ABSTRACT

ALLEN, JOSHUA LEE. Molecular Interactions of the Difluoro(oxalato)borate Anion and Its Application for Lithium Ion Battery Electrolytes. (Under the direction of Dr. Wesley A. Henderson).

Understanding the molecular interactions within electrolyte mixtures is essential for designing next generation electrolyte materials for high-voltage lithium ion (Li-ion) battery applications. Despite significant advancements in Li-ion battery electrode materials, which have theoretically enabled cell operation in excess of 5 V (vs. Li/Li\(^+\)), the state-of-the-art electrolyte formulation has remained largely unchanged over two decades after its initial commercialization. To optimize the electrolyte properties, it is crucial to understand and relate the molecular-level interactions to the measured bulk properties. In the present study, these interactions have been explored through the use of the following techniques: phase diagrams (DSC analysis), X-ray single crystal structural determination, spectroscopic vibrational analysis (Raman) of the solvent and anion bands, and other techniques for determining electrolyte physical and electrochemical properties (density, viscosity and ionic conductivity).

The primary focus of the present work is on the difluoro(oxalato)borate (DFOB\(^-\)) anion and how the properties of this anion differ from other anions used in Li-ion battery electrolyte mixtures. The synthesis of highly pure LiDFOB is reported, along with the X-ray single crystal structural analysis of the neat salt and its dihydrate (LiDFOB\(\cdot\)2H\(_2\)O). The ion coordination behavior of the DFOB\(^-\) anion is compared with the structurally similar BF\(_4^-\) and lithium bis(oxalato)borate (BOB\(^-\)) anions. The decomposition mechanism and Raman vibrational band assignments for the LiDFOB salt are also compared with those for LiBF\(_4\) and LiBOB.
The carbonate-based solvents ethylene carbonate (EC) and propylene carbonate (PC) are of extraordinary importance due to their applications in state-of-the-art electrolytes. The Raman analysis of EC- and PC-based electrolyte mixtures to determine solvation numbers, without appropriate correction factors, is inherently flawed due to varying Raman scattering activities of the coordinated and uncoordinated solvent bands. In this study, correction factors are identified through joint quantum chemistry (QC) and experimental analysis techniques that enable the accurate analysis of EC and PC-based mixtures with lithium salts. From this analysis, the ionic association strength of the DFOB\(^{-}\) anion was determined and compared to various lithium salt anions (PF\(_6\)\(^{-}\), TFSI\(^{-}\), BOB\(^{-}\), ClO\(_4\)\(^{-}\), BF\(_4\)\(^{-}\), CF\(_3\)SO\(_3\)\(^{-}\), CF\(_3\)CO\(_2\)\(^{-}\)).

Understanding the ionic association (Li\(^{+}\)...anion) and ion solvation (Li\(^{+}\)...solvent) interactions is crucial for an informed design process (i.e., electrolytes-on-demand) if these interactions can be directly linked to the physical and electrochemical properties of electrolyte mixtures. Thus, the solvation behavior of carbonate and lactone-based electrolytes with three lithium salts (LiBF\(_4\), LiDFOB and LiBOB) was investigated. Based upon the analysis of the solution structure of these mixtures, the electrolyte transport properties (viscosity and conductivity) were readily explainable. A direct link was therefore made between the solution structure of the electrolyte mixtures and the physicochemical properties they possess.

LiDFOB has proven to be a highly versatile lithium salt, displaying many favorable battery properties including the formation of amorphous mixtures (even in mixtures with EC), relatively high ionic conductivity, and favorable electrode passivation layer properties when mixed with appropriate electrolyte solvents. Thus, alternative applications of the DFOB\(^{-}\) anion have been explored, such as its use as an ionic liquid (IL) anion. \(\text{N-}\text{Alkyl-}\text{N-}\)
methylpyrrolidinium difluoro(oxalato)borate (PY$_{1R}$DFOB) ILs have been synthesized and characterized. These ILs are liquid at room temperature and have favorable Al corrosion properties, as well as a large electrochemical stability window.

The present study provides a useful set of tools for scrutinizing a new electrolyte material; from the initial synthesis and purity evaluation, to examining ionic association and ion solvation interactions in electrolyte mixtures, and investigating alternative uses of the material for utilization in a myriad of applications. With the use of such techniques, the guided development of electrolyte materials can be employed instead of the purely empirical approach that is commonly used in the battery electrolyte research community to date.
Molecular Interactions of the Difluoro(oxalato)borate Anion and Its Application for Lithium Ion Battery Electrolytes

by
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DEDICATION

This dissertation is dedicated to my parents,

Andy and Jeannie Allen,

And all of my family,

Without whom none of my success would be possible.
BIOGRAPHY

Joshua Allen was born in Cleveland, TN to parents Andy and Jeannie Allen. At age 4, he moved to Goldsboro, NC, where he was raised with his brother and sister, Anthony and Amy. After graduating from Rosewood High School in 2004, he attended North Carolina Wesleyan College in Rocky Mount, NC. After receiving his Bachelor of Science degrees in Chemistry and Mathematics in 2008, Joshua joined the Department of Chemical and Biomolecular Engineering at North Carolina State University. In the fall of 2008, he joined the ILEET research group, advised by Dr. Wesley Henderson. Joshua was awarded a SMART Graduate Research Fellowship in the spring of 2010 by the Department of Defense and the American Society for Engineering Education. Following completion of his graduate studies, Joshua will join Dr. Richard Jow at the United States Army Research Laboratory in Adelphi, MD to fulfill his SMART Graduate Research Fellowship commitment.
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to call big sister; I greatly look up to you and the fine parent you have become. To my parents Andy and Jeannie, God could not have blessed me with more loving, encouraging parents; I am forever indebted. To my loving wife Lettie, I truly could not have done this without your constant love and support. I do not think it was mere coincidence we met during my first year of graduate school, and I am grateful for God’s continuous blessings on our lives together.

_Trust the Lord completely; don't ever trust yourself. In everything you do, put God first, and He will direct you and crown your efforts with success._

_-Proverbs 3:5-6_
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CHAPTER 1: Introduction

The goals of this research project were to (1) investigate the molecular-level interactions present within mixtures of a relatively new lithium salt (lithium difluoro(oxalato)borate or LiDFOB) and aprotic solvents, (2) link the physicochemical properties of such electrolytes to these interactions, and (3) investigate alternative applications for the DFOB$^-$ anion, such as its use as a counter ion in ionic liquids.

1.1. Importance of Battery Technologies

Although renewable energy sources are plentiful in many parts of the country, they are also highly fickle. For instance, the sun does not always shine and the wind can blow too strongly (or not at all). Many forms of renewable energy could benefit greatly from energy storage devices, such as batteries. In these instances, energy can be generated via solar/wind technology, stored in a battery, and then transferred where the energy is needed when it is needed. One of the most wasteful activities is travel. Most forms of travel utilize petroleum-based fossil-fuels as a source of energy, thus they are thermodynamically inefficient as much of the stored energy is lost in the form of heat through combustion reactions. Battery technologies, however, have tremendous implications for transforming the auto industry as plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) may be charged using renewable energy sources (e.g., wind, solar, biofuel, hydroelectric, etc.) and display significantly higher efficiencies than conventional engines. Additionally, PHEVs utilizing battery technologies may be commercialized rapidly, requiring minimal infrastructure
changes for initial market entry [1]. However, PHEVs/EVs are not cost effective using current state-of-the-art technologies. According to the most recent DOE estimates, a hybrid electric vehicle (i.e., Toyota Prius) will become cost effective (by comparing fuel savings vs. incremental vehicle cost) after ~17.5 years, a PHEV (i.e., Chevy Volt) requires ~23 years, and an EV (i.e., Nissan Leaf) requires ~15 years [2]. These values, however, do not take into account the lifetime of the state-of-the-art battery (~10 years) and the cost of a replacement battery pack; this surely abates the desire for informed consumers to purchase such vehicles (aside from the inherent environmental benefits). The future of PHEV/EV technologies is largely dependent on the progression of next-generation battery technologies such that vehicles can travel further distances in more efficient ways, utilizing safer batteries that are economical for the consumer. The large-scale adoption of PHEV/EVs will be imperative for reducing demand for foreign imported oil as, in the near term, battery storage is the only technology that is able to meet the challenging requirements necessary for revolutionizing the electrification of transportation.

The implementation of electrified transportation on a large-scale, however, necessitates the development of a “Smart Grid.” To date, transmission systems do not have a large buffering ability for matching peak load levels while maintaining a lower standard operating level. Thus, generation levels must be maintained at near peak levels to prevent system overload and failures/blackouts. Due to this, power plants are highly inefficient with regards to the power generated vs. power used. Figure 1.1 displays the percentage of energy lost due to electrical generation, transmission and distribution inefficiencies (> 55%) [3,4]. These generation inefficiencies may be reduced through Smart Grid technologies/infrastructure. In
its most general definition, a Smart Grid is an electrical grid that is able to gather information about the energy used and distribute energy more efficiently. Battery technologies could be used extensively in a Smart Grid for large scale energy storage. This concept can be imagined as follows: During off-peak hours, energy is generated by the power company, but not used by consumers. This energy could be applied to battery storage units (i.e., PHEVs/EVs) and sold to the consumer at a reduced rate. During peak hours, if a consumer has a generous amount of energy stored, the power company could buy back the energy (recovered from the vehicles) at a higher rate than it was sold. After peak hours, the power company could then recharge the device back to its original state. Such a scenario is beneficial to the consumer as they are able to make money by “selling” power back to the grid at a rate higher than they paid. This scenario is also beneficial to power companies as they are able to generate power at a lower level with the option to use stored energy as a means to meet load demands during peak hours (load-leveling). By generating less energy, the efficiency of the power plant increases tremendously as energy is not wasted when demand is low. The increased efficiency of the power plant (and reduced standard generation levels) can significantly lessen the production of greenhouse gases and thus help slow global climate change. If such a scenario is achievable, the importance of high-capacity battery technologies is incontestable.
1.2. What is a Battery?

Alessandro Volta (1745-1827) was one of the earliest scientists to study a new phenomenon known as electricity. The first suggested use of static electricity, known as an “electric pistol,” consisted of an electrical wire placed inside a jar filled with methane gas. Upon sending an electrical spark through the wire, the methane gas would ignite and the jar would explode [5].

In 1800, expanding upon experiments performed by Luigi Galvani in 1780, Volta discovered that this electrical force could be generated by utilizing certain fluids as
conductors to promote chemical reactions between metal plates. Furthermore, Volta discovered that the voltage would increase when voltaic cells were stacked on top of each other (known as a voltaic pile). Figure 1.2 displays this phenomenon as sketched by Volta and published in his original article submitted to the Royal Society of London [6]. The combination of multiple galvanic (or voltaic) cells is recognized today as a battery.

A voltaic cell is a device that converts chemical energy directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction. A battery consists of one or more voltaic cells, each of which consists of two half-cells connected in series by an ionically conductive electrolyte. The chemical energy initially present is contained within the active materials and is converted to electrical energy on-demand, thus a battery is considered a storage device.

