An Adhesive Vinyl-acrylic Electrolyte And Electrode Binder For Lithium Batteries

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AN ADHESIVE VINYL-ACRYLIC ELECTROLYTE AND ELECTRODE BINDER FOR LITHIUM BATTERIES

by

BINH TRAN
B.S. University of Central Florida, 2009

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy of Chemistry in the Department of Chemistry in the College of Sciences at the University of Central Florida Orlando, Florida

Spring Term
2013

Major Professor: Lei Zhai
This dissertation describes a new vinyl-acrylic copolymer that displays great potential for applications in lithium ion batteries by enabling processes that are novel, faster, safer, and less costly than existing manufacturing methods. Overall, the works presented are based on tailored chemical synthesis directly applied to lithium ion battery manufacturing. Current manufacturing methods still have many flaws such as toxic processes and other time consuming if not costly steps. Understanding the chemistry of materials and processes related to battery manufacturing allows the design of techniques and methods that can ultimately improve the performance of existing batteries while reducing the cost. Chapter 1 provides an introduction to lithium batteries in terms of energy output, standard electrode and electrolyte materials, and processes for fabricating battery components. In this chapter, slightly more emphasis is placed on the electrolyte aspects of lithium battery technology, namely the plasticization of gel polymer hosts by liquid electrolyte and the standalone solid polymer electrolytes. Chapter 2 focuses on the free radical polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA), methyl methacrylate (MMA), and isobutyl vinyl ether (IBVE) monomers to afford a vinyl-acrylic poly(PEGMA-co-MMA-co-IBVE) random copolymer and its detailed properties as a soluble, amorphous, and adhesive electrolyte that is able to permanently hold 800 times its own weight. Such material properties envision a printable battery manufacturing procedure, since existing electrolytes lack adhesion at a single macromolecular level. Without adhesion, the cathode and anode layers easily delaminate from the cell assembly, not to mention weak interfacial contact and poor mass transfer with the electrolyte. Many soft matter type electrolytes have been reported, but they lack either adhesive strength or ease of solubility. Obtaining both properties in
a single material is a rarity. Chapter 3 aims at improving the ionic conductivity of the poly(PEGMA-co-MMA-co-IBVE) copolymer electrolyte by studying the effect of internal and external plasticizers, molecular weight of PEGMA monomer, and addition of inorganic solid state electrolytes. The inorganic electrolyte additives include Li_{(1+x+y)}Al_xTi_{(2-x)}Si_yP_{(3-y)}O_{12}, Li-Li_2WO_4 mixture, Li_7La_5Zr_2O_{12}, and Li_2S-P_2S_5 as part of an organic-inorganic hybrid approach. Electrolytes can also be used as an electrode binder so long as it has structural integrity and allows ion transfer to and from the active electrode material during insertion/extraction processes. In Chapter 4, the use of this electrolyte as a water-soluble binder for the aqueous fabrication of LiCoO_2 cathodes is presented. Results of this study demonstrated the first aqueous process fabrication of thick, flexible, and fully compressed lithium ion battery electrodes by using commercial nickel foam as a supporting current collector. This feat is rather impressive because these properties are far superior to other aqueous binders in terms of material loading per electrode, specific area capacity, durability, and cell resistance. Finally, Chapter 5 expands on this concept by using the poly(PEGMA-co-MMA-co-IBVE) copolymer for the aqueous fabrication of a low voltage Li_{4}Ti_{5}O_{12} anode type electrode. Each component of a lithium ion battery serves a distinct role and undergoes unique electrochemical processes during cycling. The fact that this poly(PEGMA-co-MMA-co-IBVE) copolymer can be used in all three components, albeit for only about 50 cycles in a liquid half cell setup, demonstrates as a proof of concept that switching the current toxic manufacturing of lithium-ion batteries to an aqueous process is highly feasible. Furthermore, new electrode manufacturing techniques are also deemed possible. A conclusive summary along with directions for future work concerning the
novelties of this unique multifunctional vinyl-acrylic copolymer as an electrolyte, a cathode
binder, and an anode binder are discussed in Chapter 6.
ACKNOWLEDGMENTS

It has been said that the most beautiful things in life cannot be touched or seen, but must be felt with the heart. In my pursuits, there are many people I would like to thank for making this dissertation possible, each of whom has passed on valuable ethics for me to carry on in life, and that words alone can never describe. I thank my family not so much for helping me with Chemistry, but for all the laughter, love, and times of deep true caring. Most of them are too young at this point to understand what a Ph.D. is, but without a doubt, they have been the inner flames that constantly motivate me to strive beyond my limitations.

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Zhai’s lab and am now completing a dissertation under his guidance, his continual support for the past six years will be deeply remembered.
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<th>Description</th>
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<tbody>
<tr>
<td>1,3-DL</td>
<td>1,3-dioxalane</td>
</tr>
<tr>
<td>2-Me-THF</td>
<td>2-methyl-tetrahydrofuran</td>
</tr>
<tr>
<td>γ-BL</td>
<td>γ-butyrolactone</td>
</tr>
<tr>
<td>ac</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant Phase Element</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DMAc</td>
<td>N,N-dimethylacetamide</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethoxyethane</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EA</td>
<td>Ethyl Acetate</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene Carbonate</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl methyl carbonate</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel phase chromatography</td>
</tr>
<tr>
<td>GPE</td>
<td>Gel polymer electrolyte</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>IBVE</td>
<td>Isobutyl vinyl ether</td>
</tr>
<tr>
<td>Li-Ion</td>
<td>lithium ion</td>
</tr>
<tr>
<td>LIB</td>
<td>lithium-ion battery</td>
</tr>
<tr>
<td>LiTf</td>
<td>Lithium triflate</td>
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<tr>
<td>LiTFSI</td>
<td>Lithium bis-(trifluoromethanesulfonyl)imide</td>
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<tr>
<td>LCO</td>
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<td>LTO</td>
<td>Li₄Ti₅O₁₂</td>
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<td>MAG</td>
<td>Massive aggregate graphite</td>
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<tr>
<td>MMA</td>
<td>Methyl methacrylate</td>
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<td>Ni-Cd</td>
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<td>NMR</td>
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<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
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<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
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</tr>
<tr>
<td>PE</td>
<td>Polymer electrolyte</td>
</tr>
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<td>PEG</td>
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<td>PEGMA</td>
<td>Poly(ethylene glycol) methyl ether methacrylate</td>
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<td>PEO</td>
<td>Poly(ethylene oxide)</td>
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<td>Poly(methyl methacrylate)</td>
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<td>PVDF</td>
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<td>Solid polymer electrolyte</td>
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<td>Stainless steel</td>
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<td>SSIP</td>
<td>Solvent separated ion pair</td>
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<td>X-Ray Diffraction</td>
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</tbody>
</table>
CHAPTER 1:
INTRODUCTION TO LITHIUM BATTERIES

Ch. 1 Abstract: Lithium batteries have advantages and disadvantages compared to other energy storage devices in terms of energy density, safety, and rate of energy conversion. How they compete in the market and motives for their research and development are highlighted. State of the art materials involved in lithium-ion batteries are discussed which include insertion electrodes (i.e. LiCoO₂, graphite, Li₄Ti₅O₁₂) and electrolytes (i.e. liquid, gel, solid). Techniques for synthesizing these materials as well as the processes for assembling them are also briefly discussed, with more emphasis placed on electrolytes.

1.1. Introduction

High energy density rechargeable batteries are in ever greater demand as present day technologies (e.g. smart phones, laptops, electric vehicles) consume energy in larger quantities and at faster rates. Lithium secondary batteries are promising in fulfilling such needs because of their high intrinsic discharge voltage and lightweight. As the lightest and one of the most electropositive elements, lithium has the highest electrode potential and releases the most energy per electron of all the alkali metals as listed in Table 1-1.¹
Table 1-1:
Oxidation energies of Alkali Metals

<table>
<thead>
<tr>
<th>Alkali Metal</th>
<th>( \text{E}^0_{\text{oxidation}} ) (V vs. SHE)</th>
<th>( \Delta G^0 ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li → Li(^+) + e(^-)</td>
<td>3.04</td>
<td>293.3</td>
</tr>
<tr>
<td>Na → Na(^+) + e(^-)</td>
<td>2.71</td>
<td>261.5</td>
</tr>
<tr>
<td>K → K(^+) + e(^-)</td>
<td>2.93</td>
<td>282.7</td>
</tr>
<tr>
<td>Rb → Rb(^+) + e(^-)</td>
<td>2.98</td>
<td>287.5</td>
</tr>
<tr>
<td>Cs → Cs(^+) + e(^-)</td>
<td>3.03</td>
<td>292.0</td>
</tr>
<tr>
<td>Fr → Fr(^+) + e(^-)</td>
<td>2.90</td>
<td>279.8</td>
</tr>
</tbody>
</table>

*potentials are vs. standard hydrogen electrode (SHE)

Fundamental relationships exist between electrode potential, chemical potential, and Gibbs energy. Assuming no volumetric work and at constant temperature, pressure, and composition of cell components, the only work done by a cell is electrical work which is equal to the Gibbs free energy of the cell:

\[
dG = -EdZ
\]

where \( G \) is the Gibbs free energy, \( E \) is the cell voltage, and \( Z \) is the charge transferred.

Substitution of \( Z = nF \) into equation and integrating yields

\[
\Delta G = -nFE
\]

where \( n \) is the number of moles of electrons transferred, and \( F \) is the Faraday’s constant (96,485 coulombs/mol e\(^-\)). Equation only considers the free energy for work coming from electrical work. In a lithium battery, the anode that releases electrons through an external circuit also
releases lithium ions into the electrolyte, both of which are simultaneously captured by the cathode at the other end. Therefore, changes in composition occur that are directly coupled to the amount of charge transferred. The chemical potential ($\mu$) is defined as:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_j, n_k} \quad (1-3)$$

Under isobaric and isothermal conditions, Eq. 1-3 can be expressed as

$$dG = \sum_i \mu_i dn_i \quad (1-4)$$

A cell can be defined as a two component system (labeled $a$ or $b$), existing in a lithiated state or de-lithiated state, respectively.

$$dG = \mu_a dn_a + \mu_b dn_b \quad (1-5)$$

If the system is closed, then by material balance conditions:

$$dn_a + dn_b = 0 \text{ (closed system)} \quad (1-6)$$

$$-dn_a = dn_b \quad (1-7)$$

Substituting Eq. 1-7 into Eq. 1-5 yields

$$dG = (\mu_a - \mu_b)dn_a \quad (1-8)$$

$$\int_1^2 dG = \int_{n_a}^{n_a^2} (\mu_a - \mu_b)dn_a \quad (1-9)$$

$$\Delta G = (\mu_a - \mu_b)n_a \quad (1-10)$$

Combination of Eqs. 1-10 and 1-2 results in the following relation:

$$-nFE = (\mu_a - \mu_b)n_a \quad (1-11)$$
Therefore, electrode potential and chemical potential are directly related. Work done on the cell as electrons are passed through a potential difference $E$ must equal the difference in chemical potential between the two electrodes ($\mu_a - \mu_b$). In this sense, electrodes are said to store chemical energy.\(^3\)

Consider a cell with a generic metal oxide (MO$_x$) as a ‘host’ electrode and lithium metal as the ‘guest’ electrode as depicted in Figure 1-1. The chemical potential of Li in the host and in the Li metal are denoted as $\mu_a$ and $\mu_b$, respectively. For every electron passed through the external circuit, one lithium ion is intercalated into the host electrode. Thermodynamics requires that as the concentration of guest ions in the host increases, $\mu_a$ increases so that $E$ (potential difference, $E^+ - E^-$) decreases. When $E = 0$, the chemical potential of the guest is the same in its bulk form and inside the host. Therefore, the cell reaches equilibrium when the chemical potential of each component is constant throughout the entire system.
Batteries are often rated by energy storage capability which can be calculated according to the following relations:

\[
\text{Energy Density: } \frac{J}{L} = \frac{W \cdot s}{L} \propto \frac{W \cdot h}{L} \quad (1-12)
\]

\[
\text{Specific Energy: } \frac{J}{g} = \frac{W \cdot s}{g} \propto \frac{W \cdot h}{g} \quad (1-13)
\]

Joules (J) is the SI unit for energy which is equal to one watt-second, divided by the volume or mass to yield the energy density or specific energy, respectively. In practice, the energy term is expressed as watt-hour (W·h), where one W·h is the electrical energy of a one watt load drawing power for one hour.

The motive to develop lithium-based batteries originates from the highest energy densities, whether per volume (Wh/L) or mass (Wh/g), that are theoretically possible with this system. For a given size, conventional nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), and lead acid batteries pale in comparison to the energy densities potent in lithium-based batteries as graphically illustrated in Figure 1-2.
Rechargeable lithium batteries, i.e. lithium-ion (Li-Ion) and Li-Ion polymer, have high energy densities of about 400 Wh/g or 500 Wh/L which translates to devices that deliver twice the energy of Ni-MH batteries for the same size or weight. Other general advantages of lithium batteries are high efficiencies and moderate-to-high rate capability. Secondary lithium batteries have additional advantages over their primary counterparts which include plasticized electrolytes and internal bonding of cathode, separator, and anode components. These issues make materials processing and cell engineering more versatile, such as a lamination process for manufacturing. On the downside, lithium-ion batteries are relatively expensive, prone to fire hazards from over-charging or over-discharging, and have poor low temperature performance.
Table 1-2:
2005 Worldwide demand (millions of cells).\(^5\)

<table>
<thead>
<tr>
<th>Application</th>
<th>Cell type</th>
<th>Ni-Cd</th>
<th>Ni-MH</th>
<th>Li-Ion cylindrical</th>
<th>Li-Ion prismatic</th>
<th>Li-Ion laminated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellular</td>
<td></td>
<td>50</td>
<td></td>
<td>898.16</td>
<td>125.85</td>
<td></td>
</tr>
<tr>
<td>Notebook</td>
<td></td>
<td>22</td>
<td>422.68</td>
<td>16.34</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Movie camera</td>
<td></td>
<td>2</td>
<td>4</td>
<td>67.98</td>
<td>11.91</td>
<td></td>
</tr>
<tr>
<td>Digital camera</td>
<td></td>
<td>56</td>
<td>18.88</td>
<td>48.17</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Power tools</td>
<td></td>
<td>575</td>
<td>53</td>
<td>20.14</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

Market demands are competitive among the Li-Ion, Ni-Cd, Ni-MH, and lead acid battery chemistries, although Li-Ion technologies are gradually replacing Ni-MH batteries in most applications with the development of higher performance electrode materials. From Table 1-2, cellular and smart phone applications are seen to dominate the unit cell production, followed by notebook computers and movie cameras. Digital cameras are often stored without continuous usage, so this market is transitioning to Li-Ion batteries which have superior shelf life over traditional Ni-MH batteries that self-discharge about 1% on a daily basis. Hand power tools have been a niche application for Ni-Cd batteries for their very high rate performance, so it would be difficult for Li-Ion batteries to penetrate this market.
Early work in lithium batteries began with primary batteries using lithium metal as an anode which provides the maximal cell voltage when coupled to any cathode material (Figure 1-3). Preliminary cathode materials were TiS$_2$ and V$_2$O$_5$, although they are low voltage materials and were eventually replaced by much more potent active materials. With lithium having the stronger reducing potential, electrons spontaneously discharge from the lithium anode to the cathode. By releasing electrons, lithium metal also releases lithium ions which dissolve in the electrolyte phase, migrate through the electrolyte under an applied potential, and are captured by the cathode through an electrochemical reaction of some sort. A porous polymer separator between the electrodes prevents short-circuiting while allowing permeation of liquid electrolyte. Though the terms cathode and anode are only strictly correct during a discharge, the chemical nature of the cathode and anode determines the energy output, while the electrolyte controls the rate of mass flow within the cell. However, as a result of lithium having one of the highest
reducing potentials, it is generally expected that nothing is stable against its surface. Developing an electrolyte for a lithium battery was initially hindered by the instability of solvents against a lithium surface, consequently leading to hazardous reactions or contamination of the anode. For example, protic solvents like water and alcohol are easily reduced by lithium in a strongly exothermic reaction. In the 1950s, a number of nonaqueous solvents were demonstrated to be compatible with lithium despite its reactivity. For example, protic solvents like water and alcohol are easily reduced by lithium in a strongly exothermic reaction. In the 1950s, a number of nonaqueous solvents were demonstrated to be compatible with lithium despite its reactivity.6

![Diagram](image)

Figure 1-4: Schematic illustration of SEI formation on a fresh lithium surface.

These electrolyte solvents ranged from organic propylene carbonate (PC) to inorganic thionyl chloride. Stabilization was attributed to a passivation film that forms between the electrolyte and the lithium surface, creating a solid electrolyte interface (SEI) that prevents a sustained reaction between the two.7 As the name suggests, a SEI layer on the lithium surface does not impair cell performance by acting as a solid state electrolyte protective barrier, i.e. it is ionically conductive but electronically insulating. Figure 1-4 illustrates the formation of an instantaneous SEI layer between PC, the electrolyte solvent, and a lithium surface. Although the exact mechanism is unclear as it can proceed via one or two electron reactions, the products are
Li$_2$CO$_3$ and CH$_3$-CH=CH$_2$. Li$_2$CO$_3$ is then the protective barrier, or solid-state electrolyte, at the electrolyte/lithium interface.$^8$

Up through the 1970s, a series of lithium-based primary cells were commercialized,$^9,10$ but efforts to expand into secondary rechargeable batteries were halted by another failure mode. It was realized that needle-like crystals (dendrites) of lithium deposited on the lithium surface during each charge.$^{11,12}$ Upon discharge, nonuniform dissolution rates along the dendrite morphology caused them to detach and become electrically isolated from the electrode as illustrated in Figure 1-5.

![Figure 1-5: Schematic illustration of lithium dendrite growth on lithium surface and its electrical isolation during subsequent discharge.$^{13}$](image)

Repetitive dendrite growth and isolation with charging-discharging leads to overconsumption of the lithium anode since excess lithium must replace the lost amount. Isolated ‘dead lithium’ crystals have a high reactive surface area which also imposes serious hazards like thermal
runaway and explosion. In the worst case scenario, a complete dendrite pathway can develop between the electrodes, leading to an internal short-circuit.\textsuperscript{13}

Strenuous but fruitless efforts to stop dendrite growth ended the general enthusiasm of lithium anodes, prompting the search for alternative anode materials that lack destructive morphological transformations during cycling. Throughout the 1970-1980s, ‘host-guest’ chemistries were strongly considered, also known as ‘intercalation’ or ‘insertion’-type electrodes, since they had shown marvels through the works of Whittingham\textsuperscript{14} and Goodenough.\textsuperscript{15} Several experiments conceptually confirmed the application of \( \text{Li}_6\text{Fe}_2\text{O}_3 \) and \( \text{LiWO}_2 \) intercalation anodes against \( \text{WO}_3, \text{TiS}_2, \text{LiCoO}_2, \) and \( \text{V}_2\text{O}_5 \) cathodes, but because of the poor cycle life, these systems never commercialized.\textsuperscript{16,17} A scientific breakthrough came in 1990 when carbonaceous materials were revisited as an intercalation host.\textsuperscript{18} Not only is lithiated carbon very close to the potential of lithium (only 0.1 - 0.2 V difference), but lithium residing in it exists in an ionic rather than a metallic state, so the possibility of dendrite growth is eliminated (Figure 1-6).

Figure 1-6: Carbonaceous intercalation anodes.\textsuperscript{13}
Carbon’s low cost and elemental abundance also eased its way to commercialization by Sony,\textsuperscript{19} Bell Communications,\textsuperscript{20} Rayovac,\textsuperscript{21} and Moli\textsuperscript{22} soon after. Although lithium dendrites were no longer a problem, the SEI layer that forms on the anode surface remained. Because the composition of the SEI layer depends on the chemical nature of the electrolyte, carefully engineering this interface is vital to enabling reversible cell chemistries. Reduction of the electrolyte at the reactive anode surface is generally expected, although this process is very complicated and still under scrutiny.\textsuperscript{23} Many solvents have a negative impact on the graphite structure but ethylene carbonate was found to protect the crystalline structure of graphite,\textsuperscript{22} thus making it an essential component of electrolyte formulations today.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure1-7.png}
\caption{Schematic of lithium ion “rocking-chair” cell.\textsuperscript{13}}
\end{figure}
Li-Ion technology is often said to be truly born from the implementation of carbonaceous anodes. Intercalation cathodes had already been employed, so the introduction of an intercalation carbon anode led to an energy storage process completely based on lithium ions (Figure 1-7). Earlier terms for this type of cell chemistry were “rocking chair”\textsuperscript{24} or “shuttle-cock”\textsuperscript{25} batteries, but “lithium-ion” became the generally accepted term. In the time period from 1991-2002, fundamental understanding of battery materials and processes for manufacturing were the main focus as Li-Ion batteries rely on an intercalation reaction rather than conventional chemical reactions. The processing of materials, cell designs, and production equipment became highly sophisticated during this decade.

![Figure 1-8: Divergence in Li-Ion market.\textsuperscript{5}](image)

Shifts in market applications appeared soon after and the development of Li-Ion batteries diverged into two major sectors as shown in Figure 1-8. One sector focused on higher capacity
and higher performance electrodes to compete with cellular phones and notebook computers. Several stellar materials including LiMn$_{1/3}$Co$_{1/3}$Ni$_{1/3}$O$_2$, LiMn$_{1/2}$Ni$_{1/2}$O$_2$, and LiFePO$_4$ cathodes and nanostructured metal alloy anodes were welcomed with great success. The other sector did not focus on energy storage capability, but rather on lowering the cost of battery manufacturing through process design or material processing.

In line with the latter sector of Li-Ion technology, the works presented in this thesis are focused on the development of a novel adhesive electrolyte and electrode binder for lithium-ion batteries with the goal of reducing the cost of manufacturing. Electrolytes do not determine the power output of a cell, but rather they mediate the rates of charging and discharging. An often overlooked responsibility of electrolytes is that they are also the ‘glue layer’ between the electrodes. Without an ion-conducting medium in direct interfacial contact with the electrode, there can be no mass (Li$^+$) transfer. Supposing that all material requirements are met (i.e. ionic conductivity, solubility, adhesion, cost), solid polymer electrolytes offer a lamination or printable type of processing that is not restricted to prismatic or cylindrical designs. Well-developed coating technologies become available for the expedient production of thin, flexible, and self-adherent high energy density lithium-ion batteries.

Improvements in binder materials may also reduce costs associated with manufacturing. Millions of cells are produced each year that rely on a poly(vinylidene fluoride) polymer to bind electrode materials together, but this polymer only dissolves in toxic and high boiling point solvents. Costly distillation towers must then be integrated into manufacturing plants to recycle the spent solvent, not to mention the hazardous environment that workers are placed in. In addition to the development of an adhesive vinyl-acrylic copolymer as a solid polymer
electrolyte, it is also used as a binder for the first ever aqueous process fabrication of thick, flexible, and fully compressed lithium-ion battery electrodes. A sharp transition from a toxic distillation process to a water-based process drastically reduces the cost of materials, eliminates safety hazards, and speeds up manufacturing. Before transitioning directly to the topics of focus, a brief overview of Li-Ion battery electrodes (section 1.2) and electrolytes (section 1.3) are covered. The electrolytes section is discussed in more detail to provide further understanding of polymer electrolytes and binder materials.

1.2. Electrodes

To ensure that electrochemical reactions at an electrode are sufficiently complete at faster rates, the electrode material needs high electronic and ionic conductivity. However, separating electronic and ionic contributions from instrumental techniques such as electrochemical impedance spectroscopy (EIS) is inconvenient, if not uncertain, despite lithium diffusion coefficients often being used to predict ionic transport in an electrode material. Transition metal oxides used as electrodes are often low in electronic conductivity (less than $10^{-6}$ S/cm), therefore carbon black additives are used to boost the electronic conductivity. Enhancements up to 0.1 S/cm can often support rates near or above 1C, which can be achieved by using 5-8% carbon additives. A few select electrode materials are briefly discussed, with particular attention on LiCoO$_2$ cathode and Li$_4$Ti$_5$O$_{12}$ anode since they are relevant to the works presented in this dissertation.
1.2.1. Cathodes

To date, the most popular candidates among cathode materials involve a select few of crystal structures, these including, but not limited to, the layered metal oxides and spinels where void spaces are available in the form of 2D layers or 3D tunnels for lithium ion insertion, respectively. The salient structural features of layered metal oxides are blocks of two hexagonally close-packed oxygen layers between which transition metals are coordinated by prismatic or octahedral oxygens. That is, MO$_2$ layers are formed by edge-sharing [MO$_6$] octahedra in a face-centered unit cell. Various arrangements of the O-M-O layers result in different polymorphs, but the important aspect is the Van der Waals gap between the O-M-O sheets.

