

1.7 Organization of Thesis

This thesis focuses on the different aspects of electrolytically formed battery development, illustrating different issues that arose during self-formation and solutions to these problems.

Chapter 2 gives background information on the different electrochemical and structural characterization methods used during this thesis work.

Chapter 3 presents a detailed study on cathode development in an electrolytically formed battery. This study presents data showing that during cell formation the PVP-iodine-Lil based cathode region develops significant electronic and ionic conductivity making it an idea candidate for a cathode material. This
ex-situ study related these conductivity properties, both ionic and electronic, to structural changes that occur in the both the polymer, PVP, and the polyiodide species present.

After an understanding of cathode development is given in chapter 3, chapter 4 will show how two different pathways were taken to allow cell functionality. Using these methods we are able to form a stable interphase over our lithium metal anode. The first method was to alter our starting nano-composite which allowed more stable materials to form as our SEI compared to the LiI SEI layer which is used in today’s non rechargeable lithium/P2VP- iodine pacemaker batteries. The second method was to alter current collector material, adding one more component to assist in formation of a different SEI. Each method offers certain advantages over the other, such as ease of fabrication and overall available energy which will be discussed, but each method allows for formation of a secondary electrolytically formed LiI battery.
1.8 References


[34] http://www.google.com/imgres?imgurl=http://www.webelements.com/_media/compounds/Li/I1Li1-10377512.jpg&imgrefurl=http://www.webelements.com/compounds/lithium/lithium_iodide.html&usg=_A7iSzjc_ec1xHdOqoSV6rWmdgxw=&h=300&w=400&sz=22&hl=en&start=0&sig2=vh_h9tZCHSvei92aREV1mg&zoom=1&tbnid=TbYqCXQB4dPzbM:&tbnw=178&ei=3TldTaTO6bKb4wQHPr6kB&prev=/search?q=lithium+iodide+crystal+structure&um=1&hl=en&sa=N&biw=1280&bih=866&tbm=isch&umsp=34&ved=1t:429,r:1,s:0&tx=94&ty=41


2.0 Experimental

2.1 Introduction

During the investigation of an electrolytically formed battery various characterization techniques were used to understand from both a fundamental view, to actual functionality, how these cells form and cycle. From fabrication of the different materials, using milling techniques, to actual cell assembly and characterization of the different components formed in-situ, an in-depth explanation of each fabrication and characterization technique will be discussed and defined in the following section.

2.2 Materials

The following is a listing of the materials used in our experimental research. Poly (vinyl-pyrrolidone) (Aldrich, Average MW=1×10^4 g/mol), anhydrous LiI beads (Aldrich, 99%), Iodine (Aldrich, ≥99.8% chips), LiI·3H2O (Aldrich, 98%), Indium metal (Alfa Aesar, 99.9% tear drop bead), Aluminum foil (Aldrich, 99.999%), Tin (Puratronic, 99.998%), Lead foil (McMaster Carr), Titanium foil (Aldrich, 99.7%), Gallium (Aldrich 99.99%), and Lithium metal (Johnson Matthey). All materials prepared were kept in a helium atmosphere glove box containing minimal moisture.
2.3 Fabrication of Materials

2.3.1 High Energy Milling

High Energy Milling (HEM) is a process used for many different applications, a few being; the size reduction of particles, thoroughly mixing materials, alloying metals, and the synthesis new materials in either equilibrium or non-equilibrium phases at temperatures and rates in which they would not normally occur [1]. Using this high energy technique for our experimental purposes we are able to both thoroughly mix materials, or force chemical reactions, forming new products.

The fundamental theory behind high energy milling is fairly straightforward. Powders are added to sealable milling cell, milling media is added, and the cell is sealed in typically a neutral environment. The milling process then forces intimate interaction to take place between all materials present by either catching the material between colliding milling media or between the milling media and the wall of the cell. When performing HEM on materials different parameters must be chosen to gain optimal results, such as; the powder to ball mass ratio, which milling media and cell to use (composition and size), time, and speed. Using a planetary ball mill (Fig. 2.1) the sample milling cells rotate in the opposite direction to the center sun disc, typically at a ratio of either 1:1 or 2:1.
For our material mixing and fabrication a Retsch™ PM100 planetary ball mill was used with a zirconium oxide milling cell and media sealed under an inert helium glove box atmosphere. The milling speed was set at 400 RPM and milled for one hour. Once completed, the sealed cell was moved into a glove box to ensure no interaction with the environment.

Anhydrous LiI bead and LiI hydrate were high energy milled at the appropriate ratios to form different hydrations of LiI(xH$_2$O), where x=1, 1.5, and 2. High energy milling was also used for the fabrication of different ex-situ prepared cathode composites. These were different composites containing LiI (anhydrous and hydrated), iodine, and PVP which were mixed at ratios of (yI$_2$:(1)PVP – nLiI:(1)I$_2$) where y = 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0 and n =0.0, 0.5, 1.0, 2.0, 4.0.

High energy milling was also used to create an intimately mixed starting composite of LiI (anhydrous or hydrated) and PVP. Proper amounts of each material was added to the milling cell and milled in order to create a homogenous mixture of the two materials.
2.3.2 Current Collector Material

Half inch disc of different metals (Sn, Ti, Stainless Steel, In, Ga, Pb, Li, and Al) were used as either the positive current collector, negative current collector, or both. When foils were available they were used without modification and discs were punched out at the appropriate size. Indium metal beads were formed into a foil by using a jeweler’s rolling mill and rolling the indium to a size where a half inch disc could be punched out of the film. In the case of gallium metal, the metal was melted between two large stainless steel plates with a shim (200 micron) placed between the plates. The plates were then allowed to cool to room temperature and then removed leaving a gallium foil of 200μm.

2.4 Cell Fabrication

2.4.1 Swagelok Cell Fabrication

Swagelok™ cells were used in the majority of experimental cells. These cells (Fig. 2.2) allow for easy disassembly which assisted in characterization of cycled battery material.
Various amounts of the prepared nano-composites were added to a modified Swagelok™ cell with an insulating Mylar inner layer and pressed to 280 MPa between two stainless steel plungers. These final pellets ranged in thickness from 100-300μm, although for some surface resistance studies pellets were made up to a thickness of 800μm. For some experimental studies, once a pellet was formed through pressing, one or both of the stainless plungers was removed and a half inch diameter metal (Sn, In, Ga, Pb, Li, Al, or Ti) disc was added to the cell. The plunger was then replaced and the cell was lightly pressed to ensure a good contact between added metal and the pellet.

2.4.2 Melt Formed Cells

For planar cell fabrication a melt forming technique was used. This method could only be used for hydrated starting composites due to its lower melting temperature, LiI(1H₂O) = 128C [3], compared to anhydrous lithium iodide.
which melts at 469°C. For melt cell fabrication the overall temperature had to be kept below the degradation temperature of our polymer additive, PVP (MW = 10K) which is approximately 150°C. In cell fabrication the cell was heated to 140°C on a hot plate and then the lithium iodide polymer nanocomposite was added to the cell. Once the material melted it was doctor bladed to ensure a uniform layer across the area of the planar cell.

2.5 Material Characterization

2.5.1 X-ray Diffraction

X-ray diffraction is a characterization technique which is used for a variety of applications with some of the most common ones being; material/phase identification or determination of unit cell parameters. The overall theory of XRD involves an incident beam with a defined direction and angle to a sample. The electromagnetic radiation has a defined frequency and when it strikes an electron, the electrons oscillate at the same frequency. This results in a diffracted X-ray. In the large majority of directions this diffracted energy results in destructive interference, where all diffracted waves are out of phase with one another, cancelling each other out resulting in no energy leaving the sample. In crystalline materials there is regular pattern of atoms, where at some angles the result is constructive interference, where the waves leaving the samples are in phase with one another, meaning energy leaves the sample and strikes the
detector resulting a peak on a XRD spectra. The angles where these peaks occur are defined by Bragg Law which states:

\[ n\lambda = 2d \sin \theta \] (2.1)

Where \( n \) is an integer, \( \lambda \) is the wavelength of the incident beam, \( d \) is the spacing between the planes of the atomic lattice and \( \theta \) is the angle between the incident beam and the scattered planes. This is more easily illustrated in figure 2.3 below.

![Diagram](image)

Figure 2.3: demonstrating theory of X-ray diffraction, where at different angles get either constructive or destructive interference [4].

For our experimental purposes XRD was used for unknown phase identification, determining sample purity, and to confirm the correct phases were formed during a HEM process. X-ray diffraction was performed on a Bruker D8 advanced diffractometer with a CuKα source in the 2θ range from 10-80° at a scan rate of 1.0°/min. The samples were placed on a glass slide under a
Kapton™ film in a helium filled glove box, which was then sealed with vacuum grease to ensure no interaction with the environment.