![Figure 1.2 Variations of Volta’s electric battery in which silver and zinc discs are separated by a brine-soaked cloth.](image)
1.2.1. Primary vs. Secondary Batteries

Electrochemical cells are generally classified as either primary (non-rechargeable) or secondary (rechargeable), depending upon whether they are able to be electrically recharged back to their original state. Primary batteries have largely non-reversible chemistries in which the active materials may not return to their original oxidation states. These batteries are able to produce current immediately upon assembly and are intended to be discarded after use.

Secondary (rechargeable) batteries may be restored back to their initial state by passing current through the device opposite the direction of the discharge current. Unlike primary batteries, these cells require an initial charge before use as they are typically assembled with the active materials in a discharged state. Once discharged, the chemical reactions that occur during the battery discharge process may then be reversed as the battery is recharged. The most well-known rechargeable battery is the lead-acid battery, which is used extensively by the automotive industry.

1.2.2. Understanding Battery Parameters

At each electrode, a relationship exists between the electronic current $I$ and the mass $m$ of the active material (i.e., the substance which donates/consumes electrons). This relationship, known as Faraday’s First Law, states that the mass of a substance altered during electrolysis is directly proportional to the quantity of electricity transferred [7]. Faraday’s law is summarized in Eq. 1.1 where $m$ is the mass of the substance that undergoes a redox reaction, $Q$ is the total electric charge passed, $F$ is the Faraday constant (96,485 C mol$^{-1}$), $M$ is the
molar mass of the substance, $z$ is the number of electrons transferred per ion during the redox reaction and $N$ is the number of moles of the substance liberated (i.e., $N = m/M$).

$$m = (QM/Fz) \quad \text{or} \quad Q = nFN$$  \hspace{1cm} \text{Eq. 1.1}

The total electric charge, $Q$, of a battery is one of the primary factors used to determine which battery chemistry will be utilized for specific applications. While Faraday’s Law is important for calculating the theoretical capacity (units of coulombs (C) or amp hours (Ah)) that an electrode/cell may yield, of equal importance is the voltage (V) at which this capacity is obtained. Voltage, commonly called potential or potential difference, is the difference in the redox potential of the two electrodes. For a specific redox reaction, the voltage is commonly referenced to a reference electrode, such as the standard hydrogen electrode (SHE). For lithium batteries, the voltage is often referenced to a Li/Li$^+$ electrode. If a cell is constructed, for example using lithium metal (0.0 V vs. Li/Li$^+$) and LiCoO$_2$ (3.9 V vs. Li/Li$^+$) electrodes, then the cell voltage is 3.9 V (vs. Li/Li$^+$). When the overall voltage of the cell is multiplied by the capacity, the energy (units of Joule, J) is obtained (Eq. 1.2). A Joule is the work required to move an electric charge of one coulomb (C) through an electrical potential difference of one volt. Thus a joule can also be described as a Watt second (Ws). In order to determine the power that is able to be generated, the energy is calculated as a function of time. Therefore, the power (Watts) of a battery is determined by dividing the energy (J) by a specific amount of time (h) as summarized in Eq. 1.3.
Current driving forces are to develop materials with improved performance in terms of power/energy density, safety, and price. One way to decrease the price of batteries is to derive more energy from a single unit, thus reducing the cost of the non-active components (cell construction material, current collectors, etc.). According to Eqs. 1.2 & 1.3, the energy and power of the battery are influenced by both the voltage and capacity, thus an optimal design displays both a higher potential energy difference between the electrodes and also a high specific capacity. Since the capacity is typically normalized on a per gram basis, it is more advantageous to have cell chemistries of low molecular weight. As the voltage of the battery is increased, however, the electrolyte materials tend to be less stable. It follows that any technological breakthrough that promotes the use of higher voltage cathodes must be met with improvements to state-of-the-art electrolytes.

1.2.3. Development of Li-Ion Batteries

While nickel-cadmium (NiCd) and nickel-metal hydride (NiMH) cells yield ~1.2 V, and alkaline and lead-acid cells yield 1.5 V and 2.0 V, respectively, the low reduction potential of Li/Li⁺ (-3.0 V vs. SHE) naturally attracted attention as an electrode material. Cells that include lithium metal typically possess voltages > 3.0 V with values as high as 5.0 V achievable. Additionally, lithium metal is attractive as an anode material (in primary cells) because of its light weight and corresponding high theoretical capacity of 3860 mAh g⁻¹,
resulting in very high gravimetric and volumetric energy densities, respectively. Due to these inherent properties, lithium-based batteries (both primary and secondary) have dominated the development of high-performance batteries for the past three decades [7].

Lithium battery technology was pioneered in 1912 by Gilbert N. Lewis, whom is most well-known for the discovery of the covalent bond and his Lewis dot structures published in the 1916 paper “the Atom and the Molecule” [8]. One of the first successful implementations of lithium chemistries into a battery was achieved in the 1970s with the invention of the Li/MnO₂ system [9–11]. During this time, intercalation phenomenon was also being investigated with alkali and alkali earth metals [12–18]. In 1972, Exxon initiated a large scale project that utilized lithium metal as an anode material combined with layered TiS₂, the best intercalation cathode available at the time [9]. Such materials are able to electrochemically intercalate (insert) Li⁺ cations into the TiS₂ crystal structure in order to balance the charge within the layered structure of the cathode as the cathode is reduced (during battery discharge) to form LiTiS₂.

Despite initial successes with TiS₂ and other intercalation cathodes, secondary lithium metal batteries inevitably suffer from anomalies associated with lithium electroplating during recharge. During cell discharge, metallic lithium is oxidized into Li⁺ cations which are intercalated in the cathode. During recharge, the Li⁺ cations are electroplated (i.e., reduced to lithium metal) on the anode. Herein lies one critical problem—lithium metal is highly reactive with respect to the electrolyte and forms a passivation film by irreversibly reacting with the molecular solvent(s) (and/or lithium salt) shortly after initial cell construction. This passivation film, however, is disrupted upon cycling. Thus, the act of discharging/recharging
a cell causes continuous decomposition of the electrolyte, which reduces the amount of lithium available for subsequent cycling and ultimately results in tremendous capacity fading (i.e., loss of available energy).

Another critical problem that has limited the usefulness of lithium metal secondary batteries is the risk of battery explosions. If lithium is plated in a non-uniform fashion, as is often the case, dendrites can form that lead to an internal short-circuit (i.e., a spontaneous reaction of these dendrites when they make contact with the cathode). If a cell short-circuits, the chemical reactions within the battery occur quickly, which releases large amounts of energy in the form of heat. This further increases the reaction rate, which leads to a higher level of heat generation. This continuous cycle, known as a thermal runaway reaction, often leads to solvent vaporization and, given the flammability of common solvents, may ultimately lead to an explosion. Suffice it to say, large-scale commercialization of secondary lithium metal batteries has not occurred to date due largely to safety concerns due to the replating of lithium and the possibilities of thermal runaway.

Lithium ion (Li-ion) batteries replace the metallic lithium anode with a carbon (i.e., graphite) electrode which largely eliminates these problems. The ability to replace lithium metal was enabled by early research into “high-voltage” cathode materials (primarily LiCoO$_2$) that were able to achieve up to 4.0 V with a lithium anode [19,20]. As a result of this discovery, it was realized the sufficiently high positive potentials of the cathode materials could enable the use of a second intercalation material that may be used as a negative (anode) electrode (and still maintain a relatively high potential difference for the cell) [9,21–23]. Since metallic lithium was no longer present in the cell (i.e., the ions are
shuttled back-and-forth as Li$^+$ cations), the term “Li-ion cell” became commonplace to describe the new, safer electrode couples that solved the problems associated with dendrite formations.

Anodes utilized in Li-ion cells are almost exclusively carbonous, typically graphite or coke. Early research had shown that various materials could be intercalated between the graphene sheets of graphite [24–26]. Subsequent studies showed that graphite was able to host a single Li$^+$ cation per six carbon atoms (forming LiC$_6$) [24]. Additionally, carbon is widely available from many different sources and is highly economical. Thus, the first Li-ion battery, commercialized in 1991 by Sony, combined the high-voltage LiCoO$_2$ cathode with a graphite anode (C/LiCoO$_2$). Although the theoretical capacity of these early Li-ion cells was relatively low (~130 mAh g$^{-1}$), the cell had a voltage (> 3.6 V) and gravimetric energy density (120-150 Wh kg$^{-1}$) that were three and two-three times higher, respectively, than a typical Ni-Cd battery [9]. Despite significant advances in alternative battery materials, which will be discussed in more details in the following sections, a large fraction of portable electronics continue to utilize the C/LiCoO$_2$ Li-ion battery over 25 years after its initial commercialization.

1.2.4. How Li-Ion Batteries Work

Typical Li-ion cells are composed of three major components: an anode (negative electrode), cathode (positive electrode), and an electrolyte (which is typically dispersed within a separator). Each of these components can be seen in Figure 1.3. Li-ion cells are assembled in an uncharged state and must be initially charged before use. Thus, the cathode
material contains Li\(^+\) cations (i.e., LiCoO\(_2\)) while the anode material does not (i.e., neat graphite). The Co atoms therefore have an oxidation state of Co\(^{3+}\). As the battery is charged, electrons are extracted from the cathode (i.e., the Co\(^{3+}\) is oxidized to Co\(^{4+}\)), causing Li\(^+\) cations to be deintercalated from the electrode (i.e., forming Li\(_{1-x}\)CoO\(_2\)) and the graphite becomes negatively charged. To balance this charge, Li\(^+\) cations are intercalated into the graphite structure. The electrode reactions that take place during cell charging can be seen in Eqs. 1.4-1.6.

\[
\text{Cathode: } \text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \quad \text{Eq. 1.4}
\]

\[
\text{Anode: } x\text{Li}^+ + xe^- + C_6 \rightarrow \text{Li}_x\text{C}_6 \quad \text{Eq. 1.5}
\]

\[
\text{Overall: } C_6 + \text{LiCoO}_2 \rightarrow x\text{LiC}_6 + \text{Li}_{1-x}\text{CoO}_2 \quad \text{Eq. 1.6}
\]

Once the Li-ion battery has been charged, the electrode materials are maintained in a thermodynamically unstable state. When an external circuit is applied, the electrodes are thus driven to return to their thermodynamically favorable state and the cell is discharged. Upon discharge, Co\(^{4+}\) is reduced to Co\(^{3+}\) and Li\(^+\) cations are intercalated into the cathode to balance the excess electrons (forming LiCoO\(_2\)). As the Li\(^+\) cations are removed from the electrolyte, they are simultaneously deintercalated from the anode (forming nonlithiated graphite). The electrode reactions that take place during cell discharge can be seen in Eqs. 1.7-1.9.

\[
\text{Cathode: } \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiCoO}_2 \quad \text{Eq. 1.7}
\]

\[
\text{Anode: } \text{Li}_x\text{C}_6 \rightarrow x\text{Li}^+ + xe^- + C_6 \quad \text{Eq. 1.8}
\]

\[
\text{Overall: } x\text{LiC}_6 + \text{Li}_{1-x}\text{CoO}_2 \rightarrow C_6 + \text{LiCoO}_2 \quad \text{Eq. 1.9}
\]
The multi-step reactions described above are limited primarily by the efficiency in which the electrolyte is able to deliver the Li\(^+\) cations to the electrodes. Li-ion batteries are often referred to as “rocking-chair” batteries or “shuttle batteries” as the Li\(^+\) cations are effectively shuttled between the electrodes (through the electrolyte). A schematic of a typical Li-ion battery during discharge can be seen in Figure 1.3.