![Figure 1-9: Representative drawing of layered rock salt structure exemplified by lithium transition metal oxides LiMO$_2$ (M = Co, Ni, Mn).](image)

This space is reversibly occupied during lithium insertion in the form of [LiO$_6$], and then emptied when lithium is extracted from the metal oxide (Figure 1-9). Diffusion of Li$^+$ expands
the host structure in the c-axis (typically 10%), and the inter-layer Van der Waals forces are replaced by coulombic interactions. The inter-layer space also contains octahedral and tetrahedral sites for lithium occupation, where the octahedral sites are generally thermodynamically favored and the tetrahedral sites are kinetically favored. As a result, octahedral sites are filled (and emptied) via the tetrahedral sites.\(^{32}\)

The cubic rock salt structure can be identified as a face-centered unit cell based on cubic close packing of oxygen anions with all octahedral sites filled by cations. Alternating planes of cubic close-packed [MO\(_6\)] and [LiO\(_6\)] rock salt structures generates a layered rock salt structure. Lithium diffusion coefficients usually range from \(10^{-11} - 10^{-12}\) m\(^2\)/s in layered rock salts.\(^{33-36}\) Isostructures of this sort include LiCoO\(_2\), LiNiO\(_2\), and LiMnO\(_2\) which are of industrial importance. Common methods for synthesizing these lithium transition metal oxides are via solid state or sol-gel calcinations of carbonate,\(^{37}\) hydroxide,\(^{38}\) nitrate,\(^{39}\) and acetate\(^{40}\) precursors as shown in the following reactions.

\[
\begin{align*}
\text{Li}_2\text{CO}_3 + 2\text{CoCO}_3 + \frac{1}{2}\text{O}_2 & \xrightarrow{800-900^\circ \text{C}} 2\text{LiCoO}_2 + 3\text{CO}_2 \\
\text{LiOH} + \text{Ni(OH)}_2 & \xrightarrow{600-850^\circ \text{C}} \text{LiNiO}_2 + \text{H}_2\text{O} \\
\text{LiNO}_3 + \text{Mn(NO}_3)_2 & \xrightarrow{800-900^\circ \text{C}} \text{LiMnO}_2 + 3\text{NO}_2 + \frac{1}{2}\text{O}_2 \\
4\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O} + 8\text{Mn(CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O} + 43\text{O}_2 & \xrightarrow{750^\circ \text{C}} 4\text{LiMn}_2\text{O}_4 + 40\text{CO}_2 + 70\text{H}_2\text{O}
\end{align*}
\]

High temperatures up to 900°C are generally required to synthesize powders of well-defined crystallinity. Above this point, Li\(_2\)O tends to volatilize which then renders the material electrochemically inactive.

LiCoO\(_2\) is considered a standard cathode material because of its demonstrated reliability in terms of crystalline purity, relatively high conductivity, decent capacity (140 mAh/g), and long cycle life. However, some drawbacks of using LiCoO\(_2\) are the high cost and toxicity.
associated with cobalt. LiNiO₂ offers higher capacity and lower cost than LiCoO₂, but it is difficult to synthesize LiNiO₂ of high purity. Above 600°C, which is necessary to complete the oxidation of nickel from Ni²⁺ to Ni³⁺ in oxygen atmosphere, a broad phase distribution of 0 ≤ x ≤ 0.4 in Li₁₋ₓNiₓO₂ forms that is very sensitive to synthesis conditions. And then above 850°C, LiNiO₂ decomposes to become the electrochemically inactive LiₓNi₁₋ₓO (0 < y < 0.3) due to loss of Li₂O. Hence, LiNiO₂ of stoichiometric composition is difficult to prepare, especially in comparison to other transition metal oxides that crystallize efficiently at high temperatures.⁴¹,⁴²

Layered LiMnO₂ is another alternative that offers very low cost from abundant and non-toxic precursors. Its capacity is significantly higher than both LiCoO₂ and LiNiO₂, rated at 285 mAh/g. But despite these great prospects, LiMnO₂ is not electrochemically stable, i.e. it is metastable. Repeated cycling within 2 – 4.3 V induces irreversible structural transformations that degrade is capacity, going from a layered rock salt structure (285 mAh/g) to an orthorhombic structure (230 mAh/g), and finally to its spinel form LiMn₂O₄ (148 mAh/g).⁴³

![Figure 1-10: Spinel tunnel structure exemplified by LiMn₂O₄.](image-url)
Spinel LiMn$_2$O$_4$ (Figure 1-10) exemplifies another class of active crystal structures for Li-Ion battery electrodes. Unlike the layered structures which have 2D planes for lithium diffusion, the spinel structure is a 3D framework with cross-linked channels for ion transport. The advantages here are: (1) reduced volumetric expansion/contraction during lithium insertion/extraction and (2) the possibility to avoid co-insertion of molecules. Spinel LiMn$_2$O$_4$ can be identified as a face-centered lattice (F$_{3}$dm space group) of cubic close-packed oxygen anions with lithium cations occupying one-eighth of the tetrahedral sites and manganese cations occupying one-half of the octahedral sites. Empty octahedral and tetrahedral sites are interconnected such that diffusion pathways are available for lithium ion movement. The chemical diffusion coefficient for spinel LiMn$_2$O$_4$ is reported to be in the $10^{-8} – 10^{-14}$ m$^2$/s range. Substantial variations have been noticed depending on synthesis conditions and experimental technique.

At any rate, spinel LiMn$_2$O$_4$ has rather poor cyclability compared to standard LiCoO$_2$ for several reasons. First, the instability of organic electrolytes at high voltages ($\geq$ 4.5 V) causes the electrolyte to electrochemically break down, quickly leading to deteriorating cell performance. LiMn$_2$O$_4$ itself is also prone to slowly dissolving in the electrolyte from the disproportionation of Mn$^{3+}$ to Mn$^{2+}$ and Mn$^{4+}$, where Mn$^{2+}$ is the soluble species. Deeply discharged LiMn$_2$O$_4$ undergoes a Jahn-Teller effect which shifts the cubic symmetry of the spinel structure to a tetragonal symmetry. This asymmetric lattice distortion negatively affects the reversible expansion/contraction properties of LiMn$_2$O$_4$ during discharge/charge reactions.
Table 1-3:
Comparison of Active Cathode Materials.

<table>
<thead>
<tr>
<th>Active Material</th>
<th>LiCoO$_2$</th>
<th>LiNiO$_2$</th>
<th>LiMnO$_2$</th>
<th>LiMn$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Voltage</td>
<td>4.2 V</td>
<td>4.1 V</td>
<td>4.5 V</td>
<td>4.5 V</td>
</tr>
<tr>
<td>Safety</td>
<td>toxic</td>
<td>less toxic</td>
<td>non-toxic</td>
<td>non-toxic</td>
</tr>
<tr>
<td>Relative cost</td>
<td>high cost</td>
<td>moderate cost</td>
<td>low cost</td>
<td>low cost</td>
</tr>
<tr>
<td>Capacity</td>
<td>140 mAh/g</td>
<td>150 mAh/g</td>
<td>285 mAh/g</td>
<td>148 mAh/g</td>
</tr>
<tr>
<td>Other Comment</td>
<td>stable</td>
<td>broad phase distribution</td>
<td>metastable</td>
<td>electrolyte unstable</td>
</tr>
</tbody>
</table>

Table 1-3 is a brief comparison of the merits of each active cathode material mentioned earlier. LiCoO$_2$ is lower in capacity, toxic, and more expensive than the Ni- and Mn-based alternatives, but it has demonstrated significantly better stability and cyclability than its other competitors. Hence, LiCoO$_2$ is a commonly used standard cathode material for both fundamental studies and industrial applications.

1.2.2. Anodes

Lithium metal has a large theoretical capacity of 3.86 Ah/g (27 times that of LiCoO$_2$) as an anode material but as mentioned before, two persistent failure modes have shunned its use. Interphase films that form between lithium and the electrolyte are often destructive for both cell components, and accurately studying these interactions for further understanding is an onerous task. Needle-like dendrite crystals that form upon charging become electrically isolated from the anode during discharging due to non-homogeneous dissolution rates. These isolated metallic species are highly reactive and consume the anode as dead weight.
Lithium can alternatively be stored in a large variety of carbonaceous materials having varying degrees of crystallinity which depend on heat treatment during carbonization (< 1200°C) or graphitization (> 2000°C). Different forms of carbon can roughly be categorized as either amorphous carbons having any mixture of sp\(^3\), sp\(^2\), and sp\(^1\) sites, or graphite which has sp\(^2\) hybridized carbons only. Several amorphous carbon electrodes were initially investigated including carbon fiber, pyrolytic carbons, and petroleum coke, but it turned out that graphites offer higher capacity as a result of a more crystalline structure. High temperature treatments above 2000°C produce highly crystalline graphite, below which carbons tend to be disordered and lack long range order. The intercalation of lithium into carbon proceeds according to the reversible reaction:

\[
xLi^+ + 6C + xe^{-} \xrightarrow{\text{charging}} Li_xC_6
\]

where x < 1 for amorphous carbon, x \(\approx\) 1 for graphite, and x > 1 for mesoporous hard carbon. Complete utilization of the crystalline structure of graphite corresponds to a theoretical capacity of 372 mAh/g. Interestingly, mesoporous hard carbons are synthesized from cross-linked polymeric precursors that do not graphitize with heat treatment. They have demonstrated significantly higher capacities (> 400 mAh/g) by relying on surface and interfacial charging, although poor reproducibility, volume expansion, low capacity retention, and short cycle life have been problematic issues.
Figure 1-11: Carbonaceous anodes based on (a) carbon fiber, (b) natural flaky graphite, and (c) mesoporous hard carbon.

Figure 1-11 shows scanning electron microscopy (SEM) images of amorphous carbon fiber, natural flaky graphite, and mesoporous hard carbon. Graphite itself is a multilayer structure based on a regular stacking of 3-dimensional flat layers, called graphenes, along the c-axis which resembles a planar honeycomb-like structure. The in-plane distance between C-C atoms is 1.42 Å through covalent bonding, and the out-of-plane distance between carbon layers is about 3.35 Å held together by weak Van der Waals forces (Figure 1-12). Stacking of graphene layers can occur in rhombohedral (ABCABC) or hexagonal (ABAB) fashion, both of which are present in natural graphites such as spherical or flaky graphites. Irrespective of its constituent phase(s), graphite comes devoid of lithium and intercalation of lithium ions during a charging process shifts its phase to a repeating AAA type structure once the stage-1 structure is formed. The usual notation is that a stage-\( n \) structure has guests in every \( n \)th layer.
Consequently, the rhombohedral and hexagonal phases of graphite provide the same reversible capacity.\textsuperscript{68} Some studies have suggested that the rhombohedral phase is less prone to exfoliation\textsuperscript{69} and can provide more capacity through grain boundary effects,\textsuperscript{70} although the hexagonal phase is more thermodynamically stable. Therefore, artificial graphites obtained from high temperature synthesis typically contain only trace amounts of the rhombohedral phase. On the industrial scale, the synthesis of massive artificial graphite (MAG) constitutes the majority of the anode market. MAG is made up of flat particles randomly aggregated together. It warrants numerous desirable properties including a nearly pure hexagonal structure, low voltage of intercalation (0.1 V), nearly theoretical capacity (362 mAh/g), semi-metallic conductivity, high charge/discharge rates, 100\% coulombic efficiency, and greater than 94\% capacity retention on a highly reproducible basis. These properties are marked improvements over other anode materials which merits its industrial application since the early 1990s.

Considering the impressive performance of graphite, its manufacturing is actually very tedious because of the need to carefully form the initial SEI layer during the first charge process, and expansion/contraction issues must also be properly engineered in the cell design. The
interlayer spacing between graphene layers increases from 3.35 Å to 3.70 Å which is about 10%, but due to solvent co-intercalation interactions, the expansion of graphite during operation is actually more than 150%.\textsuperscript{71} To measure up to the performance of graphite anodes, another novel anode material appeared in 1999, this time a spinel lithium titanate (Li$_4$Ti$_5$O$_{12}$) synthesized via solid state calcination.\textsuperscript{72,73}

$$4\text{TiO}_2 + \frac{5}{2}\text{Li}_2\text{CO}_3 + \frac{3}{4}\text{O}_2 \xrightarrow{850^\circ\text{C}} \text{Li}_4\text{Ti}_5\text{O}_{12} + \frac{5}{2}\text{CO}_2$$

Stoichiometric amounts of anatase (TiO$_2$) and lithium carbonate (Li$_2$CO$_3$) are calcined together in oxygen atmosphere to produce spinel Li$_4$Ti$_5$O$_{12}$. It belongs to a class of defect spinels of the type Li[Li$_{1/3}$M$_{5/3}$]O$_4$ where M = Ti in this case, and the strong M-O bonds maintain the metal oxide framework during insertion and extraction.\textsuperscript{74} Under an applied current, Ti$^{4+}$ ions are reduced to Ti$^{3+}$ to accommodate the insertion of three lithium ions.

$$\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3e^- \xrightarrow{\text{charging}} \text{Li}_7\text{Ti}_5\text{O}_{12}$$

$$\text{Li}_7\text{Ti}_5\text{O}_{12} \xrightarrow{\text{discharging}} \text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3e^-$$

Lithium and titanium atoms are randomly distributed in one-half of the octahedral (16c) sites in addition to lithium atoms also occupying one-eighth of the tetrahedral (8a) sites within a face-centered oxygen close packed lattice. The three incoming lithium ions, as well as the original lithium ion occupying an 8a site, move to occupy adjacent 16c sites via the 8a sites to transform the spinel structure to a layered rock salt (Figure 1-13).\textsuperscript{73}
This process is completely reversible as during the de-intercalation process, lithium is emptied from the 16c sites via the 8a sites in reverting back to the spinel structure. Intimate mixing interactions between 8a and 16c sites characterizes Li$_4$Ti$_5$O$_{12}$ as a solid solution which is beneficial for lithium mobility compared to the ordered coexistence of 8a and 16c domains. Lithium resides partly in both 8a and 16c sites, and the presence of such defects is believed to be responsible for the high lithium diffusivities and rate capabilities of Li$_4$Ti$_5$O$_{12}$.\textsuperscript{76}

The volume of the original face-centered cubic unit cell (F$_{3\text{dm}}$) changes only 0.3%\textsuperscript{77} compared to the 150% volume expansion of carbon during intercalation. Minimal volumetric alteration identifies Li$_4$Ti$_5$O$_{12}$ as a zero-strain insertion material, in addition to it also demonstrating excellent cyclability in a wide voltage window (1 – 5 V),\textsuperscript{78} high lithium diffusivity,\textsuperscript{79} absence of a solid electrolyte interface (SEI),\textsuperscript{72} and superior safety.\textsuperscript{80} Figure 1-16 reveals the intercalation of lithium into the spinel structure of Li$_4$Ti$_5$O$_{12}$ proceeding at 1.55 V and extraction at 1.5 V vs. Li/Li$^+$. In general, controlling the particle structure also affects cell
performance. Bulk $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles consistently deliver weaker rate performance than mesoporous particles, this trend being attributed to the greater surface area offered by mesoporous particles to enhance reaction kinetics.$^{81}$

Within the 1.0 – 3.0 voltage window, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is completely free of side reactions with the electrolyte.$^{72}$ So long as voltages less than 1.0 V are not imposed, $\text{Li}_4\text{Ti}_5\text{O}_{12}$-based cells have actually demonstrated excellent cyclability within the 1.0 – 5.0 V range.$^{80}$ It is often claimed to be a SEI free electrode material, but strictly speaking, this is only true if it operates above 1.0 V. Since its lithium intercalation voltage occurs around 1.5 V, this condition is easy to meet, but avoiding SEI formation comes with the drawback of sacrificing the voltage output. For example, a $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiCoO}_2$ cell provides an operating voltage of about 2.4 V as opposed to a 3.0 V cell if lithium were the anode. Graphite anodes also offer a much lower voltage (0.1 V) than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (1.0 V), and therefore higher energy densities when coupled to a higher voltage cathode material, although $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is generally free of SEI reactions and volumetric expansion that burden the use of graphite.

1.3. Electrolytes

Electrodes determine the power output of a cell while the electrolyte controls the rate of mass flow within the cell. High ionic conductivities allow faster charge and discharge rates at a given temperature. Lithium-ion conducting electrolytes consist of a lithium salt dissolved in a solvent which forms a solution that exists as a liquid, gel, or solid phase. The conductivity of the
Electrolyte is then directly related to the specific lithium salt, the solvent or conducting medium for the ions, and the physical structure of the electrolyte.

![Schematic illustration of electrolyte networks](image)

**Figure 1-14**: Schematic illustration of electrolyte networks; (a) liquid electrolyte pathways in a porous polyolefin (Celgard) membrane separator; (b) a gel electrolyte consisting of semicrystalline regions for structural support and amorphous regions swollen with liquid electrolyte; (c) a solid polymer electrolyte where Li⁺ (red dot) moves along entangled polymer chains.⁴

Schematic illustrations of various electrolyte systems are shown in Figure 1-14. Liquid electrolytes are based on lithium salt dissolved in liquid solvent. Cells assembled using purely liquid electrolyte must also rely on a porous polyolefin (brand name Celgard) membrane as a separator to prevent direct contact between the positive and negative electrodes while allowing permeation of liquid electrolyte. A gel electrolyte is a polymer host swollen with liquid electrolyte, where structural rigidity is maintained by crystalline regions within the polymer host, and amorphous regions increase electrolyte uptake. By doing so, the gel plays the dual role as an electrolyte and a separator. If the solvent becomes a solid, typically being high molecular weight organic polymer bearing similar chemical functionality as liquid solvents, then lithium ions are
coordinated by polymer chains and move along the polymer assisted by the random thermal motion of polymer chains.\textsuperscript{4}

![Graph showing ionic conductivity vs. liquid electrolyte percentage.]

**Figure 1-15:** The ionic conductivity of electrolyte films based on its phase using PVDF as a model polymer host.\textsuperscript{82}

Under the application of an electric field, and depending on the polarity of the working electrode, lithium ions migrate toward an electrode where it is ‘captured,’ so to speak. If the polarity is reversed, then the lithium ions migrate toward the opposite electrode. The basic property of an electrolyte in a battery is that it allows the reversible conduction of ions, but not electrons. Hence, it should have high ionic conductivity but low electronic conductivity. Any appreciable electronic conductivity in the electrolyte potentially causes spontaneous self-discharge of the battery when it is not in use. Because the solvents for lithium-ion electrolytes are organic and tend to have low inherent electronic conductivity, self-discharge is usually not a problem. But in other systems such as the Ni-MH electrolyte which is a 3-6 M KOH solution,
sufficient electronic conductivity in the electrolyte results in a 1% self-discharge on a daily basis.\textsuperscript{83}

1.3.1. Lithium Salts

Electrochemical activity of electrolytes originate from dissolved lithium salts which are abundant in chemical diversity but the selection becomes limited from certain restrictions: (1) it must completely dissolve or dissociate in nonaqueous media; (2) its ion mobility should be high; (3) both the cation and anion must remain inert to other cell components (e.g. separator, electrolyte, anode, cathode); (4) it should be non-toxic and resistant to thermally induced reactions. The importance of ion dissociation and ion mobility are reflected by their influence on the ionic conductivity ($\sigma$) from the relation:

$$\sigma = \sum_i n_i u_i Z_i e$$  \hspace{1cm} (1-14)

where $n_i$ is the number of free ions, $u_i$ is the ion mobility, $Z_i$ is the valence number of the ionic species $i$, and $e$ is the unit charge of electrons.\textsuperscript{84} Ionic conductivity depends on the concentration of charge carriers and their mobility as charged species. Both of these variables weigh against each other because while it may appear that ionic conductivity increases with increasing concentration of dissolved salt, the conductivity usually reaches a maximum at a relatively low concentration of ions. The downturn in conductivity thereafter is attributed to frictional forces that impede the ion’s mobility, despite increasing salt concentration, as expressed by the Stokes-Einstein formula:\textsuperscript{84}

$$u_i = \frac{1}{6\pi\eta r_i}$$ \hspace{1cm} (1-15)
where $\eta$ is the viscosity and $r_i$ is the solvation radius of the ion. From this relation, ion mobility is inversely proportional to the viscosity of a given solution and the solvation radius of dissolved ions. Different lithium salts have varying ion mobilities due to changes in the solvation sheath of the anion, considering that the solvation size of the lithium cation remains constant. It is therefore expected that salts having larger anions are lower in mobility compared to smaller salts, and hence, lower conductivities. In extreme cases where the anion is polymeric and very large, reduced ion mobility from the anion drastically lowers the overall ionic conductivity.\(^{85}\)

Setting aside the effects of the anion’s size, for a given solute, increasing solute concentration affects the viscosity of the solute-solvent mixture, for which lithium salts are known to raise the solution viscosity.

![Graph showing conductivity and viscosity of NaClO$_4$ and LiClO$_4$ model salts in $\gamma$-Butyrolactone.\(^{86}\)](image)

The conductivity and viscosity of NaClO$_4$ and LiClO$_4$ model salts in $\gamma$-butyrolactone solvent are plotted against salt concentration in Figure 1-16.\(^{86}\) As the salt concentration increases, the solution viscosity rises. The conductivity initially increases as the free ion number
increases until it reaches a maximum, after which the conductivity continually decreases as the high viscosity reduces the mobility of solvated ions under an applied electric field. Low viscosity solvents are, therefore, a necessity to maintain high ion mobilities and high ionic conductivities. Ion mobility can also be tuned by modifying the solute volume, but for practical applications, the available selection of lithium salts is very limited because of safety and stability issues. Without considering ionic radius as an experimental parameter to enhance conductivity, liquid electrolytes for lithium-ion batteries are based on finely tuned solvent mixtures having low viscosity.

Most simple salts of lithium (e.g. LiF, LiCl) are weakly soluble in nonaqueous media because of the ‘hardness’ of both the lithium cation and the simple anion which bond strongly. Setting other factors aside, increasing the ‘softness’ of the anion by replacing it with Br⁻, I⁻, or S²⁻ would increase the salt’s solubility in nonaqueous solvent, but salts of these anions are nonetheless anodically unstable above 4.0 V. Those that meet both solubility and voltage stability requirements are based on the anions of Lewis superacids including lithium perchlorate (LiClO₄), lithium hexafluoroarsenate (LiAsF₆), lithium tetrafluoroborate (LiBF₄), lithium triflate (LiTf), and lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) as shown in Table 1-4.
Firstly, LiClO$_4$ is an attractive solute for laboratory testing\textsuperscript{20} because of its high conductivity and anodic stability up to 5.1 V vs. Li/Li$^+$.\textsuperscript{87} On the serious downside, the high oxidation state of chlorine (VII) makes it a powerful oxidant capable of reacting violently with organic species at high temperatures or under high charge-discharge currents.\textsuperscript{88} Thus, its lack of safety has averted it from industrial use. LiAsF$_6$ has suffered from a similar problem. Although it has the highest conductivity in EC/DMC for this series of solutes,\textsuperscript{89} any electrochemical reduction of As(V) during cell operation to either As(III) or As(0) would produce highly toxic species.\textsuperscript{90} As such, LiAsF$_6$ is suited for small scale studies but its toxicity prohibits large scale application. On the other hand, LiBF$_4$ is claimed to be less toxic than LiAsF$_6$ and safer than
LiClO$_4$\textsuperscript{91} However, it has a low ionic conductivity due to a poor balance between its highest ion mobility and low dissociation constant.\textsuperscript{92} The use of LiBF$_4$ has been rare because of its inferior conductivity.

Unlike LiClO$_4$, LiAsF$_6$, and LiBF$_4$ which are the anion form of inorganic superacids, LiTf and LiTFSI represent the conjugate bases of organic superacids. The triflate and TFSI anions are based on sulfonate groups having strong electron-withdrawing CF$_3$ functional groups. High acidities are realized by a combination of both inductive and resonance effects that stabilize the anion. As the simplest member of this class of organic anions, LiTf affords the lowest conductivity due to relatively low dissociation constant and moderate ion mobility.\textsuperscript{93} A larger chemical relative of LiTf appeared in 1984 in the form of LiTFSI, bearing a chemical structure composed of two triflic groups with a lone electron-pair nitrogen between them.\textsuperscript{94} Its larger delocalized electronic structure compared to LiTf result in electrolytes that are highly conducting, safe, and thermally stable. In fact, ionic association has been experimentally confirmed to be essentially absent for this anion.\textsuperscript{95,96} Commercialization by 3M Corporation in the 1990s further popularized LiTFSI for mostly research purposes since triflate-based salts undergo corrosive reactions with aluminum, an essential low cost cathode current collector substrate.\textsuperscript{97}

Considering the advantages and often vital flaws of the aforementioned lithium salts, LiPF$_6$ was eventually selected for commercialization not because it excelled in any area, but because of its overall well-balanced properties. For a brief comparison, LiPF$_6$ has a lower conductivity than LiAsF$_6$,\textsuperscript{98} lower dissociation constant than LiTFSI,\textsuperscript{98} lower ion mobility than LiBF$_4$,\textsuperscript{98} and slightly lower anodic stability than LiAsF$_6$.\textsuperscript{99} It so happens that none of the other
salts are able to meet these multifaceted requirements as well as LiPF$_6$, as described in the following trend:

Average ion mobility: LiTFSI $<$ LiTf $<$ LiAsF$_6$ $<$ LiPF$_6$ $<$ LiClO$_4$ $<$ LiBF$_4$

Dissociation constant: LiTf $<$ LiBF$_4$ $<$ LiClO$_4$ $<$ LiPF$_6$ $<$ LiAsF$_6$ $<$ LiTFSI

Acquiring both high ion mobility and high dissociation constant cannot be achieved by any individual lithium salt. LiPF$_6$ has intermediate values and has demonstrated success in real device applications, thereby gaining general acceptance from both research and industrial perspectives.