2.5.2 Raman and FT-IR Spectroscopy

Raman and FT-IR spectroscopy are two absorbance spectroscopy characterization techniques that are typically used in conjunction with one another and characterize materials by measuring the energy difference of vibrational levels within a molecular structure. The reason both techniques are used is that some vibrational transitions that are seen in FTIR cannot be seen using Raman spectroscopy and vice versa. For a sample to show vibration bands in FTIR it must have a permanent dipole moment, while in Raman this is not a requirement.

IR spectroscopy works by passing a beam of infrared light (usually 4000-400cm\(^{-1}\)) through a sample and monitoring the transmitted light at each wavelength. Comparing this transmitted light value with the transmitted light passed through a blank sample holder results in energy differences at specific wavelengths corresponding to vibrational energies within the samples structure. This technique can either be done by scanning each wavelength individually or by using a Fourier Transform IR and scanning all wavelengths at once.

With Raman spectroscopy, a beam of monochromatic light, typically higher energy than the wavelengths measured using FT-IR, is focused on a sample. This energy excites the molecule bonds to virtual energy states, which
then relax emitting a photon. In most cases the released photon or relaxation energy is the same energy as the incident laser resulting in Rayleigh scattering. In some cases the photon energy is slightly less (Stokes shift), or slightly more (Anti-Stokes shift), with this energy difference being related to the samples different vibrational and/or rotational energies. This concept is illustrated in figure 2.4 shown below. Using different wavelength lasers in Raman spectroscopy can affect sample fluorescence, with typically higher energy, lower wavelength lasers resulting in more fluorescence from the sample. Also higher energy lasers can cause sample destruction, sample heating, and be more expensive, although an advantage of using a high energy laser is Raman scattering efficiency is increased giving more pronounced peaks.
Figure 2.4: Showing difference infrared and Raman absorbance spectroscopy techniques. IR energy differences directly relates to the energy difference between a ground vibrational energy state and an excited vibrational energy state of bond within the molecule structure. Raman absorbance occurs excited the material to a virtual energy state, which then relaxes giving off light with an energy difference corresponding to the vibrational energies of a bond in the sample [5].

ATR-FTIR was performed using a Thermonicolet 8700 FT-IR spectrometer with a diamond window. Five hundred and twelve scans were made with a selected resolution of 4 cm$^{-1}$ and ranged from 4000-400cm$^{-1}$. Samples were loaded in a helium filled glove box and sealed using lead tape to isolate the sample from the atmosphere while the IR scans were being run.

Raman spectroscopy was conducted on an Enwave EZRaman-L series Raman system with excitation wavelength of 670nm (Enwave optronics, Inc.). Samples were once again sealed in a helium filled gloved box in a custom made sample holder using a transparent quartz window to be certain the samples remained isolated from the atmosphere. For each sample measured using Raman spectroscopy only 20% = 40mW, of the power source was applied while exposure time was also limited. This low power and sample exposure time insured no laser induced damage occurred, which was confirmed by running multiple scans of the same sample. All FTIR and Raman scans were performed in a dry room (Room temperature 25 °C, humidity < 2%).
2.5.3 AC Impedance and DC Polarization Conductivity Measurements

AC impedance measurements were performed to measure overall sample conductivity (combination of ionic and electronic), while DC polarization methods were used as a method to separate the overall conductivity into its electronic ($\sigma_e$) and ionic ($\sigma_i$) portions. The AC impedance measurements were performed on a combination of two machines, the first being a Solartron SI 1287 impedance analyzer, and the second being a Bio-Logic VMP3 (Bio-Logic, Claix, France). The measurements were run from 1MHz – 0.1Hz and 500 kHz – 0.1Hz respectively for each machine while a 20mV AC potential sweep was applied. All cell impedance was measured by using the Swagelok cell fabrication method previously described. The resistance of the cell was found from the low frequency X intercept in a Nyquist plot (Fig. 2.5). This intercept was found by using a circle data (ZPlot) included with the Solartron software.

Figure 2.5: Representative Nyquist plot [6].
Using this low frequency intercept the overall material conductivity was calculated using the following equation:

\[
\text{Conductivity} = \sigma = \left(\frac{1}{R}\right) \times \left(\frac{t}{A}\right)
\]  

(2.2)

Where \( R \) is the cell resistance (ohm), \( t \) is the thickness of the active material (cm), \( A \) is the surface area of one surface of the pressed pellet, which in a Swagelok cell was 1.226cm\(^2\). Using this equation the final conductivity of the material was found in units of siemens per cm (S/cm).

DC polarization measurements were performed using a Bio-Logic VMP3 (Bio-Logic, Claix, France). Using DC polarization, the overall conductivity was separated into its electronic and ionic portions through the use of ionically blocking electrodes. A 200mV potential above open circuit voltage was applied to a Swagelok cell and the resulting current was monitored as a function of time. A representative polarization curve is shown in Fig. 2.6. At the start of the polarization measurements the initial current was proportional to the overall conductivity of the cell. As the polarization continued, all ions present in the material were polarized toward their oppositely charged current collectors and the current dropped until it reached a plateau. This constant current reading represented the electronic conductivity of the cell, and the difference between the starting current and plateau current represents the ionic conductivity.
Figure 2.6: DC polarization of a sample for separation of ionic and electronic conductivity.

In general, the overall conductivities of the composites using the AC impedance and DC polarization methods showed a strong agreement for all samples tested. Although there were slight differences, this was most likely due to the difference in polarization voltage (DC = 200mV, AC impedance = 20mV). One concern was possible redox or shuttle mechanisms, in samples containing large concentrations of iodine, induced by an I$^-$ $\leftrightarrow$ I$_3^-$ reaction, but as shown in the following figure there is a very mild effect on conductivity as a function of bias voltage.
Figure 2.7: Conductivity of sample at different bias voltages, measured using AC impedance spectroscopy (20-640mV).

In determining the material conductivity, some contact resistance issues did occur between the electrodes and the composite, and this problem remained fairly constant for all compositions. The texture of the composites changes with the ratios of I₂, PVP, and LiI (monohydrate or anhydrous). The compositions with higher conductivities resemble a thick paste, while some of the composites remain in a powder form. To isolate and identify the degree of contact resistance, soft indium electrodes were placed against the pressed pellets and lightly pressed to ensure good contact between the indium and the formed pellet. Cells of different thickness were made and their conductivity was measured using AC impedance for both the stainless and indium current collectors. The resistance was constant for different thickness cells using indium electrodes, and
when stainless was used the resistance reached a constant as thickness increased. This can be seen in Fig 2.8. where a sample with a 0.5:1:1 ratio of I$_2$:LiI:PVP was used.

![Resistance vs. Thickness](image)

**Figure 2.8:** Change in resistance as a function of thickness.

When using AC impedance to determine the resistance of the material, the ratio of current collector area to thickness is used. As the thickness of our cells increased the effect area has becomes less and less of a factor, until it is negligible and the resistance of the material reaches a constant. Independent of material in the composite, samples using stainless steel current collectors all
gave a curved resistance vs. thickness plot similar to that shown in Fig. 2.8, again confirming that the contact problem was present is all samples.

The indium current collectors could only be used for cells containing a high percentage of lithium iodide. When used with cells containing high concentrations of iodine, the indium and iodine would react making an insulating \( \text{InI}_3 \) layer, affecting the measured cell resistance. Since the majority of the samples tested were around 0.25 mm in thickness, the conductivity of these samples compared to a sample with near ideal contact (Indium CC) had similar offsets.