![Schematic representation of a typical Li-ion battery.](image)

**Figure 1.3** Schematic representation of a typical Li-ion battery.
1.3. Li-Ion Battery Components

Although Li-ion cells are typically described as being composed of three major functional components (anode, cathode and electrolyte), each of these major components consists of mixtures of different materials. For instance, the anode and/or cathode may contain an active material, a binder, a conductive additive, and perhaps other additives, all of which are supported on a current collector. Regardless of the active materials used, most electrodes contain these general components. Battery electrolytes, however, vary greatly depending upon the properties desired/required (e.g., reduced flammability, low/high temperature performance, rate capability, etc.). Furthermore, the voltage and/or capacity of a battery can be selected directly by choosing the appropriate anode and cathode that meets the specific demand, thus the energy capacity of the battery is dependent primarily upon the identity and mass of the anode and cathode active materials. The electrolyte, contrarily, may be tailored to each specific application and largely affects the battery power (i.e., charge/discharge rate), safety, lifetime, and operating temperature range. Each of these components will be discussed in more detail in the following sections.

1.3.1. Electrolyte Materials

The role of an electrolyte in a battery is to enable the transfer of ions between electrodes. The electrolyte must therefore be an ionic conductor, but also an electronic insulator to prevent internal self-discharge and/or short-circuit. An overwhelming majority of electrolytes utilized in electrochemistry are concentrated aqueous solutions of acids or salts. Aqueous electrolytes, however, are impractical in lithium battery applications due to the reactivity of...
water with the electrodes and/or its electrolysis at higher potentials [27]. Therefore, organic solvents with lithium salts have largely been utilized in Li-ion cells due to the electrolyte’s stability and sufficiently high ionic conductivity. Carbonate-based solvents have dominated the market of non-aqueous electrolytes for Li-ion batteries and continue to be used in commercial state-of-the-art cells. The lithium salt anions utilized in Li-ion batteries are traditionally fluorinated (or oxygenated) in order to increase the electrolyte’s conductivity. Of these salts, lithium hexafluorophosphate (LiPF₆) is almost exclusively used due to its ability to meet the multifaceted requirements needed for the battery to operate.

One of the most demanding properties required of electrolytes utilized in state-of-the-art batteries is the formation of a protective solid-electrolyte interface (SEI) layer. Graphite anodes rely heavily on the formation of a protective SEI layer, which forms from insoluble electrolyte decomposition products formed during the first several charge cycles and prevents the co-intercalation of solvent. Thus far, only a few electrolyte materials have been identified that can form an effective SEI layer. Most of these materials are only marginally stable at high potentials due to decomposition on the cathode surface. As new electrode technologies emerge that operate at higher voltages, battery electrolytes have quickly become the limiting technology for the utilization of next generation Li-ion batteries. Advanced electrolyte materials will be discussed in more detail in Section 1.4.

1.3.2. Anode Materials

Carbon anodes have dominated the battery market since their initial utilization in the first commercial Li-ion battery. Carbon anodes possess a markedly lower capacity than
lithium metal anodes (3860 mAh g⁻¹ for Li and 372 mAh g⁻¹ for LiC₆) (Table 1.1). They are much safer, however, since they do not suffer from dendrite formations and are significantly less reactive towards the electrolyte components (once an SEI is formed). Graphite electrodes operate at a potential only a few millivolts above the potential of the Li/Li⁺ redox couple and thus suffer negligible losses in voltage as compared with a lithium anode. Furthermore, the flat potential-capacity profile of graphite anodes is very favorable for electronic devices because the cell provides a stable voltage over the duration of the discharge.

Although carbon anodes have proven difficult to replace, due largely to their relatively low cost and low operating potential, one significant problem exists with carbon-based anodes that limits their compatibility with a variety of solvents. The co-intercalation (with Li⁺ cations) of solvents such as propylene carbonate can exfoliate the graphene sheets and cause cell failure [28–31]. One approach to perhaps eliminate the necessity of forming an SEI is to use anode materials that operate at a higher potential, hence reducing the decomposition of the electrolyte. Transition metal oxides such as Li₄Ti₅O₁₂ (LTO) and TiO₂ have gained significant attention as an alternative to carbon. One undesirable consequence of the high operating potential of LTO and TiO₂ (1.55 V and 1.85 V, respectively) is an astonishing loss in energy (Table 1.1) [9]. Therefore, the use of these anodes in concert with high-voltage cathodes may be counterproductive as the increase in cathode potential is offset by the increase in anode potential.

Considering that graphite (i.e., LiC₆) possesses one of the lowest reduction potentials, it is difficult to increase the energy of the battery by designing a lower potential anode. An alternative to this approach, however, is to design anode materials that have a higher
capacity. Elemental crystalline silicon anodes have a maximum theoretical capacity of 4198 mAh g⁻¹, which is based upon a stoichiometry of Li₂₂Si₅ or approximately 4.4 Li per Si (as compared with 0.167 Li per C for graphite anodes) (Table 1.1) [9]. Silicon anodes, however, suffer extensively from large volume changes, upwards of 300%, that result in extremely poor cycling in full cells. Although numerous Si-based alloys have been developed (i.e., with carbon and TiO₂ or the development of Si nanotubes to accommodate the large volume changes), silicon anodes are yet to be commercialized as an anode material capable of sustaining long term cycling [9].

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Specific Capacity (mAh g⁻¹) (theoretical/observed)</th>
<th>Potential vs. Li⁺/Li</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li Metal</td>
<td>3860/-</td>
<td>0.0</td>
<td>High capacity, dendrite formation</td>
</tr>
<tr>
<td>Graphite</td>
<td>372/330</td>
<td>0.1-0.2</td>
<td>LiC₆, volume change: ~11%</td>
</tr>
<tr>
<td>Soft Carbon</td>
<td>-/&lt;700</td>
<td>&lt;1</td>
<td>High capacity, sloping voltage profile</td>
</tr>
<tr>
<td>Hard Carbon</td>
<td>-/600</td>
<td>&lt;1</td>
<td>High capacity, sloping voltage profile</td>
</tr>
<tr>
<td>Li₄Ti₅O₁₂</td>
<td>175/170</td>
<td>1.55</td>
<td>High voltage, no volume change</td>
</tr>
<tr>
<td>TiO₂</td>
<td>168/168</td>
<td>1.85</td>
<td>High voltage, Cheap, volume change: ~4%</td>
</tr>
<tr>
<td>SnO₂</td>
<td>782/780</td>
<td>&lt;0.5</td>
<td>Large initial irreversible capacity loss</td>
</tr>
<tr>
<td>Sn</td>
<td>993/990</td>
<td>&lt;0.5</td>
<td>Poor cycling, volume change: 257%</td>
</tr>
<tr>
<td>Si</td>
<td>4198/≤3500</td>
<td>0.5-1</td>
<td>Poor cycling, volume change: 297%</td>
</tr>
<tr>
<td>Al</td>
<td>2235</td>
<td>&lt;0.3</td>
<td>Poor cycling, volume change: 238%</td>
</tr>
<tr>
<td>Bi</td>
<td>385</td>
<td>&lt;0.8</td>
<td>Volume change: 115%</td>
</tr>
</tbody>
</table>
1.3.3. Cathode Materials

Since the initial utilization of the LiCoO₂ cathode material in Li-ion batteries, significant advances have occurred to yield higher voltage cathode materials. Although LiCoO₂ still remains the dominant cathode material in commercial Li-ion batteries [9], various materials have been adopted by industries as a potential replacement, including LiNiO₂ [32–35], LiMn₂O₄ [36–39], LiNiₓMnᵧCo₂O₂ [40,41], and LiFePO₄ [42,43] (see Table 1.2).

Each cathode material can be classified by the crystal structure it possesses: layered, spinel, or olivine (Figure 1.4) [9]. Layered compounds, such as LiCoO₂ and LiNiO₂ are currently used in commercial Li-ion batteries due to their sufficiently high capacity (< 180 mAh g⁻¹) and a reasonably long cycle/service life. However, batteries composed of LiCoO₂ are prone to thermal runaway reactions that are exacerbated when the battery is overcharged. Further, cobalt is quite expensive (and toxic) when compared with other layered transition metals (i.e., Ni and Mn). Thus, researchers have focused on replacing Co with other transition metals in various fractions to maintain the properties of LiCoO₂ cathodes, but at a lower cost and with improved safety. It has been noted, however, that the elements that help maintain a stable layered structure decrease effectiveness in the order Co > Ni > Mn, which coincides with the cost of the elements [44–46]. One approach, however, is to combine the various metals such that the benefits of each are obtained. LiNiₓCoᵧMn₂O₂ (commonly called NMC) has been combined in various ratios to obtain a relatively cheap, stable cathode material. Due to the complexity of the various metals with differing redox potentials, such electrodes can be charged to a variety of voltages. Although increasing the charge voltage of a given electrode inevitably leads to an increase in the discharge capacity (and thus energy
density), there is a tradeoff with the cell cycle life. For example, discharging a LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ half-cell (with a lithium metal anode) from 4.2 V to 3.0 V (vs. Li/Li$^+$) yields a discharge capacity of 134.4 mAh g$^{-1}$ and energy density of 513.4 mWh g$^{-1}$ (with an average cell voltage of 3.8 V) [47]. Discharging the same half-cell configuration from 4.7 V to 3.0 V yields a discharge capacity of 198.1 mAh g$^{-1}$ and energy density of 788.4 mWh g$^{-1}$ (with an average cell voltage of 4.0 V). When the same NMC cathodes are assembled in a full-cell configuration (with a carbon anode), however, and tested over 500 cycle, the cell charged to 4.2 V maintains ~88% of its initial capacity after 500 cycles while the cell charged to 4.7 V maintains only 25% of its initial capacity after only 150 cycles [47]. Thus, a charge voltage limit is often imposed that optimizes the cell capacity and cycle life.

One of the most successful high-voltage cathode materials currently under development is the LiMn$_2$O$_4$ spinel. Manganese is attractive, both economically and environmentally, due to abundant precursors and its nontoxicity. However, the structure of LiMn$_2$O$_4$ is unstable during cycling due largely to the disproportionation of Mn$^{3+}$ into Mn$^{4+}$ and Mn$^{2+}$, as well as the dissolution of the latter in the electrolyte. Therefore, other ions (such as Co, Ni, Fe, Cr, Al or Mg) have been investigated as partial substitutes to yield spinel cathodes with LiMn$_{1-x}$M$_x$O$_4$ chemistries [48–56]. Many of these, especially LiMn$_{1.5}$Ni$_{0.5}$O$_4$, have shown great promise as next-generation cathode materials for high voltage applications which do not suffer from capacity fading due to Mn disproportionation reactions [57,58].