1.3.2. Liquid Electrolytes

Ionic conductivity is a direct consequence of solvent properties which include the free charge number and ion mobility. Just as ion mobility is affected by the viscosity, the free charge number is influenced by the dielectric constant of the solvent ($\varepsilon$) according to the relation:

$$q = \frac{|z_i z_j| e^2}{8\pi \varepsilon_0 \varepsilon kT}$$

(1-16)

where $q$, $z$, $e$, $\varepsilon_0$, $k$, and $T$ correspond to the critical distance for ion pair formation, valence order of ions, unit charge of electrons, dielectric constant of vacuum, dielectric constant of the solvent, Boltzmann’s constant, and temperature, respectively. Ions in solution exist as aggregate ions, contact ion pairs, or solvent separated ion pairs, of which only separated ion pairs are conductive. For a solvated ion to migrate, non-conducting ion pairs must be prevented from forming. Ion
pairing occurs at a distance less than the critical distance q, so high dielectric solvents work by lowering the critical distance in order to keep ions separated by solvent interactions. They are more effective at shielding ion-ion interactions, which means that counter-ions must come closer than otherwise to pair up. By reducing ion association kinetics, high dielectric solvents increase the free ion number which then improves the conductivity.

An ideal electrolyte solvent should therefore meet the following criteria: (1) it should have a high dielectric constant to sufficiently dissolve lithium salts; (2) its fluid viscosity (\(\eta\)) should be low for facile ion transport; (3) it should remain inert during cell operation; (4) its physical state should be a liquid within a wide temperature range; (5) it should also be safe, non-toxic, and economical. Requirements (1) and (2) are actually in conflict with each other since high dielectric solvents are highly viscous, whereas low viscosity solvents are poor dielectrics. To illustrate this point, commonly used polar aprotic solvents fall into the class of organic esters and ethers as shown in Table 1-5.
Table 1-5:
Organic Esters as Electrolyte Solvents.\textsuperscript{13}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>$M_w$</th>
<th>$T_m$ (°C)</th>
<th>$T_b$ (°C)</th>
<th>$\eta$ (cP)</th>
<th>$\varepsilon$</th>
<th>$d$ (g/mL)</th>
</tr>
</thead>
</table>
| DMC     | \[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\] | 90    | 4.6       | 91         | 0.59        | 3.107       | 1.063       |
| DEC     | \[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\] | 118   | -74.3     | 126        | 0.75        | 2.805       | 0.969       |
| EMC     | \[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\] | 104   | -53       | 110        | 0.65        | 2.958       | 1.006       |
| EC      | \[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\] | 88    | 36.4      | 248        | 1.90        | 89.78       | 1.321       |
| PC      | \[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\] | 102   | -48.8     | 242        | 2.53        | 64.92       | 1.200       |
| $\gamma$-BL | \[
\begin{array}{c}
\text{O}
\end{array}
\] | 86    | -43.5     | 204        | 1.73        | 39          | 1.199       |

Linear esters shown in Table 1-5 include dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). They generally have a wide liquid range and low viscosity, but their dielectric constant is insufficiently low for dissolving lithium salts. On the other hand, cyclic esters (carbonates) including ethylene carbonate (EC), propylene carbonate (PC), and $\gamma$-butyrolactone ($\gamma$BL) are highly viscous liquids ($\eta = 1.7 – 2.6$) that offer outstanding dielectric constants ($\varepsilon = 34 – 90$). The dielectric constant of EC ($\varepsilon \sim 90$) is remarkably even higher than that of water ($\varepsilon = 79$). Significantly higher dielectric constants inherent in cyclic esters come from intramolecular strain of the cyclic structure which favors the alignment of
molecular dipoles, whereas the open and flexible structure of linear esters results in the mutual cancellation of dipoles.

Considering the contradicting elements of singular solvent species, mixtures of solvents are therefore used in order to perform various functions simultaneously. It was confirmed during the early 1990s that using PC, THF, and 2-Me-THF co-solvents resulted in large irreversible capacities, while the ethers were unstable at high voltages. In 1994, Tarascon and Guyomard reported the use of DMC, a linear ester, as a co-solvent for EC. Surprisingly, an EC/DMC mixture has a synergistic effect such that it is electrochemically stable up to 5.0 V vs. Li/Li+. Each individual solvent also refined the properties of the resultant mixture through: (1) the anodic stability of EC; (2) the high solvating power of EC for lithium salts; (3) the low viscosity of DMC to facilitate ion transport. This formulation quickly set a new benchmark for state-of-the-art lithium ion electrolytes. Various linear esters such as DEC and EMC were explored for the same purpose, and their electrochemical characteristics were found to be nearly identical.
Shown in Figure 1-17 is the molar conductivity (Λ) of a 1 M LiClO₄ solution in a PC/DME solvent. At either extreme when the solvent composition is pure PC or DME, the conductivity is lower than if a mixture is used. Without any DME, the electrolyte conductivity is relatively low but serially adding DME continually lowers the viscosity which subsequently increases the conductivity up to an order of magnitude at about 60% DME. In this region, lowering the viscosity brings about a net increase in conductivity even if the dielectric constant suffers some loss because the dielectric constant is still high enough to ensure ion solvation. Thus, ionic conductivity in this region is dominated by ion mobility, or termed the viscosity effect. Increasing the DME composition beyond this point then leads to a decline in conductivity, because although the viscosity is continually lowered (which may be beneficial for
ion mobility), the dielectric constant becomes insufficiently low for dissolving salts. As a result, the solution becomes deprived of free ions for conduction, also called the ion-pairing effect. The ion-pairing effect apparently outweighs the viscosity effect beyond this critical percentage of DME. Properly balancing solvent mixtures according to the properties of the individual components brings out the superior advantages of binary systems. EC deserves special attention since its dielectric constant is ideal for solvating ions, but its melting temperature is inconveniently above room temperature. To date, electrolyte formulations that are used in the over 1 billion lithium ion cells manufactured each year are based on a mixture of EC for high $\varepsilon$ and a linear ester for low $\eta$.

1.3.3. Gel Electrolytes

Gels comprise a particular state of matter that is neither liquid nor solid, and interestingly they exhibit both the cohesive properties of a solid and the diffusive properties of a liquid. A gel polymer electrolyte (GPE) is based on a polymer network that is swollen with electrolyte solvent, whereby the solvent is dissolved in the polymer matrix. In the process of gelling or plasticizing a polymer host, the infiltrated liquid grants chemico-physical properties to the hybrid network structure. The role of the polymer host then is a physical support to contain the liquid electrolyte and prevent leakage. A secondary function of gel electrolytes is a physical separator between the cathode and anode to prevent short-circuiting.

Ideally, polymer hosts must have chemical resistance, thermal stability, and high voltage stability. Polymers that meet these requirements generally include polyfluorocarbons, of which poly(vinylidene fluoride) (PVDF) is an exemplar material. Fluorine’s highest electronegativity
leads to tight binding of its valence electrons, where the electronegativity difference between carbon and fluorine is 2.5 vs. 4.0, respectively.\textsuperscript{109} Highly polar covalent C-F bonds result in high bond energies (thermal stability), while the low polarizability of CF\textsubscript{x} functional groups translates to weak intermolecular interactions and chemical inertness.\textsuperscript{110} Furthermore, PVDF has a dielectric constant ($\varepsilon$) of 8.4 which slightly assists in the ionization of a salt and production of more charge carriers.

\begin{align*}
\text{PVDF} & \quad [\overset{\scriptscriptstyle{C}}{\overset{\scriptscriptstyle{C}}{H}}_{n} \overset{\scriptscriptstyle{F}}{\overset{\scriptscriptstyle{F}}{C}}_{n} ] \\
\text{P(VDF-HFP)} & \quad [\overset{\scriptscriptstyle{C}}{\overset{\scriptscriptstyle{C}}{H}}_{x} \overset{\scriptscriptstyle{F}}{\overset{\scriptscriptstyle{F}}{C}}_{y} ]_{CF_{3}} 
\end{align*}

Figure 1-18: Chemical structures of PVDF and P(VDF-HFP).

Plasticization of PVDF by liquid electrolyte induces ionic conductivity, during which the polymer is swollen to a gel state. Although they plasticize sufficiently, chemical functionalization of PVDF polymers have sought ways to generate microporous structures to improve its solubility parameters. Both of these factors are to improve the ionic conductivity of such gel polymer electrolytes. A polymeric variant of PVDF, the poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) copolymer, is a modest improvement upon its parent polymer (chemical structures are shown in Figure 1-18). Amorphous HFP units incorporated into the copolymer entrap large amounts of liquid electrolyte to improve the gellation, while the crystalline PVDF phase still acts as a mechanical support for the polymer.
Despite methods to improve material properties, gel polymer hosts lose their mechanical strength regardless when plasticized by liquid electrolyte. Acquiring high ionic conductivity in the gelled polymer is adversely accompanied by loss of mechanical strength. To overcome this problem, special processing techniques have been devised to retain the mechanical properties of gel films while improving ion transport properties. Phase inversion methods are mostly used to prepare flexible membranes of controllable pore structure.

Figure 1-19: P(VDF-HFP) copolymer membrane prepared by phase inversion technique.\textsuperscript{111}

A film prepared from phase inversion is depicted in Figure 1-19. To ensure film homogeneity, the copolymer is first fully dissolved in high boiling point solvent (i.e. NMP, DMF, DMAc) and casted onto a glass substrate carrier. This film is then immersed in non-solvent such as water, during which the polymer precipitates out of solution and the non-solvent replaces the solvent to produce a porous polymer structure. After careful drying, the polymer film is activated by immersing in electrolyte solution to afford a gel polymer electrolyte with an ionic conductivity exceeding $10^{-3}$ S/cm and voltage stability up to 5.0 V vs. Li/Li$^+$. Also known
as non-solvent induced phase separation (NIPS), this technique has demonstrated widespread success, most notably in Bellcore’s plastic rechargeable lithium-ion batteries. NIPS is a nearly ideal process for preparing gel membranes because most of the treatment occurs outside and only the activation step is done in a dry room. The major disadvantage is the need for high boiling point and toxic solvents to fully dissolve the PVDF polymer so that homogeneous films can be casted. Toxicity is such a problem that strict regulations are enforced to recycle the spent solvent.112

Judging by material properties, GPEs begin as soluble polymer precursors that after activation, have adequate mechanical rigidity, ionic conductivity, and high voltage stability. These properties are not only suitable for an electrolyte separator, but also as an electrode binder. Lithium-ion battery electrodes consist mainly of active material, but because of the low inherent conductivity of active materials, carbon black is added at low percentages to boost the conductivity to appropriate levels. Both the active material and carbon black are pure solids without any structural cohesion, so polymers are used to withhold the electrode ingredients. Electrode fabrication is based on a slurry coating process where the polymer binder is first dissolved, and then active material and carbon black are dispersed in the polymer solution. This slurry or dispersion is then casted onto a current collector (usually aluminum foil for cathode or copper foil for anode), dried to remove solvent, and then soaked in liquid electrolyte. PVDF polymers make superb binders for the same reasons that they are used as GPEs: adequate structural cohesion and rigidity, high ionic conductivity, and wide electrochemical window. But as before, the major shortcoming that comes hand in hand with using PVDF polymers is the usage of toxic solvents. Casting electrode slurries of PVDF requires costly distillation towers for
solvent recovery. Because of this major problem, numerous research efforts have focused on methods that rely on solvents that are safer and less costly.

1.3.4. Solid Polymer Electrolytes

Low lattice energy alkali salts (e.g. lithium salts) form ionically conductive complexes when they are solvated by polymers, and such complexes have a low interfacial resistance and broad voltage stability which make them suited for diverse energy storage applications. Although they are generally lower in conductivity compared to liquid and gel electrolytes, solid polymer electrolytes have many prospective advantages that merit their use in lithium-ion batteries. First, a continuous, non-porous solid electrolyte membrane is able to suppress the growth of lithium dendrites that otherwise form when using a gel electrolyte or polymer separator, both of which rely on a permeating liquid electrolyte. A second advantage of SPEs is reduced reactivity against a lithium or carbonaceous anode (the voltage difference between lithium and lithiated graphite is only 0.1 V). While SPEs still passivate against lithium, its solid-like nature inhibits the dissolution and re-growth of the passivation layer which is a common failure mode of lithium-ion batteries. Simultaneously, the lack of liquid also means lowered risk to explosion and better tolerance to shock, vibration, and mechanical deformation. Shape flexibility and improved mechanical properties is an invaluable asset for process design issues. Such films are not restricted to rectangular or cylindrical batteries, but spray-on, dip-coating, and an automatic laminating process become available via well-developed coating technology. In practice, polymer electrolytes are mostly based on polyether-inorganic salt complexes that have a low T_g. Exemplar materials for solid polymer electrolytes include methoxy-terminated
PEG and oligoether functionalized polysiloxane\textsuperscript{113} and polyphosphazene\textsuperscript{114} as shown in Figure 1-20.

![Chemical Structures](image)

Figure 1-20: Solid Polymer Electrolytes for Lithium-Ion Batteries

Because electrolytes are in direct contact with a highly reducing anode, PEG must be end-terminated with methoxy units to remove reactive protons. PEG has been the most extensively studied solid polymer electrolyte because it has higher conductivity than polypropylene oxide, poly(methyl methacrylate), and poly(acrylonitrile). From a synthetic perspective, methods for incorporating oligoether or polyether units onto a parent molecule to induce ionic conductivity are abundant and can be facile. Polysiloxanes and polyphosphazenes are, in fact, inorganic backbones of which oligoether branches are attached. Similarly to complexation by organic carbonate solvents, PEG dissolves lithium salts by tetrahedral coordination of the metal center which requires two PEG chains, each chain acting as a bidentate ligand. Ion transport in PEG occurs through the random thermal motion of lithium ions coordinated by PEG chains above the glass transition temperature of the complex. Conduction of lithium ions is accommodated by the segmental rearrangement of ether units as the lithium ions are transported predominately in an intra-chain fashion along the PEG network, as
illustrated in Figure 1-21. Inter-chain transport also contributes to the conductivity but occurs much less frequently.\textsuperscript{115}

![Figure 1-21: Cartoon illustration of ion motion in a polymer host.\textsuperscript{115}](image)

PEG usually has a $T_g$ well below room temperature, but one of the major setbacks is that high molecular homopolymers form crystalline lamellae through chain folding or chain elongation. Despite the polymer being amorphous, crystalline regions within the material strongly impede ion transport, resulting in very low conductivities at room temperature. Heating PEO above its melting point (ca. 60°C) causes it to liquefy which then leads to an abrupt increase in ionic conductivity. Practical conductivities ($10^{-4}$ S/cm) are therefore only breached at high temperatures of about 60°C-80°C when the solid electrolyte melts.

**1.4. Introduction Summary**

A brief overview of lithium battery technology has been presented. The primary incentives for the development of lithium batteries are high energy densities, high rate capability, and long cycle life. Disadvantages to consider are high cost and difficulties of manufacturing
which arise from the high reactivity of lithium metal and hygroscopicity of lithium ion electrolytes. Commercial liquid electrolytes are based on finely tuned mixtures of linear and cyclic esters with LiPF$_6$ as solute. Gel electrolytes are usually PVDF-based polymers casted by phase inversion techniques to produce a highly porous electrolyte membrane. Solid polymer electrolytes are mostly polyether-inorganic salt complexes that are ionically conductive at room temperature. An electrolyte can also serve as an electrode binder so long as it offers mechanical strength without hindering transport processes within an electrode. Chapter 2 presents the synthesis of a soluble, amorphous, and adhesive solid polymer electrolyte based on PEG. This chapter is based on a recently published article titled “Adhesive Poly(PEGMA-co-MMA-co-IBVE) Copolymer Electrolyte” in the journal Solid State Ionics.$^{116}$ Chapter 3 focuses on improving the conductivity of the poly(PEGMA-co-MME-co-IVE) copolymer electrolyte through the addition of inorganic electrolyte additives. Chapter 4 is an investigation of this copolymer as a binder for lithium-ion battery cathodes, namely the standard LiCoO$_2$ electrode, and is also based on scientific work published in Journal of the Electrochemical Society titled “Thick LiCoO$_2$ Cathode Prepared by an Adhesive and Water-Soluble PEG-Based Copolymer Binder.”$^{117}$ Chapter 5 describes the use of this solid polymer electrolyte as an anode binder, and this article has also been published as “Adhesive PEG-Based Binder for Aqueous Fabrication of Thick Li$_4$Ti$_5$O$_12$ Electrode” in Electrochimica Acta.$^{118}$ Overall, a poly(PEGMA-co-MMA-co-IBVE) copolymer demonstrates outstanding versatile functions as a vinyl-acrylic electrolyte and electrode binder that is facilely synthesized and enables novel, faster, safer, and less costly processes for fabricating lithium-ion batteries.
1.5. References


CHAPTER 2:
ADHESIVE POLY(PGMA-CO-MMA-CO-IBVE) COPOLYMER ELECTROLYTE

Ch. 2 Abstract: The synthesis of a soluble, amorphous, and adhesive electrolyte based on poly(ethylene glycol) is presented. A high molecular weight poly(PEGMA-co-MMA-co-IBVE) random copolymer with the lithium ion conductivity of 4.8x10^{-5} S/cm at room temperature is synthesized through a facile statistical copolymerization of poly(ethylene glycol) methyl ether methacrylates (PEGMA), methyl methacrylate (MMA), and isobutyl vinyl ether (IBVE). The polymer composition, thermal properties, adhesion, and electrochemical properties are discussed. Such a copolymer has the adhesion strength to permanently hold 800 times its own weight, and high solubility in water and organic solvents for easy material processing. Its unique and versatile properties belong to a class of multifunctional soft matter electrolytes.

2.1. Introduction

Ethers such as dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyl-tetrahydrofuran (2-Me-THF), 1,3-dioxolane (1,3-DL), and 4-methyl-1,3-dioxolane (4-Me-1,3-DL) were once regarded as potential candidates as electrolyte solvents during the 1980s largely due to improved lithium morphology during cycling, but lithium-ion cells had poor capacity retention and dendrites formed over the long term anyways. Furthermore, ether functional groups tend to oxidize at the cathode surface at 4.0 V compared to the 5.0 V stability of ester
mixtures.\textsuperscript{5} The failure of ether solvents amidst the widespread application of potent cathode materials exceeding 4.0 V (e.g. LiCoO\textsubscript{2}, LiMnO\textsubscript{2}, LiNiO\textsubscript{2}) quickly diminished research interest in liquid ether electrolyte formulations.

In contrast to low molecular weight ethers, high molecular weight polyethers such as poly(ethylene oxide) (PEO or PEG) have long been among the materials of choice as polymer electrolytes, next to poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), and poly(vinylidene fluoride) (PVDF), although several commonly encountered problems with this material include its ionic conductivity and adhesion ability. Unlike the benchmark PVDF polymers which have demonstrated acceptable adhesion and ionic conductivity in gel electrolytes,\textsuperscript{6} PEO has generally suffered from weak adhesion\textsuperscript{7} in addition to its inherent low ionic conductivity at room temperature.\textsuperscript{8} One of the simpler strategies to circumvent this problem has been to use very high molecular weight PEO in combination with a low molecular weight plasticizer,\textsuperscript{9,10} ionic liquid,\textsuperscript{11,12} inorganic ester,\textsuperscript{13} or plastic crystal\textsuperscript{14,15} in order to produce semi-solid or solid-state electrolytes with improved ionic conductivity and interfacial interactions.

Recent trends in electrolyte research have shown a considerable degree of evidence for the use of ‘soft matter,’ as opposed to strictly solid-state, electrolytes for energy storage applications. Such materials include functionalized copolymers and cross-linked polymers which have demonstrated improved ionic conductivity and mechanical properties. For example, ‘solid-state’ electrochromic windows\textsuperscript{16} and lithium-ion batteries\textsuperscript{17} have been fabricated by PEO-based copolymers. It has furthermore been shown that PEO alone may hinder the dissolution of sulfur in Li/S batteries\textsuperscript{18} or the growth of lithium dendrites when applying a cross-linked gel
against a lithium anode, thereby imparting a dual electrolyte/separaror functionality for polymeric electrolytes. Many cross-linked acrylonitrile and methacrylic-based polymeric systems have afforded gel-like polymer electrolytes that have superior properties in terms of stability against lithium, compatibility with plasticizing liquid electrolyte solution, ionic conductivity, and physico chemical properties. Thus, soft matter type materials have shown many prospective advantages for battery applications.

This study presents the synthesis of an adhesive PEO-based electrolyte membrane by the statistical copolymerization of PEGMAs, MMA, and IBVE to produce a high molecular weight poly(PEGMA-co-MMA-co-IBVE) random copolymer by a thermal curing process. Generally, the free radical syntheses of statistical or random copolymers methodically avoid expensive polymerization catalysts or chain transfer agents which reduce the cost and time of manufacturing, although they lack in molecular weight control of the growing chains. Hence, this method is selected based on its ease of producing multifunctional copolymers at a macromolecular level without the use external plasticizers or additives. The properties of the synthesized poly(PEGMA-co-MMA-co-IBVE) random copolymer are discussed in terms of its composition, thermal properties, adhesiveness, lithium ionic conductivity, and electrochemical stability. It demonstrates excellent contact adhesion and tackiness to surfaces including stainless steel, borosilicate glass, and rubber latex. Testing the adhesion strength of the copolymer validates that it can permanently hold up to 800 times its own weight. A maximum ionic conductivity of $4.8 \times 10^{-5}$ S/cm at room temperature and $1.69 \times 10^{-4}$ S/cm at 40°C are achieved using LiTFSI as lithium salt. Lastly, its ease of solubility in water and organic solvents allow for facile processing.
2.2. Experimental

2.2.1. Materials and methods

Poly(ethylene glycol) methyl ether methacrylate (average $M_n$ 300, 475, and 950), 2,2’-azobisisobutyronitrile 98% (AIBN), methyl methacrylate (99%), isobutyl vinyl ether (99%), ethyl acetate (99%), hexanes (99%), tetrahydrofuran (anhydrous) were purchased from Sigma Aldrich and used as received. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was purchased from 3M, vacuum dried at 200°C overnight prior to use, and stored in an argon filled dry box. Lithium foil (0.75mm x 19mm, 99.9%) was purchased from Alfa Aesar and also stored in an argon filled dry box.

The molecular weight and molecular weight distribution were measured using a JASCO gel permeation chromatograph equipped with a refractive index (RI) detector, using HPLC grade THF as eluent and monodistribution polystyrene as standards. FT-IR spectra were scanned by a Perkin-Elmer Spectrum-100 spectrometer. $^1$H NMR spectra were scanned using a 300 MHz Oxford Labs instrument using CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Differential scanning calorimetry (DSC) was performed using a DSQ-1000 instrument. For DSC, samples were hermetically sealed in aluminum pans and measurements were performed under nitrogen gas flow from -50°C to 200°C at a rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on a TGA-1000 instrument (TA Instruments) at a heating rate of 10°C/min from 50°C to 380°C under air or nitrogen gas flow of 110 psi. Sample weights ranging from 35-50 mg were loaded onto a platinum crucible. Prior to ramping the temperature, the samples were incubated under gas flow for 10 minutes.
Rheological properties were measured by a rheometer (Rheometric Scientific, Ares) at 1% strain which was within the linear viscoelastic regime of the copolymer, using 25 mm plates at 1 mm gap. Adhesion tests were designed by applying 15 mg of the copolymer between two aluminum blocks and compressed to 10 um thickness with the aid of 10 µm stainless steel foil spacers. Weights were serially added until a permanent adhesion between the two aluminum blocks was no longer maintained. These tests were performed inside a glove box to avoid moisture contamination.

2.2.2. Synthesis of poly(PEGMA-co-MMA-co-IBVE)

![Reaction scheme of the statistical copolymerization of poly(PEGMA-co-MMA-co-IBVE).](image)

Figure 2-1: Reaction scheme of the statistical copolymerization of poly(PEGMA-co-MMA-co-IBVE).

PEGMAs of different molecular weights ($M_n$ 300, 475, 950) were polymerized together with MMA and IBVE as depicted in Figure 2-1. Although the monomers contained only one double bond which precluded cross-linking reactions, PEGMA (Aldrich) contained reactive
diacrylate impurities which caused cross-linking. As a part of the synthetic strategy, PEGMA\textsubscript{475} and PEGMA\textsubscript{950} were added as reactive diluents to control cross-linking. MMA and IBVE were internal plasticizers. In a typical reaction, 1.0 g PEGMA\textsubscript{300}, 0.40 g PEGMA\textsubscript{475}, 0.20 g PEGMA\textsubscript{950}, 0.20 g MMA, 0.20 g IBVE, 0.040 g AIBN initiator, and 0.50 mL ethyl acetate were dissolved together in a glass container and sealed under ambient temperature and pressure. The mixture was heated at 95°C in an oil bath with stirring for 30 minutes, during which the color turned deep orange and faded to light yellow, and the mixture became very viscous. After this heating period, the sample was removed from heat and allowed to cool down. Purification was achieved by repeated dissolving/precipitation in ethyl acetate/hexane thrice, and the pale yellow product was then vacuum dried for 36 hours to afford a light yellow, transparent gum-like substance. Typical yield was 1.7 g (85%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ 0.7-0.9 (s, 7.2H), δ 0.9-1.1 (s, 4.5H), δ 1.6-2.0 (m, 7.4H), δ 3.4 (s, 9.2H), δ 3.6 (s, 67H), δ 4.2 (s, 5.4H). The molecular weights (M\textsubscript{n}) and polydispersity indices (PDI) of the poly(PEGMA-co-MMA-co-IBVE) random copolymers using various polymerization times are listed in Table 2-1.