### 2.6 Electrochemical Characterization

Electrochemical characterization was performed using either a Biologic Macpile cycler or a Biologic VMP3 (Claix, France). Experiments were run in both potentiostatic and galvanostatic modes. For electrolytically formed hydrated cells the material was charged potentiostatically at 4.0V and discharged down to a cutoff voltage of 2.0V. In anhydrous formed cells where an alloying negative current collector was used, the cells were charged potentiostatically at 3.4V and discharged down to a cutoff voltage of 1.4V. Alternate charge protocols were also utilized using a combination of galvanostatic and potentiostatic segments which will be noted where used in the results section.
2.7 References

3.0 Transport Properties of a Polyiodide Based Cathode for an Electrolytically Formed Battery (EFB)

3.1 Introduction

During polarization and formation of an electrochemically self-formed lithium iodide cell, lithium metal is plated down as the cell anode and the iodide ions formed coordinate with our polymer additive to form a polyiodide based cathode. Therefore as a cell is charged, stoichiometrically it moves from a sample containing exclusively lithium iodide and PVP, to one which contains lithium metal, lithium iodide, PVP, and iodine. As the charging continues the ratio of I$_2$:PVP and I$_2$: LiI increases. The following chapter presents an understanding of the evolution of conductivity (ionic and electronic), and structural properties for different ratios of LiI (anhydrous and monohydrate), I$_2$, and PVP. As well as the effect alternate alkali halide salts such as KI have on these characteristics. Using the vibrational characterization techniques outlined in the experimental sections we can see how polyiodide conductivity is developed from both the structure and the polyiodides and the polyiodide-PVP interaction. Ex-situ composites are prepared to represent various cathode materials that would form in an electrochemically self-formed cell.
3.2 Structural Characterization and Conductivities of a Pure I$_2$: PVP System

PVP is a polymer that contains a carbonyl group on its pyrrole ring which is well known to complex with metal cations. The carbonyl group can induce a redox disproportionation [1] or large degree of polarization in the iodine leading to the formation of polyiodide groups.

\[ \text{PVP + nI}_2 \rightarrow \text{PVP-I}_{2n}^- \]  
(3.1)

Polyiodides are known semiconductors and can impart good electronic conductivity depending on the polyiodide length, structure, and percolation with other polyiodide chains. Raman spectroscopy was utilized to study the influence of PVP on polyiodide formation. Fig. 3.1 shows the Raman spectra of samples containing different ratios of iodine to PVP.
As the amount of iodine is increased, the peak red shifts from the 186 cm\(^{-1}\) band characteristic of pure I\(_2\) to lower wave numbers. This is consistent with the formation of various lower average oxidation state polyiodide chains. The characteristic wavelengths of various polyiodides have been established in literature. However, changes in the excitation wavelength, intensity of laser, and compound associated with the polyiodide formation can effect the location of this region along with the intensity of peaks in one region relative to another [2]. In general, I\(_3^-\) polyiodide chains appear between 110 and 130 cm\(^{-1}\). Multiple peaks can arise in this region depending if the band is from symmetrical or
asymmetrical stretching of the molecule [2]. It should also be noted that longer polyiodide chains (≥ I₇⁻) containing an I₃⁻ within their system will also show a peak in the 110-120 range if the tri-iodide is symmetric or a peak in the 130-155 range if the tri-iodide is asymmetric [3]. Penta-iodide units, I₅⁻, show peaks between 140 and 165cm⁻¹. This large range is due to the fact that penta-iodide units can either be comprised of an I₃⁻ and an I₂ molecule, or 2I₂ and an iodine ion [3]. For longer polyiodides, the peaks are located between 170cm⁻¹ and that of pure iodine, 186cm⁻¹. In this region it is difficult to distinguish each polyiodide chain to a distinct peak location, however, as polyiodide chain length is increased, there is a decrease in I-I bond distance, and this distance has a linear relation to peak location within the spectra [2,4]. An I₇⁻ unit would have more weakening of the I-I bonds leading to a peak at a lower wave number than that of an I₉⁻ chain.

Samples with low ratios of iodine to PVP, such as a ratio of 1:10, form a majority of I₃⁻ units with small amount of higher order polyiodides present. The triiodide Raman peaks in these samples, and the I₃⁻ peaks presented in our higher iodine concentration samples are located at the same energy. Based off this relationship, it is believed that our systems contain both pure I₃⁻ units along with symmetric and asymmetric I₃⁻ units contained in the longer polyiodide chains.

Raman spectra also confirm a saturation of iodine occurring within the composite at an I₂:PVP ratio greater than 1.5. This can be seen in Fig. 3.1. As more I₂ is added above a concentration of 1.5-1, the peak begins to blue shift toward that of molecular iodine (186cm⁻¹) suggesting free I₂ is formed. It is
critical to note that just the presence of $I_2$ in the locale of PVP is sufficient to form the polyiodides and no iodide content from a salt such as LiI is necessary, this can be seen in all samples represented in Fig. 3.1.

If the PVP induced formation of polyiodides were the result of the aforementioned redox disproportionation, the coordination of the polyiodide unit should have a noticeable effect on the vibration band of the PVP carbonyl group as determined by FTIR. In FTIR spectroscopy, the carbonyl peak is located at 1665 cm$^{-1}$ (Fig. 3.2).

![Figure 3.2: FTIR of pure Poly (vinyl-pyrrolidone). 10,000MW. 500 scans in the range of 4000-600 cm$^{-1}$](image)

Fig. 3.3 shows the FTIR spectra of the PVP-$I_2$ composites discussed above along with the spectra of pure PVP.
When I\textsubscript{2} and PVP composites are reacted to form polyiodides, the carbonyl peak at \(\approx1665\text{ cm}^{-1}\) systematically decreases in intensity and a new peak at \(\approx1600\text{ cm}^{-1}\) forms. As the ratio of I\textsubscript{2} : PVP (monomer unit) increases, the intensity of the new 1600 cm\(^{-1}\) peak increases systematically. When the iodine to PVP ratio is \(\geq 2\), there is little change in peak intensity between the two peaks. This suggests that the coordination of polyiodides with the carbonyl is saturated. This is in complete agreement with the aforementioned polyiodide Raman study where compositions at \(\geq2:1\) ratio of I\textsubscript{2} : PVP resulted in a phase saturation and the subsequent formation of a two phase system of PVP:I\textsubscript{n}\(^-\) and molecular iodine. During the addition of iodine to PVP no other changes to the spectra were observed.
The polyiodide formation shown by the Raman parallels the PVP-\(I_n^-\) complex formations shown in the FTIR results, and as we will show, were found to correlate well with the development of electronic conductivity. From the interpretation of the two previous spectra we would expect the peak in electronic conductivity to occur when there is the maximum number of polyiodide chains with the least volume of pure iodine in the composite. In actuality this is the case. As shown in Fig. 3.4, the maximum in electronic conductivity occurs at an \(I_2\):PVP ratio of 1.5, while the maximum for the ionic conductivity, of mobile \(I^-\), occurs at a ratio of 2.

![Figure 3.4: Conductivity of \(I_2\):PVP samples, as a function of the \(I_2\) concentration](image)

The maximum in electrical conductivity is consistent with the theoretically smaller bandgap and higher conductivity expected for continuous chains of \(I_3^-\) as opposed to chains \(\geq I_5^-\) [5]. In short, these results show the electronic
conductivity is increased by the addition of iodine to PVP and that conjugated polymers such as P2VP are not necessary for the development of significant electronic conductivity. For samples containing only iodine and PVP the maximum electronic conductivity found was \(2.0 \times 10^{-6}\) S/cm, where the peak conductivity for iodine:P2VP composites is \(~1 \times 10^{-3}\) S/cm and occurs at an \(I_2: P2VP\) ratio of 8:1. Although the value of electronic conductivity can be perceived as low, it is on the order of the Li ion conductivity in a typical solid state LiI electrolyte. It should again be restated that a P2VP conjugated polymer cannot be utilized in an electrochemically formed cell due to the need for high temperature annealing after the cell is formed. From Fig. 3.4, it can be seen that the majority of the total conduction comes from electronic conductivity, and that the I\(^{-}\) ion, although present, contributes only slightly to the overall conductivity peak.

### 3.3 Effect of Adding Lithium Iodide

Even though polyiodides were formed without the addition of an ionic iodide salt, it was still of interest to observe the effect of lithium iodide on the resulting electrical and structural properties. To each of the \(I_2\)-PVP composites discussed above, various amounts of LiI were added in concentrations ranging from a LiI-\(I_2\) ratio of 0.5 to a ratio of 4. As LiI is added to samples containing low concentrations of \(I_2\), a shift in the carbonyl band similar to the pure \(I_2^-\) PVP composites (1600 cm\(^{-1}\)) occurs. A shift also occurs with the PVP C-N bands at 1268 and 1283 cm\(^{-1}\) which was not observed with pure iodine addition. From the
initial addition of LiI a blue shift is seen in the C-N band. Increasing the LiI concentration results in a larger shift up to a LiI : PVP ratio of 1 (Fig. 3.5).

![Graph showing blue shift in C-N bands](image)

**Figure 3.5:** Blue shift in the C-N bands as a result of coordination with LiI. Ratios shown are LiI-I\textsubscript{2}-PVP.

As the shift occurring in the C-N bands occurs for samples containing LiI only, the I\textsuperscript{-} ion could be coordinating with the nitrogen, and the Lithium may be interacting with the carbonyl creating a shift similar to that seen in the I\textsubscript{2}-PVP systems.