The final classification of cathode materials in Table 1.2 is based upon an olivine crystal structure (Figure 1.4) [9]. Olivine cathode materials typically possess the formula LiMPO$_4$ (M = Fe, Co, Mn or Ni), with the most widely studied being LiFePO$_4$ [42]. Although
LiFePO$_4$ operates at a relatively low potential, LiMnPO$_4$ and LiCoPO$_4$ provide a higher voltage plateau of 4.1 V and 4.8 V (vs. Li/Li$^+$), respectively. By charging up to a voltage of 4.8 V (with a theoretical capacity of 166 mAh g$^{-1}$), the theoretical energy density of LiCoPO$_4$ is nearly 1.35 times larger than that of LiFePO$_4$. However, operating at such high potentials has a profound effect on the stability of the electrolyte. Therefore, many researchers have focused on LiMnPO$_4$, which is largely compatible with the state-of-the-art electrolyte due to a voltage plateau similar to LiCoO$_2$. In order to take advantage of cathode chemistries that operate at 4.8 V (LiCoPO$_4$) or 5.1 V (LiNiPO$_4$), more stable electrolytes must be developed that resist oxidation at such high potentials.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Specific Capacity in mAh g$^{-1}$ (theoretical/observed)</th>
<th>Potential (Li/Li$^+$)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>273/160</td>
<td>3.9</td>
<td>First cathode, expensive</td>
</tr>
<tr>
<td>LiNiO$_2$</td>
<td>274/180</td>
<td>3.6</td>
<td>Cheaper than LiCoO$_2$</td>
</tr>
<tr>
<td>LiNi$_x$Co$_y$Mn$_z$O$_2$</td>
<td>~270/150-180</td>
<td>3.8</td>
<td>Cheap and stable</td>
</tr>
<tr>
<td>LiNi$_x$Co$_y$Al$_z$O$_2$</td>
<td>~250/180</td>
<td>3.7</td>
<td>Stable</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>148/130</td>
<td>4.1</td>
<td>Unstable cycling</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.5}$O$_4$</td>
<td>146/130</td>
<td>4.7</td>
<td>High voltage, cheap</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>170/160</td>
<td>3.45</td>
<td>Low voltage, safe, cheap</td>
</tr>
<tr>
<td>LiMnPO$_4$</td>
<td>171/80-150</td>
<td>4.1</td>
<td>Slow kinetics, cheap, high voltage</td>
</tr>
<tr>
<td>LiNiPO$_4$</td>
<td>166/-</td>
<td>5.1</td>
<td>No suitable electrolyte</td>
</tr>
<tr>
<td>LiCoPO$_4$</td>
<td>166/60-130</td>
<td>4.8</td>
<td>Expensive</td>
</tr>
</tbody>
</table>
Figure 1.4 Classifications of cathode materials: (a) layered structure (LiMnₓNi₁₋ₓCo₂O₄), (b) spinel structure (LiMn₂O₄), and (c) olivine structure (LiFePO₄).

1.4. Advanced Electrolyte Materials

Li-ion batteries rely heavily on the composition of the electrolyte to perform many functions within the battery. It has been stated that “recent advances in cathode and anode materials have refocused attention on electrolytes as the technological bottleneck limiting the operation and performance of lithium-battery systems” [59]. Not only is the Li⁺ cation containing electrolyte the source of Li⁺ cation transfer, but the counter-anion and solvent are essential in forming the stable interfaces (i.e., SEI) that protects the electrolyte from complete decomposition when in contact with the electrodes. State-of-the-art Li-ion batteries have an
electrolyte typically composed of 1M LiPF₆ in a mixture of ethylene carbonate (EC) and a non-cyclic carbonate such as diethyl carbonate (DEC), dimethyl carbonate (DMC) or ethyl methyl carbonate (EMC) [60,61]. The high polarity and dielectric constant of EC enables dissolution of the lithium salt to suitably high concentrations, but such solutions are highly viscous. The addition of linear carbonates (DEC, DMC or EMC), which are less polar with low dielectric constants, lowers the viscosity of the overall electrolyte and promotes a more rapid Li⁺ cation transport [59]. In the subsequent sections, the advantages and disadvantages of the various lithium salts available are discussed. Additionally, the various solvents used in Li-ion battery electrolytes are discussed, each of which are selected to achieve specific performance requirements (i.e., low/high temperature, high voltage, non-flammable, etc.).

1.4.1. Lithium Salts

Various lithium salts have been developed since the discovery of Li-ion battery technologies. In order for a lithium salt to be utilized in a Li-ion cell, it must meet (at least) the following requirements: (1) it should dissociate (dissolve) in the aprotic solvents, (2) the resulting solvent-salt mixtures should have a sufficient conductivity (~10 mS cm⁻¹) to enable a rapid discharge of the battery (i.e., high power), (3) the anion must be stable (but not too stable) to oxidation/reduction reactions at the active electrodes such that a passivation reaction occurs, but does not continually decompose the material and (4) the anion must remain inert towards non-active components (separator, current collector, cell packing material, etc.). Ideally, the lithium salt should also be safe/non-toxic and thermally stable with aprotic solvents. With this complex list of requirements, various salts have been
proposed and widely studied in Li-ion battery research. The most common lithium salts are described in greater detail below:

\textit{LiPF}_6: \textit{LiPF}_6 is almost exclusively used in commercial Li-ion batteries because of its favorable battery electrolyte properties, including the formation of stable interfaces with battery current collectors (preventing corrosion) [62,63]. Carbonate electrolytes containing \textit{LiPF}_6, however, have poor performance at low temperatures (< -10°C) due to a rapid rise in viscosity (or the formation of crystalline solvates), and decompose at elevated temperatures (> 60°C) (forming HF byproducts) [63,64]. Due to the toxic byproducts of \textit{LiPF}_6 in the presence of cathode materials (\textit{Li}_x\textit{MO}_2, where \textit{M} is Co, Ni or Mn), the need for an environmentally benign, high performance lithium salt is growing as industry attempts (unsuccessfully thus far) to replace \textit{LiPF}_6 [65].

\textit{LiTFSI:} Lithium bis(trifluoromethanesulfonyl)imide (\textit{LiN(SO}_2\textit{CF}_3)_2 or \textit{LiTFSI}) is a promising lithium salt due to the anion’s extensive resonance, resulting in a high degree of charge delocalization. In addition, \textit{LiTFSI} is quite flexible and can adopt both \textit{cis} and \textit{trans} conformations, which hinders solvate crystallization or reduces the melting temperature of solvates (relative to \textit{LiPF}_6 solvates). Furthermore, electrolyte mixtures containing \textit{LiTFSI} typically display conductivity values approaching those of \textit{LiPF}_6, which is imperative for high charge/discharge rates. Although there are a multitude of reasons why \textit{LiTFSI} is suitable for battery applications, one substantial disadvantage is the fact that traditional carbonate-based electrolytes with \textit{LiTFSI} significantly corrode the cathode Al current collector at high potentials (> 4.0 V vs. Li/Li\textsuperscript+). Since it is almost universally established among battery
manufacturers that Al is irreplaceable as a current collector, electrolytes based upon LiTFSI have largely not been utilized in commercial Li-ion battery applications [66–68].

**LiFSI**: Lithium bis(fluorosulfonyl)imide (LiN(SO₂F)₂ or LiFSI) is a relatively new lithium salt that behaves similarly to LiTFSI. Electrolytes with LiFSI generally have conductivity values which are comparable to those with LiPF₆ [69]. LiFSI electrolytes are also quite difficult to crystallize (as for LiTFSI electrolytes), often resulting in amorphous mixtures even for high salt concentrations. Like LiTFSI, carbonate-based electrolytes with LiFSI are known to corrode Al and have thus far not been utilized in high-voltage applications (> 4.0 V vs. Li/Li⁺) [70].

**LiBF₄**: Lithium tetrafluoroborate (LiBF₄) has been studied in Li-ion batteries since their initial development stages. LiBF₄ is a promising salt due to its exceptional low temperature performance (< -20°C). LiBF₄ is less affected by temperature changes than LiPF₆, as evidenced by an improved conductivity at lower temperatures. However, carbonate-based solvent mixtures with LiBF₄ have a lower conductivity at room temperature and above (than comparable LiPF₆ electrolytes) and are thus rarely utilized in Li-ion batteries due to a loss in power performance. LiBF₄ has been used extensively, however, in applications that require improved low temperature performance [71,72].

**LiBOB**: Lithium bis(oxalato)borate (LiBOB) was introduced as a potential alternative to LiPF₆ due to its ability to form protective passivation layers. Although the solubility of LiBOB is low, and the conductivity of comparable mixtures is inferior, it has seen great success as an electrolyte additive. Even in trace additive concentrations, LiBOB has been shown to promote SEI formation on graphite in common electrolyte mixtures [73]. LiBOB
has also been shown to stabilize high-voltage cathode materials such as LiNi_{0.8}Mn_{1.5}O_{4} [57]. Despite these successes, LiBOB has failed to replace LiPF_{6} as a primary lithium salt and has largely been replaced as an additive by LiDFOB.

**LiDFOB**: Lithium difluoro(oxalato)borate (LiDFOB) was developed as a hybrid salt that contains boron-fluorine bonds (similar to LiBF_{4}) and an oxalate moiety (similar to LiBOB). The combination of these features yields a salt that has a higher conductivity (than LiBOB and LiBF_{4}) when mixed with common solvents, participates in electrode passivation layer formation, and is beneficial in high and low temperature applications [74–87]. Additionally, LiDFOB has been shown to stabilize various cathode materials for high-voltage applications [76,77,84,88,89] and protect the Al current collector from corrosion [90,91].

### 1.4.2. Solvents and Solvent Properties

The solvents utilized in Li-ion batteries can generally be categorized as dipolar aprotic solvents. These are useful in batteries because of their superior electrochemical stability (compared with protic solvents) and sufficiently high dissolution of common lithium salts; aprotic solvents are able to break ionic bonds within the lithium salt and form coordination bonds, effectively dissolving the salt. Although there are various classes of aprotic solvents that are applicable to Li-ion batteries, most of these solvents share similar properties that are highly beneficial for optimum cell performance. In order for a molecular solvent to be considered in a Li-ion cell, it must meet (at least) the following requirements: (1) dissolve an appropriate lithium salt at a suitable concentration, (2) maintain a high level of mobility for the solvates or ion-pairs formed (i.e., a sufficiently high ionic conductivity), (3) have a low
viscosity (high fluidity) to optimize surface wettability, (4) remain inert when in contact with
the charged surfaces of the anode/cathode, (5) display a large liquidus range with no
solvate/complex formation (low melting point ($T_m$) and high boiling point ($T_b$)), and (6) be
safe (i.e., non-flammable or have a high flash point ($T_f$))[63].

The various parameters discussed above are often used when discussing how well a
solvent is able to perform as an electrolyte medium. There is arguably no single solvent that
meets all of these requirements, thus binary solvent systems have become essential for
optimum cell performance. A common example of this phenomenon is the composition of
the state-of-the-art solvent system—a binary mixture of EC and a linear carbonate (i.e.,
DMC, DEC, or EMC) in a 3:7 ratio [60]. The high permittivity ($\varepsilon$) of EC enables dissolution
of the lithium salt to a very high salt concentration, but such solutions are highly viscous and
solvates crystallize near room temperature (or above). Since high $\varepsilon$ solvents tend to have
strong interactions with one another (and thus a higher viscosity), it is beneficial to have a
lower permittivity co-solvent to decrease the viscosity of the solution. The addition of a
linear carbonate solvent lowers the viscosity of the overall electrolyte and promotes a more
rapid Li$^+$ cation transport. Additionally, the use of multiple solvents disrupts crystallization
and commonly results in mixtures that vitrify (form glassy solids at low temperature), rather
than crystallize, resulting in a larger liquidus range.