2.2.3. Cell fabrication and electrochemical tests

Pouch cells were assembled for electrochemical testing and all cell fabrication procedures were performed in an argon filled glove box equipped with an activated carbon solvent trap. Prior to cell fabrication, the copolymer was vacuum dried at 40°C for 24 hours in an environmental chamber connected to a glovebox to remove trace solvent. A schematic of the cell fabrication procedure is illustrated in Figure 2-2.
For ac cells, the polymer sample was dissolved in THF to 10 wt% concentration, LiTFSI (5 – 100 mol% based on average Mₙ of EO units) was added and dissolved, and the solution was drop-casted onto two polished stainless steel substrates (type 304) of 1 cm² area. The samples were allowed to dry for 1 hour, after which they were vacuum dried at room temperature for 12 hours to remove residual solvent. The two substrates were then pressed together at 10 psi to sandwich the electrolyte layer between the electrodes, resulting in a stainless steel/polymer electrolyte/stainless steel (SS/PE/SS) cell which was sealed in a metalized plastic bag. Film thicknesses ranged from 120-250 µm as determined by a thickness gauge. Electrochemical impedance spectroscopy (EIS) was performed using an IM6e Zahner ac impedance analyzer scanned from 10 mHz to 100 kHz. The ionic conductivity was determined from the Nyquist plot impedance and measured with stainless steel blocking electrodes in a temperature range from 23°C to 80°C while the sample was incubated in an environmental chamber.

For cyclic voltammetry (CV) studies, the polymer electrolyte was drop-casted onto a stainless steel substrate of 1 cm² area, dried in the same manner as described before, and then a
750 µm lithium foil of 1.4x1.4 cm² area was pressed on the electrolyte layer at 10 psi to form a SS/PE/Li cell. Lithium served as the reference and counter electrode while stainless steel was used as the test electrode. Measurements for CV were taken at a scan rate of 2 mV/s from -0.5 V to 4.0 V while the sample was kept in an environmental chamber stabilized at 40°C.

2.3. Results and Discussion

2.3.1. Polymer composition

![Figure 2-3: ¹H NMR spectrum of Poly(PEGMA-co-MMA-co-IBVE) copolymer in CDCl₃ solvent.](image)

Analysis of the ¹H NMR spectrum confirms a true statistical copolymerization (Figure 2-3) of the co-monomers. To confirm the presence of the various components, several diagnostic comparisons are used. The experimental peak integration ratio between the signals at 3.3 ppm
and 4.1 ppm is 1.7, and the ratio between the signals at 0.8 ppm and 1.0 ppm is 1.6. These values agree with theoretical calculations for the proton signals of isobutyl vinyl ether and methyl methacrylate, respectively. Furthermore, the large signal at 3.6 ppm confirms the copolymerization of the PEGMAs. Thus, the polymer composition in terms of weight is 50% PEGMA$_{300}$, 20% PEGMA$_{475}$, 10% PEGMA$_{950}$, 10% MMA, and 10% IBVE. Overall, the polymer composition can be designated as poly(PEGMA$_{0.8}$-co-MMA$_{0.1}$-co-IBVE$_{0.1}$). The synthesis of this copolymer proceeds according to the respective input of monomers without unexpected losses or un-reactive units.

Table 2-1:
Molecular weight of copolymers and adhesive load.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$M_n$ (g/mol)</th>
<th>PDI</th>
<th>Adhesive load (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>31.2 x 10$^3$</td>
<td>4.21</td>
<td>767</td>
</tr>
<tr>
<td>P-2</td>
<td>36.4 x 10$^3$</td>
<td>4.27</td>
<td>833</td>
</tr>
<tr>
<td>P-3</td>
<td>38.5 x 10$^3$</td>
<td>4.29</td>
<td>833</td>
</tr>
<tr>
<td>P-4</td>
<td>40.2 x 10$^3$</td>
<td>4.32</td>
<td>833</td>
</tr>
</tbody>
</table>

The molecular weight of the copolymer with different polymerization times are listed in Table 2-1. Samples P-1, P-2, P-3, and P-4 correspond to copolymers having polymerization times of 20, 30, 40, and 60 minutes, respectively. Generally, the number average molecular weight ($M_n$) as estimated by GPC increases with polymerization time ranging from 31,200 to 40,200 g/mol, and the polydispersity index ($M_w/M_n$) also increases accordingly. Due to the
nature of the free radical polymerization, high polydispersity indices exceeding 4.0 are obtained throughout the samples.

Figure 2-4 shows the trend in molecular weight as it is affected by the polymerization time. A larger increase in $M_n$ is observed from P-1 to P-2, and subsequent samples show a continually depreciated increase in molecular weight. Part of the reason for this non-linear trend is the increased viscosity of the reaction mixture which kinetically reduces the rate of polymer growth.

2.3.2. Thermal properties

Amorphousness is an important property of polymeric electrolytes as it affects mass transport in the system. In studying the thermal properties of the copolymer, the DSC scan (Figure 2-5) from -50°C to 200°C shows that it is amorphous within this temperature range, with
no indications of a glass transition temperature ($T_g$), melting temperature, or crystallization temperature.

![DSC Profile](image)

Figure 2-5: DSC Profile of poly(PEGMA-co-MMA-co-IBVE) copolymer showing no phase transitions within the temperature range.

Similar DSC profiles are obtained for both the P-1 and P-4 samples which demonstrate a negligible effect of molecular weight on the DSC profile. Although the $T_g$ is not detectable, a poly(PEGMA$_{300}$) homopolymer has a reported $T_g$ value of -57°C.\textsuperscript{28} Unfortunately, a lower temperature scan is beyond the operation range of the DSC instrument available. There is also no sign of a side reaction possibly due to reactive impurities. All of these factors indicate that the copolymer is thermally stable with no phase transitions within this temperature range. It is important to note that in the absence of a melting or crystallization process and without chemical additives, the poly(PEGMA-co-MMA-co-IBVE) copolymer is advantageous over other systems.
where volatile plasticizers are used which introduce flammable risks or concerns for chemical leeching arise.

Figure 2-6: TGA and differential weight loss curves of copolymers from 50°C to 380°C.

Thermal stability is investigated by TGA and carried out under air and nitrogen gas flows to verify the decomposition behavior of the copolymer in different gaseous environments (Figure 2-6). Samples selected for this study include P-1 and P-4 to also determine the effect of relatively low and high molecular weight on thermal decomposition. Under air environment, the decomposition for both P-1 and P-4 copolymers starts to occur after 200°C. From the derivative of the weight loss depicted in the lower break of Figure 2-5, maximum decomposition occurs at 286°C, after which most of the material mass is consumed and further losses proceed rather slowly. When switching to nitrogen, the onset of decomposition is delayed until after 250°C and there is also no abrupt decomposition process. The weight loss differential for these samples shows a gradual increase with higher temperature. Thus, the weight of the copolymer decreases
rapidly in air, but more gradually in nitrogen. Air has the effect of lowering the decomposition temperature and accelerating the rate of decomposition. Further evidence to support this assertion is that samples heated in air are volatilized by $380^\circ$C when recovering the platinum crucible, whereas a brown liquid remains after $380^\circ$C heating for samples heated under nitrogen. Similar decomposition behavior is found regardless of the molecular weights of the copolymer studied.

2.3.3. Rheological and adhesion properties

Adhesion is closely associated with the viscoelasticity of a material as it includes all bonding and de-bonding processes. A plot of the storage modulus ($G'$) vs. frequency ($\omega$) is shown in Figure 2-7 for the P-1 through P-4 samples.

![Figure 2-7: Storage Modulus ($G'$) vs. frequency of copolymer samples.](image)
Starting from low frequency, the storage modulus increases rather linearly until it undergoes a plateau around 0.1 Hz – 100 Hz, which characterizes an overall increase in elasticity with frequency (or decrease in elasticity over time). At lower frequencies (longer time), the copolymers display liquid-like viscous behavior by the quasi-linear relationship of $G'$, but at higher frequencies the plateau describes a solid-like elastic response. Hence, the nonlinear time-dependence of $G'$ indicates that the material exhibits viscoelastic behavior. Tack and peel properties are nominally defined at 0.1 Hz and 10 Hz, respectively, to describe the time frames during which these adhesive events take place. In an ideal adhesive, the tack and peel resistances are balanced in the form of a flat plateau so as to maintain a steady elasticity at either high or low rates. For example, a weak adhesive has high elasticity at high rates (peel resistance), or low elasticity at low rates (tack resistance), which causes the adhesive to either rip a substrate during peeling or stick inadequately. From the modulus curves, $G'$ is consistently lower at 0.1 Hz than at 10 Hz, thus classifying the copolymers as non-ideal adhesives based on their storage moduli. The difference in $G'$ between the tack and peel regions is about half an order of magnitude for the P-4 sample, but is more than an order of magnitude for the P-1 sample. Higher molecular weight copolymers display a more balanced $G'$ value between the tack and peel regions, in addition to a viscoelastic response that persists to lower frequencies. At high frequency, $G'$ values approach a maximum of $3.6 \times 10^5$ Pa for the samples under study.
Figure 2-8: (a) Adhesion ability of the copolymer electrolyte when applied on borosilicate glass and (b) a setup to test the adhesion strength.

Figure 2-8a is a sample demonstration of the adhesiveness of the material when applied onto borosilicate glass. It has a tackiness and resilience that can adhere to a wide range of materials including stainless steel, rubber latex, and Teflon. In an effort to test the adhesion strength of the material, 15 mg of the copolymer is applied between two aluminum plates and pressed at 100 psi to produce a 10 µm thick polymer layer (Figure 2-8b). Weights are serially added to one of the aluminum plates until a permanent adhesion between the plates is no longer preserved. Table 2-1 lists the permanent adhesive loads possible using the various copolymer samples. Using this setup, the P-2, P-3, and P-4 samples can permanently support slightly more than a 12 g load, which is more than 800 times its own weight. Heavier weights are still attachable, but gradual displacement is observed over time. The P-1 sample demonstrates weaker adhesion strength which can be related to its storage modulus profile where there is a large difference between its tack and peel elasticity. Interestingly, the P-2 through P-4 copolymers display similar adhesion strengths using this test despite small differences in the storage moduli. Another advantage of the material, this being provided by its polar and
polyether nature, is its solubility in water and polar organic solvents including tetrahydrofuran, acetone, ethyl acetate, and chloroform. Its ease of solubility and thermal stability ensure facile processing protocols in the fabrication of electrochemical devices, such as by spray deposition or dip-coating.

2.3.4. Electrochemical characterization

For electrochemical studies, only the P-2 sample is selected based on the premises that the thermal and adhesion properties of the poly(PEGMA-co-MMA-co-IBVE) copolymer do not change significantly among the P-2, P-3, and P-4 samples. Coordinating the P-2 copolymer with 5, 10, 25, 50, 75, and 100 mol% LiTFSI based on average \( M_n \) of EO units produces the polymer electrolytes PE-2A through PE-2F, respectively.

Figure 2-9: (a) Representative Nyquist plots using PE-2B as an example, measured from 23°C to 80°C and (inset) zoomed-in image of the high frequency region; (b) an equivalent circuit.
Nyquist plots from ac impedance spectroscopy show a typical semicircle at high frequency followed by a sloping line at low frequency. For brevity, only the Nyquist plots of sample PE-2B from 23°C to 80°C are illustrated in Figure 2-9a as an example, since each set of profiles are similar throughout the EIS experiments. In the inset of Figure 2-9a is the zoomed-in image of the high frequency region to reveal the depressed semicircles as they become depreciably condensed at higher temperatures. An equivalent circuit is shown in Figure 2-9b to interpret the Nyquist impedance plots, where CPE is a constant phase element characterizing the capacitive double layer response at the electrode/electrolyte interface, and $R_b$ is the bulk resistance connected in parallel to the total capacitance ($C$). From the Nyquist impedance plot, the high frequency semicircle corresponds to $R_b$ and the low frequency sloping line characterizes the CPE. At low frequencies, $C$ is considered to be open and the equivalent circuit is reduced to $R_b$ connected in series with CPE. Since the low frequency end of the semicircle and the high frequency end of the sloping line coincide along the x-axis, the $R_b$ values are obtained directly from Nyquist impedance plots and used in Eq. (2-1) to compute the ionic conductivities:

$$\sigma = \frac{t}{R_b A}$$ (2-1)

where $\sigma$ is the conductivity (S/cm), $t$ is the thickness of the polymer electrolyte layer between the two stainless steel electrodes (cm), $R_b$ is the bulk resistance ($\Omega$), and $A$ is the area of the cell (1 cm$^2$).
Table 2-2:
Conductivity of PE-2 Samples with LiTFSI concentration from 23°C to 80°C.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>mol %</th>
<th>$\sigma_{23}$ (S/cm)</th>
<th>$\sigma_{40}$ (S/cm)</th>
<th>$\sigma_{50}$ (S/cm)</th>
<th>$\sigma_{60}$ (S/cm)</th>
<th>$\sigma_{70}$ (S/cm)</th>
<th>$\sigma_{80}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-2A</td>
<td>5</td>
<td>2.42 x 10^{-6}</td>
<td>1.37 x 10^{-5}</td>
<td>1.93 x 10^{-5}</td>
<td>3.73 x 10^{-5}</td>
<td>5.14 x 10^{-5}</td>
<td>8.85 x 10^{-5}</td>
</tr>
<tr>
<td>PE-2B</td>
<td>10</td>
<td>3.71 x 10^{-7}</td>
<td>3.63 x 10^{-6}</td>
<td>8.73 x 10^{-6}</td>
<td>1.80 x 10^{-5}</td>
<td>3.46 x 10^{-4}</td>
<td>6.60 x 10^{-5}</td>
</tr>
<tr>
<td>PE-2C</td>
<td>25</td>
<td>1.96 x 10^{-6}</td>
<td>1.32 x 10^{-5}</td>
<td>2.61 x 10^{-5}</td>
<td>3.73 x 10^{-5}</td>
<td>5.00 x 10^{-4}</td>
<td>8.20 x 10^{-4}</td>
</tr>
<tr>
<td>PE-2D</td>
<td>50</td>
<td>1.78 x 10^{-5}</td>
<td>8.70 x 10^{-5}</td>
<td>1.59 x 10^{-4}</td>
<td>2.30 x 10^{-4}</td>
<td>3.50 x 10^{-4}</td>
<td>5.68 x 10^{-4}</td>
</tr>
<tr>
<td>PE-2E</td>
<td>75</td>
<td>4.80 x 10^{-5}</td>
<td>1.69 x 10^{-4}</td>
<td>2.93 x 10^{-4}</td>
<td>4.33 x 10^{-4}</td>
<td>5.70 x 10^{-4}</td>
<td>8.12 x 10^{-4}</td>
</tr>
<tr>
<td>PE-2F</td>
<td>100</td>
<td>4.42 x 10^{-5}</td>
<td>1.41 x 10^{-4}</td>
<td>2.61 x 10^{-5}</td>
<td>3.46 x 10^{-4}</td>
<td>4.85 x 10^{-4}</td>
<td>6.91 x 10^{-4}</td>
</tr>
</tbody>
</table>

Acronyms: $\sigma_{xx}$ – specific conductivity at xx °C

Experimental conductivity values for the copolymer when coordinated with increasing percentage of lithium salt (LiTFSI) based on average $M_n$ of EO units are listed in Table 2.

Conductivities are measured from 23°C up to 80°C, and Arrenhius plots of the log($\sigma$) against inverse temperature are shown in Figure 2-10.
Figure 2-10: Arrhenius Plots of PE-2 samples with various concentrations of LiTFSI as a function of inverse temperature.

Ionic conduction in PEO occurs in amorphous regions, mediated by the random thermal motion of PEO chains above the T_g. Although the T_g of linear PEO is generally well below room temperature, its melting temperature lies slightly above room temperature for higher molecular weight polymers (>1000 g/mol). As such, heating a waxy or solid PEO electrolyte induces a structural phase transition whereupon amorphous domains increase and ionic conduction is greatly enhanced,\(^3\) resulting in Arrhenius plots that deviate from linearity. In contrast to linear PEO systems, the poly(PEGMA-co-MMA-co-IBVE) copolymer consists of low molecular weight PEO branches with no melting or crystallization temperature. Consequently, the Arrhenius plots in Figure 2-10 display a linear relationship as the conductivities increase steadily with temperature without any abrupt jumps. The plots are consistent with Arrhenius type charge conduction in the electrolyte and follow the relation:

\[
\sigma = \sigma_0 \exp(-E_a / kT) \tag{2-2}
\]
where $\sigma$ is the conductivity, $\sigma_o$ is a pre-exponential factor, $E_a$ is the activation energy, $k$ is the Boltzmann’s constant, and $T$ is the temperature. Activation energies of the conductivity extracted from the slope of the Arrenhius plots are calculated to be 0.342, 0.240, 0.240, 0.225, 0.182, and 0.187 eV for the PE-2A, PE-2B, PE-C, PE-2D, PE-2E, and PE-2F samples, respectively. Overall, the activation energy ranges from 0.182 eV to 0.342 eV and is larger for lower conductivity but smaller at higher conductivities.

A maximum ionic conductivity is found for the PE-2E sample which has a conductivity of $4.8 \times 10^{-5}$ S/cm at room temperature and $1.69 \times 10^{-4}$ S/cm at 40°C. These values are higher than native PEO without chemical modification, but lower than PEO having external plasticizers. Thus, the conductivity of a PEO electrolyte has been improved at a macromolecular level without introducing external plasticizers or inorganic fillers while simultaneously imparting adhesion ability. PE-2E and PE-2F are the only two polymer electrolytes that achieve $10^{-4}$ S/cm at 40°C. Other samples achieve this order of conductivity but at inconveniently higher temperatures.
Figure 2-11: Variation of conductivity with molar coordination of LiTFSI and the consistency of the trend from 23°C to 80°C.

Trends in conductivity as a function of lithium salt coordination are illustrated in Figure 2-11. Generally, the conductivity drops from 5% LiTFSI to 10% LiTFSI and then increases again until the conductivity at 25% LiTFSI is about equal to the conductivity at 5% LiTFSI. The conductivity continues to increase beyond this range until it levels off at 75% LiTFSI. This trend in conductivity remains consistent with changes in temperature which is demonstrated by the plots at different temperatures from 23°C to 80°C.

In high molecular weight PEO (exceeding 3200 g/mol), ion transport is believed to arise predominately from short-range segmental motion of polymer chains, and occasionally, inter-chain cation transfer from one chain to another. For lower molecular weight PEO, a mechanism involving polymer chain diffusion becomes important. As such, PEO electrolytes usually experience a maximum conductivity at a Li:EO ratio roughly between 1:5 to 1:20, after which the ‘down-turn’ in conductivity has been attributed to an increase in absolute temperature.
which reduces the drift velocities of the ions under the application of an electric field.\textsuperscript{33} For the poly(PEGMA-co-MMA-co-IBVE) copolymer electrolyte to experience a maximum conductivity within the 75-100 mol% lithium salt range suggests that other factors affect the conductivity. A study by Walkowiak and coworkers\textsuperscript{34} has demonstrated conductivities exceeding $10^{-3}$ S/cm at room temperature by coordinating a branched polysiloxane-based copolymer electrolyte with 100% LiTFSI. Since the polysiloxane copolymer consisted of Si-OCH$_2$CH$_2$OCH$_3$ branches along the poly(Si-O) backbone, the primary mode of ion transport is the inter-chain hopping of cations among adjacent EO units. The fact that the poly(PEGMA-co-MMA-co-IBVE) copolymer electrolyte also consists of low molecular PEO branches along a polymer backbone with a maximum conductivity in the 75-100 mol% LiTFSI range suggests that inter-chain charge transfer plays a large role in the ion conduction mechanism.

Figure 2-12: Cyclic Voltammetry profile of the copolymer electrolyte (+75% LiTFSI), showing the first, fifth, and tenth cycles scanned at 2 mV/s. The first cycle shown here has a sharp peak at +0.065 V.
The electrochemical stability of the copolymer electrolyte is demonstrated by the cyclic voltammetry profile (up to ten cycles) of the PE-2E sample as shown in Figure 2-12. Before continuous scanning, the cell is first cathodically swept from an open-circuit voltage of 3.2 V to -0.5 V, followed by an anodic sweep up to 4V. The peaks corresponding to lithium plating on the stainless steel electrode (-0.3 V) and lithium stripping (+0.3 V) are clearly present throughout all of the scans. During the first cycle, an additional peak is observed during the stripping process at +0.065 V which is attributed to lithium plating in two different environments.\textsuperscript{35,36} When lithium deposits onto the stainless steel electrode, the first layer adsorbs more strongly on the metal surface, and then subsequent layers of lithium deposit on this initial layer. Consequently, stripping the upper fractions of lithium occur at a potential closer to the formal Li\textsuperscript{+}/Li potential (+0.065 V), whereas the more strongly adsorbed initial layer is stripped at a slightly more positive potential (+0.3 V). After the first several cycles, the peak at +0.065 V is no longer observed, and subsequent cycles only show a single potential for lithium stripping or plating. A small oxidation peak at +1.5 V during the anodic scan is related to an irreversible reaction at the electrolyte/lithium interface where a passivation layer is formed. Altogether, the CV profile shows that lithium plating/stripping is a fully reversible chemical reaction using this electrolyte, and that the electrolyte is stable up to 4 V vs. Li/Li\textsuperscript{+}, which is typical of PEG-based polymer electrolytes.
2.4. Conclusion

An adhesive PEG-based copolymer is synthesized by the statistical copolymerization of poly(PEGMA-co-MMA-co-IBVE). A relatively high room temperature conductivity of $4.8 \times 10^{-5}$ S/cm is achieved and $10^{-4}$ S/cm is readily achievable above 40°C. These values are higher than native PEG, but lower than PEG having external plasticizers. Thus, we have improved the conductivity of PEG as a single macromolecule while also introducing adhesion ability. A 10 μm thick film of the copolymer supports up to 800 times its own weight. This material possesses many interesting properties that could envision numerous applications in the manufacturing of electrochemical devices. It offers low cost, facile synthesis, safety, and scalability. As a high molecular weight polymer that is thermally stable and readily soluble in water and organic solvents, it is ideal for large area sprayed, dip-coated, and printed adhesive electrolytes for flexible batteries and electrochromic screens. What could be more appealing is its potential as a gel polymer electrolyte with appropriate use of cross-linking agent, or electrode binder due to its adhesiveness, inherent ionic conductivity, ease of solubility, and low temperature drying.

2.5. References

CHAPTER 3:
IMPROVING THE IONIC CONDUCTIVITY OF POLY(PEGMA-CO-MMA-CO-IBVE) COPOLYMER ELECTROLYTE

Ch. 3 Abstract: A study to improve the ionic conductivity of a poly(PEGMA-co-MMA-co-IBVE) copolymer electrolyte is presented. Inorganic solid state electrolytes used as additives include Ohara Glass, LiI- Li$_2$WO$_4$ mixture, Li$_7$La$_3$Zr$_2$O$_{12}$, and Li$_2$S-P$_2$S$_5$. Effects of the methyl methacrylate and isobutyl vinyl ether internal plasticizers are also studied. Maximum conductivities approach but do not exceed 10$^{-4}$ S/cm with any organic-inorganic hybrid system.

3.1. Introduction

Since early on, solid state electrolytes garnered enormous research interest due to the possibility of eliminating dendrite growth by inhibiting lithium dissolution in the electrolyte phase. Bypassing this failure mode would enable the use of lithium metal anodes in lithium secondary batteries which are far superior in energy density compared to pervasive graphitic anodes. Chapter 2 demonstrated the synthesis of a soluble, amorphous, and adhesive copolymer electrolyte based on the statistical copolymerization of poly(ethylene glycol) methyl ether methacrylate, methyl methacrylate, and isobutyl vinyl ether in optimal proportions. Its solid state ionic conductivity was confirmed to be within the 10$^{-5}$ S/cm range at room temperature which is inadequate for fast rate performance. Improving the ionic conductivity to levels above
10^{-4} \text{ S/cm} is necessary to compete with gel polymer electrolytes whose conductivities are often about 10^{-3} \text{ S/cm} or higher.

The design of an adhesive and elastomeric poly(PEGMA-co-MMA-co-IBVE), abbreviated P(PEGMA-MMA-IBVE), copolymer electrolyte offers a strategy for improving the structural properties of inorganic electrolytes through an organic-inorganic composite material. Inorganic (ceramic) electrolytes are typically more stable against lithium, have wider electrochemical windows, and offer better thermal stability than their organic counterparts. Despite these admirable attributes, inorganic electrolytes lack structural integrity since they are powders synthesized from solid state calcinations. Assembling cells with a ceramic electrolyte requires it to be compressed into a free-standing pellet, which then calls into question its mechanical durability and interfacial contact to the electrode surface. In their compressed form, inorganic electrolytes are hard, brittle solids that lack flexibility and contact adhesion. Furthermore, a post-annealing (sintering) step is required to increase grain sizes so that the grain boundary resistance is minimized.\textsuperscript{1}

For solid state electrolytes to become practical, adhesion and ionic conductivity must both be properly resolved. Li\textsuperscript{+} conductivity is known to be sensitive to the composition and microstructure of the conductor. A ceramic phase dispersed in a continuous elastomeric phase minimizes ineffective solid-on-solid interfaces while negating pinholes and cracks that may otherwise form.