### 3.3.1 Electronic Conductivity
For pure $I_2$:PVP compositions, a specific $I_2$: PVP (1.5:1) ratio (Fig. 3.4) results in the highest electronic conductivity. Similarly, there is a very sharp and distinct maximum for the electronic conductivity at a $I_2$ : PVP ratio of 1.5 ($I_3^-$) (Fig. 3.6-B) regardless of the Lil content. This suggests the lithium salt ($Li^+$ and $I^-$) plays little role in the development of the electronically conductive polyiodide network after initial additions. Although not as dramatic as the additions of $I_2$, the initial addition of Lil to the composite did increase the electronic conductivity approximately an order of magnitude for the sample with a 1.5-1 $I_2$ : PVP ratio. After which, further addition of the electronically insulating Lil is believed to only take up volume ($Lil:I_2 \geq 1:1$) resulting in the observed decrease of the electronic conductivity of the composite.
Figure 3.6: The ionic (3.6-A) and electronic (3.6-B) conductivities of samples containing a fixed ratio of LiI to I\textsubscript{2}, varying the I\textsubscript{2} to PVP ratio

3.3.2 Ionic Conductivity

The peaks in the ionic conductivity plot of composites containing LiI (Fig. 3.6-A) cannot be explained as simply as the peaks in electronic conductivity, due to the fact that the composites contain two ions (Li\textsuperscript{+}, I\textsuperscript{-}) which interact with each other and most likely interact differently at different ratios. At lower iodine concentrations the trend seems to follow that of the electronic conductivity, giving a conductivity ridge at 1.5-1 \( \text{I}_2 : \text{PVP} \), pointing toward the fact that at these lower iodine concentrations the majority of the ionic conduction comes from the I\textsuperscript{-} ion and the polyiodide chains. While at higher iodine concentrations (I2:PVP > 2:1) the peaks occur less uniformly and this may be explained by the dual ion conductivity.
The two previous plots again confirm that the ratio of I$_2$:PVP is primarily responsible for the peaks and conductivity ridges in both the ionic (possibly related to I$^-$) and electronic conductivity. This suggests that the majority of conductivity comes from the polyiodide chains. If this were indeed the fact then a change in the alkali salt should have little to no effect on the conductivity. To investigate this effect, KI was substituted for LiI. Indeed, little change in conductivity (ionic or electronic) was observed. The fact that the ionic conductivity did not change although a drastic change in alkali size was induced suggests that the majority of the observed ionic conductivity may be that of the iodide ion. It should be noted that the salt to polymer ratio is much greater than one in these samples, at which point it is believed that no salt dissociation or coordination is occurring and the salt simply acts as an insulator.

<table>
<thead>
<tr>
<th>Mole %</th>
<th>XI:I$_2$</th>
<th>S/cm AC</th>
<th>S/cm DC</th>
<th>$\sigma_E$</th>
<th>$\sigma_I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI</td>
<td>10</td>
<td>10</td>
<td>1.79E-07</td>
<td>2.26E-07</td>
<td>2.16E-07</td>
</tr>
<tr>
<td>LiI</td>
<td>10</td>
<td>10</td>
<td>1.22E-07</td>
<td>2.08E-07</td>
<td>1.99E-07</td>
</tr>
</tbody>
</table>

Table 3.1: Demonstrating effect alkali halide salt plays in polyiodide formation and therefore conductivity. Small change in ionic conductivity noticed a change in salt suggests polyiodide species are major ion conductors in composite.

3.3.3 Structural effect of Lithium Iodide
The independence of the peak conductivity on the salt composition and concentration suggests that, after the initial addition, minimal interaction between the salt and the polyiodide formation occurs. In order to investigate this interaction Raman studies were performed as a function of either I$_2$:PVP (0.5:1 → 4:1) ratio at a fixed Li$_2$ to I$_2$ ratio (1:1) or as a function of Li$_2$ content for a fixed I$_2$:PVP (1.5:1) ratio. Raman spectra of various I$_2$:PVP ratios at a fixed Li$_2$ content show significant changes in peak positions and ratios as a function of iodine content (Fig. 3.7).

Figure 3.7: Raman Spectra from 60 to 220 cm$^{-1}$ with a fixed Li$_2$-I$_2$ ratio. Changing the ratio of I$_2$-PVP
In sharp contrast to this result, when the I$_2$:PVP ratio is fixed and the LiI content is varied (LiI: I$_2$ ratio of 0:1 $\rightarrow$ 4:1), very little change in the Raman spectra occurs (Fig. 3.8), supporting little interaction between the salt and the polyiodide as shown in the conductivity plots. The iodine: PVP ratio (1.5:1) in Fig. 3.8 is the ratio that gave the highest electronic conductivities.

![Figure 3.8: Raman spectra of samples containing samples of fixed I$_2$-PVP ratio altering the LiI content. Three is little to no shift in spectra as change LiI Mole %.

The systematic approach to this system would be to expect that as more I$_2$ is added to the system, longer polyiodide chains would grow until a saturation of iodine occurred. From the previous Raman and FTIR spectra this saturation...
occurs where there is the peak in electronic conductivity, which is at 1.5 I\textsubscript{2}:PVP. As a greater concentration of iodine is added, the ratio of peaks increases (higher order polyiodides : I\textsubscript{3}⁻) until this saturation point is reached. At this point further addition of iodine induces a much smaller change in ratios, and a blue shift in the higher order polyiodide peak towards molecular I\textsubscript{2} (186 cm\textsuperscript{-1}). This effect can also be seen in Fig 3.7.

A three dimensional plot was made for each component of the conductivity; ionic and electronic. These plots more easily illustrate the high conductivity ridge that occurs at 1.5 I\textsubscript{2}:PVP for a very wide range of compositions. The compositions in Fig. 3.7 and 3.8 each represent a line in the following set of 3D plots, perpendicular to one another. The samples in Fig. 3.8 correspond to the high conductivity ridge in electronic conductivity shown in Fig. 3.9.
As can be seen in this figure, electronic conductivity is viewed to systematically decrease as a function of Lil content again confirming the structural results that it has little role in polyiodide formation at an Lil : PVP ratio greater than 1. Although this initial addition of Lil to samples did increase electronic conductivity very little change in Raman spectra was observed. Figure 3.10 shows the ionic conductivity of the same samples shown in figure 3.9.
Figure 3.10: 3-Dimensional plot of the ionic conductivity of samples containing different mole percents of Lil (anhydrous), I₂ and PVP.

3.4 Effect of Hydration on Structure and Conductivity

In order to investigate the effect of hydration on the polyiodide and transport properties, Lil monohydrate was utilized as the source of Lil. Lil (1)H₂O has a perovskite ABO₃ structure. The A positions are filled with I⁻ ions. The center of these iodine cubes, B position, holds the water molecule, and one third of the FCC positions are occupied by Li⁺ ions [6]. Raman spectra were collected
to compare the polyiodide formation as a function of samples utilizing anhydrous
LiI vs. monohydrate LiI for a variety of compositions. In almost all spectra, the
samples contained two main peaks in the region between 110 cm\(^{-1}\) – 220 cm\(^{-1}\).
The peak located at \(\approx 120\) cm\(^{-1}\) is from I\(_3^-\) units, while the peak located between
170 cm\(^{-1}\) and 185 cm\(^{-1}\) is from the longer >I\(_5^-\) polyiodide chains.

The Raman spectra of twenty eight sample pairs (one anhydrous, one
monohydrate), were compared, and the majority of spectral comparisons show
nearly identical peak location and intensity between the anhydrous and
monohydrate sample. In the few pairs that did not coincide well, the spectra with
the lower energy (shorter chain), higher order polyiodide peak (170-185 cm\(^{-1}\))
showed a more intense I\(_3^-\) peak.

Similar to the anhydrous samples, the monohydrate samples exhibit a
high conductivity ridge in the electrical conductivity plot (Fig. 3.11). This ridge is
located at the same ratio of I\(_2\) : PVP (1.5:1) as for the anhydrous samples, again
proving that it is only the ratio of iodine to PVP that is responsible for the
polyiodide formation, and thus conductivity in both the hydrated and anhydrous
samples.
Figure 3.11: 3-D plot of electronic conductivity for samples containing LiI-monohydrate.

In a comparison of conductivities between the anhydrous and hydrated samples, hydration does increase the absolute conductivity in the composites, and the majority of this increase occurs in the ionic conductivity. Figure 3.12 shows a 3D plot of ionic conductivity for the hydrated composite.
Out of the twenty eight sample pairs investigated, the electronic conductivity increased an order of magnitude for two of these pairs, and the average increase due to hydration was approximately 330%, while the ionic conductivity increased on average around 845%. Fig. 3.13 is a plot comparing the ionic conduction between the samples made using anhydrous and monohydrate Lil. The general trends seen in this plot are representative for samples containing different ratios of Lil to I$_2$. 