When looking at solvent properties alone, a molecular solvent like PC might seem to be
preferred, as it shares beneficial properties with EC, but displays a significantly lower
melting point. However, PC is well known to intercalate within the graphene layers and
disrupt the graphite structure [28–31]. Contrary to this, EC does not intercalate and instead
forms a highly protective SEI layer that prevents further solvent degradation, but allows rapid Li$^+$ cation transport for successful battery operations [59,60,92]. Although various other solvents have been proposed for Li-ion batteries, including lactone- and sulfone-based solvents, each of these mixtures requires EC for SEI layer formation. For this reason EC is almost exclusively used as a co-solvent in Li-ion batteries, in concert with other relevant molecular solvents. Solvent structures and physical properties can be seen in Table 1.3 [93–95].
Table 1.3 Physical properties of molecular solvents used in Li-ion batteries.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molecular Formula</th>
<th>Chemical Structure</th>
<th>Properties</th>
</tr>
</thead>
</table>
| ethylene carbonate (EC)  | C₆H₄O₃            | ![Chemical Structure](ethanol.png) | M.W.: 88.06 g mol⁻¹  
M.P.: 36.5°C  
B.P.: 238°C |
| propylene carbonate (PC) | C₄H₆O₃            | ![Chemical Structure](propylene.png) | M.W.: 102.09 g mol⁻¹  
M.P.: -54.53°C  
B.P.: 242°C |
| dimethyl carbonate (DMC) | C₆H₄O₃            | ![Chemical Structure](DMC.png) | M.W.: 90.08 g mol⁻¹  
M.P.: 4.6°C  
B.P.: 90°C |
| diethyl carbonate (DEC)  | C₅H₁₀O₃           | ![Chemical Structure](DEC.png) | M.W.: 118.13 g mol⁻¹  
M.P.: -43°C  
B.P.: 126.8°C |
| ethyl methyl carbonate (EMC) | C₅H₈O₃         | ![Chemical Structure](EMC.png) | M.W.: 104.10 g mol⁻¹  
M.P.: -14.5°C  
B.P.: 107°C |
| γ-valerolactone (γ-BL, GBL) | C₆H₈O₂          | ![Chemical Structure](γ-BL.png) | M.W.: 86.09 g mol⁻¹  
M.P.: -43.53°C  
B.P.: 204°C |
| γ-valerolactone (γ-VL, GVL) | C₆H₈O₂           | ![Chemical Structure](γ-VL.png) | M.W.: 100.12 g mol⁻¹  
M.P.: -31°C  
B.P.: 207-208°C |
1.5. Electrolyte Solution Structure-Property Relationships

In an electrolyte mixture, consisting of a lithium salt and any number of molecular solvents, there are two competitive interactions that occur. The interaction between Li$^+$ cations and solvent molecules is known as ion solvation. Ion solvation is dependent upon both the lithium salt(s) (i.e., anions) and the molecular solvent(s) present. Ion solvation, however, is typically referred to as a property of the solvent and thus a higher ion solvation is indicative of a system in which solvent molecules preferentially coordinate the Li$^+$ cations. The second type of interaction that exists in an electrolyte mixture is between Li$^+$ cations and anions. This type of interaction is known as ionic association. Ionic association is also dependent upon the solvent(s) and salt(s) present, but is generally expressed as a property of the anion of the lithium salt (i.e., the PF$_6^-$ anion is often considered highly dissociated and thus has low ionic association interactions). Although the physical properties of the electrolyte are highly dependent upon the ionic association and ion solvation present within the system, very little information is available regarding these interactions. In order to link the molecular-level interactions within an electrolyte to the electrolyte’s physical properties, a more in-depth understanding of the interactions that occur is necessary.

1.5.1. Phase Diagrams and Crystalline Solvate Structures

When investigating an electrolyte mixture, it is highly informative to first determine the thermal properties of the mixtures. Thermal characterization of solvent-lithium salt mixtures may be done using differential scanning calorimetry (DSC) to identify thermal events, such as the $T_m$ of crystalline solvates and $T_g$ of amorphous compositions. DSC thermograms of
solvent-lithium salt mixtures of varying composition enable the preparation of solid-liquid phase diagrams, which readily display the thermal phase behavior of the mixtures. The crystalline solvate phases denoted in the phase diagrams provide key information about both the ion solvation and ionic association interactions present in the mixtures (see Appendix A). In the phase diagram in Figure 1.5, two crystalline solvate phases (represented by vertical lines) are evident at concentrations of 6/1 and 5/1 (acetonitrile/Li$^+$ cation ratio) [96]. Unlike solvates in the solution phase, the crystalline solvates have a defined structure that is determined by the solvent and ion packing constraints and the competitive cation-anion and cation-solvent interactions. The ion coordination in the 6/1 and 5/1 crystalline solvates, as determined by single crystal X-ray diffraction, is shown in Figure 1.6 [97,98]. Understanding the solvate structures that are present in the solid phases provides an invaluable tool, when linked with other characterization methods, for examining how ions and solvent molecules interact with one another in the liquid state.
1.5.2. Ion Solvation and Solvation Numbers

Although two distinct interactions exist within an electrolyte, these interactions are non-exclusive; ionic association and ion solvation typically exist in a dynamic equilibrium.
Despite the dynamic conditions, investigating the solvation behavior within an electrolyte is crucial. Solvation species can generally be classified as solvent-separated ion pair (SSIP), contact ion pair (CIP) or aggregate (AGG) solvates, depending upon whether the anion is coordinated to zero, one, or more than one Li⁺ cation, respectively. These classifications can be further divided by the method in which the anions are coordinated; for example, CIP-I solvates exist when a single anion is coordinated to a single Li⁺ cation through a single donor atom, while CIP-II solvates indicate a single anion coordinated to a single Li⁺ cation through two donor atoms (i.e., bidentate).

When investigating the solvation behavior within an electrolyte, it is important to discuss the donor number (DN) of the solvent. A DN is a quantitative measure of the Lewis basicity of a solvent, i.e., the ability to donate electrons to a Lewis acid in order to form a Lewis acid/base complex. When a dissociated lithium salt is mixed with a molecular solvent that displays a high DN and a low acceptor number (AN), the anion is immediately displaced by solvent molecules and the salt is effectively dissolved. In such a case, the cation-anion interactions are low and the Li⁺ cations are effectively fully solvated by the high DN solvent; these mixtures therefore contain principally SSIP solvates and the anions remain uncoordinated. If instead a molecular solvent with a lower DN or a more associated lithium salt is used, the solvent molecules may not be able to fully solvate the Li⁺ cations. Thus, CIP and AGG solvates will be present due to the increased cation-anion interactions. A comparison of solvent DN, AN, and ε can be seen in Table 1.4 [93–95].
Table 1.4 Polarization parameters of solvents used in Li-ion batteries.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DN</th>
<th>Dielectric Constant (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene carbonate (EC)</td>
<td>16.4</td>
<td>90.4</td>
</tr>
<tr>
<td>propylene carbonate (PC)</td>
<td>15.1</td>
<td>65.0</td>
</tr>
<tr>
<td>dimethyl carbonate (DMC)</td>
<td>15.1</td>
<td>3.1</td>
</tr>
<tr>
<td>diethyl carbonate (DEC)</td>
<td>16.0</td>
<td>2.8</td>
</tr>
<tr>
<td>ethyl methyl carbonate (EMC)</td>
<td>–</td>
<td>2.4</td>
</tr>
<tr>
<td>γ-butyrolactone (γ-BL, GBL)</td>
<td>18.0</td>
<td>42</td>
</tr>
<tr>
<td>γ-valerolactone (γ-VL, GVL)</td>
<td>–</td>
<td>34</td>
</tr>
</tbody>
</table>

The ability of solvent molecules to fully solvate Li$^+$ cations is commonly expressed as a solvation number ($N$)—the average number of solvent molecules coordinated to a single Li$^+$ cation. Solvation numbers may be calculated through the use of Raman spectroscopy due to the shift in a solvent’s vibrational bands when it coordinates a Li$^+$ cation. Neat acetonitrile, for instance, has C-C and C≡N stretching modes at 920 cm$^{-1}$ and 2250 cm$^{-1}$, respectively. When a lithium salt is added, such as LiTFSI, the acetonitrile molecules coordinate with the Li$^+$ cations and the vibrational bands of the coordinated solvent molecules are shifted to 930 cm$^{-1}$ and 2277 cm$^{-1}$, respectively. By deconvoluting the Raman spectra of a given electrolyte mixture, the solvation number may be calculated by the following equation [96,99,100]:

$$\frac{A_C}{A_C + A_U} = N \frac{c_{LiX}}{c_S}$$

Eq. 1.8

where $A_C$ and $A_U$ are the integrated area intensities of the vibrational bands for coordinated and uncoordinated solvent, respectively, $c_{LiX}$ and $c_S$ are the concentrations of the lithium salt and solvent, respectively, and $N$ is the solvation number. The solvation numbers for specific compositions and temperatures are a direct measure of the solvent's ability to preferentially
coordinate Li$^+$ cations. Thus, a higher solvation number indicates a solvent that is able to solvate the Li$^+$ cations more effectively and prevent ionic association, which is beneficial for Li$^+$ cation mobility. It has been previously discussed that both the $\varepsilon$ and $DN$ values are commonly used to describe the solvation strength of a given solvent. Discrepancies exist, however, within these values; for example, PC has a lower $DN$ than DEC, but a $\varepsilon$ over 20x higher. In contrast, solvation numbers are experimental determinants of the actual electrolyte solvation interactions. Although such numbers are highly beneficial when investigating how these interactions govern the physical properties of electrolytes, there is little information available in the literature about solvation numbers due, in large part, to the difficulties associated with interpreting Raman spectra.

1.5.3. Ionic Association

Although an examination of the ion coordination within crystalline solvates is very informative for understanding the solid-state interactions, spectroscopy is necessary to identify the solvates present in solution. Raman spectroscopy, in particular, is an excellent means for identifying solvate structures, as both the solvent and anion vibrational bands are typically shifted upon coordination to Li$^+$ cations. By investigating crystalline solvates of known configurations, and assigning fixed band position values to each type of solvate, the solution phase may be analyzed and deconvoluted to determine the fraction of anions with specific forms of coordination to Li$^+$ cations [101]. Ion solvation can also aid in the determination of ionic association, as a low solvation number inevitably means there is a higher degree of ion pairing or aggregation present. Using Raman spectroscopy, in concert
with the phase behavior and solvate crystal structures, the types of solvates in solution can be determined, as well as their approximate distribution; thus the degree of ionic association can be evaluated for solvent-salt mixtures and directly compared to the transport properties of the electrolyte solution.