The study is divided into three sections with the goal of improving the conductivity of poly(PEGMA-co-MMA-co-IBVE) copolymer electrolyte. In the first section, the effect of MMA and IBVE as internal plasticizers on the conductivity of the macromolecular copolymer

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electrolyte is studied. Second, how the molecular weight of the PEGMA monomers influence the conductivity is studied. PEG has a conductivity that is dependent on the molecular weight of the polymer chains. Ion conduction in low molecular weight PEG is dominated by polymer chain diffusion, whereas for high molecular chains, chain rearrangement plays an important role. Since the P(PEGMA-MMA-IBVE) copolymer contains both high and low molecular weight chains, it is important to clarify the exact influence of the various PEG chains on the conductivity of the macromolecule. The third section investigates four inorganic solid state electrolytes as additives to the P(PEGMA-co-MMA-co-IBVE) copolymer electrolyte. These inorganic electrolytes consist of a LiI-Li$_2$WO$_4$ mixture, Ohara Glass, Li$_7$La$_3$Zr$_2$O$_{12}$, and Li$_2$S-P$_2$S$_5$.

Table 3-1:

<table>
<thead>
<tr>
<th>Material</th>
<th>Abbreviation</th>
<th>$\sigma$ (S/cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{(1+x+y)}$Al$<em>x$Ti$</em>{(2-x)}$Si$<em>y$P$</em>{(3-y)}$O$</em>{12}$</td>
<td>Ohara Glass</td>
<td>3x10$^{-4}$</td>
<td>2</td>
</tr>
<tr>
<td>LiI-Li$_2$WO$_4$</td>
<td>LiI-LWO</td>
<td>3x10$^{-3}$</td>
<td>3</td>
</tr>
<tr>
<td>Li$_7$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>LLZ</td>
<td>2x10$^{-4}$</td>
<td>4</td>
</tr>
<tr>
<td>Li$_2$S-P$_2$S$_5$</td>
<td>LSPS</td>
<td>3x10$^{-3}$</td>
<td>5</td>
</tr>
</tbody>
</table>

*the x and y fractions of Ohara Glass are unspecified from the manufacturer

Table 3-1 lists the abbreviations and conductivities of the glassy inorganic electrolytes under study. All are considered lithium superionic conductors (LISICONs) since their conductivities exceed 10$^{-4}$ S/cm. Combining inorganic and organic electrolytes, both of which are considered
solid state, results in organic-inorganic hybrid solid state electrolytes with improved ionic
c Conductivity to varying degrees.

3.2. Experimental

3.2.1. Materials and methods

Poly(ethylene glycol) methyl ether methacrylate (average Mₐ 300, 475, and 950), 2,2’-
azobisisobutyronitrile 98% (AIBN), methyl methacrylate (99%), isobutyl vinyl ether (99%),
ethyl acetate (99%), hexanes (99%), poly(ethylene glycol) dimethyl ether (PEGDME) and
tetrahydrofuran (anhydrous) were purchased from Sigma Aldrich and used as received.
The ionic liquid electrolyte (ILE) 1-methyl-3-propylpyrrolidinium bis
(trifluoromethanesulfonylimide (P₁₃TFSI) and lithium bis(trifluoromethanesulfonylimide
(LiTFSI) were purchased from 3M Corporation and vacuum dried at 200°C for 24 hours prior to
use. Li₂S-P₂S₅ (LSPS, 99%) in a weight ratio of 70:30 was purchased from Idemitsu Kosan,
Japan. Lithium foil (0.75mm x 19mm, 99.9%) was purchased from Alfa Aesar. All of these
reagents were stored in an argon filled glove box.

Ohara Glass lithium ion conducting glass (LICG) grade was purchased from Ohara
Corporation and vacuum dried at 80°C for 4 hours prior to use. Li₇La₃Zr₂O₁₂ was synthesized
according to published procedure. Briefly, stoichiometric amounts of LiOH, La₂O₃, and ZrO₂
were ball-milled with YSZ beads at 300 RPM for 12 hrs in 2-propanol in an air-sealed YSG ball-
mill jar. The powder mixture was then heated at 1125°C for 24 hours to afford a light gray
powder.
The molecular weight and molecular weight distribution were measured using a JASCO gel permeation chromatograph equipped with a refractive index (RI) detector, using HPLC grade THF as eluent and monodistribution polystyrene as standards. $^1$H NMR spectra were scanned using a 300 MHz Oxford Labs instrument using CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard.

3.2.2. Synthesis of poly(PEGMA-co-MMA-co-IBVE)

PEGMAs of different molecular weights (M$_n$ 300, 475, 950) were polymerized together with MMA and IBVE. In a typical reaction, 1.0 g PEGMA$_{300}$, 0.40 g PEGMA$_{475}$, 0.20 g PEGMA$_{950}$, 0.20 g MMA, 0.20 g IBVE, 0.040 g AIBN initiator, and 0.50 mL ethyl acetate were dissolved together in a glass container and sealed under ambient temperature and pressure. The mixture was heated at 95°C in an oil bath with stirring for 30 minutes, during which the color turned deep orange and faded to light yellow, and the mixture became very viscous. After this heating period, the sample was removed from heat and allowed to cool down. Purification was achieved by repeated dissolving/precipitation in ethyl acetate/hexane thrice, and the pale yellow product was then vacuum dried for 36 hours to afford a light yellow, transparent gum-like substance. Typical yield was 1.7 g (85%). $^1$H NMR (CDCl$_3$): δ 0.7-0.9 (s, 7.2H), δ 0.9-1.1 (s, 4.5H), δ 1.6-2.0 (m, 7.4H), δ 3.4 (s, 9.2H), δ 3.6 (s, 67H), δ 4.2 (s, 5.4H). The molecular weights (M$_n$) and polydispersity indices (PDI) of the poly(PEGMA-co-MMA-co-IBVE) random copolymers using various polymerization times are listed in Table 2-1.
3.2.3. *Cell fabrication and electrochemical tests* 

Pouch cells were assembled for electrochemical testing and all cell fabrication procedures were performed in an argon filled glove box equipped with an activated carbon solvent trap. Prior to cell fabrication, the copolymer was vacuum dried at 40°C for 24 hours in an environmental chamber connected to a glovebox to remove trace solvent. For *ac* cells, the polymer sample was dissolved in THF to 10 wt% concentration, LiTFSI (5 mol% based on average \( M_n \) of EO units) was added and dissolved. For ac studies without any inorganic additives, the copolymer electrolyte solution was drop-casted onto two polished stainless steel substrates (type 304) of 1 cm\(^2\) area. Optionally, external plasticizers (ILE and PEGDME) were added and dissolved before casting. The samples were allowed to dry for 1 hour, after which they were vacuum dried at room temperature for 12 hours to remove residual solvent. The two substrates were then pressed together at 10 psi to sandwich the electrolyte layer between the electrodes, resulting in a stainless steel/polymer electrolyte/stainless steel (SS/PE/SS) cell which was sealed in a metalized plastic bag. Film thicknesses ranged from 120-250 µm as determined by a thickness gauge. Electrochemical impedance spectroscopy (EIS) was performed using an IM6e Zahner *ac* impedance analyzer scanned from 10 mHz to 100 kHz. The ionic conductivity was determined from the Nyquist plot impedance and measured with stainless steel blocking electrodes in a temperature range from 23°C to 80°C while the sample was incubated in an environmental chamber. A typical Nyquist plot consisted of a single semicircle starting at the origin at high frequency and a sloping line at lower frequency. Bulk resistances were extracted from the Nyquist plot by taking the real resistance (\( R' \)) when the imaginary resistance (\( R'' \)) was
minimal (x-intercept) at the low frequency region. Ionic conductivity was calculated from the relation:

\[ \sigma = \frac{t}{R_b A} \]  

(3-1)

where \( \sigma \) is the conductivity (S/cm), \( t \) is the thickness of the polymer electrolyte layer between the two stainless steel electrodes (cm), \( R_b \) is the bulk resistance (\( \Omega \)), and \( A \) is the area of the cell (1 cm\(^2\)).

For electrolyte samples containing inorganic additives (organic-inorganic composite electrolyte), the P(PEGMA-MMA-IBVE) copolymer was first dissolved in THF to 10wt% concentration and 5 mol% LiTFSI was added and dissolved. Inorganic electrolyte was then added to the specified amount (10 – 20 wt%) and 20 yttrium stabilized zirconium oxide (YSZ) beads (Across International, 6 mm diameter) were added. This mixture was then ball-milled at 100 RPM for 12 hours. Dispersions were then casted onto stainless steel substrate, dried, and \( ac \) cells were prepared similar manner as described above. Film thicknesses were within the same range.

3.3. Results and discussion

3.3.1. Effect of internal plasticizers – MMA and IBVE

MMA and IBVE are internal plasticizers for the poly(PEGMA-co-MMA-co-IBVE) copolymer and so their influence on the ionic conductivity of the macromolecule is important to understand at least from a practical level. Two experiments were performed, one in which the IBVE portion was not added during polymerization, and another where the MMA portion was not added. In a separate set of experiments, external plasticizers (ILE and PEGDME) were
added at 10 wt% to the polymer electrolyte solution before casting the film. Ionic conductivities of these electrolyte films as computed from ac impedance are listed in Table 3-2.

Table 3-2:
Effect of plasticizers on ionic conductivity of P(PEGMA-MMA-IBVE)

<table>
<thead>
<tr>
<th>P(PEGMA-MMA-IBVE)</th>
<th>$\sigma_{25}$ (S/cm)</th>
<th>$\sigma_{40}$ (S/cm)</th>
<th>$\sigma_{50}$ (S/cm)</th>
<th>$\sigma_{60}$ (S/cm)</th>
<th>$\sigma_{70}$ (S/cm)</th>
<th>$\sigma_{80}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no change</td>
<td>5.35x10^{-6}</td>
<td>1.49x10^{-5}</td>
<td>2.99x10^{-5}</td>
<td>5.10x10^{-5}</td>
<td>7.02x10^{-5}</td>
<td>1.01x10^{-4}</td>
</tr>
<tr>
<td>PEGMA-MMA</td>
<td>6.64x10^{-7}</td>
<td>1.97x10^{-6}</td>
<td>5.27x10^{-6}</td>
<td>1.14x10^{-5}</td>
<td>2.11x10^{-5}</td>
<td>3.14x10^{-5}</td>
</tr>
<tr>
<td>PEGMA-IBVE</td>
<td>5.84x10^{-6}</td>
<td>1.61x10^{-5}</td>
<td>3.24x10^{-5}</td>
<td>5.51x10^{-5}</td>
<td>7.64x10^{-5}</td>
<td>1.10x10^{-4}</td>
</tr>
<tr>
<td>10% ILE</td>
<td>1.69x10^{-5}</td>
<td>3.22x10^{-5}</td>
<td>5.01x10^{-5}</td>
<td>7.47x10^{-5}</td>
<td>1.00x10^{-4}</td>
<td>1.33x10^{-4}</td>
</tr>
<tr>
<td>10% PEGDME</td>
<td>2.82x10^{-5}</td>
<td>5.43x10^{-5}</td>
<td>7.97x10^{-5}</td>
<td>1.03x10^{-4}</td>
<td>1.31x10^{-4}</td>
<td>1.79x10^{-4}</td>
</tr>
</tbody>
</table>

Conductivities are then plotted as an Arrhenius plot by using log$\sigma$ as y-axis and 1000/T (inverse temperature) as x-axis. The Arrhenius plots from these initial studies are shown in Figure 3-1.

Figure 3-1: Variation of conductivity with internal and external plasticizers.
Removing IBVE from the copolymer (i.e. PEGMA-MMA) results in significantly reduced conductivity, whereas removing MMA (i.e. PEGMA-IBVE) does not alter the conductivity to any appreciable extent. Actually, the P(PEGMA-IBVE) copolymer shows a very slight increase in conductivity but the difference is about 1-3%. While MMA is used to add structural strength to the copolymer, it has a negative effect on the conductivity of the macromolecular electrolyte. The negative effect is offset by the introduction of a more flexible unit IBVE. From this study, it can be said that the selection of internal plasticizers is appropriate.

Unlike MMA and IBVE which are internal plasticizers covalently bonded to the parent polymer, ILE (P_{13}TFSI) and PEGDME are external plasticizers which are dissolved by the polymer. Introducing a liquid phase to a solid electrolyte increases ion mobility to enhance the conductivity. For example, high molecular weight PEG plasticized by ILE has shown conductivities within $10^{-4} - 10^{-3}$ S/cm,\(^6\) and PEGDME (a low molecular weight PEG) has similarly affected enhancements up to $4\times10^{-4}$ S/cm.\(^7\) In this study, plasticization of the P(PEGMA-MMA-IBVE) copolymer electrolyte by 10% ILE shows an enhancement ranging from 300% at 25°C to 30% at 80°C. PEGDME used in the same weight percentage results in even higher conductivities: greater than 500% at 25°C and about 75% increase at 80°C. The reason for PEGDME being a more effective plasticizer than ILE is attributed to their viscosities which are 1.03 g/mL and 1.44 g/mL, respectively. Both are used in equivalent weight amounts but on a volume basis, more PEGDME is used than P_{13}TFSI. In all cases, the target $10^{-4}$ S/cm is not achieved even with the use of external plasticizers. It seems possible that increasing the
amount of external plasticizers (i.e. ILE, PEGDME) would likely reach such a level of conductivity at room temperature. However, electrolyte films lost adhesion with higher amounts of external plasticizer and actually became freely flowing viscous liquid itself which is not suitable for solid-state studies.

3.3.2. Effect of molecular weight of PEGMA monomers

Synthesizing the P(PEGMA-MMA-IBVE) copolymer proceeds with PEGMA monomers with various molecular weights. As a more in-depth study, the effect of the molecular weight of PEGMA monomers on the conductivity of the P(PEGMA-MMA-IBVE) copolymer electrolyte is studied by eliminating either the PEGMA$_{950}$ or PEGMA$_{475}$ portion to result in the PEGMA$_{475}$-MMA-IBVE or PEGMA$_{950}$-MMA-IBVE copolymers, respectively. Both of these samples contain the original amount of monomers although the subscript might be misleading.

Table 3-3:
Ionic conductivity of PEG$_{475}$-MMA-IBVE copolymer electrolyte

<table>
<thead>
<tr>
<th>PEG$_{475}$-MMA-IBVE</th>
<th>$\sigma_{25}$ (S/cm)</th>
<th>$\sigma_{40}$ (S/cm)</th>
<th>$\sigma_{50}$ (S/cm)</th>
<th>$\sigma_{60}$ (S/cm)</th>
<th>$\sigma_{70}$ (S/cm)</th>
<th>$\sigma_{80}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% LiTFSI</td>
<td>2.37 x 10^{-6}</td>
<td>9.44 x 10^{-6}</td>
<td>1.70 x 10^{-5}</td>
<td>3.77 x 10^{-5}</td>
<td>5.03 x 10^{-5}</td>
<td>6.50 x 10^{-5}</td>
</tr>
<tr>
<td>25% LiTFSI</td>
<td>3.39 x 10^{-6}</td>
<td>1.14 x 10^{-5}</td>
<td>2.72 x 10^{-5}</td>
<td>4.08 x 10^{-5}</td>
<td>5.16 x 10^{-5}</td>
<td>7.44 x 10^{-5}</td>
</tr>
<tr>
<td>50% LiTFSI</td>
<td>7.18 x 10^{-6}</td>
<td>3.09 x 10^{-5}</td>
<td>6.58 x 10^{-5}</td>
<td>8.83 x 10^{-5}</td>
<td>9.61 x 10^{-5}</td>
<td>1.16 x 10^{-4}</td>
</tr>
<tr>
<td>75% LiTFSI</td>
<td>2.80 x 10^{-5}</td>
<td>8.16 x 10^{-5}</td>
<td>1.20 x 10^{-4}</td>
<td>1.61 x 10^{-4}</td>
<td>2.24 x 10^{-4}</td>
<td>2.82 x 10^{-4}</td>
</tr>
<tr>
<td>100% LiTFSI</td>
<td>2.16 x 10^{-5}</td>
<td>4.74 x 10^{-5}</td>
<td>7.82 x 10^{-5}</td>
<td>1.18 x 10^{-4}</td>
<td>1.23 x 10^{-4}</td>
<td>1.56 x 10^{-4}</td>
</tr>
</tbody>
</table>

acronym: $\sigma_{xx} = \sigma$ at xx °C
Table 3-3 lists the conductivities of the PEGMA$_{475}$-MMA-IBVE copolymer electrolyte with LiTFSI loading from 10% to 100%. Conductivities from Table 3-3 are then plotted as an Arrhenius plot for ease of comparison which is shown in Figure 3-2.

The trend in conductivity is similar to published literature. From 10% to 75% LiTFSI, the ionic conductivity of the copolymer continually increases after which it appears to level off. Samples having 100% LiTFSI demonstrate slightly lower conductivity than at 75% LiTFSI. Polymer incorporated with 50% LiTFSI shows rather a rather non-linear Arrhenius plot which may be due to experimental error and can be improved by performing more tests. A separate set of experiments is carried out in a similar manner for a copolymer having the PEGMA$_{475}$ portion.
replaced by PEGMA\textsubscript{950}. Conductivities obtained for such the PEGMA\textsubscript{950}-MMA-IBVE are listed in Table 3-4 and corresponding Arrhenius plots are shown in Figure 3-3.

Table 3-4:
Ionic conductivity of PEG\textsubscript{950}-MMA-IBVE copolymer electrolyte

<table>
<thead>
<tr>
<th>PEG\textsubscript{950}--MMA-IBVE</th>
<th>$\sigma_{25}$</th>
<th>$\sigma_{40}$</th>
<th>$\sigma_{50}$</th>
<th>$\sigma_{60}$</th>
<th>$\sigma_{70}$</th>
<th>$\sigma_{80}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S/cm)</td>
<td>(S/cm)</td>
<td>(S/cm)</td>
<td>(S/cm)</td>
<td>(S/cm)</td>
<td>(S/cm)</td>
<td>(S/cm)</td>
</tr>
<tr>
<td>10% LiTFSI</td>
<td>4.63 \times 10^{-6}</td>
<td>1.95 \times 10^{-5}</td>
<td>3.40 \times 10^{-5}</td>
<td>5.39 \times 10^{-5}</td>
<td>8.63 \times 10^{-5}</td>
<td>1.41 \times 10^{-4}</td>
</tr>
<tr>
<td>25% LiTFSI</td>
<td>5.38 \times 10^{-6}</td>
<td>2.13 \times 10^{-5}</td>
<td>4.36 \times 10^{-5}</td>
<td>5.74 \times 10^{-5}</td>
<td>9.68 \times 10^{-5}</td>
<td>1.44 \times 10^{-4}</td>
</tr>
<tr>
<td>50% LiTFSI</td>
<td>1.05 \times 10^{-5}</td>
<td>3.00 \times 10^{-5}</td>
<td>5.71 \times 10^{-5}</td>
<td>7.31 \times 10^{-5}</td>
<td>1.26 \times 10^{-4}</td>
<td>1.98 \times 10^{-4}</td>
</tr>
<tr>
<td>75% LiTFSI</td>
<td>2.18 \times 10^{-5}</td>
<td>6.26 \times 10^{-5}</td>
<td>1.22 \times 10^{-5}</td>
<td>1.93 \times 10^{-4}</td>
<td>2.19 \times 10^{-4}</td>
<td>3.08 \times 10^{-4}</td>
</tr>
<tr>
<td>100% LiTFSI</td>
<td>1.56 \times 10^{-5}</td>
<td>5.35 \times 10^{-5}</td>
<td>8.86 \times 10^{-5}</td>
<td>1.72 \times 10^{-4}</td>
<td>1.96 \times 10^{-4}</td>
<td>2.70 \times 10^{-4}</td>
</tr>
</tbody>
</table>

acronym: $\sigma_{xx} = \sigma$ at xx °C

Figure 3-3: Arrhenius plot of conductivity of poly(PEGMA\textsubscript{950}-co-MMA-co-IBVE) copolymer electrolyte with various loading of LiTFSI
For comparison, Figure 3-3 is the conductivity of poly(PEGMA_{950}-co-MMA-co-IBVE) copolymer electrolyte with various loading of LiTFSI. Conductivities obtained from these experiments are plotted together as a superposition shown in Figure 3-4.

Figure 3-4: Arrhenius plot superposition of Figure 3-2 and Figure 3-3

A minor improvement in conductivity is apparent at room temperature when replacing PEGMA_{475} with PEGMA_{950}. As the LiTFSI concentration increases, this effect lessens nonetheless. It is difficult to make any general conclusions from these experiments, other than that there appears to be no significant consequence between using PEGMA_{475} and PEGMA_{950} in these amounts. For both of the experimental sets, the conductivities are within nearly the same range, and the effect of lithium salt concentration is in agreement with published reports. Ion conduction in a PEGMA-based random copolymer is believed to occur through intra-chain and
inter-chain transfer. In contrast to Arrhenius plots of plasticized organic polymer electrolyte from Figure 1, the conductivity without external plasticizers is not such a well-defined linear fit.

3.3.2. Effect of inorganic solid state electrolyte additives

Table 3-5:
Conductivity of P(PEGMA-co-MMA-co-IBVE) with inorganic additives

<table>
<thead>
<tr>
<th>P(PEGMA-MMA-IBVE)</th>
<th>( \sigma_{25} ) (S/cm)</th>
<th>( \sigma_{40} ) (S/cm)</th>
<th>( \sigma_{50} ) (S/cm)</th>
<th>( \sigma_{60} ) (S/cm)</th>
<th>( \sigma_{70} ) (S/cm)</th>
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Figure 3-5: Inorganic solid state electrolyte additives

Ohara glass belongs to a class of defect phosphate glasses possessing high ionic conductivities, chemical resistance, and thermal stability. The general molecular structure of lithium ion conducting phosphate glasses is lithium phosphate (Li$_3$PO$_4$) with a fraction of the lithium substituted with various metals. Li$_3$PO$_4$ alone is an ion conductor, albeit a very poor one, based on an orthorhombic structure where all octahedral sites are occupied by cations (three Li$^+$ for every P$^{5+}$ ion) in a four-fold oxygen anion close-packed lattice. Generally, crystalline solids
are not ionic conductors, but generating defect sites greatly enhances the conductivity. Partial substitution (or doping) of P$^{5+}$ by two or more cations (e.g. Al, Si, Ti) produces such defect sites. For example, Li$_3$PO$_4$ doped with Li$_4$SiO$_4$ produces the Li$_{(3+x)}$P$_{(1-x)}$Si$_x$O$_4$ system, where a pentavalent P$^{5+}$ cation is partially substituted by two cations, Si$^{4+}$ and Li$^+$. In maintaining charge neutrality during the substitution of P$^{5+}$ for Si$^{4+}$ and Li$^+$, numerically more cations are introduced than there are vacant sites. Excess Li$^+$ therefore occupy migratory spaces between the MO$_4$ tetrahedrons. The addition of Ohara Glass to the P(PEGMA-MMA-IBVE) electrolyte film whether in 10 wt% or 20 wt% yields minor improvements. A moderate improvement in conductivity is found at room temperature but at higher temperatures, this effect diminishes.

Similarly to Li$_3$PO$_4$, LiI is a weak ion conductor by itself ($10^{-7}$ S/cm). Chemical interactions between LiI and Li$_2$WO$_4$ form a new conducting phase that is believed to be responsible for high, but short-lived, conductivity in a LiI-Li$_2$WO$_4$ mixture. Over a period of about 10 days with slight heating, the conductivity of LiI-LWO drops below $10^{-6}$ S/cm, which is attributed to the vaporization of LiI. As LiI is responsible for free lithium ions for conduction, its disappearance quickly degrades ionic conductivity. In these studies, the addition of a LiI-LWO mixture did not produce a pronounced effect on the conductivity of the composite electrolyte. It may be due to the fact that LiI is dissolved in the P(PEGMA-MMA-IBVE) copolymer which then restricts its interactions at the surface of a Li$_2$WO$_4$ particle surface. Consequently, the conductive intermediate phase of LiI-LWO is only partially, or not at all, formed. A slight improvement in the room temperature conductivity is observed but is still an order of magnitude below $10^{-4}$ S/cm.
Li$_2$La$_3$Zr$_2$O$_{12}$ (LLZ) is an interesting and relatively newly developed solid state electrolyte based on the garnet structure whose conduction mechanism remains elusive.$^{11}$ Its advantages over the unstable LiI-LWO and phosphate glass systems are stability against lithium metal, moisture, and air, and electrochemical stability above 5.5 V vs. Li/Li$^+$. Still, many technical problems such as relatively low ionic conductivity, high cost, and processing issues have hindered its large-scale application. Using an adhesive elastomeric electrolyte to bind LLZ particles where the weight percentage of LLZ is 10 – 20% results in consistent, improved conductivities. 10% LLZ results in about 350% conductivity enhancement at room temperature and 80% increase at 80°C. 20% LLZ is another bold improvement by about 600% at room temperature and 230% at 80°C. These values are considerably larger than the Ohara Glass and LiI-LWO additives but still less than the target value $10^{-4}$ S/cm.