Figure 3.12: 3-D plot of the ionic conductivity of cells containing Lil-monohydrate.
Figure 3.13: Comparison of sample conductivities for samples containing the same ratios of LiI:I₂:PVP changing hydration.

The increase in ionic conductivity can be explained by an increase in the conductivity of lithium ions, iodide ions, protons or a combination of all three. Initial tests were done to separate the total ionic conductivity into its Li⁺ and I⁻ portions using a combination of blocking and non-blocking electrodes. Although the initial results look promising, a more in-depth analysis has not been performed up to this point and will be discussed in a future manuscript. Pulse gradient NMR may be the best approach to accurately isolate the ion transport behavior.

If a reaction leading to the increase in the electronic conductivity involved the hydration during the milling process, or a dissociation of the water from the
LiI, we would then expect the electronic conductivity to increase as the percentage of LiI(1)H₂O increased. This is not the case. One explanation is that the protons are assisting in the formation of higher conducting $I_3^-$ [7]. At this ratio of $I_2$:PVP, there may be the maximum number of cross links between triiodide species, possibly induced by hydration, creating an electronically conductive network of almost infinite polyiodide species through the polyiodide based composites.

3.5 Conclusions

The search for an electrochemically stable additive that induces highly intrinsically conductive polyiodide networks has revealed that PVP is an excellent candidate. PVP has the ability to form high concentrations of stable polyiodide species, which result in an electronically and ionically conductive material. The development of ionic and electronic conductivity is not due to the introduction of holes to the polymer structure, as seen in the P2VP iodine composites, but from the polyiodide species themselves. When ratios of $I_2$:PVP and lithium iodide (anhydrous and monohydrate) are milled together at various concentrations, a high electronic conductivity ridge at a constant $I_2$: PVP ratio develops. This peak ratio of iodine to PVP of 1.5:1 coincides with the saturation of the polymer by the iodide species as shown in both FTIR and Raman spectra. This trend was found to be independent of LiI, KI or the addition of hydration.
3.6 References

4.0 Pathways to Enabling Solid State Electrolytically Formed Batteries; The Solid Electrolyte

4.1 Introduction

Polarizing/charging an anhydrous lithium iodide/PVP composite between two stainless steel current collectors results in the formation of soft, healable shorts in an EFB. Healable shorts are defined for the purposes of this manuscript as soft shorts which disappear when the charging current is removed and the cell reverts to an OCV near that of a lithium polyiodide couple. As demonstrated in Fig. 2a, polarizing the composite at 4V leads to extreme spikes in current in direct correlation to the formation of electronically conductive dendrites which transverse the composite. There are two possible sources for these electronically conductive dendrites. First, despite the presence of a truly solids state electrolyte, it is possible that when lithium metal is plated on the stainless steel negative current collector, lithium dendrites can form [1]. The short develops when the lithium metal grows through the electrolyte material coming in contact with the highly electronically conductive in-situ formed polyiodide cathode (Figure 4.1-C).
Figure 4.1: A: Schematic of an uncharged cell. B: representation of ideal anode and cathode development. C and D: Two possible situations where soft shorts form in an electrochemically self-formed cell beginning with an anhydrous LiI starting nanocomposite.

Scenario two would occur where the highly conductive polyiodide cathode growth occurs throughout the electrolyte material contacting the lithium anode also resulting in healable shorts (Figure 4.1-D). Figure 1 also includes a schematic of an uncharged EFB (Figure 4.1-A), and a charged/formed EFB (Figure 4.1-D). In
both cases where dendrite growth occurs, the electronically conductive lithium and polyiodide come in contact as the dendrite develops and act as a shorting point for the electronic current. If the cell is relaxed, OCV redevelops as an insulating LiI is reformed at the interface. As such, an EFB was not able to be developed with simple anhydrous LiI.

Two pathways were taken to correct the formation of these healable shorts, which in turn enabled the in-situ formation and subsequent cycling of a lithium iodide EFB. One, engineering the starting composite to form an in-situ formed stable solid electrolyte interphase (SEI) over the plated lithium metal anode thereby eliminating the possibility of contact between the anode and cathode. The second pathway uses a different material for the negative current collector which both alloys with lithium, eliminating lithium dendrites, and which reacts with our cathode forming a highly insulating material. The first pathway discussed will be formation and characterization of a SEI in a lithium iodide EFB.

4.2. SEI formation

Within traditional Lithium - iodine battery chemistry a very effective LiI "SEI" forms when one brings in contact lithium and a polyiodide containing material. In the EFB the electrolytic action destroys such interphase as it is the basis for the cell formation. Therefore SEIs of higher resistance to electrolytic decomposition are required. Table 4.1 shows a number of lithium salts that can
form in our cell as possible SEI materials with their corresponding decomposition potential.

<table>
<thead>
<tr>
<th>Possible SEI Material</th>
<th>Redox Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/LiH/H₂</td>
<td>0.35V</td>
</tr>
<tr>
<td>Li/LiOH</td>
<td>2.24V</td>
</tr>
<tr>
<td>Li/LiI/I₂</td>
<td>2.79V</td>
</tr>
<tr>
<td>Li/Li₂O/O₂</td>
<td>2.91V</td>
</tr>
<tr>
<td>Li/Li₂O₂/O₂</td>
<td>2.95V</td>
</tr>
</tbody>
</table>

Table 4.1: Possible SEI components that can form in a hydrated EFB with corresponding redox potential.

As can be inferred from table 4.1, one approach is developing a Lithium oxide based (Li₂O, Li₂O₂) solid electrolyte interphase.

Using a hydrated lithium iodide starting composite [2], we have shown the development of a stable SEI in hydrated EFB compared to cells formed using anhydrous composites. This more stable SEI is believed to form from a reaction between the lithium metal anode, which is deposited during the charging process, and the water of hydration that is present in the original starting composite. The hydrated SEI layer forms a strong boundary across the anode eliminating the formation of soft shorts. Proof of this effectiveness can be seen in Figure 4.2, where the anhydrous EFB develop high current shorts after a brief charge period due to the lack of a stable SEI and soft shorts occurring. In contrast, hydrated samples, where the lithium iodide is approximately a 50-50
composite of LiI-H$_2$O and LiI 2H$_2$O, continue to charge for well over 200 hours without the formation of soft or healable shorts as evidenced by the low current.
Figure 4.2-A and 4.2-B: Difference in current evolution profiles for two hydrated (B) and two anhydrous (A) samples during charge at 4V. Anhydrous samples short after short charge period, while hydrated samples show no shorts forming in over 150 hours of charging.

Further proof of the formation of a stable SEI layer can be found in AC impedance measurements. AC impedance experiments were previously performed by our group using one lithium metal current collector (equivalent of a charged cell) and one stainless steel current collector [2]. When using a hydrated composite of lithium iodide and PVP there is a large change in impedance spectra from a reaction between the lithium metal anode and the hydration of the composite, developing a semicircle corresponding to considerable charge transfer resistance, shown in Fig. 4.3-A labeled R$_2$. 
Figure 4.3: A: AC impedance spectra of a hydrated LiI:PVP nano-composite. R1 corresponds to material resistance using two stainless steel current collectors while R2 shows resistance of cells using one stainless steel and one lithium metal current collector. B: AC impedance spectra of an EFB showing similarities between our ex-situ SEI impedance and impedance from a formed cell. R3 represents the cathode impedance.

The product of this Lithium metal-LiI(H₂O) reaction is referred to as an Ex-Situ formed SEI. In cells prepared with anhydrous materials there is no change in impedance spectra with time. From the lack of change in our anhydrous composites impedance spectra, this experiment also confirms that lithium metal does not react with our polymer additive PVP. This ex-situ formed SEI layer shows similarities in both shape and magnitude with that of an actual charged hydrated EFB, when comparing AC impedance spectra (Fig. 4.3-B).

4.3 Ex-Situ formed SEI characterization

From the impedance spectra it is believed that our increase in cell impedance from the use of a lithium metal current collector is caused by a thin SEI layer forming on the lithium metal surface. Although XPS and TEM/EELS would have given detailed SEI information, the reactivity of the anode during physical transfer precluded us from using such techniques with a degree of
Using atmosphere controlled FTIR and XRD we are able to characterize this ex-situ formed SEI layer.