1.5.4. Transport Properties

The transport properties of electrolyte mixtures are commonly determined to optimize electrolyte formulations. Various studies have been performed on the transport properties of electrolytes, including conductivity, transference numbers, and diffusion of Li\(^+\) cations [102–109]. Despite extensive information with regards to the transport behavior of electrolyte mixtures, these studies focus exclusively on how the properties affect the overall performance of the battery. Little to no information is currently available as to how the solution structure of the electrolyte affects the transport properties of the electrolyte, most importantly the conductivity. Since the conductivity of the electrolyte relies solely on the transfer of charged species, it is highly beneficial to determine the fraction of a given electrolyte mixture that is composed of CIP or AGG solvate species (which may be charge neutral) as opposed to SSIP solvates (which are charged). Solvation analysis of electrolyte mixtures may also be helpful in examining the transport properties; if a solvent has a large solvation number with salt \(x\) over salt \(y\), it follows that solvent-salt \(x\) mixtures may have a higher conductivity than solvent-salt \(y\) mixtures. By investigating the solution structure of various electrolytes, in parallel with the transport properties, a direct correlation may be observed.
1.6. Motivation for this Study

Due to the development of high-voltage, high-capacity cathode materials, there is nearly universal agreement that electrolyte technology is the bottleneck in the development of next-generation Li-ion batteries. Not only is the electrochemical stability of electrolytes in question, the high/low temperature performance is of utmost importance for safety, especially in PHEV/EV applications. Although Li-ion battery electrolyte research is considered a “mature” field of study, the present approach to electrolyte development is anything but mature. The current development process for next-generation electrolytes is based entirely on a trial-and-error approach.

In this work, an entirely new approach, developed by our laboratory, is taken to investigate the molecular-level interactions that exist within the electrolyte mixtures. The competitive solvation and anion (ionic) association interactions with the Li$^{+}$ cation largely govern the electrolyte properties. Our approach is to investigate the molecular interactions that exist within various electrolyte mixtures, determine the electrochemical properties displayed by similar mixtures, and directly compare/relate the molecular-level interactions with the observed electrochemical properties. Such an analysis is highly dependent upon systematic characterization methods (phase diagrams, solvate crystal structures, Raman spectroscopy, conductivity/viscosity/density measurements, etc.) to fully understand how electrolyte mixtures can be rationally designed to fulfill specific applications in the vast field of battery research.

DFOB$, the anion of principal interest in the present body of research, was first reported in 2006, a mere two years before the present work began [110]. Since the original
publication, interest in the DFOB\textsuperscript{−} anion has grown markedly due to its stabilization of high-voltage cathodes in common solvents (Section 1.4.1). However, a large portion of this work was commercially driven and performance based. In the present work, the following steps were performed in order to fully characterize the DFOB\textsuperscript{−} anion and its potential as a salt for Li-ion battery electrolytes: (1) determine the crystal structure of the neat LiDFOB salt and its dihydrate, (2) investigate the molecular interactions of LiDFOB with common carbonate and lactone-based solvents, (3) relate the molecular interactions of solvent-LiDFOB mixtures with electrolyte physical/electrochemical properties, and (4) investigate alternative applications of the DFOB\textsuperscript{−} anion, such as for the preparation of ionic liquids.
1.7. References


CHAPTER 2: Experimental Methods

2.1. Materials

2.1.1. Lithium Salts

The molecular structures and acronyms of the lithium salts used for this study are shown in Figure 2.1. LiBF₄ (anhydrous, 99.99%), LiPF₆ (electrolyte grade), and LiClO₄ (battery grade, 99.998%) were purchased from Sigma-Aldrich or Novolyte and used as-received. LiTFSI (electrolyte grade, 3M) and LiCF₃CO₂ (95%, Sigma-Aldrich) were dried under high vacuum at 120°C for 24 h prior to use. LiCF₃SO₃ (99.995%, Sigma-Aldrich) was used as-received. LiFSI (> 99.5%, Suzhou Fluolyte Company) was used as-received. LiBOB (≥ 99.9%, Chemetal) was purified by recrystallization in acetonitrile and dried at 105°C for 24 h. LiDFOB (≥ 99.9%) was synthesized and purified by a technique previously reported. This synthesis technique will be explained in greater detail in Chapter 3.

![Molecular Structures](image)

Figure 2.1 Structures and acronyms of the lithium salts used in this study.
2.1.2. Solvents

The molecular solvents and acronyms used in this study are shown in Figure 2.2. Acetonitrile (AN, 99.8%), ethyl acetate (EA, 99.8%), dimethyl carbonate (DMC, ≥ 99%), ethyl methyl carbonate (EMC, 99%), ethylene carbonate (EC, 99%), propylene carbonate (PC, 99.7%), γ-butyrolactone (GBL, > 99%) and γ-valerolactone (GVL, 99%) were purchased from either Sigma-Aldrich, Novolyte, Fisher Scientific, Ferro Corporation and/or TCI America. The solvents were dried over 3 Å molecular sieves, if necessary, until the water content was verified to be negligible (< 20 ppm) using a Mettler Toledo DL39 Karl Fischer coulometer.

![Figure 2.2 Structures and acronyms of molecular solvents used in this study.](image)

2.2. Sample Preparation

Samples were prepared in a Vacuum Atmospheres inert atmosphere (N₂) glovebox (< 1 ppm H₂O) by adding the appropriate amounts of solvent(s) to salt(s) in hermetically-sealed vials and heating/stirring until a homogenous solution was obtained. The composition of each mixture/solvate is described using the following three notations: (1-x) solvent-(x) LiX,
Various techniques were used to obtain single crystals for X-ray crystallography. Primarily, mixtures were made at the desired solvate stoichiometry and allowed to sit at temperatures slightly below the solvate melting points (as obtained from phase diagrams). Typically, samples were stored either at room temperature (20°C), in the refrigerator (4°C) or in the freezer (-23°C). Single crystals obtained for LiDFOB and its hydrate will be discussed in Chapter 3. The crystals obtained were used for three different purposes: crystal structure determination via X-ray crystallography, DSC analysis to determine the melting point of solvate, and/or the Raman analysis of solvate vibrational bands. For DSC analysis, the single crystals were directly added to the sample pans and tested. For the Raman analysis, the solvate crystals were ground into a fine powder (in the glovebox) with a mortar and pestle. In some cases, for solvates with a $T_m$ below ambient temperature, the solvates were formed by crystallizing the homogeneous solutions in the Raman Linkam stage by cycling/annealing the samples at subambient temperature until the solvates formed.

### 2.3. Instruments and Techniques

#### 2.3.1. Differential Scanning Calorimetry (DSC)

DSC analysis was performed using a TA Instruments Q2000 differential scanning calorimeter. The instrument was calibrated with cyclohexane (solid-solid phase transition at -87.06°C, $T_m$ at 6.54°C) and indium ($T_m$ at 156.60°C). Each sample was hermetically-sealed in an Al sample pan in the glovebox. The samples were cooled to -150°C and heated at a rate
of 5°C min⁻¹ to 100-300°C, depending upon the temperature necessary for melting and/or decomposition. All samples were cycled/annealed multiple times below/above their $T_g$ until crystallization was observed. If crystallization was not achieved after five cycles, it was assumed that the sample could not be crystallized (with the procedures used). Neat lithium salts were not annealed, but rather cooled to -150°C and heated until decomposition was observed. Only the final heating traces are reported. Peak values were recorded from the final heating thermograms and this data was used to construct the reported phase diagrams.

2.3.2. Thermogravimetric Analysis (TGA)

TGA measurements were performed using a TA Instruments Q5000 thermogravimetric analyzer. Lithium salts were heated at a rate of 5°C min⁻¹ from 25°C to 400°C. Ionic liquids were heated at a rate of 10°C min⁻¹ from 25°C to 150°C (to remove residual moisture absorbed during sample loading), equilibrated for 90 min, cooled to 25°C, and heated at a rate of 5°C min⁻¹ to 550°C. The TGA furnace was maintained under N₂ gas during all of the measurements.

2.3.3. Raman Spectroscopy

Raman measurements were performed on a Horiba-Jobin Yvon LabRAM HR VIS high resolution confocal microscope using a 632 nm⁻¹ He-Ne laser as the excitation source and a Linkam heating/cooling stage for temperature control and protection from ambient moisture. A 50X long distance optical objective was necessary for use with the Linkam stage. Samples were added to a stainless steel microscope slide with a well milled into the slide. The slide
was then sealed (inside the glovebox) in the Linkam stage and transferred to the spectrometer. The instrument was calibrated with a two point calibration of the Raman laser line at 0.0 nm and a monocrystalline Si wafer at 520.7 cm\(^{-1}\). Spectra were typically collected at 60°C, where most samples are liquid, using a 10-30 s exposure time and 20 accumulations to ensure high resolution spectra were obtained. Raman spectra were deconvoluted with a Gaussian-Lorentzian function using LabSpec software.

### 2.3.4. X-Ray Diffraction

Structural analysis of single crystals was performed by Dr. Paul D. Boyle in the Department of Chemistry at North Carolina State University. Crystals were typically mounted on a nylon loop with a small amount of Paratone N oil. Samples composed of carbonate solvents required the use of a quartz fiber for mounting due to the dissolution of the nylon loop. All X-ray measurements were performed on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were calculated from a symmetry constrained fit of the reflections. The data collection strategy varied for the different samples. The frame integration was performed using SAINT [1]. The raw data were scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS or TWINABS (if twinning was present) [1]. The structures were solved by direct methods using either XS or SIR92 [2,3]. All non-hydrogen atoms were obtained from the initial solutions. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural models were fit to the data using full matrix least-squares based on \(F^2\). The calculated spectra factors included corrections for
anomalous dispersion from the usual tabulation. The structures were refined using the XL program from SHELXTL [2].

2.3.5. Nuclear Magnetic Resonance (NMR)

NMR was performed to verify the purity of solvents, salts and ionic liquids. For liquid samples, approximately three drops of sample was added to a 5 mm NMR tube along with 0.6 ml of deuterated solvent (varies by sample). For solid samples, approximately 2-3 mm of the NMR tube was filled with the solid and deuterated solvent was added to dissolve the salt. Care was taken to ensure that the liquid samples were miscible and the solid samples were soluble in the deuterated solvent. $^1$H-NMR was performed on a Varian Mercury 300 MHz spectrometer internally referenced to the solvent used; if overlap existed between the samples and deuterated solvent peaks, the samples were referenced to tetramethylsilane at 0.0 ppm. $^{11}$B-NMR was performed on a Bruker AVANCE 500 MHz spectrometer externally referenced to LiBOB at 6.60 ppm. $^{19}$F-NMR was performed on a Varian Mercury 300 MHz spectrometer externally referenced to LiPF$_6$ at 65.00 ppm.