Li$_2$S-P$_2$S$_5$ (LSPS) is a sulfide glass that interestingly, has one of the highest conductivities of inorganic electrolytes in addition to stability against lithium.$^{12}$ Like many other inorganic systems, technical difficulties involving compression, sintering, and film strength has complicated its development. Using LSPS as an additive for the P(PEGMA-MMA-IBVE) polymeric system results in well-dispersed suspensions and electrolyte films with improved ionic conductivities. At 10 wt% loading, the conductivity increased by 250% and 25% at 25°C and 80°C, respectively. With 20%, the conductivity increased by more than a factor of 12, nearly reaching $10^{-4}$ S/cm. An unexpected shortcoming is that electrolyte films containing 20 wt% LSPS became weakly self-adherent. Adhesion of the electrolyte film to the stainless steel current collectors was poor which required very meticulous and careful handling of such samples. Furthermore, stable EIS data were not obtainable at 80°C, possibly due to side
reactions of LSPS with polymer or potential loss of volatile species. For this reason, a data point for 20% LSPS at 80°C is labeled ‘not available’ (n/a).

Figure 3-6: Effect of inorganic fillers

For a straightforward comparison of the inorganic fillers in organic-inorganic composite solid state electrolytes, Figure 3-6 is a superposition of Figures 3-5a – 3-5d. Ohara glass seems to have an equivalent effect in enhancing the conductivity as a LiI-LWO mixture, but both are rather weak additives. LLZ has a much more apparent boost in conductivity that is higher than Ohara Glass and LiI-LWO additives. LSPS at 10 wt% is lower than LLZ, but at 20%, LSPS increase the conductivity more than all of the other inorganic additives. Therefore, the trend in conductivity enhancement from these inorganic electrolyte additives is generally: Ohara Glass ≤ LiI-LWO < LLZ < LSPS. Inorganic solid state electrolytes suffer a large deal from processing
and engineering issues. Reported conductivity values vary markedly depending on synthesis conditions, compression level, and interfacial contact to electrodes, since grain boundary effects play a large role in transport mechanism.

![Graph showing conductivity vs. temperature for different hybrid electrolytes.](image)

**Figure 3-7:** Effect of 20% inorganic filler on conductivity of P(PEGMA-MMA-IBVE) copolymer electrolyte.

Figure 3-7 is a simplified version of the results summary showing only the hybrid electrolytes having 20 wt% inorganic fillers. Ohara Glass and Li-LWO seem to have little effect on the conductivity. The room temperature conductivity is slightly enhanced with these two systems, although at higher temperatures there appears to be no bonus effect to the conductivity. LLZ and LSPS demonstrate an apparent improvement in the conductivity at low and high temperatures. Despite LSPS appearing as a potent inorganic additive for the system, it is one of
the most hazardous electrolytes to handle. All procedures must be carried out under inert atmosphere as LSPS releases pungent and toxic H$_2$S upon reaction with moisture.

The maximum conductivity of inorganic electrolytes comes from sintering (heat-pressing) so as to reduce grain boundary resistance. Large differences in conductivity between bulk powder and sintered pellets are often an order of magnitude or greater. In these experiments, neither high compression nor sintering was performed, and hence, enhancements in conductivity were drawn from mostly the bulk conductivity of the ion conducting particles.

3.4. Conclusions

Results obtained from these studies are empirical so as to better understand the limitations of this electrolyte system. Many factors are involved include chemical compatibility between the organic and inorganic systems, the inorganic particle size, its dispersion efficiency, and interfacial contact to the electrodes. Not all of these factors are on equal footings with each other, and it would actually be difficult to do so considering the hygroscopic and sometimes toxic nature of inorganic solid state electrolytes. At all times, handling was kept under inert gas, which excludes transferring of samples to characterization instruments such as x-ray diffraction or electron microscopy. Instead, these experiments were an attempt to purchase or synthesize readily available inorganic electrolytes to determine whether high conductivities well within the $10^{-4}$ S/cm range are possible through an organic-inorganic composite approach. The highest conductivities were achieved with LSPS as inorganic filler where approximately $6 \times 10^{-5}$ S/cm was obtained. Nonetheless, this experiment was based more on conceptual grounds, since LSPS
is severely toxic. Even so, sample reproducibility becomes compromised at 20 wt% loading with all fillers. Therefore, results are subject to changes with minute differences in preparation method.

It should also be noted that using an organic-inorganic hybrid system such as the ones studied here eliminate the possibility of solution-based deposition, and only dispersion-type depositions are possible. Therefore, the low conductivities combined with onerous processability are dissuasive from the viewpoint of practicality. Lack of control of film thickness is another concern when trying to compare the results on equal grounds. In these instances, results are more accurate than precise. More exact control of experimental parameters would certainly yield more precise measurements. Reproducibility is poor from these studies, but the important aspect is the conclusions that can be drawn. Trends of polymer electrolyte properties are established, and its limitations as a material are better understood.

Reproducibility is poor mostly from dispersion issues. In most cases, addition of inert inorganic fillers did not result in dramatic improvements in the conductivity, which could be related to grain boundary processes in bulk solids. Ion conduction at the grain boundary and the solid-elastomer interface is generally lower than within the bulk solid electrolyte. Inorganic electrolytes possess conductivities above $10^{-4}$ S/cm, some of them (i.e. LSPS) beyond $10^{-3}$ S/cm when properly pelletized and sintered. The marriage of the two systems resulted in intermediate conductivities. LSPS increased the conductivity the most, although $10^{-4}$ S/cm remains beyond reach. General conclusions from this study suggest that an organic-inorganic hybrid electrolyte using an adhesive poly(PEGMA-co-MMA-co-IBVE) copolymer electrolyte as a gluing or
binding agent for inorganic solid state electrolyte particles can increase the conductivity when compared to the organic component alone.

The full power of an organic-inorganic hybrid electrolyte is not drawn out, most likely due to poor interfacial adhesion of the electrolyte films above 20 wt% doping concentration. Electrolyte samples containing 20% LSPS experienced difficulty in acquiring consistent ac impedance measurements, which may have been due to volatile reactions, loss of sulfur as gas, or reaction with polymer electrolyte. The reasons why are unclear as it was not possible to transfer the sample for characterization. Ohara Glass and LiI-LWO were relatively ineffective additives, and they also caused almost equivalent changes in the conductivity. They were more effective at room temperature but became ineffective at higher temperatures. It appears that it is difficult to exceed $10^{-4}$ S/cm with many of the inorganic electrolytes, and the maximum at higher temperature coincided with the conductivity of the polymer electrolyte itself. At lower temperatures, there is an enhancement in conductivity but the effect diminishes at higher temperatures. Part of the reason for this trend may be attributed to the polymer dominating the electrolyte composition ($\geq 80$ wt%). Ion transport at lower temperatures may occur preferentially through the inorganic phase, but at higher temperatures, ion transport in the polymer phase becomes more frequent.

3.5. References


CHAPTER 4:
THICK LITHIUM COBALT OXIDE CATHODE PREPARED BY AN ADHESIVE AND WATER-SOLUBLE PEG-BASED COPOLYMER BINDER

Ch. 4 Abstract: This study presents the first aqueous process fabrication of thick, flexible, and fully compressed lithium ion battery cathodes exceeding 200 µm in thickness using an adhesive, elastomeric, and ionically conductive PEG-based copolymer binder. The binder is synthesized through the statistical copolymerization of poly(ethylene glycol) methyl ether methacrylates (PEGMA), methyl methacrylate (MMA), and isobutyl vinyl ether (IBVE) in optimal proportions. Using standard LiCoO₂ as active material, dense and flexible cathode films can withhold active mass loadings over 30 mg/cm² which deliver 4.53 mAh/cm² with 94% capacity retention at C/2-rate. Electrodes were fabricated by casting aqueous cathode slurries onto nickel foam, followed by drying and hard calendar compression at 10 tons/cm². Coordinating the binder with lithium salt plays a crucial role in activating the cathode.

4.1. Introduction

One of the major dilemmas in electrode preparation for lithium-ion batteries has been the selection of binder material, as each type comes with associated inconveniences. Although poly(vinylidene fluoride) (PVDF) polymers are the most prevalent in use, their major downside is the usage of highly toxic solvent (e.g. N-methyl-2-pyrrolidone (NMP), N,N-
dimethylformamide (DMF), and N,N-dimethylacetamide (DMAc)) that is required for dissolution so that homogeneous films can be casted (Figure 4-1).

![Chemical structures of NMP, DMF, and DMAc](image)

Figure 4-1: True solvents for PVDF polymers

This problem leads to strict environmental regulations when using PVDF in electrode formulations, where it must be removed and recovered during the drying stage. Many systems including rubber poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(ethylene glycol) (PEG), latex, carboxymethyl cellulose (CMC), poly(acrylic acid) (PAA), and poly(vinyl alcohol) (PVA) have been studied as aqueous binders.
PAN and PMMA are advantageous over PVDF by being more readily soluble in organic aprotic solvents such as PC\textsuperscript{16} or THF,\textsuperscript{17} respectively. Plasticized PAN possesses high ionic conductivity on the order of $10^{-3}$ S/cm and voltage stability around 4.5 V vs. Li/Li$^+$,\textsuperscript{2} but its instability against lithium metal anode has rendered it impractical.\textsuperscript{18} Furthermore, it does not exactly excel in any area and has weak complexing interactions with lithium salts in the presence of liquid electrolyte.\textsuperscript{19} PMMA as a polymer matrix has resulted in reduced conductivity which is believed to arise from strong association between the polymeric chains and ionic species.\textsuperscript{3} PEG is water-soluble and even dissolves inorganic salt to become an ionic conductor, but it also dissolves in the plasticizing liquid electrolyte solution which makes it chemically incompatible.\textsuperscript{4}

Despite their low cost and environmental benignity, CMC and PAA are very stiff materials which lead to aggregated or delaminated coatings. Hence, a rubber such as styrene-butadiene rubber (SBR)\textsuperscript{20-23} is often added to improve the structural integrity of the electrode, but at the cost of drastically reducing its conductivity.\textsuperscript{20} Furthermore, SBR-CMC and SBR-PAA
binders are weak absorbents of liquid electrolyte, resulting in the formation of a resistive interface for lithium ion transport, particularly at the active material interface.\textsuperscript{24,25} PVA as a standalone or composite binder has also experienced similar problems, although it has better adhesion.\textsuperscript{26,27}

Owing to their ineffective processing and electrochemical inertness, research studies employing the aforementioned aqueous binders have usually been limited to electrodes that are very thin or have low mass loadings. Otherwise, the conductivity and mechanical properties are too poor for thicker films which result in rapidly deteriorating performance. And for the same reasons, thick films cannot be fully compressed due to the electrode’s fragile structure. Herein, we report the first fabrication of densely packed, fully compressed, thick, and flexible cathodes through an aqueous process using a high molecular weight poly(PEGMA-co-MMA-co-IBVE) random copolymer as a unique and multifunctional binder. Unlike other PEG based non-adhesive materials which lost contact with the active materials or current collectors,\textsuperscript{28-30} poly(PEGMA-co-MMA-co-IBVE) exhibits strong adhesion and tacky properties in the form of an amorphous gum-like substance. Our strategy involves using the adhesive, elastomeric, and lithium ion conductive binder to cast aqueous cathode slurries onto a nickel foam current collector, followed by low temperature drying and a high pressure calendaring at 10 tons/cm\textsuperscript{2}. Using the standard LiCoO\textsubscript{2} active material, the obtained LiCoO\textsubscript{2}/nickel foam cathodes can effectively sustain over 30 mg/cm\textsuperscript{2} loading of active material and deliver an average of 4.53 mAh/cm\textsuperscript{2}, which corresponds to 20 times the active mass loading of thin LiFePO\textsubscript{4} (LFP) cathodes prepared by CMC.\textsuperscript{31} For a more relevant comparison, the area specific capacity is 50% greater than the thick LFP/cellulose cathodes prepared by Porcher and coworkers\textsuperscript{32} in which the
slurries were tape-casted and compressed at 2 tons/cm² to produce 100-150 µm thick films. We demonstrate that even with a lower capacity active material such as LiCoO₂, a substantial increase in the specific area capacity is achievable. In addition to the boost in area capacity, we validate that inducing ionic conductivity in the binder is necessary for the cell to function. A preliminary optimization of the procedure is discussed.

4.2. Experimental

4.2.1. Materials and methods

Poly(ethylene glycol) methyl ether methacrylate (Mₙ = 300, 475, 950), methyl methacrylate (99%), isobutyl vinyl ether (99%), 2,2’-azobisisobutyronitrile (AIBN, 99%), ethyl acetate (99%), tetrahydrofuran (THF, HPLC grade), and hexanes (99%) were purchased from Sigma Aldrich and used as received. De-ionized water (18 MΩ resistivity) was used in the preparation of the copolymer binder solution and cathode dispersions. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99%) was purchased from 3M and stored in an argon filled dry box. Lithium foil (0.75mm x 19mm, 99.9%) was purchased from Alfa Aesar and stored in an argon fill dry box. Nickel foam was purchased from Linyi Gelon New Battery Materials Co., model number FN –I (Shandong, China). Prior to use, the nickel foam was cleaned by soaking in dilute Alkanol 6112 surfactant purchased from Sigma Aldrich, DI water, and acetone, each for 30 minutes. Afterwards, it was rinsed with water and dried in air at 150°C for 30 minutes.
The molecular weight of the copolymer binder was measured using a JASCO gel permeation chromatograph equipped with a refractive index detector using THF as eluent and monodistribution polystyrene as standards. $^1$H NMR characterization was carried out using a 300 MHz Oxford Labs instrument using CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. The crystallographic structure and morphology were studied by thin-film X-ray diffraction (XRD, Rigaku) and a high resolution scanning electron microscope (SEM, Zeiss Ultra).

4.2.2. Synthesis of Poly(PEGMA-co-MMA-co-IBVE) copolymer binder

PEGMAs of various molecular weights ($M_n$=300, 475, 950) were copolymerized together with MMA and IBVE. Briefly, 1.0 g PEGMA$_{300}$, 0.4 g PEGMA$_{475}$, 0.2 g PEGMA$_{950}$, 0.2 g MMA, 0.2 g IBVE, 0.04 g AIBN, and 0.5 mL ethyl acetate were dissolved together in a glass container and sealed at ambient pressure. The mixture was heated in an oil bath at 95°C for 30 minutes with stirring, during which the color turned deep orange and faded to light yellow. After this, the sample was cooled down to room temperature, and purified by repeated dissolving/precipitation in ethyl acetate/hexane three times. Finally, the sample was vacuum dried for 36 hours to remove residual solvent, affording a pale yellow, transparent gum-like substance. Typical yield is 1.7 g (85%). $^1$H NMR (CDCl$_3$): δ 0.7-0.9 (s, 7.2H), δ 0.9-1.1 (s, 4.5H), δ 1.6-2.0 (m, 7.4H), δ 3.4 (s, 9.2H), δ 3.6 (s, 67H), δ 4.2 (s, 5.4H). The average molecular weight against polystyrene standards is 36,400 with a polydispersity index ($M_w/M_n$) of 4.27. This copolymer is soluble in water and organic solvents such as tetrahydrofuran, ethyl acetate,
and acetone. In ethylene carbonate (EC) / propylene carbonate (PC) liquid electrolyte solutions, it swells without dissolving.

4.2.3. Fabrication of LiCoO$_2$/nickel foam cathode

Aqueous cathode dispersions were prepared by first dissolving the poly(PEGMA-co-MMA-co-IBVE) copolymer in water to 30 wt% concentration, and then coordinated with 20 wt% LiTFSI based on the weight of the polymer. This amount corresponds to a Li:EO ratio of 1:20. The positive electrode consisted of LiCoO$_2$ powder (Alfa Aesar, 97%), poly(PEGMA-co-MMA-co-IBVE) copolymer binder (with LiTFSI), and carbon black (Timcal, Super P), and water is added at 250 wt% based on solutes. For reference, the details of the cathode formulations are listed in Table 3-1. This mixture was sonicated (Sonics & Materials, model CV33, 500W 20 kHz) for five minutes, and then applied onto a nickel foam (area = 5 cm x 2 cm) with a doctor blade at 90°C. A small strip of the nickel foam along the edge (1 cm x 2 cm) was left uncoated to serve as the current collector. Once the cathode was dried for 10 minutes at this stage, it was further dried at 170°C for one hour, cold calendared between two tool steel blocks at 100 tons with a hydraulic press, and then vacuum dried at 80°C for two hours before transferring it into a glove box for cell assembly. The active material loading of the cathode ranged from 20 to 42 mg/cm$^2$.

In replacing the binder with PVDF for the PED-X cathode, PVDF (Kynar 2801) was dissolved in NMP at 30 wt% concentration, after which LiCoO$_2$ powder and Super P are added. The suspension was mixed for 6 hours at 80°C, pasted onto a nickel foam substrate, and vacuum dried at 120°C for 12 hours before calendaring.
In an argon filled glove box, lithium-ion cells were assembled using the nickel foam of the cathode as current collector, a cathode of active area 2.4x2.4 cm$^2$, a Celgard 2325 (25 µm thick) separator, a lithium foil as anode, and 1M LiPF$_6$ in EC/PC (1:1 wt% mixture) electrolyte purchased from Novolyte. The LiCoO$_2$/separator/Li half cells were assembled in a metalized plastic pouch and sealed under argon. Before electrochemical characterization (rate test and effective resistance test), cells were cycled for ten cycles at C/2 rate to ensure electrochemical stability.

4.2.4. Electrochemical measurements

Nyquist Plots from alternating current (ac) electrochemical impedance spectroscopy (EIS) were obtained using an IM6e Zahner electrochemical analyzer, scanned from 10 mHz to 100 kHz at open circuit voltage (OCV). Electrochemical performance was evaluated by preparing half cells against a lithium anode. Cells were tested using a Maccor tester Series 4000, with cutoff voltages of 4.2 V for charging and 3.0 V for discharging. All cell testing and characterization were performed at 25°C.
4.3. Results and Discussion

Table 4-1:
Experimental cathode formulations

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*all formulations are diluted by 250 wt% water based on solutes and the binder is coordinated with LiTFSI.

4.3.1. Structure and morphology of the LiCoO₂/Ni foam cathode

Studying the morphology of the cathode film by SEM indicates that the surface morphology is smooth and the particle sizes are on the submicron scale.
A high resolution SEM image (Figure 4-3a) of the cathode reveals the presence of two distinct sets of particle sizes. The larger particles that are about 200 nm – 1 µm in size correspond to the LiCoO₂ particles since they are used as purchased, while the smaller particles that are 30-40 nm may mostly be composed of the Super P carbon black. Although the amorphous polymer binder is not clearly discernable, all of the particles are intimately linked together, especially the carbon black particles for electrical contact, without signs of detachment from each other. The cross-sectional view (Figure 4-3b) shows the density of the free-standing film, the compact and non-aggregated distribution of the material throughout the entire nickel foam, and the absence of any delaminating. Although the film appears to be rigid and dense, it is actually flexible and bendable with a thickness of about 220 µm owing to the elastomeric poly(PEGMA-co-MMA-co-IBVE) binder. Some nickel foam protrusions are also distinguishable from the discontinuity in the material structure, showing its role as a skeletal support. Altogether, these images confirm that the dispersion of LiCoO₂ and carbon black in the aqueous cathode slurry is adequate in casting crack-free and non-aggregated films. Otherwise, large colloids or clustered regions
would be observed. The formation of such a uniform film is attributed to the various components of the copolymer which have different levels of solubility in water, granting surfactant-like ability to improve the dispersion efficiency of the cathode slurries.

A standard binder such as PVDF was also used to produce the cathode as a controlled sample. Compared with cathodes fabricated using poly(PEGMA-co-MMA-co-IBVE) binder, the cathode film using PVDF as a binder is non-homogeneous (Figure 4-3c), and composed of easily delaminating layers. During the calendaring, a significant portion of electrode material squeezed out of the film, resulting in loss of material as well as a reduction in the thickness. Moreover, the cathode materials tend to spontaneously detach during handling since the film is not self-adherent due to PVDF’s poor adhesiveness. It is generally expected that if the surface energy of an ‘ink’ is higher than that of a substrate, then poor wettability and adhesion incur.

Nickel has a higher surface energy of 1770 dynes/cm compared to NMP (41 dynes/cm) or water (73 dynes/cm), which means that both the organic and aqueous solvents should have adequate wettability on the nickel surface. Additionally, PVDF as a polyfluorocarbon has a low surface energy due to the high electronegativity of fluorine and low polarizability of C-F bonds. Hence, the organic PVDF-based slurry should have proper wetting on the nickel current collector, if not better wettability than the aqueous PEG-based slurry. Weaker adhesion of PVDF onto the nickel foam compared to the PEG-based binder is rather due to the mitigated intermolecular attractive forces present in PVDF, again due to the low polarizability of its chemical structure. Although increased Van der Waals interactions may be responsible for the improved interfacial contact between the PEG-based copolymer and the nickel surface, the drying rate of the solvent is also an important consideration. Unlike the aqueous process which
undergoes 10 minutes at 90°C in the first stage of drying, NMP takes a much longer time to dry which allows for binder re-distribution to the surface layers of the evaporating solvent. Continuous upward migration of non-adsorbed binder during the slow drying has detrimental effects on the uniformity and adhesion of electrode materials to the current collector.\textsuperscript{35} The cathode using a PVDF binder did not undergo a half cell test because of the highly irreproducible procedure.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{film_thickness.png}
\caption{Figure 4-4: Calibration of film thickness after compression as a function of material loading into the nickel foam. Measurements are averaged over three samples, nine measurements per sample.}
\end{figure}

The relationship between the amounts of mass loading into the foam and the final thickness after compression is depicted in Figure 4-4. Samples for this study correspond to formulations of PED-1, PED-2, and PED-3. Thicknesses vary from 173 µm, 222 µm, and 273 µm when the average active material loading is 21, 33, and 42 mg/cm\textsuperscript{2}, respectively. Typically, the standard deviation of the thickness is about 4-5%. With these loading amounts, the thickness of the film did not significantly change when undergoing 8 tons/cm\textsuperscript{2} to 10 tons/cm\textsuperscript{2} compression,
which suggests that the films were fully compressed when applying 10 tons/cm$^2$ for cathode fabrication.

Figure 4-5: XRD pattern of PED-2 cathode indicating pristine active material and nickel foam after drying in air at 170°C/1 hr and then hard-calendaring.

Examineing the cathode film by XRD reveals that it consists of only two crystalline structures (Figure 4-5). All of the peaks in the XRD pattern match exactly with reported values for LiCoO$_2$\textsuperscript{36} with the exception of the three signals at 44.6, 51.8, and 76.4 degrees (2$\theta$) which correspond directly to synthetic nickel.\textsuperscript{37} Thus, the composition of the cathode is free of defective phases or the oxidation of the nickel foam during the brief heat treatment. The possible formation of hydroxides such as cobalt or nickel hydroxide associated to the aqueous route processing are apparently absent in the XRD pattern, albeit the close similarities in their respective XRD spectra.
4.3.2. Optimization of aqueous cathode formulation

A typical charge-discharge profile of a LCO/Li half cell prepared from this process is shown in Figure 4-6.

Figure 4-6: Representative charge-discharge profile from 4.2 – 3.0 V of LCO/Li half cell.

Starting from an open circuit voltage (OCV) of about 3.8 – 4.0 V, cells begin by charging lithium ions and electrons to the lithium anode until the cell potential is 4.2 V. After the initial charge, LCO/Li half cells repeatedly discharge to 3.0 V and then charge to 4.2 V, of which only the first two full cycles are shown in Figure 3-4 for illustrative purposes. The charge and discharge curves are smooth without deviation from known behavior (e.g. voltage plateaus, discontinuities), indicating that the electrochemical properties of the thick LiCoO$_2$ electrode are unaltered from this aqueous fabrication process. Figure 4-6 plots the according to time (min) along the x-axis. Capacities (mAh/g) are computed from the software by using the known
current (mA) for charging/discharging and multiplying by the time (h), divided by the weighed mass (g) of the active material.

The optimal amount of contents in the formulations is determined in three stages. In the first stage, the maximum amount of loading is determined by performing a rate test on samples that are loaded with different amounts using the same recipe, as shown in Figure 4-7a.

Based on these results, cathodes having active mass loadings ranging from 21 to 33 mg/cm² do not show an appreciable difference in rate capability, while cathodes having 42 mg/cm² loading show dramatically reduced performance. Thus, the percolation threshold seems to be slightly above 30 mg/cm² of material loading before rate capability becomes compromised. For the PED-2 sample, a C/4 and C/2 discharge produced 134 and 132 mAh/g, respectively, while a C-rate discharge produced 127 mAh/g (Figure 4-7b). Compared to the theoretical value of 140
mAh/g for LiCoO$_2$, these values equate to 96%, 94%, and 91% capacity retention at C/4, C/2, and C-rate, respectively.

Figure 4-8: Effect of the concentration of carbon black and binder additives on the rate capability of the LiCoO$_2$/Ni foam half cells.