Fig. 4.4 shows a FTIR spectra of the lithium metal surface cleaved from two ex-situ formed SEI samples along with a LiOH standard and the original hydrated LiI composite. Both ex-situ formed SEI samples show a broad hydration peak, 3200 cm\(^{-1}\)-3500 cm\(^{-1}\), comparable to our starting composite, caused by residual LiI\((x\text{H}_2\text{O})\) remaining attached to the now formed SEI layer. The SEI FTIR spectra also show one distinct peak at 3675 cm\(^{-1}\), a doublet peak located at \(\sim3620\) cm\(^{-1}\), along with a small absorbance peak at 3575 cm\(^{-1}\).
Figure 4.4: FTIR spectra showing a comparison of absorbance spectra for; LiI (3H$_2$O), two ex-situ formed SEI layers and a LiOH standard.

Based on agreement with a standard, one of the SEI absorption peaks is from the formation of a LiOH layer on the lithium surface. It should be noted that lithium hydroxide is not thermodynamically stable against Lithium metal and some amounts of Li$_2$O and LiH would be expected to form at the lithium surface. Also, LiH reacts with hydration forming LiOH and hydrogen gas so LiH would not be expected to be found on the surface of the SEI, against the hydrated nano-composite, but more towards the Li [3]. XRD of the SEI clearly reveals the presence of LiH along with the aforementioned FTIR identified LiOH (Fig. 4.5)
In an attempt to recreate the remaining unknown FTIR absorbance peaks present in our ex-situ formed SEI FTIR spectra, located at 3575 and 3620 cm$^{-1}$, various hydrations of LiI and anhydrous LiOH were mixed in a mortar and pestle under helium atmosphere. After mixing a 1:1 ratio of LiI(A):LiOH no change in absorbance spectra is seen and the only FTIR absorbance peak present is from lithium hydroxide (Fig. 4.6). Mixing a 1:1 molar ratio of LiI(1H$_2$O) with LiOH in a mortar and pestle causes a large change in absorbance spectra from that of the raw materials. The lithium hydroxide peak is still present in this material along with three new peaks forming, which are in excellent agreement with the unknown peaks present in the ex-situ SEI FTIR. Mortar and pestle mixing a 1:1 ratio of LiI(3H$_2$O) with LiOH also caused a large change in absorbance spectra with the formation of new peaks.
Figure 4.6: FTIR spectra comparing the ex-situ formed SEI layer with that of a mortar and pestle mixed samples. All samples were 1:1 molar ratio of LiI(xH$_2$O):LiOH, where $x = 0, 1, 3$. Also shown in spectra is hydrated lithium iodide standard.

It should be noted that all that is needed for the formation of these absorbance peaks is hydrated LiI in the locale of LiOH and no high energy milling or reaction be forced. The XRD spectra of the mortar and pestle mixed 1:1 LiI(1H$_2$O) with LiOH material, Fig. 4.7, revealed the formation of no new peaks.
Figure 4.7: XRD spectra of the mortar and pestle mixed 1:1 molar ratio of LiI(H2O):LiOH, showing no new crystal phases formed.

The spectra shows only the initial raw LiOH and LiI (1H2O) components and the formation of no new crystalline phases that can be attributed to the newly developed FTIR bands.

Since a strong correlation was observed between the FTIR of the mortar and pestle mixed samples of LiI(1H2O) and LiOH and our ex-situ formed SEI, various ratios of these materials were mixed to observe if peak location changed as a function of the ratio of raw materials. Fig. 4.8 shows the FTIR spectra of a 1:4, 1:1 and 2:1 ratio of LiI(1H2O): LiOH.
Figure 4.8: FTIR spectra of ex-situ formed SEI compared with LiI(H$_2$O) and LiOH mixed at different ratios.

No shifts in peak location are noticed. Also, the relative intensity of the unknown peaks appears to remain at a constant ratio with our known LiOH absorbance peak, suggesting that our LiOH plays an important role in the formation of our unknown peaks.

In summary new FTIR absorbance peaks were formed through a light interaction between LiOH and LiI(1H$_2$O), and no new crystalline phases present in an XRD of the material. An examination of the literature related to FTIR performed on hydroxyl containing materials, and the interaction of these materials with different compounds was performed [4,5,6,7]. Based on our literature research it is
believed that as our hydrated lithium salt comes in contact with lithium hydroxide there is the formation of hydrogen bonds between these materials, consistent with the low energy interaction require to develop the new vibration band in the FTIR spectra. The red shifted peaks present in our spectra, relative to that of a pure LiOH sample, are attributed to the formation of these hydrogen bonds, and one author noted the extent of this shift is a direct factor of the number of bonds [5]. This hydration-hydroxide coordinated shift has been noted in different materials, with shifts of different energy being dependent on the materials involved.

4.4 In-Situ formed SEI characterization

Forming a stable SEI enabled the concept of an EFB, which in turn allows the formation of a secondary EFB similar to the cell shown in Fig. 4.9. For Fig. 4.9, the charge current was 15mA charged to 20% theoretical capacity and a discharge current of 2.5μA was used. Although efficiency was not 100%, (~20% for cell shown) the importance of the SEI cannot be understated.
Figure 4.9: Voltage profile and applied current for hydrated LiI starting composite showing cell formation and cyclability.

Efficiency of ~60% can be achieved in EFBs at lower depths of charge, but to obtain competitive energy densities cells should be charged to higher percentages. The following figure shows discharge efficiencies for EFBs charged to different percentages of the total capacity.
Figure 4.10: Discharge efficiency for EFBs for cells charged to different percentages of the total available capacity.

All characterization to this point was for an ex-situ formed SEI where bulk Li metal is placed in direct content with our salt nanocomposite. This was to give enhanced spectral response allowing characterization of the sample. Following the interpretation of our ex-situ SEI spectra, FTIR was performed on the in-situ formed SEI, which forms on the deposited Li metal. Figure 4.11 shows the FTIR spectra of an in-situ formed SEI sample compared to a sample formed by the ex-situ technique (i.e. placing lithium metal against a hydrated composite).
Figure 4.11: Comparison of an Ex-situ and In-situ formed SEI layer vs. material a short distance from the in-situ formed SEI.

The spectra of the in-situ sample contained the exact bands that were identified in the ex-situ FTIR (LiOH and LiOH-LiI-H₂O complex), but in much different intensity ratios. The in-situ sample spectrum shows the formation of LiOH occurring at the anode/composite interface as a component of the SEI layer. Also, it was observed that as FTIR spectra were taken of the battery material after charging, the LiOH and coordinated hydroxyl peaks present disappeared as the distance from the anode increased, confirming that LiOH formation is only occurring near the anode surface, this is also shown in Fig. 4.11.

The formation of these new hydroxyl peaks would be expected in our in-situ formed SEI. As shown earlier when LiOH and LiI(1H₂O) are lightly mixed, new peaks are formed from a hydrogen bonding occurring between hydration and the
hydroxyl group in LiOH. As our SEI layer is formed in an EFB, the lithium anode reacts with the hydration present in our starting composite forming LiOH which would be in contact with more hydrated battery material causing an effect similar to our earlier experiments. Figure 4.12, shows a schematic of what we believe our SEI composition to be and where each component is located within the SEI structure.

![Figure 4.12: Schematic showing possible SEI composition as a function of distance from the anode](image)

Initially, our plated lithium metal anode will react with the hydration forming LiOH. Over time the LiOH material adjacent to our anode will decompose and for a region of both Li₂O and LiH. Although small amounts of LiH have been identified in aforementioned studies, the Li₂O could not be isolated. It is to be expected that this inorganic phase to be a sub 50nm Li₂O insulating layer due to its self-limiting growth and below the detection limits of the characterization used in this manuscript.
4.5 Enabling Anhydrous Lithium iodide nano-composite

While adding hydration to the starting composite enables formation of an EFB, there is a significant loss in available volumetric and gravimetric energy along with concerns of impedance increase as a result of lithium interaction with excess hydrate with storage time. There are a few ways to add a preformed SEI, however this is against the philosophy of this work and this challenge must be addressed via in-situ formed methodologies.