2.3.6. Conductivity Measurements

The ionic conductivity of the electrolytes was measured with a Biologic VMP3 Potentiostat/Galvanostat/EIS analyzer. The temperature was controlled with a Binder or Tenney Jr. environmental chamber. The conductivity cells, purchased from Materials Mates Italia, consist of a glass body insert with two identical platinum electrodes. The glass body insert was screwed into a glass vial with a cap/gasket, yielding a hermetically-sealed cell.
The cells were assembled inside the glovebox and transferred into an environmental chamber for testing. Cell constants were calculated for each cell with a 11.67 mS cm\(^{-1}\) KCl standard at 20\(^{\circ}\)C (Sigma-Aldrich). For the determination of the ionic conductivity, the impedance of the samples was determined by scanning from 1 MHz to 20 Hz with a 10 mV AC perturbation. A Nyquist plot was generated for each measurement and the conductivity was evaluated using the point where the impedance curve intersected the real axis [4–6].

2.3.7. Corrosion Testing

Samples (mixed solvent-LiX or IL-LiX mixtures) were prepared in a N\(_2\) filled glovebox. The concentrations of the mixed carbonate-based and IL-based mixtures were 1.0 \(m\) and 0.5 \(m\), respectively. The later concentrations (for the IL-LiX mixtures) were selected due to LiX salt solubility limitations. These compositions are comparable to those typically reported in the related studies [7-11]. CR2032 Al-clad coin-cells were constructed in a dry room (RH < 0.1% at 20\(^{\circ}\)C) with 7/16” (0.97 cm\(^{2}\)) Al working electrodes, Celgard 3501 separators, and Li/Li\(^+\) counter/reference electrodes (FMC Lithium). Cyclic voltammograms (CVs) were performed on a Solartron SI-1287 electrochemical interface by cycling each cell from OCV to 6.0 V (vs. Li/Li\(^+\)) for two cycles at a rate of 1 mV s\(^{-1}\). Data was processed with CorrView (v. 2.3) software. Upon completion of the cycles, each electrode was removed from the cell, rinsed with AN, and observed through a Nikon Eclipse LV100 illuminated microscope. Optical photos were taken using the microscope and ACT-1 software (v. 2.63) with 100x, 20x and 5x objectives using brightfield or darkfield illumination.
2.3.8. Electrochemical (Oxidation/Reduction) Stability

Ceramic patterned cells were obtained from Pine Research Instrumentation that consist of patterned Pt working and counter electrodes. A reference electrode (Ag/Ag\(^+\)) was made by immersing a Ag wire in a 10 mM solution of AgCF\(_3\)SO\(_3\) (AgTf) in PY\(_{14}\)TFSI with a fine glass frit. This reference electrode is reported to be stable to within ±1 mV over a period of three weeks with a reference electrode potential of 3.40 V (±5 mV) vs. Li/Li\(^+\) [12-14]. The Pt electrodes were cleaned before each test by cycling in the range ± 0.8 V in 0.5 M H\(_2\)SO\(_4\) (with a Ag wire immersed as the reference electrode), rinsing with deionized H\(_2\)O and EA, and drying in the oven at 120°C for 1 h. The final scan of this H\(_2\)SO\(_4\) cycling was used to calculate the real surface area of the Pt electrode by hydrogen absorption [15]. The surface area was calculated before each test to ensure accuracy, with a typical value of 0.80 cm\(^2\). To determine the electrochemical stability of each IL and IL-LiX mixture, the samples were added to a low-volume voltammetry cell (Pine Research Instrumentation) in the glovebox, along with a clean Pt-patterned cell and the Ag/Ag\(^+\) reference electrode. The samples were cycled (5 mV s\(^{-1}\)) three times from OCV (approx. -0.5 V) to 2.4 V and from OCV to -4.0 V by a Biologic VMP3 potentiostat/galvanostat/EIS. Data was processed with EC-Lab (v. 10.21) software. For convenience, all of the data was converted to a Li/Li\(^+\) reference using the potential noted previously. The notation used for cathodic and anodic scans refers to scanning the potential to lower or higher values, respectively.
2.3.9. Density/Viscosity Measurements

The dynamic viscosity and density of the samples were measured with an Anton Paar SVM 3000 Stabinger viscometer. The instrument was calibrated using Cannon viscosity/density standards with a four point calibration curve, with calibration points above and below the expected testing range of the samples. Tests were performed from 0°C to 100°C with data collection every 10°C. All samples were tested in duplicate with a fresh sample after each analysis. The moisture content of the samples was tested before and after each test to ensure water contamination did not affect the results. The instrument was cleaned after each set of measurements with either EA or H2O, depending upon the solubility of the sample, and flushed with N2 gas.

2.3.10. Quantum Chemistry Calculations

Most of the DFT calculations were performed using a B3LYP functional that showed excellent predictive capabilities for the Raman spectra of the solvents [16]. A limited set of calculations was also performed using M06-L and M05-2X density functionals. The M06-L (local) functional was chosen because it yielded the most accurate EC/Li+ binding energy among the functionals tested (LC-wPBE, M05-2X, B3LYP, HSE06). Both small 6-31+G(d,p) and large aug-cc-pvTz (denoted as Tz) basis sets were used. A polarized continuum model (PCM) with either EC or PC parameters was employed in all of the calculations to implicitly incorporate solvation effects unless noted otherwise. For clarity, Raman bands calculated by DFT analysis are preceded by ca, whereas Raman bands that do not contain ca are indicative of experimental results. Solvent complexes with Li+ cations
have been denoted as solvent\textsubscript{ip}/Li\textsuperscript{+} or solvent\textsubscript{ip}/LiX when referring to DFT calculations and (solvent)\textsubscript{n}-LiX when referring to experimental mixtures. Calculated Raman spectra were predicted using the SWizard program with a Gaussian peak shape and a full-width-at-half-maximum (FWHM) of 15 cm\(^{-1}\) [17,18].

### 2.4. References


CHAPTER 3: Crystal Structure and Physical Properties of LiDFOB

Abstract

The structural characterization and properties of LiDFOB are reported. LiDFOB was synthesized as previously described in the literature via direct reaction of boron trifluoride diethyl etherate with lithium oxalate. The crystal structure of the salt was determined from single crystal X-ray diffraction yielding a highly symmetric orthorhombic structure ($Cmcm$, $a = 6.2623(8)$ Å, $b = 11.4366(14)$ Å, $c = 6.3002(7)$ Å, $V = 451.22(9)$ Å$^3$, $Z = 4$ at 110 K). Single crystal X-ray diffraction of a dihydrate of LiDFOB yielded a monoclinic structure ($P2_1/c$, $a = 9.5580(3)$ Å, $b = 12.7162(4)$ Å, $c = 5.4387(2)$ Å, $V = 634.63(4)$ Å$^3$, $Z = 4$ at 110 K). Along with the crystal structures, additional structural information and the properties of LiDFOB (via $^{11}$B and $^{19}$F NMR, DSC, TGA and Raman spectroscopy) have been compared with those of LiBF$_4$ and LiBOB to better understand the differences between these lithium battery electrolyte salts.
3.1. Introduction

From the initial Li-ion technology demonstrated in the 1970’s, there has been a steady improvement in electrode materials, in part to meet the demands for hybrid and electric vehicles [1]. Since commercialization of the first Li-ion battery by Sony Corp. in 1991, however, electrolyte compositions (i.e., LiPF₆-carbonate mixtures) have remained largely unchanged [2]. LiPF₆ has been the dominate lithium source in most electrolyte compositions for two decades, due largely to its high conductivity in carbonate-based solvents (~10 mS cm⁻¹ at room temperature) and its ability to limit the corrosion of Al current collectors [3–6]. Unfortunately, LiPF₆ is known to decompose at elevated temperatures, resulting in the formation of LiF and PF₅, which is accelerated in the presence of carbonate-based solvents [7–9].

For Li-ion batteries to be used as a power source for electric vehicles, significant improvements must be made to state-of-the-art electrolyte formulations to moderate the continuous capacity fade seen with current electrodes, which limits the lifetime of existing batteries. Many new lithium salts have been proposed as replacements for LiPF₆. Thus far, none of the proposed salts have been able to meet the myriad property requirements necessary for commercial Li-ion batteries. Some of the lithium salts, however, have shown significant promise as additives to (i) increase ionic conductivity, (ii) decrease electrolyte flammability and/or (iii) promote interfacial stability (improved solid-electrolyte interface (SEI) formation, reduced Al corrosion, etc.).

Of the lithium salts that have been developed in the past decade, one of the most promising to date is LiDFOB. LiDFOB has been shown to form in cells containing both
LiBF₄ and LiBOB at higher temperatures, similar to the formation of lithium tetrafluoro-(oxalato)phosphate (LiF₄OP) from LiPF₆ and LiBOB [10–12]. LiDFOB combines the benefits of its two parent salts, LiBF₄ and LiBOB [13–19]:

Like LiBOB, LiDFOB has the innate ability to form an SEI on the surface of a graphite anode, even in high concentrations of PC [16]. This intrinsic property of a lithium salt dominating SEI formation is necessary for the replacement of the high-melting EC that is typically required for SEI formation. LiDFOB also possesses the characteristics of LiBF₄, such as an exceptional ability to passivate Cu and Al current collectors [20].

Although LiDFOB is one of the most promising additives for battery electrolyte technologies, and numerous reports are available on its thermal/electrochemical benefits [21–35], no crystallographic data has been reported thus far. Such information provides both insight into the manner in which the anions coordinate Li⁺ cations, as well as the necessary background required for computational analysis of the anion. In this study, the structural determination of LiDFOB based on single-crystal X-ray diffraction is reported. The effect of displacing fluorine atoms on BF₄⁻ with oxalate ligands on the thermal degradation behavior and Raman spectra has also been investigated.
3.2. Synthesis of LiDFOB

LiDFOB was synthesized by the direct reaction of excess boron trifluoride diethyl etherate (BF$_3$-ether) with lithium oxalate (oxalic acid dilithium salt, anhydrous), both used as-received from Sigma-Aldrich [21]. The reagents were combined in a sealed vessel and stirred for 24 h at 80°C, allowing the solid-state reaction to occur. After decanting and rinsing multiple times with ether to remove unreacted BF$_3$-ether, the crude lithium salt was extracted with dimethyl carbonate (DMC) and filtered to remove solid impurities (LiF, lithium oxalate, etc.). The crude lithium salt, dissolved in DMC, was roto-evaporated until small crystals formed, at which time the solution was removed, placed in a N$_2$ glovebox (< 0.5 ppm O$_2$ and H$_2$O) and allowed to crystallize for > 48 h. After decanting, the isolated crystals were then recrystallized a total of five times in DMC by supersaturating the solution, vacuum filtering, and allowing the solution to slowly cool to promote large crystal growth. After the fifth recrystallization, LiDFOB was dried at 105°C for 48 h, yielding a high purity salt. All actions, except the initial roto-evaporation, were performed in a N$_2$ glovebox. The salts (LiBF$_4$, LiDFOB and LiBOB) were dissolved in DMSO-$d_6$ for NMR analysis. Figure 3.1 displays the $^{11}$B- and $^{19}$F-NMR results, respectively, for the three salts. $^1$H-NMR was also performed, but yielded no detectable impurities and therefore is not reported.
**Figure 3.1** $^{19}$F- and $^{11}$B-NMR spectra of LiBF$_4$, LiDFOB and LiBOB (in DMSO-$d_6$) externally referenced to LiPF$_6$ at 65.00 ppm (not shown) and LiBOB at 6.60 ppm, respectively.