After determining the optimal amount of loading, the amounts of Super P and poly(PEGMA-co-MMA-co-IBVE) binder were tuned to investigate their effects on rate performance (Figure 4-8). Starting from 8.3% of both Super P and binder additives (PED-2), the amount of binder was held constant while decreasing (PED-4) or increasing (PED-5) the amount of Super P. Then, the amount of Super P was held constant while decreasing the amount of binder (PED-6) or increasing it (PED-7). Comparing the effect of the concentration of Super P and binder additives on the rate capability of the LiCoO$_2$/Ni foam half cells shows that PED-2, PED-5 and PED-7 demonstrate similar performance excelling those of PED-4 and PED-6 when either of the additives was decreased. Since using the lowest amounts of carbon and binder
additives is preferred in order to keep the maximum volumetric energy density, the optimal contents for the formulation are 83.3% LiCoO$_2$ powder, 8.3% Super P, and 8.3% binder (PED-2). Using more of either the Super P (PED-5) or binder (PED-7) does not substantially improve the rate performance. However, reducing the concentration of Super P (PED-4) or binder (PED-6) lowers the rate performance presumably due to insufficient conductivity in the cathode or inadequate material contacts, respectively.

Figure 4-9: Effect of drying temperature with fixed time on the cycle performance of the PED-2 half cells, cycled at C/2 rate.

The PED-2 samples were dried at 150°C, 170°C and 200°C for one hour and the resulting samples were subjected to half cell cycling evaluation to find the optimized drying temperature for the cathode (Figure 4-9). Samples dried at 150°C or 170°C show somewhat similar cycling performance, although the sample dried at 170°C demonstrates slightly better stability over long-term cycling. In contrast, 200°C drying has a serious negative impact on the cell performance.
which can be seen in the diminished capacities. The fast loss in capacity is most likely due to the
decomposition of the binder when held at elevated temperatures for lengthy periods, as the
polymer binder contains PEG.\textsuperscript{38}

![Graph showing discharge potential and applied current](image)

**Figure 4-10:** Effective Resistance ($R_e$) measurements during C/5 discharge of representative
PED-2 half cell and (inset) zoomed-in image of the induced voltage drops by using consecutive
current pulses.

To take a step further in establishing a standard for assessing quality control, the effective
Resistance ($R_e$) of the cells is determined by a pulsed current test, as illustrated in Figure 4-10.
In contrast to Nyquist plot impedance when the cell is in a static state, measuring the resistance
during cell operation provides a more pragmatic value. Furthermore, the $R_e$ takes into account
all resistive contributions (ionic and electronic) and is simpler to measure, whereas the total
resistance is complicated to calculate with complex impedance data. During the discharge, a
series of synchronized current pulses are applied which induce instantaneous voltage drops.
Since the applied current pulse is known, and the voltage drop is measurable, the corresponding resistance is calculated according to the relation:

\[ R = \frac{V}{I} \]  

(4-1)

where \( R \) is the resistance (\( \Omega \)), \( V \) is the induced voltage drop (mV), and \( I \) is the current pulse (mA). Three current pulses are applied to the PED-1 sample, where the 2 mA, 3 mA, and 5 mA current pulses are identified as PED-1a, PED-1b, and PED-1c, respectively, in Table 4-2.

<table>
<thead>
<tr>
<th>Measurement #</th>
<th>Current Pulse (mA)</th>
<th>Voltage Drop (mV)</th>
<th>Resistance Calculated (( \Omega ))</th>
<th>Area Specific Resistance (( \Omega \text{•cm}^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PED-1a</td>
<td>2</td>
<td>19.5</td>
<td>9.75</td>
<td>56.16</td>
</tr>
<tr>
<td>PED-1b</td>
<td>3</td>
<td>27.9</td>
<td>9.3</td>
<td>53.57</td>
</tr>
<tr>
<td>PED-1c</td>
<td>5</td>
<td>42.7</td>
<td>8.54</td>
<td>49.19</td>
</tr>
<tr>
<td>PED-1-average</td>
<td>--</td>
<td>--</td>
<td>9.2</td>
<td>52.97</td>
</tr>
<tr>
<td>PED-2-average</td>
<td>--</td>
<td>--</td>
<td>9.65</td>
<td>55.58</td>
</tr>
<tr>
<td>PED-3-average</td>
<td>--</td>
<td>--</td>
<td>14.35</td>
<td>82.66</td>
</tr>
</tbody>
</table>

Based on these three current pulses, an average resistance of the cell is calculated and labeled as PED-1-average. The same \( R_e \) test was performed on PED-2 and PED-3 half cells, and the averaged numerical results of those tests are listed in Table 2 as PED-2-average and PED-3-average. Considering the cathode’s area which is 5.76 cm\(^2\), the area specific resistance is also calculated and shown in the last column of Table 3-2. Results indicate that the optimized
cathode (PED-2) has a resistance of 55.85 Ω•cm², and a cathode with reduced material loading (PED-1) has a proximal resistance of 52.97 Ω•cm². However, the PED-3 cell which has excessive material loading has a higher resistance of 82.66 Ω•cm².

4.3.3. Electrochemical performance of LiCoO₂/Ni foam half cells

Nyquist plots obtained from ac impedance spectroscopy are shown in Figure 4-11, where a measurement is made for a freshly assembled half cell, after a single cycle of charge-discharge, and then again after 20 complete cycles.

![Figure 4-11: Nyquist plots of PED-2 half cell when freshly assembled, after 1 cycle of charge-discharge, and after 20 cycles.](image)

In a typical lithium-ion cell, a Nyquist plot shows a depressed semicircle at high frequency which represents the solid electrolyte interface (SEI) resistance (R_{SEI}), a second semicircle at
medium frequency representing the charge transfer resistance ($R_{CT}$), and a sloping line at low frequency characterizing the Warburg impedance.\(^{39}\) A zoomed-in image of the impedance spectra at low frequency is shown in the inset to reveal the depressed semicircles. Nyquist plots show a gradual increase in both the $R_{SEI}$ and $R_{CT}$ over repetitive cycling, although a slight decrease in $R_{CT}$ is observed after the first cycle. This minor initial decrease in $R_{CT}$ might be related to the infiltration of liquid electrolyte into the cathode which slightly decreases polarization. The increase in $R_{SEI}$ is accountable for both the anode and cathode surfaces. On the lithium anode side, it is well known that a passivation layer is formed upon contact with liquid electrolyte, and continual dissolution and re-growth of the SEI occurs with each cycle.\(^{40}\) Eventually, the electrolyte is damaged due to dendritic growth which contributes to capacity fading. A SEI layer also forms on the cathode surface, attributed to side reactions between strongly oxidizing Co\(^{4+}\) cations in the active material’s de-lithiated state and the electrolyte present at the surface.\(^{41}\) According to a previous study by Wang and Chen,\(^{42}\) LiCoO\(_2\) also undergoes solvent storage-induced degradation over time, which likely explains another contribution to the cathode resistance. In addition to the $R_{SEI}$ and $R_{CT}$, the bulk resistance ($R_B$) was also found to increase with the number of cycles, which is usually extracted from the start of the impedance scan located at the x-axis interception.
Figure 4-12: Area capacity vs. cycle number of PED-2 half cell with and without LiTFSI coordinated in the binder, along with coulombic efficiency (right and bottom axes).

Finally, the cycle life of a representative PED-2 half cell is shown in Figure 4-12. Cycled at C/2 rate, the cell is able to consistently deliver an average of 4.53 mAh/cm² without any significant capacity fading over 50 cycles. Along with the high area capacity, the Coulombic efficiency maintained an average of 98.7% efficiency throughout these cycles. As a standard for comparison, another half cell was constructed in which the poly(PEGMA-co-MMA-co-IBVE) binder was not coordinated with LiTFSI. PEG has a unique ability to switch from an ionic insulating state to a conducting state through the coordination of lithium salt in its polyether structure. As a test to validate the effect of ionic conductivity in the binder on cell performance, it is confirmed that cells without LiTFSI coordinated into the PEG-based binder were completely defective.
Charge-discharge curves for the ‘inactive’ cells are shown in Figure 3-13. Numerous flaws can be noticed including the lowered OCV, discontinuous charge and discharge curves, an intercalation voltage lower than normal on the first discharge, and then sudden cell death after the second charge. Not only do such cells fail to properly deliver a full discharge, they cease to function after two weak, incomplete cycles.
Consequently, the cathode structure can be described (Figure 4-14a) as active material being dispersed in an electronically conducting network of carbon black, and the surface of these particles is then covered and bound together by an ionically conducting elastomer, which is then adhered onto a nickel foam structure. When liquid electrolyte is added, the binder which covers the particle surface becomes wetted so as to further facilitate a permeable path for lithium ions. In the case that the binder is not coordinated with LiTFSI, then the hindered transport of lithium ions to and from the active material leads to cell failure. Ion transport when using an elastomeric binder such as the poly(PEGMA-co-MMA-co-IBVE) copolymer is much different than standard PVDF binder, as depicted in Figure 4-14b. PVDF has a semi-crystalline structure and is solid, so polymer chains are not exactly bound to a particular surface. It more or less relies on swelling to for ion transport, and as a polymer binder, PVDF does not affect inter-particle interactions in the same way as an elastomeric binder.\textsuperscript{21}
4.4. Conclusions

It is demonstrated as a proof of concept that 200+ µm thick and densely compressed cathodes are produced through an aqueous route, in this case using a binder that is adhesive and elastomeric to maintain the cohesion of the electrode, and also ionically conductive to improve lithium ion transport kinetics within the dense film. In terms of aqueous processing, the level of packing density, compression, thickness, and area capacity surpasses previous reports.\textsuperscript{23,27} Despite the low cycle life, it nonetheless surpasses previous studies of aqueous-processed LiCoO\textsubscript{2} cathodes.\textsuperscript{22,44} Using standard LiCoO\textsubscript{2} as active material for this process, the optimized cathodes deliver up to 4.53 mAh/cm\textsuperscript{2}. Particular emphasis must be placed on the ionic conductivity of the PEG-based binder, because cells do not function at all when it is not coordinated with lithium salt. The poly(PEGMA-co-MMA-co-IBVE) random copolymer exemplifies a unique class of multifunctional materials which enable the exploration of novel processes for electrode manufacturing. Its combination of versatile properties as a binder offers additional benefits including a one-step synthesis, safety, and low cost. Future investigations are aimed at experimenting with different active materials and to extend the cycle life.

4.5. References


CHAPTER 5:
ADHESIVE PEG-BASED BINDER FOR AQUEOUS FABRICATION
OF THICK LITHIUM TITANATE ELECTRODE

Ch. 5 Abstract: Fully compressed Li₄Ti₅O₁₂ electrodes are fabricated by an aqueous process. An adhesive, elastomeric, and lithium ion conductive PEG-based copolymer is used as a binder for the aqueous fabrication thick, flexible, and densely packed Li₄Ti₅O₁₂ (LTO) electrodes. Self-adherent cathode films exceeding 200 µm in thickness and withholding high active mass loadings of 28 mg/cm² deliver 4.2 mAh/cm² at C/2 rate. Structurally defect-free electrodes are fabricated by casting aqueous cathode slurries onto nickel foam, dried, and hard-calendared at 10 tons/cm². As a multifunctional material, the binder is synthesized by the copolymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA), methyl methacrylate (MMA), and isobutyl vinyl ether (IBVE) in optimal proportions. Furthermore, coordinating the binder with lithium salt is necessary for the electrode to function.

5.1. Introduction

An important aspect of manufacturing lithium-ion batteries is the selection of binder materials. Polymers based on poly(vinylidene fluoride) (PVDF) have been highly praised for their excellent performance and high thermal, chemical, and electrochemical stability. However, their major shortcoming is the solvent that is required for complete dissolution. Usually, toxic and high boiling point solvents such as N-methyl-2-pyrrolidone (NMP), N,N-
dimethylformamide (DMF), and N,N-dimethylacetamide (DMAc) are recommended to fully swell PVDF polymers so that homogenous films can be casted. In the strive to develop safer alternatives, aqueous binders including carboxymethylcellulose (CMC), poly(acrylic acid) (PAA), and poly(vinyl alcohol) (PVA) have been evaluated. These materials in general are stiff and brittle, consequently leading to cracked films that can delaminate from the current collector either during cell fabrication or cell cycling. Thus, an additional rubber such as styrene-butadiene rubber (SBR) has been used to improve the overall cohesion of the electrode, although the rubber does not contribute towards the dispersion efficiency of cathode slurries and has a negative impact on the conductivity of the electrode. In all cases, these water-soluble binders are not electrochemically active and their presence serves as impedance to lithium ionic conduction, most notably at the active material interface.

In pursuit of more effective binders, research efforts have clarified the need for an adhesive binder capable of conducting lithium ions, with particular emphasis placed on a poly(ethylene glycol) (PEG)-based system because of its ability to coordinate metal salts. This claim holds true to the fact that cathodes assembled by the aforementioned aqueous binders are very thin, low in material loading, or fragile against compression due to the poor mechanical and electrochemical properties of the respective binder. In a stride towards the aqueous processing of 200+ µm thick and fully compressed lithium ion battery cathodes, we report the use of an adhesive, elastomeric, and ionically conductive binder to cast aqueous LTO cathode slurries onto nickel foam current collector, followed by drying and compression at 10 tons/cm². Such a unique and multifunctional binder is synthesized through a one-step statistical copolymerization of PEGMAs, MMA, and IBVE to produce a high molecular poly(PEGMA-co-
MMA-co-IBVE) random copolymer. High material loadings using this procedure allow up to 28 mg/cm$^2$ of active material, which results in a high area specific capacity of 4.2 mAh/cm$^2$ at C/2 rate. This level of material loading, area capacity, and compression substantially surpasses previous reports of aqueous binders. For example, the active mass loading is nearly 20 times that of thin LiFePO$_4$ (LFP)/CMC electrodes,$^{23}$ the area capacity is more than 200% greater than weakly compressed LTO/CMC/rubber electrodes,$^{24}$ and the calendaring pressure is 250% higher than thick LFP electrodes having rubber/CMC binder.$^{25}$ Also, we validate that coordinating the PEG-based binder with lithium salt plays a crucial role in ‘activating’ the cathode. As an electrode, spinel lithium titanate possesses many attractive qualities including zero-strain volume change,$^{26}$ high lithium diffusivity,$^{27}$ absence of a solid electrolyte interface (SEI),$^{28}$ and excellent safety.$^{29}$ Herein, it is demonstrated that significant improvements in material processing can be achieved by using a novel binder material along an aqueous route. A procedure for electrode fabrication and the performance of LTO/nickel foam half cells are discussed.

5.2. Experimental

5.2.1. Materials and methods

The following reagents were purchased from Sigma Aldrich and used as received: poly(ethylene glycol) methyl ether methacrylate (average $M_n = 300, 475, 950$), methyl methacrylate (99%), isobutyl vinyl ether (99%), ethyl acetate (99%), hexanes (99%), 2,2’-azobisisobutyronitrile (AIBN, 99%). De-ionized water having 18 MΩ resistance was used in cathode formulations. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99%) was
purchased from 3M, lithium foil (0.75mm x 19mm, 99.9%) was purchased from Alfa Aesar, and these materials were stored in an argon fill dry box. Nickel foam was purchased from Linyi Gelon New Battery Materials Company model number FN–I (Shandong, China). Prior to coating the foam, it was cleaned by soaking in 1 wt% Alkanol 6112 surfactant (Sigma Aldrich) solution, DI water, and acetone, each for 30 minutes. Then, it was rinsed copiously with water and dried in air at 150°C for 30 minutes.

The molecular weight of the copolymer was measured using a JASCO gel permeation chromatograph equipped with a refractive index detector (THF eluent; monodistribution polystyrene standards). ¹H NMR spectra were obtained using a 300 MHz Oxford Labs instrument (CDCl₃ solvent). The structure and morphology were studied by thin-film X-ray diffraction with Cu Kα radiation (XRD, Rigaku) and a high resolution scanning electron microscope (SEM, Zeiss Ultra).

5.2.2. Synthesis of Poly(PEGMA-co-MMA-co-IBVE) copolymer binder

The reaction was a one-step free radical copolymerization consisting of PEGMA’s (Mₙ = 300, 475, 950), MMA, IBVE, 2 wt% thermal initiator (AIBN), and minimal solvent to control cross-linking. To a glass container was charged 1.0 g PEGMA₃₀₀, 0.4 g PEGMA₄₇₅, 0.2 g PEGMA₉₅₀, 0.2 g MMA, 0.2 g IBVE, 0.04 g AIBN, and 0.5 mL ethyl acetate. This mixture was dissolved together and sealed at ambient temperature and pressure. Then, it was heated in an oil bath at 95°C for 30 minutes with stirring, during which the color turned deep orange and faded to light yellow. After the 30 minutes duration, the sample was cooled down to room temperature and purified by repeated dissolution/precipitation in ethyl acetate/hexane three times. Finally,
the sample was vacuum dried for 36 hours to afford a pale yellow, transparent gum-like substance. Typical yield was 1.7 g (85%). $^1$H NMR (CDCl$_3$): $\delta$ 0.7-0.9 (s, 7.2H), $\delta$ 0.9-1.1 (s, 4.5H), $\delta$ 1.6-2.0 (m, 7.4H), $\delta$ 3.4 (s, 9.2H), $\delta$ 3.6 (s, 67H), $\delta$ 4.2 (s, 5.4H). The average molecular weight determined against polystyrene standards was 36,400 with a polydispersity index ($M_w/M_n$) of 4.27. The copolymer is soluble in water, acetone, tetrahydrofuran, and ethyl acetate. In ethylene carbonate (EC) / propylene carbonate (PC) liquid electrolyte solution, it swells without dissolving.

5.2.3. Fabrication of LiCoO$_2$/nickel foam cathode

Cathode slurries were prepared by first dissolving the Poly(PEGMA-co-MMA-co-IBVE) random copolymer in water to 30 wt% concentration. Based on the weight of the copolymer, 20 wt% LiTFSI was added to induce lithium ionic conduction in the copolymer, this amount corresponding to a Li:EO ratio of 1:20. By weight, the positive electrode consisted of 83.3% Li$_4$Ti$_5$O$_{12}$ spinel powder (MTI Corporation), 8.3% Super P carbon black (Timrex), and 8.3% copolymer binder (with LiTFSI salt). This mixture was sonicated (Sonics & Materials, model CV33, 500W 20 kHz) for five minutes, and then doctor bladed onto a cleaned nickel foam at 90°C. The area of the nickel foam was 5 cm x 2 cm, while an edge strip of the foam (1 cm x 2 cm) was left uncoated to serve as the current collector. After allowing the coating to dry for 10 minutes, it was further dried at 170°C for one hour, cold calendared between two tool steel blocks at 100 tons (10 tons/cm$^2$) with a hydraulic press, and then vacuum dried at 80°C for two hours before finally transferring into an argon circulated glove box. On average, the active material loading was 28 mg/cm$^2$, and the final thickness of the cathode was 250 µm.
For the LTC-X cathode where the binder is replaced by PVDF, PVDF (Kynar 2801) was dissolved in NMP at 30 wt% concentration, after which Li$_4$Ti$_5$O$_{12}$ powder and Super P are added. The suspension was mixed for 6 hours at 80°C, pasted onto a nickel foam substrate, and vacuum dried at 120°C for 12 hours before calendaring.

In an argon filled glove box, LTO/Li half cells were assembled using the uncoated strip of nickel foam spot-welded to a stainless steel current collector. The half cell contained a cathode of active area 2.4x2.4 cm$^2$, a Celgard 2325 (25 µm thick) separator, a lithium foil as the anode, and 1M LiPF$_6$ in EC/PC (1:1 wt% mixture) purchased from Novolyte as the electrolyte. The LTO/separator/Li half cells were assembled in a metalized plastic pouch and vacuum packaged under argon.

5.2.4. Electrochemical measurements

Cell performance was evaluated by preparing half cells against a lithium anode. For cell cycling, a Maccor tester 4000 Series was used with cutoff voltages of 2.5 V for charging and 1.0 V for discharging. Prior to electrochemical characterization (rate test and effective resistance test), the cells were cycled for 10 cycles to ensure electrochemical stability. Nyquist plots from AC impedance spectroscopy were measured using an IM6e Zahner analyzer, scanned from 10 mHz to 100 kHz at open circuit potential. The lithium anode was used as the reference and counter electrode while the LTO/nickel foam cathode was used as the test electrode.
5.3. Results and discussion

5.3.1. Electrode structure and morphology

For reference, samples were loaded with an average of 20, 28, or 39 mg/cm\(^2\) of active material and they are identified as lithium titanate cathode LTC-1, LTC-2, or LTC-3, respectively. A survey of the structure and morphology of the compressed LTO/nickel foam cathode film is performed by SEM.

Figure 5-1: SEM images of (a) nickel foam before material loading; (b) after material loading and drying; (c) after compression; (d) high-resolution SEM image of LTC-2 cathode surface; (e) its cross-sectional view; and (f) the LTC-X cathode when the binder is replaced by PVDF.

Figure 5-1 illustrates the stepwise procedure starting from a bare nickel foam (Figure 5-1a), followed by coating with the aqueous cathode slurry (Figure 5-1b), and after compression at 10
tons/cm$^2$ (Figure 5-1c). From these images, it is clear that this process yields non-aggregated coatings as well as smooth surfaces, which are attributed to the unique properties of the poly(PEGMA-co-MMA-co-IBVE) binder. Firstly, the different components of this copolymer have varying degrees of solubility in water, thereby granting surfactant-like ability to efficiently disperse the electrode suspensions. Its amorphous and elastic properties allow the compression of the film without detachment or segregation of materials, while the adhesion property ensures the overall cohesion of the electrode once it is calendared. A high resolution image of the LTC-2 cathode surface (Figure 5-1d) reveals two distinct sets of submicron particle sizes. Smaller particles (30-40 nm) that seem to have extensive coverage throughout the film are mostly attributed to the Super P carbon black, while the larger particles (200-500 nm) enclosed by the carbon black are characteristic of the LTO particles since they are used as received. Thus, the carbon black particles are in intimate contact with each other, thereby preserving a well-connected electronic pathway throughout the electrode. And secondly, all of the particles are well-adhered together by the copolymer binder although it may not be clearly visible due to its amorphousness. A cross-sectional view of the cathode film in Figure 5-1e shows a 250 µm thick and defect free structure, although slight delaminating is observed which is presumably due to cutting the sample prior to SEM. Nickel foam protrusions are also discernable from discontinuities in the film morphology, thereby showing its role as a physical support. Because the redox potential of Ni/Ni(II) is 2.80 V vs. Li/Li$^+$ which is above the operational voltage of the cell (1.0 – 2.5 V),$^{30}$ the stability of the nickel foam as a current collector is expected. Overall, electrode materials with the elastomeric binder are densely packed into the compressed nickel foam, producing a flexible and bendable electrode.
In an attempt to produce a control sample, a cathode is made using PVDF as the binder (LTC-X) instead of the poly(PEGMA-co-MMA-co-IBVE) copolymer. After compression, the cross-sectional view of this cathode (Figure 5-1f) indicates that the film suffers from severe delaminating and also the electrode materials are not homogeneous throughout the film. During the calendaring, substantial portions of materials are forced out of the nickel foam. Moreover, electrode materials spontaneously detach with handling because of the poor adhesiveness of PVDF. Because of the highly irreproducible nature of this process, a half cell test using the LTC-X cathode is not performed.

![Figure 5-2: Calibration of cathode thickness with material loading after compression; standard deviations are 4-5%.

A calibration of the thickness of the LTO/Ni foam electrode as a function of material loading is shown in Figure 5-2. Active material loadings of 20, 28, and 39 mg/cm² results in average film thicknesses of 185, 245, and 305 µm, respectively. These measurements are
averaged over three samples, each sample contributing nine measurements. The standard deviations in thickness are usually 4-5%. There is no noticeable difference in thickness when calendaring at 8 tons/cm$^2$ or 10 tons/cm$^2$, suggesting that the electrode is fully compressed when applying 10 tons/cm$^2$. Thus, this aqueous procedure allows a high level of freedom for producing films of varying thickness and with reasonable accuracy.

![XRD Pattern](image)

Figure 5-3: XRD pattern of Li$_4$Ti$_5$O$_{12}$/Nickel foam cathode indicating pristine active material and nickel foam after aqueous dispersion, drying in air, and compression.

To confirm the crystallographic structure of the cathode, the XRD pattern is shown in Figure 5-3. The peaks identified by XRD verify that the cathode consists of two crystalline structures which can be indexed to spinel$^{31}$ Li$_4$Ti$_5$O$_{12}$ and synthetic nickel.$^{32}$ All of the peaks from 10 – 80 degrees (2θ$^o$) are characteristic of LTO, except for the peaks at 44.5, 51.9, and 76.4 (2θ$^o$) which characterize the crystal structure of synthetic nickel. Therefore, it can be concluded
that the aqueous process using this poly(PEGMA-co-MMA-co-IBVE) copolymer does not significantly alter the chemistry of the active material. In any case, Fongy and coworkers have reported the dissolution of lithium from Li₄Ti₅O₁₂ during an aqueous suspension. And due to the annealing in air, other impurity species which might have formed are the nickel (II) and nickel (III) oxides, although the peaks for these materials are also absent. At the end of the brief heat treatment, the material composition remains highly pristine.

5.3.2. Optimization of cathode fabrication procedure

A typical charge-discharge profile of a LTO/Li half cell is shown in Figure 5-4, revealing the characteristic plateaus at 1.5 – 1.55 V from lithium insertion/extraction reactions.