4.5.1 Dual Functionality Current Collector

The use of an alloying current collector would impart a lateral driving force for the uptake of lithium at the anode and should greatly eliminate the formation of lithium dendrites. Silver metal is well known to alloy with lithium and preliminary experiments were accomplished using an anhydrous lithium iodide starting composite with a silver negative current. Upon partial formation of the cell, a lower OCV developed (~2.6V) consistent with Li-Ag formation [8]. Despite this, little to no improvement was seen in the prevention of healable/soft shorts during the first formation charge relative to a similar anhydrous lithium iodide cell using stainless steel current collectors. This suggests Li dendrites are not the traversing electronic species inducing shorts and that it is mostly dendrites induced by polyiodide formation. More importantly, it further demonstrates that control of the interfacial insulating SEI is key to moving such technology forward.
The next step taken was the identification of a metal anode current collector with dual functionality. The candidate would be one that both alloyed with lithium and more importantly, reacted with the polyiodide based cathode to form an insulating material as per equation 4.1.

\[ M^{\circ} + xI^{-} \rightarrow M_{y} \text{(Insulating)} \]  \hspace{1cm} (4.1)

This SEI would be stable to anodic decomposition during the electrolysis occurring at the anode interface. Figure 4.13 shows schematics showing four possible situations that occur in our EFB.
Figure 4.13: Schematic of cell passivation for configuration of the ESAB: (A): Using an anhydrous LiI starting composite; lithium and polyiodide dendrite growth occurs resulting in soft shorts. (B): LiI xH2O composites allow for a stable oxide based SEI to form resulting in cell functionality. (C): Using an anhydrous LiI composite with an alloying negative current collector eliminates lithium dendrites, but shorts still occur through polyiodide dendrite growth. (D): Using a dual function current collector with anhydrous LiI eliminates lithium dendrites through alloying and also reacts with polyiodide dendrites forming an insulating metal iodide product eliminating shorts through electrolytic decomposition of the SEI.

Fig. 4-13-A, as mentioned earlier, shows shorting from both anode and cathode dendrite growth. This occurs with anhydrous composites where no stable SEI growth occurs. In Fig. 4.13-B, using a hydrated composite, and the basis for the first part of our results section, shows when hydration is added to our composite a stable lithium-oxygen based SEI is formed allowing cell formation and eliminating contact between our anode and cathode. Fig. 4.13-C suggests that when using an alloying current collector, we eliminate lithium metal dendrite growth, but shorts still occur from our cathode/polyiodide dendrites. Fig. 4.13-D offers a pathway to allow cell formation and cycling with an anhydrous LiI starting composite. The alloying negative current collector will eliminate lithium metal dendrites while any polyiodide dendrite growth that occurs with react with our current collector material formatting this electronically insulating metal iodide product.
To survey candidates and evaluate the feasibility of such goal, various metals were incorporated as the *positive* current collector in a cell made with a LiI-PVP-I$_2$ composite. If the in-situ formed Ml$_y$ was of high enough electronic resistance and stability vs. anodic (high voltage) electrolytic decomposition, the cell current would drop precipitously during the cell and interphase formation. The cell was charged, forming a polyiodide based cathode at the metal surface which forced an interaction between the metal current collector and newly formed polyiodide species. Of the different metal chosen (Pb, Sn, In, Ga, Al, Ti, and stainless steel), indium, aluminum, tin, lead, and gallium showed the most promising results, Fig. 4.14.
Figure 4.14: Cells polarized at 3.5V vs. Li/Li+ using a LiI-I₂-PVP composite (6-1.5-1) placed against different metal positive current collectors. Presents blocking ability of reactive In, Al, Sn, Pb and Ga current collectors to electrolytic decomposition of their in-situ formed iodides opposed to essentially non-blocking Ti and stainless steel.

As the cell charges and the reaction between the reactive metal current collectors and the polyiodide cathode occurs, the current decreases toward zero. This is caused by the formation of an insulating product at the current collector-cathode interface which did not electrolytically decompose even though the voltage is well beyond that of the thermodynamic electrolytic decomposition potential for the metal iodide materials, $E^\circ/V < 1.5V$.

Of the metals in Fig. 4.14 which shown positive results, indium was chosen for the initial experiments for its low modulus and subsequent ability to form an intimate interface with the composites of interest. To again show that our indium-iodine reaction product is insulating and occurs spontaneously, indium metal was placed against an anhydrous LiI-PVP-I₂ composite, which is representative composition of an EFB cathode material after formation. AC impedance measurements were taken as a function of time. Fig. 4.15 shows the change in impedance over time for a reactive indium current collector against our ex-situ formed cathode material compared to the same experiment performed with a non-reactive stainless steel current collector vs. the same polyiodide composite.
Figure 4.15: Increase in cell impedance from growth of insulating indium iodide layer at indium surface when placed in contact with 1.5:6:1 I₂:LiI:PVP composite. Data is shown relative to lack of growth on SS current collector. (Time interval from zero to ten hours)

The stainless steel current collector results in a small semicircle representing ion transfer in the polyiodide composite along with a large 45 degree response at the low frequency which represents a Wardburg semi-infinite diffusion response. The latter is relatively stable with time and represents a degree of ion diffusion within the stainless steel bulk. Indium shows a similar small semicircle representative of the ion transfer in the composite but has a low frequency response in sharp
contrast to the stainless steel. Indeed this response consists of a large semicircle representative of high interfacial impedance which grows substantially with time. This suggests the in-situ formation of an InIₓ barrier which is both electronically and ionically resistive to a great degree. Indeed, XRD of the In surface (Fig. 4.16) from a cell similar to that shown in Fig. 4.15 revealed the formation of a InI phase at the In-polyiodide interface.

![XRD of Indium Surface](image)

**Figure 4.16**: XRD of indium metal surface previously placed against anhydrous LiI-I₂-PVP composite, showing formation of insulating indium iodine complex.

A cell was fabricated using an anhydrous Li-PVP composite to confirm the functionality of the indium metal. Figure 4.17 shows that when indium metal is
used as the negative current collector for an anhydrous EFB, it not only enables charging/formation of the cell (eliminating shorts), but also allows for the formation of a secondary cell. Cell in Fig. 4.17 was charged potentiostatically at 3.4V to 20% theoretical capacity, and discharged at 2.5µA. Although the discharge efficiency of this cell is relatively low (approx. 20-30% at this point) it confirms our previous work where the key to battery functionality in an EFB is the stabilization of the anode/electrolyte interphase.
Figure 4.17: EFB using anhydrous lithium iodide-PVP nanocomposite. with first a stainless steel negative current collector (see formation of soft shorts), and second an indium negative current collector. Demonstrates the enabling ability of a dual functionality current collector. Using indium allows for cell formation and eliminated the formation of soft shorts.

For a standard Li/Lil/I\textsuperscript{−} cell there is an OCV of 2.8V. Using an indium current collector produces an OCV is ~2.2V. To verify that the lower OCV is from having a Li\textsubscript{x}In alloyed anode, lithiation of indium metal was performed using an anhydrous solid state Lil electrolyte vs. lithium metal. This lithiation reveals a 0.6V plateau for Li-LiIn which corresponds to our 0.6V loss in potential when using an indium current collector. The alloying voltage profile also confirms a wide alloying range up to 2.5 Li per indium. Also, literature shows that after the first cycle lithium extraction and columbic efficiency are near 100% [9]. After cycling an EFB, characterization of the anode was performed to again confirm the formation of a Li-In alloy as the cells anode and verify indium iodine formation at the anode surface. Fig. 4.18 shows two XRD spectra of different areas of our alloyed anode, one where normal cell formation has occurred showing lithium indium alloy formation, and one on an area where polyiodide dendrites have contacted the indium current collector showing the formation of indium (I) iodide which we believe is the stabilizing interphase comparable to figure 4.13-D. The latter lends support to our proposed mechanism of stabilization.
Figure 4.18: XRD of indium negative current collector after cycling has occurred.

Shows formation of Li-In alloy and InI consistent with ex-situ studies.

4.6 Discussion

One would expect that InI should not be stable at the negative electrode interface as the following reaction should take place:

\[
\text{InI} + \text{Li} \rightarrow \text{LiI} + \text{In} \rightarrow \text{LiI} + \text{Li}_{x}\text{In}
\]  

(4.2)

However, the experimental data suggest that InI is stable towards the cathodic reaction with lithium described in this equation. This can only be accomplished if
the formed SEI is multi-layer and no electronic pathway exists between the lithium anode and the InI interphase. Below, we propose a mechanism for this isolation.
Figure 4.19: Schematics showing formation of electronically insulating layers between anode and cathode. A: Initial contact between cathode and alloyed Li$_x$In anode. B: results in formation of both InI and Lil. C. InI layer not stable against lithium metal in anode, reduces InI to In and forms Lil product. D: Newly formed indium metal reacts with cathode forming more InI material, eventually isolating the InI from contact with the negative electrode and further insulting anode from cathode.