![Figure 5-4: representative charge-discharge profile from 2.5 – 1.0 V of LTO/Li half cell.](image)
From the open circuit voltage (OCV) of about 3.2 – 3.4 V, cells go directly to discharge mode as Li$_4$Ti$_5$O$_{12}$ comes in a lithium deficient state. After the initial discharge, cells repeatedly charge to 2.5 V and then discharge to 1.0 V, of which only the first two full cycles are shown in Figure 5-4. The charge and discharge curves are smooth without abrupt discontinuities, indicating that the electrochemical properties of the thick Li$_4$Ti$_5$O$_{12}$ electrode are unaltered from this aqueous fabrication process.

The optimal amount of material loading into the nickel foam is determined by performing a rate test on the LTC-1, LTC-2, and LTC-3 half cells which have different weight loadings as shown in Figure 5-5.

![Figure 5-5](image)

**Figure 5-5:** (a) Rate capability test of half cells from 0.2C to C rate; and (b) representative discharge curves using LTC-2 sample (28 mg/cm$^2$).

In testing the rate capability, half cells are cycled at various rates ranging from 0.2C to 1C rate (Figure 5-5a). Comparing the results of the rate tests indicates that the percolation threshold for
material loading is about 28 mg/cm$^2$, since increasing beyond this point negatively affects the rate capability. Figure 5-5b shows the discharge curves of the LTC-2 sample which reveal the flat plateaus at 1.55 V. For the LTC-2 half cell, a C/5 and C/2 discharge produces marginal differences of 158 mAh/g and 154 mAh/g, respectively. Based on the theoretical capacity of 175 mAh/g for Li$_4$Ti$_5$O$_{12}$, these values correspond to 90.3% and 88% capacity retention, respectively. Interestingly, the LTC-1 and LTC-2 samples demonstrate similar rate capability, including the C-rate discharge where they deliver 143 mAh/g which equates to 81.7% capacity retention. Such limited rate capability is attributed to a combination of the film thickness and inherently low conductivity of the active material.$^{33}$

Figure 5-6: Effect of drying temperature on performance LTC-2 half cell.

An experiment to determine the most appropriate drying temperature is expediently performed by drying a LTC-2 cathode at 170°C or 200°C for one hour each. Assembling half
cells of these cathodes and comparing their cycle life (Figure 5-6) indicates that drying at 170°C results in extended cyclability, while 200°C diminishes the cycle life. These results are rather anticipated since PEG, which comprises most of the binder, typically decomposes above 200°C.\textsuperscript{34} Drying samples at this temperature for an extensive period deteriorates the cathode structure and impairs the cell performance.

After optimizing the electrode fabrication procedure, an additional measure to assess quality control involves a pulsed current test to determine the effective resistance (\(R_e\)) of the cell during operation (Figure 5-7).

![Figure 5-7: \(R_e\) test during C/3 discharge of LTC-1 half cell and (inset) zoomed-in image of the induced voltage drops.](image)

This procedure is selected because of its simplicity to determine all resistive contributions in the cell construct, in contrast to the use of complex impedance data to calculate the total cell
resistance. In order to measure the $R_e$, the current is momentarily paused during a C/3 discharge, causing the cell voltage to rise and then stabilize. Once the potential is steady, instantaneous current pulses are applied in a consecutive manner, each one inducing a measurable voltage drop. The $R_e$ is then calculated according to the relation:

$$R = \frac{V}{I}$$  \hspace{1cm} (5-1)

where $R$ is the resistance (Ω), $V$ is the voltage drop (mV), and $I$ is the current pulse (mA).

Shown in Table 4-1 are the results of the $R_e$ test, where the 2 mA, 4 mA, and 8 mA current pulses are labeled as LTC-1a, LTC-1b, and LTC-1c, respectively.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Current Pulse (mA)</th>
<th>Voltage Drop (mV)</th>
<th>Resistance Calculated (Ω)</th>
<th>Area Specific Resistance (Ω•cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTC-1a</td>
<td>2</td>
<td>16.6</td>
<td>8.3</td>
<td>47.81</td>
</tr>
<tr>
<td>LTC-1b</td>
<td>4</td>
<td>34</td>
<td>8.5</td>
<td>48.96</td>
</tr>
<tr>
<td>LTC-1c</td>
<td>8</td>
<td>66</td>
<td>8.25</td>
<td>47.52</td>
</tr>
<tr>
<td>LTC-1-average</td>
<td>--</td>
<td>--</td>
<td>8.35</td>
<td>48.10</td>
</tr>
<tr>
<td>LTC-2-average</td>
<td>--</td>
<td>--</td>
<td>9.25</td>
<td>53.28</td>
</tr>
<tr>
<td>LTC-3-average</td>
<td>--</td>
<td>--</td>
<td>16.45</td>
<td>94.75</td>
</tr>
</tbody>
</table>

Averaging these resistances yields a value of 8.35 Ω for the LTC-1 half cell which is labeled as LTC-1-average. For a cell with an area of 5.76 cm², the area specific resistance equates to 48.10 Ω•cm². The same test is performed on the LTC-2 and LTC-3 half cells and the averaged numerical results are identified in Table 1 as LTC-2-average and LTC-3-average, respectively.
Obtaining the $R_c$ of the half cells provides some insight into their performance because the rate capabilities of the LTC-1 and LTC-2 samples are nearly identical and their specific resistances are also similar. However, the LTC-3 sample has substantially higher resistance and its rate capability is also dramatically reduced.

### 5.3.3. Electrochemical characterization of LTO/Ni foam half cells

Nyquist plots of the optimal LTC-2 half cells are obtained for a freshly prepared cell, after one cycle of charge-discharge, and after 20 cycles, as illustrated in Figure 5-8.

![Nyquist plots](image)

**Figure 5-8**: Nyquist plots of freshly assembled LTC-2 half cell, after 1 cycle of charge-discharge, and after 20 cycles of charge/discharge.
A typical profile of a LTO/Li half cell shows a depressed semicircle at high frequency for the solid electrolyte interfacial resistance (R_{SEI}), a larger semicircle at medium to high frequency representing the charge-transfer resistance (R_{CT}), and a sloping line at high frequency which characterizes the Warburg impedance.\textsuperscript{35} Additionally, a bulk resistance (R_{B}) is extrapolated from the onset of the Nyquist plot at the x-axis interception. Results indicate an increase in R_{CT} with each cycle from 10.4 Ω for a fresh cell, to 10.6 Ω after one cycle, and to 12.6 Ω by 20 cycles. In contrast to the increase in R_{CT}, the R_{B} is found to slightly decrease with cycling which may be due to a combination of several events. This trend is not likely associated to cycling, but related to infiltration of liquid electrolyte into the thick cathode and also the change in the state of charge of the active material. In the cell’s discharged state, Li_{7}Ti_{5}O_{12} possesses higher electronic conductivity compared to its de-lithiated Li_{4}Ti_{5}O_{12} state for a freshly prepared cell.\textsuperscript{33} A combination of improved surface contacts with infiltration of liquid electrolyte into the densely packed cathode and lithiation of the active material bring about a lowered R_{B} in the ensuing Nyquist plots. As for the changes that occur in R_{SEI}, its presence in the Nyquist plot for a fresh cell is indicative of the instantaneous reaction between the liquid electrolyte and the lithium anode surface upon cell assembly, forming a passivation layer that is well known to be electronically insulating but ionically conductive.\textsuperscript{36} After the first cycle, the change in R_{SEI} is not so substantial, but the semicircle for the R_{SEI} becomes noticeably larger by 20 cycles. Since the LTO cathode is generally accepted to be free of SEI formation within the 1–3 V potential window,\textsuperscript{37} an increase in R_{SEI} with continuous cycling accompanies the repeated dissolution and re-growth of the passivation layer on the anode side. Taking all of these factors into
consideration, the increase in cell impedance with cycling is presumably due to consumption of the electrolyte because of repetitive SEI formation.

![Cycling performance and area capacity of LTC-2 half cell with and without LiTFSI coordinated by the binder at C/2 rate charging and discharging.](Figure 5-9).

Lastly, Figure 5-9 shows the long-term cycling of the optimized LTC-2 half cell at C/2 rate charging and discharging. An initial irreversible capacity loss is observed in the first discharge\(^{38}\) which delivers 4.67 mAh/cm\(^2\) (or 171.2 mAh/g), and then subsequent cycles consistently deliver an average of 4.2 mAh/cm\(^2\) over 47 cycles. Capacity fading afterwards is attributed to the continuous re-growth of SEI layers which deteriorate cell performance. Remarkably, the coulombic efficiency maintained 100% throughout these cycles. As a control experiment to determine the effect of ionic conductivity in the binder, a LTC-2 half cell is assembled without LiTFSI coordinated into the PEG-based binder. As well known, PEG can switch from an ionically insulating to a conducting state through the coordination of lithium salt.
in its polyether structure. Half cells constructed without LiTFSI in the binder are completely defective since they fail to deliver a full discharge and then cease to function after two weak cycles, while cells with LiTFSI in the binder continuously cycle for a much longer period. Based on these results, the cathode structure can be described as active material being dispersed with Super P particles, and the surfaces of these particles are bound together by the adhesive and elastomeric poly(PEGMA-co-MMA-co-IBVE) binder. In the case that the binder is coordinated with LiTFSI, then the addition of plasticizing liquid electrolyte causes the wetting of the particle surfaces to further facilitate the transport of lithium ions within the electrode. But in the opposite case where the binder is not coordinated with LiTFSI, serious detrimental effects relating to poor lithium ion transport lead to cell failure.

5.4. Conclusions

The aqueous route fabrication of 200+ µm thick LTO electrodes using a novel poly(PEGMA-co-MMA-co-IBVE) copolymer binder is demonstrated. High active material loadings up to 28 mg/cm² and hard calendaring at 10 tons/cm² yields thick, flexible, and fully compressed electrodes that deliver an area specific capacity of 4.2 mAh/cm² at C/2-rate. Even as a proof of concept for a new electrode manufacturing technique that is enabled by an adhesive, elastomeric, and lithium ion conductive binder, the mechanical properties of such electrodes demonstrate superior durability. Many major aspects of electrode engineering such as material loading, thickness, compression level, flexibility, and ease of processing are addressed with this method. The PEG-based copolymer binder is a unique and multifunctional material that plays
many crucial roles including the effective dispersion of electrode slurries, ensuring cohesion of electrode materials, and maintaining ionic conduction pathways throughout the electrode. While each of these roles is critical, special emphasis must be placed on the ionic conductivity in the binder since cells are only operable when lithium salt is coordinated in the binder. Additional benefits of the poly(PEGMA-co-MMA-co-IBVE) copolymer include its facile one-step synthesis, easy solubility, and safety. Although LTO is used as a cathode in these half cell constructions, this aqueous process is deemed applicable for the all-aqueous production of lithium-ion batteries where LTO is the anode against high voltage active materials.

5.5. References


6.1. Dissertation Conclusions

Careful implementation of structure-property relationships is a powerful technique for designing breakthrough materials. A viscoelastic, soft matter type electrolyte is synthesized based on a ternary random copolymer of poly(ethylene glycol) methyl ether methacrylate, methyl methacrylate, and isobutyl vinyl ether. These functional monomers classify the product as a vinyl-acrylic copolymer. Oligoether chains along the polymer backbone are able to dissolve lithium salts, which in this case LiTFSI is used to demonstrate basic electrolyte behavior in the solid state since LiTFSI is safe and is among the highest conducting salts. The ionic conductivity of the poly(PEGMA-co-MMA-co-IBVE) copolymer determined by EIS is well within the $10^{-5}$ S/cm range at room temperature and $10^{-4}$ S/cm is attainable at 40°C. Its voltage stability seems limited to 4.0 V vs. Li/Li⁺ which is common for PEG-type materials, so only the 3 V class of cathode materials (e.g. V₂O₅, LiFePO₄) are applicable in a cell configuration. However, creative chemical design may heighten the electrochemical window, such as through the incorporation of functional inorganic units, which would then open up the 4 V class of cathodes (LiCoO₂, LiMn₁/₃Co₁/₃Ni₁/₃O₂, LiMn₁/₂Ni₁/₂O₂) for higher energy density batteries.

Apart from electrolyte ability, the poly(PEGMA-co-MMA-co-IBVE) copolymer possesses strong adhesion strength capable of permanently holding 800 times its own weight as a 10 μm thin film and easy solubility in water and organic solvents for facile processing. Well developed coating technologies are therefore available for dip-coating or spraying of self-adherent,
multilayer thin films. Other possibilities are not limited to just lithium-ion batteries, but also electrochromic windows and sodium or silver ion electrolytes for various electrochemical devices.

With alternative applications in mind, this copolymer can also serve as an electrode binder for lithium-ion batteries. Once again relying on its ease of solubility, an all-aqueous process for fabricating lithium-ion battery electrodes is demonstrated for both a cathode (LiCoO$_2$) and anode (Li$_4$Ti$_5$O$_{12}$) type active material. Thick, flexible, densely packed, and fully compressed electrodes are produced by using commercial nickel foam as a current collector for an aqueous slurry coating. Electrode thicknesses exceed 200 µm and withhold active mass loadings of about 30 mg/cm$^2$, which correspond to 20 times the loading of CMC-binded electrodes. High area specific capacities of 4.5 mAh/cm$^2$ for LiCoO$_2$ or 4.2 mAh/cm$^2$ for Li$_4$Ti$_5$O$_{12}$ can withstand C/2-rate charging-discharging for about 50 cycles without fading. These area capacities are significantly higher than most commercial electrodes, taking for example, graphite anodes that usually afford 3.0 mAh/cm$^2$. Film resistances obtained with this process are among the lowest reported to date, again indicating a strong advantage over other plastic binders. As ionic conductivity is often a limiting factor for electrode kinetics, it appears that the poly(PEGMA-co-MMA-co-IBVE) binder must have dissolved lithium salt in its chemical structure to activate the electrode; plasticization by liquid electrolyte alone is insufficient. In summary, structurally defect-free electrodes are fabricated that have not been previously achieved by any water-soluble binder (i.e. PAA, SBR, CMC). Even the commercial standard P(VDF-HFP) binder, which requires toxic solvent, could not withstand the compression level (10 tons/cm$^2$) that the poly(PEGMA-co-MMA-co-IBVE) supports.
Perhaps the only discouraging aspect of this process is the low cycle life of the half cells under study, as commercialization would require an upwards of 500 cycles with at least 80% capacity retention. With further effort to successfully elongate the cycle life, this vinyl-acrylic electrolyte/binder is expected to drastically reduce the resources allocated to battery manufacturing. A sharp transition from NMP to water solvent for the fabrication of mechanically robust and free-standing electrodes provides a conceptual proof for the use of novel multifunctional binder materials, particularly ones that are adhesive, elastomeric, and ionically conductive. Cleaner processes for the production of lithium-based energy storage devices are within realization. Not only in terms of environmental benignity, but such processes are also less costly, less time-consuming, facile, and overall more expedient than existing methods for the mass manufacturing of the highest theoretical energy density batteries.

Altogether, lithium battery development consists of two major sectors, one focused on creating higher performance electrodes while the other aims at process improvement. Both sectors diverged from what originally started as fundamental understanding of materials. As detached as they may appear, both sectors are strongly interconnected and dependent on each other. Breakthroughs in electrode materials may be integrated into existing manufacturing processes, and innovative processes may likewise be applied to novel electrodes. This dissertation is in accordance with the process improvement sector by studying a vinyl-acrylic copolymer as an electrolyte and electrode binder. Standard electrode materials have been tested for the purposes of conceptualization. Further advances in this system may be possible with the invention of newer active materials, or by experimentation with nano-structured electrodes. The
works presented in this dissertation make up a contribution towards the development of cleaner technologies for producing lithium batteries and creating a more sustainable future.

6.2. Future Directions

Applications beyond portable electronics are stationary energy storage and transportation. Stationary energy storage for uninterrupted power supply has long been dominated by lead acid batteries simply due to sheer costs. Since this application is determined by costs and safety, it is unlikely for this market to be overturned by Li-Ion batteries whose high energy densities are irrelevant. Recent studies have conceptually shown that liquid metal magnesium-antimony (Mg-Sb) batteries may be more cost-effective than lead acid batteries for niche applications in stationary energy. Mg-Sb batteries operate at high temperatures (700°C) where the electrode and electrolyte layers melt from the solid state and stratify by density to form the cell multilayer structure. Instead, transportation is an immense and emerging market opportunity for Li-Ion batteries. Equipping the Toyota Prius and Tesla electric vehicles with 200+ mile range Li-Ion batteries has opened the curtain for electric propulsion.

Sea ferries have also begun employing electric car batteries for seafaring power, partially as a result of stricter regulations expected to become enforced by 2015. Traditional coal-powered sea vessels generate large amounts of SO₂ as air pollutants, and therefore, there is a strong demand for alternative seaward power sources such as batteries and liquid natural gas. A unique combination of rechargeable docking batteries that are then recharged by the electric grid allows for efficient recharging of ferry batteries. In numerous areas in the electric grid, custom
designed lithium batteries are usurping previous battery chemistries from their long-held reign. New lower-cost manganese and phosphate cathode materials provide even more incentive for the development of Li-Ion batteries and its expansion in the marketplace. New electrolyte and binder materials are not strictly limited to lithium batteries, but in principle, can apply to many battery systems.

Future directions for research and development are open and seem promising in many directions. This dissertation focuses on a singular vinyl-acrylic copolymer electrolyte having chemically tailored properties for applications in lithium batteries as an electrolyte and electrode binder. Future work may be directed towards performing a larger scale investigation of materials having similar properties, and enlarging the library of polymeric materials that can serve similar purposes. It seems optimistic at this stage that the creation of superior and more advanced polymers may improve the processing of lithium batteries to an even higher level.

Short term plans are to incorporate inorganic functional groups as a side chain or backbone to improve the voltage stability of the electrolyte. Inorganic units such as siloxanes and phosphazenes tend to provide a wider electrochemical window than organic units alone. Since PEG suffers from limited structural stability, many attempts to combine it with polymers that are more structurally stable and flexible such as polysiloxanes and polyphosphazenes have developed interesting chemistries. Polysiloxanes represent a unique class of materials that are either highly viscous or viscoelastic, and because of this property, they can overcome melting-induced failure modes that are prominent in PEG homopolymers. The synthesis of a polysiloxane precursor prior to functionalization can be facilely performed by acid catalyzed ring-opening polymerization of cyclic siloxane oligomers such as 2,4,6,8-
tetramethylcyclotetrasiloxane. This polymer precursor contains Si-H bonds that can be reacted by either Pt or B catalysts to produce an enormous range of graft, comb, star, network, and random copolymers possessing ion solvating units. With a Si-O backbone, the addition of oligoether groups can produce amorphous solid polymer electrolytes having ionic conductivities \((10^{-3} - 10^{-4} \text{ S/cm})\) surprisingly comparable to liquid and gel electrolytes. Not only that, the voltage stability typically lies in the 4.5 – 5.0 V range compared to the 4 V stability of pristine PEG. Excellent thermal stability along with superior conductivities and electrochemical stability have led to the commercialization of polysiloxane and organosilicone electrolytes, although the major obstacle for this class of polymers is their vulnerability to nucleophilic attack. Hydroxides, alcohols, or any base sufficiently electronegative are able to displace the Si-O-CH\(_2\) oligoether functional units from silicon to render it inactive or crosslink it. Even the ambient moisture in air will cause hydrolysis of improperly sealed polysiloxane samples. Therefore, all of the synthesis and handling of polysiloxanes must be carefully kept under inert atmosphere which involves cumbersome processing.

Polyphosphazene electrolytes are based on an inorganic \(-\text{P=\(\text{N}\)-} \) backbone where the phosphorus groups are functionalized with oligoether units for solvating ions. Functionalization may proceed by reacting a center-stage precursor, poly(dichlorophosphazene), with alkoxides or amines to produce a wide variety of polyphosphazene derivatives. An often recognized disparity in polyphosphazene electrolytes that is worth mentioning is a temperature dependent conductivity that deviates from true Arrhenius behavior, otherwise known as Vogel-Fulcher-Tammann (VFT) type conductivity. It is not uncommon for polymer electrolytes to delineate from Arrhenius type
conductivity, but resorting to the empirical VFT equation means that the activation energy for conductivity is also dependent on temperature in an uncertain way.

Physically grafting an elastic polymer to a rigid polymer through a polymer blend system may also produce polymer electrolytes with interesting properties. Rigidity and flexibility can be maintained by incorporating crosslinkable monomers into the co-polymer, such as isocyanates which can crosslink in the presence of epoxides, acohol, and anhydrides. At any rate, it is important to explore other polymers that have similar chemical, electrochemical, physical, and rheological properties, i.e. adhesive, elastomeric, and lithium ion conductive. All the while, water solubility is the economical driving force for application to lithium technologies.

In the longer term, binder capabilities must also be confirmed with diverse active materials. LiCoO$_2$ and Li$_4$Ti$_5$O$_{12}$ have so far been validated, and future investigations will aim at lower, intermediate, and higher voltage active materials such as Sn (0.9 V), LiFePO$_4$ (3.3 V), and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (4.3 V), respectively. Expanding the electrochemical window of active materials will potentially increase energy densities and also area-specific capacities while reducing the thickness of battery designs. Or, even thicker electrodes may be fabricated. For example, Sn alloys with Li to form LiSn with a capacity of 4000 mAh/g. Successful implementation of Sn anodes would negate the necessity of fabricating thick anodes. Thin Sn anodes may have sufficient capacity to match that of thick cathodes that are much lower in capacity (<500 mAh/g). Besides widening the voltage gap between the anode and cathode, intermediate voltage active materials present formidable advantages despite their lower energy density. LiFePO$_4$ is well known for its low cost, fast rates, and superior safety compared to other standard cathode materials. Sulfur is another strong candidate for lithium-sulfur batteries as a
Consequence of its low density, although a major obstacle is dissolution of sulfur in the liquid electrolyte phase. Solid state electrolytes that can serve the dual role of separator and binder in lithium-sulfur cells are promising in this aspect. Overall, switching the toxic PVDF binder in any of these electrodes to an aqueous processed binder is considerable for market delivery, so long as long cycle life is retained.

Conductive nanomaterials such as carbon nanotubes and graphene offer low percolation thresholds as conductive additives which may potentially replace traditional carbon black additives. Carbon nanotubes (CNTs) can be seen as one-dimensional material made by rolling up a graphene sheet. The high surface area and unique geometry of CNTs and graphene materials result in greatly enhanced molecular interactions per weight used. Electronic conductivities of electrodes can therefore be enhanced with less mass of additives for high rate performance. However, strong intermolecular Van der Waals interactions between CNTs and graphene sheets in suspension cause severe bundling or aggregation to occur which undermine their percolation efficiency. Developing an aqueous electrode binder that can effectively disperse CNTs and graphene may also further improve the processing of lithium batteries. Presently, many conjugated molecules and polymers have demonstrated very efficient dispersion of CNTs. Several examples of these dispersing agents include pyrene, fluorescein, and poly(3-hexylthiophene). Incorporating an aromatic or conjugated polymeric unit to a polymer electrolyte is also a research path worth pursuing.

In summary, PEG alone possesses fundamental electrolyte properties in the solid state that are not as apparent in other polymers such as polyesters and polynitriles. Ethers for the most part have been neglected as solvents for liquid electrolytes and polymer hosts for gel electrolytes
for various reasons. In the liquid form, ethers are low dielectrics that afford poor capacity retention and limited electrochemical stability which cannot match the performance of mixed carbonates and esters. If used as a polymer host for gel electrolytes, PEG dissolves in liquid electrolyte rather than swelling in it, therefore making it chemically incompatible as a host. As a solid polymer electrolyte, PEG itself has low ionic conductivity ($10^{-6} - 10^{-7}$ S/cm) at room temperature, and practical conductivities are only reached when the electrolyte is no longer a solid. Suppressing its crystallinity by the addition of inert inorganic fillers or incorporation of internal plasticizers can drastically boost the room temperature conductivity of PEG above $10^{-5}$ S/cm. Methods to do so involve the addition of inert inorganic fillers (Al$_2$O$_3$, TiO$_2$, SiO$_2$) or incorporation of flexible functional groups, both of which have the effect of decreasing the crystallinity of PEG to enhance ion transport. Despite the low cost of PEG and its prospected ease of processing, its lack of adhesion and poor interfacial contact to electrodes lead to inadequate cell performance. Many investigations have aimed at functionalizing inorganic polymers that are more structurally stable and flexible with oligoether units. Polysiloxanes bearing oligoether units have demonstrated excellent thermal stability, high conductivity ($10^{-3} - 10^{-4}$ S/cm), and a wide electrochemical window up to 5 V, although the processing of polysiloxanes is complicated due to easy hydrolysis of Si-O-CH$_2$ bonds and the synthesis often requires expensive catalysts. Polyphosphazene-based solid electrolytes offer relatively low conductivities ($10^{-5}$ S/cm) that are impractical when considering the high cost of the material. No system can be said to be perfect, but it suffices to say that new chemistries are continually being sought because of direct application to energy conversion. Solid polymer electrolytes have many prospective advantages that if properly executed, high energy density lithium-ion batteries
can be manufactured to be safer, less costly, and processed in versatile ways. Through chemical design, solid polymer electrolytes may potentially deliver better performance and enable novel processes for the fabrication of lithium-ion batteries.