Mechanistically, the first lithium that enters the In negative electrode would result in the formation of Li$_x$In. In parallel the polyiodide complex forms at the positive electrode to the degree that it eventually contacts the Li$_x$In negative electrode (Fig. 4.19-A). At that point both Lil and InI will form (Fig. 4.19-B). Any InI that is still in electronic contact with the negative electrode will then form Lil + In (Fig. 4.19-C and eq. 4.2). The In will then react with the polyiodide to reform additional InI and the aforementioned decomposition will continue (Fig 4.19-D). This cycle will cease when the Lil layer has built up under the reformed InI to the degree that electronic transfer from the Li$_x$In negative electrode to the InI can no longer occur. At this point the InI will be a stable crystalline species formed on top of the Lil layer. At this point the InI is in contact with the polyiodide positive electrode. We have already proven that InI is surprisingly stable to anodic decomposition and this layer now stays intact relative to the oxidizing potentials from the counter electrode. This capping interphase now protects the cell from electrolytic decomposition of the last Lil that protects the anode and enables the concept of an electrochemically formed, reversible anhydrous Lil battery.
In cycling anhydrous EFB, like the one in Fig. 4.17, which have been cycled for well over half a year, the total discharge capacity, or the sum of the capacity from all the discharges, totals more than the theoretical capacity in the original starting composite. Figure 4.20 illustrates this idea, where discharge capacity is plotted as a percentage of theoretical capacity available in the entire original starting composite. This proves that the cycling is not from partial gradual consumption of the composite but rather we are reforming the same materials through the cycles.

![Figure 4.20: Percentage of accumulated discharge capacity compared to total theoretical capacity available in entire starting composite vs. cycle number.](image-url)
4.7 Demonstration of EFB Versatility

The use of the LiI based EFB allows cell fabrication in shapes and sizes that would not be possible or extremely difficult using conventional battery multi-layer fabrication techniques. Figure 4.21 demonstrates the application of the in-situ formed cell technology to a complex interdigitated electrode (IDE) array.

*Figure 4.21: Interdigitated electrode design showing versatility of EFB chemistry. Cell fabrication using this complicated design demonstrates ability of chemistry to form electrochemical cell in any number of electrode configurations*
Hydrated Li(1.5H₂O):PVP composites (8:1) were melt cast over the top of the entire digit array for electrochemical evaluation. The IDE requires that 11 EFB cells form in parallel during the charge in a planar configuration. During the charging/formation process, Fig 4.22 shows the dark polyiodides form along the positive electrode and bright lithium metal on the negative electrode.
Figure 4.22: Small section of an interdigitated cell design showing both an uncharged IDE EFB with thin film Ti current collectors (A) and a partially formed EFB (B). The latter shows the formation of polyiodide as dark regions from the positive current collector and lithium as bright regions on the negative current collector.

The discharge curve of the cell from Fig. 4.22 is shown in Fig. 4.23. Approximately 18.0 μAh discharge capacity was resolved from the planar cell.

Figure 4.23: Voltage profile for lithium iodide EFB using interdigitated electrode configuration. Demonstrates ability of cell to form and function in complicated electrode geometry. Cell discharged at 50nA and charged potentiostatically at 4.0V.
The in-situ cell formation should allow the solid state EFB to open a pathway to easy fabrication of bipolar cell configurations. To test this, a bipolar IDE was fabricated to enable a 14V OCV. In essence five interdigitated cells are fabricated in series, using a bipolar design, utilizing duplex electrodes, where each center metal tab acts as both a positive and negative current collector, electronically conductive from the anode of one cell to the cathode of the next, while ionically isolating each individual cell. The following figure shows bipolar interdigitated design, along with the associated voltage profile. Bipolar series cell have an open circuit potential equal to 14V or 5 x 2.8V. The discharge capacity of the bipolar EFB of 22.0μAh was similar to the single cell but with an average discharge V > 12V.
Figure 4.24: Bipolar series IDE cell design utilized in high voltage EFB (A), with associated voltage profile (B). Cell charged potentiostatically at 20.0V and discharged at -50nA to a cutoff of 9V.

4.8 Conclusion

It has been shown that an effective SEI is fundamentally critical to the enablement of EFB. Two pathways were taken to enable the formation of an lithium iodide electrolytically formed battery. This was achieved by eliminating the formation of healable shorts which occurred when the cell anode and cathode were in contact after the electrolytic decomposition of the remaining LiI. Adding hydration to a LiI composite assisted in the formation of a strong solid electrolyte
interface over the plated lithium metal anode. This layered SEI is more resistant to electrolytic decomposition compared to a lithium iodide SEI layer formed using an anhydrous material. The in-situ formed SEI was characterized as being composed of LiOH, LiH, and believed to contain a thin layer of Li$_2$O.

As hydrated compositions can lead to uncontrolled impedance increase of a LiI cell with time, an alternative SEI approach was developed not requiring hydration. Current collector materials such as In, Al, and Ga were identified to have a dual functionality, a material that both alloys with lithium metal eliminating dendrite growth during the charging process, and also react to form a non-electrolytically decomposing metal iodide product with our polyiodide based cathode. This approach enabled the use of anhydrous LiI to form an electrochemically active cell.

Both techniques, while still not perfect with respect to efficiency, clearly demonstrate a path of research that enables the dream of electrolytically formed batteries where the electrodes are formed in-situ. A number of configurations were shown to be feasible ranging from simple stacked cell to a 14V series interdigitated electrode cell. Future work on such concepts will enable an era of batteries not constrained by cost of fabrication, transportation restrictions in the unformed state, and have the ability to form batteries in previously unimaginable configurations.
4.9 References

5.0 Summary

In the first steps to producing a high energy, reversible, electrolytically formed battery, we have shown, through a demonstrative lithium iodide system, that both in-situ anode and cathode electrode development are possible forming, for the first time, a secondary lithium iodide cell. This EFB chemistry allows cell design in shapes and sizes that would not be possible though conventional battery fabrication techniques. Demonstrations of these have been shown through the complicated interdigitated electrode designs, and subsequent cell formation.

Through polymer-iodine interactions a cathode material is formed which possesses both ionic and electronic conductivity, not through an irreversible polymer oxidation, which is seen in conventional P2VP-iodine cell, but through the reversible formation of polyiodide species, which themselves possess an intrinsic ionic and electronic conductivity. The transport properties are directly tied to the type of polyiodide network formed.

The key to cell formation and functionality of an EFB was the interphase stability over both a lithium metal or lithium alloy anode. This interphase stabilization eliminated the formation of soft shorts which were detrimental to cell efficiency and functionality. To stabilize the cell interphase, two different approaches were taken to form a SEI layer which was more resistant to electrolytic decomposition than our lithium iodide electrolyte material. First through the addition of hydration, and oxide bases SEI layer was formed. This
was confirmed through FTIR and Raman vibrational spectroscopy, and also though structural XRD characterization. The second method involved the use of a dual functionality current collector. This material alloyed with lithium metal and also reacted with our cathode material to form an insulating material.

Whichever interphase stabilization method was used, the outcome was the formation of a secondary electrolytically formed battery, which demonstrates an alternate pathway to battery fabrication and a step forward toward developing cells with complicated electrode designs. Success of an EFB is highly dependent on the formation of a robust SEI.
6.0 Future Work

This research dealing with electrolytically formed batteries is only the initial work in an area of research which should have a significant impact on energy storage research and battery development for many years. As battery and energy storage research continues to develop, I am certain new methods for self forming cells will be developed, but the idea behind the work, of simplifying battery fabrication, doing it at a lower cost, and developing cells in different arrays, configurations and sizes, will still remain the main motivation for this research.

Specifically to continue research dealing with lithium iodide electrolytically formed batteries, there is a large span of areas which can be developed, with a few listed here:

1. Dealing with such a hygroscopic material such as lithium iodide, at present time, the characterization techniques are limited to methods where the samples can be isolated to an inert environment. An understanding of the interphases and mechanism could be greatly improved if alternate characterization techniques could be implanted (such as EELS/TEM, XPS). Therefore, different methods to implement different characterization techniques can use continued development.

2. Electrochemically, some initial work has been performed studying different charge protocols and pulse charging techniques, with improvement in efficiency being realized. A more in-depth study of why these techniques
are resulting in improvements could show the next pathway forward in this research.

Listed are two of the more important areas which we believe will develop into a significant improvement in the cycling ability of an EFBs. Although there are only two listed there are numerous other areas which can be developed, such as alternated polymers, nano-filler effect on dendrite growth, and particle size of initial starting material.

This initial work dealing with lithium iodide self formed cells, demonstrates the feasibility of this concept, along with showing there is room for improvement and motivation for continued research. This present research highlights a pathway which can be extended to different studies dealing with self formed cell.
7.0 Curriculum Vita

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Publications


5. Mbindyo, Jeremiah K. N.; **Yourey, W.**. “Layer by layer self assembly of DNA and polyelectrolytes on Au and biodegradable polymer nanoparticles.” Abstracts, 38th Middle Atlantic Regional Meeting of the American Chemical Society, Hershey, PA, United States, June 4-7 (2006)