### 3.3. X-Ray Structural Determination

#### 3.3.1. X-Ray Analysis Strategy

*LiDFOB*: Single crystals were obtained from a highly concentrated solution of crude LiDFOB and DMC stored at 5°C for approximately 30 days. A crystal was mounted on a quartz fiber with a small amount of Paratone N oil. All X-ray measurements were acquired
on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer at a temperature of -163°C [36]. The unit cell dimensions were determined from a symmetry constrained fit of 6704 reflections with 7.42° < 2θ < 81.78°. The data collection strategy was a number of ω and φ scans, which collected data up to 84.8° (2θ).

LiDFOB·2H₂O: Single crystals were obtained from a solution of DMC and LiDFOB that was exposed to ambient moisture. A single crystal was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer at a temperature of -163°C [36]. The unit cell dimensions were determined from a symmetry constrained fit of 9916 reflections with 5.48° < 2θ < 83.72°. The data collection strategy was a number of ω scans which collected data up to 85.56° (2θ).

Refinement: The frame integration was performed using SAINT [36]. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS [36]. Details of the crystal structure data can be found in Table 3.1 and Appendix B. The structures were solved by direct methods using the XS program from SHELXS [37]. All non-hydrogen atoms were obtained from the initial solution. The hydrogen atom positions were obtained from a difference Fourier map and were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on $F^2$. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structures were refined using the XL program from SHELXTL [37].
Table 3.1 Crystal data and structural refinement for LiDFOB and its dihydrate.

<table>
<thead>
<tr>
<th>LiDFOB</th>
<th>LiDFOB·2H₂O</th>
</tr>
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<tr>
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<tr>
<td>Temperature</td>
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<tr>
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<td>6.2623(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.4366(14)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>6.3002(7)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>451.22(9)</td>
</tr>
<tr>
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<td></td>
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<tr>
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</tr>
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<td></td>
<td>wR2 = 0.0838</td>
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<tr>
<td>R indices (all data)</td>
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<tr>
<td></td>
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<tr>
<td>Δe min/Δe max (e·Å⁻³)</td>
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3.3.2. LiBF₄ Crystal Structure

The single crystal structure of neat LiBF₄ has been previously reported [38]. The ion packing in LiBF₄ is shown in Figure 3.2. Each Li⁺ cation is coordinated by 4 fluorine atoms from 4 different BF₄⁻ anions. Each BF₄⁻ anion is coordinated to 4 Li⁺ cations with each of the
4 fluorine atoms coordinating a single Li$^+$ cation. This coordination behavior yields rows of alternating Li$^+$ cations and BF$_4^-$ anions parallel to the crystallographic b-axis.

**Figure 3.2** Ion packing in the crystal structure of LiBF$_4$ [38].
3.3.3. LiBOB Crystal Structure

The crystal structure of neat LiBOB has been previously reported as calculated from powder X-ray diffraction [39]. The ion packing within the LiBOB crystal structure is shown in Figure 3.3. Each Li$^+$ cation is coordinated by five carbonyl oxygen atoms from four different BOB$^-$ anions. Three different BOB$^-$ anions coordinate the Li$^+$ cation through a single carbonyl oxygen atom, while one BOB$^-$ anion forms a bidentate coordination with two carbonyl oxygen atoms. Each BOB$^-$ anion is coordinated to four Li$^+$ cations. The carbonyl oxygens from one oxylate group forms a single coordination with two different Li$^+$ cations, while the other oxylate group forms a bidentate coordination between its carbonyl oxygens and a single Li$^+$ cation, with one of the carbonyl oxygens also coordinated to another Li$^+$ cation. This coordination results in the BOB$^-$ anions and Li$^+$ cations being arranged in a polymeric structure parallel to the crystallographic $b$-axis that is linked together by the carbonyl oxygen–Li$^+$ cation coordination bonds. Note that ellipsoids are not displayed for this structure since the results were obtained from powder X-ray diffraction instead of single crystal X-ray diffraction.
3.3.4. LiDFOB Crystal Structure

The single crystal structure of LiDFOB is a highly symmetric, orthorhombic structure with lattice parameters $a = 6.2623(8)$ Å, $b = 11.4366(14)$ Å, $c = 6.3002(7)$ Å and $\beta = 90.00^\circ$ (space group $Cmcm$). The ion packing in LiDFOB is shown in Figure 3.4. Each Li$^+$ cation is coordinated by four oxygen atoms from three DFOB$^-$ anions and two fluorine atoms from
two DFOB\(^-\) anions, with some similarities to both LiBF\(_4\) and LiBOB. Each DFOB\(^-\) anion is coordinated to five Li\(^+\) cations. The anion oxalate group coordinates three of the cations through the carbonyl oxygen atoms with one cation coordinated by both carbonyl groups. Each fluorine atom is coordinated to a single Li\(^+\) cation. This coordination results in the DFOB\(^-\) anions and Li\(^+\) cations being arranged in planar sheets which are linked together by the fluorine–Li\(^+\) cation coordination bonds.

**Figure 3.4** Ion packing in the crystal structure of LiDFOB.
3.3.5. LiDFOB·2H₂O Crystal Structure

The single crystal structure of LiDFOB·2H₂O is a monoclinic structure with lattice parameters $a = 9.5580(3)$ Å, $b = 12.7162(4)$ Å, $c = 5.4387(2)$ Å and $\beta = 106.2469(12)^\circ$ (space group $P2_1/c$). The ion packing in LiDFOB·2H₂O can be seen in Figure 3.5. Each Li⁺ cation is coordinated by two oxygen atoms from two DFOB⁻ anions and four oxygen atoms from four H₂O molecules. Each H₂O molecule is coordinated to two Li⁺ cations and the oxalate group from each DFOB⁻ anion coordinates two Li⁺ cations through a single carbonyl oxygen atom. This coordination results in polymeric chains in which the fluorine atoms from the DFOB⁻ anions and hydrogen atoms from H₂O are protruding out of the unit cell (Figure 3.5). A comparison of the Li⁺ cation and anion coordination within the LiBF₄, LiDFOB and LiBOB crystal structures is displayed in Figure 3.6.
Figure 3.5 Ion packing in the crystal structure of LiDFOB·2H$_2$O.
3.4. Thermal Properties of LiDFOB

The thermal properties of each lithium salt differ significantly in the DSC and TGA measurements (Figures 3.7 and 3.8). For instance, after a solid-solid phase transition at 28°C [40], LiBF$_4$ displays an endothermic peak at 305°C (melting and/or decomposition)(DSC). The TGA measurements, however, show that LiBF$_4$ mass loss onset occurs at ~160°C. This behavior is also seen with LiDFOB; an endothermic peak exists at 272°C (DSC), but mass loss onset occurs at ~200°C (TGA). These results indicate that vapor pressure may play a significant role in the thermal degradation of each lithium salt as the TGA measurement involves heating the sample open to flowing N$_2$ gas, whereas for the DSC measurements the
Al sample pans are hermetically-sealed in the N₂-filled glove box. These measurements are reproducible.

TGA is useful for determining the lithium salt’s decomposition products, which can aid in the identification of impurities that may exist within an electrolyte, as well as battery thermal runaway processes. The thermal decomposition mechanism of LiBF₄ is known (Eq. 3.1) [41] and can be easily related to its TGA thermogram (Figure 3.8). The loss of BF₃ correlates with a 72.3% reduction in mass, which is observed in the TGA as a single-step decomposition:

\[
\text{LiBF}_4 \rightarrow \text{LiF (s)} + \text{BF}_3 (g) \quad (3.1)
\]

The thermal decomposition of LiBOB is much more intricate. Zinigrad et al. report a multi-step thermal decomposition of LiBOB (< 350°C), which can be related to the mass loss seen in the TGA measurements (Eq. 3.2 and 3.3). The initial decomposition step at ~350°C (DSC) or 290°C (TGA) is a combination of Eq. 3.2 and 3.3, as reported in the literature [17]. These reactions account for a 61.9% reduction of mass.

\[
6 \text{LiBC}_{4}O_{8} \rightarrow 3 \text{Li}_2\text{C}_2\text{O}_4 (s) + 3 \text{B}_2\text{O}_3 (s) + 9 \text{CO} (g) + 9 \text{CO}_2 (g) \quad (3.2)
\]
\[
\text{Li}_2\text{C}_2\text{O}_4 + 3 \text{B}_2\text{O}_3 \rightarrow 2 \text{LiB}_3\text{O}_5 (s) + \text{CO} (g) + \text{CO}_2 (g) \quad (3.3)
\]

The final LiBOB decomposition step may involve the decomposition of the remaining lithium oxalate due to its reported decomposition temperature of ~520°C [42]. This decomposition step, however, has not been further investigated and has thus far not been reported in the literature.

It appears from the TGA analysis that LiDFOB may be a combination of the two decomposition mechanisms for both LiBF₄ and LiBOB. However, attempts to interpret the
decomposition products have thus far been unsuccessful. It is believed that similar products as for LiBF₄ and LiBOB will be formed, but the exact stoichiometric ratios remain unknown.

**Figure 3.7** DSC heating traces (5°C min⁻¹) of LiBF₄, LiDFOB and LiBOB.

**Figure 3.8** TGA heating traces (5°C min⁻¹) of LiBF₄, LiDFOB and LiBOB.
3.5. Raman Vibrational Modes of LiDFOB

The highest intensity peak in the LiBF₄ Raman spectra is from a symmetric B-F stretching mode, which has a characteristic peak in the 760–800 cm⁻¹ region [43]. This peak is known to shift due to varying forms of ionic association between the anion and Li⁺ cations [43,44]. The B-F stretching peak of the neat LiBF₄ can be seen in Figure 3.9 at 797 cm⁻¹.

LiBOB has been studied via vibrational spectroscopy (IR and Raman) and *ab initio* calculations [45,46]. By comparing the peak assignments of LiBOB to LiDFOB, many of the vibrational bands are shared due to a common oxalate group. Holomb *et al.* report that the BOB⁻ anion displays out-of-phase valence vibrations at ~1780 cm⁻¹ and ~1800 cm⁻¹, as well as an in-phase valence vibration at 1822 cm⁻¹, corresponding to C=O vibrations [46]. Since the DFOB⁻ anion also possesses these C=O bonds, the bands at 1762 cm⁻¹ and 1800 cm⁻¹ correspond to C=O out-of-phase and in-phase valence vibrations, respectively. The frequency of these peaks is different between the DFOB⁻ and BOB⁻ anions due to differing degrees of aggregation. These peaks shift and/or split from Li⁺ cation coordination effects that are present in the neat lithium salt and solvates in solution [45].

Other peak assignments have been analyzed based upon the similarity in structure of the DFOB⁻ and BOB⁻ anions, including a (O=C−C=O) bend at 360 cm⁻¹, (O−B−O) deformation at 722 cm⁻¹, (O−B−O) valence and (O−C−O) deformation at 946 cm⁻¹, and (C−O) valence (in-phase) and (C−C) valence at 1405 cm⁻¹ [46]. When a single Li⁺ cation is coordinated by the two oxalate carbonyl oxygen atoms, the C−C stretching vibration calculated to be 1328 cm⁻¹ (for uncoordinated BOB⁻) shifts to ~1435 cm⁻¹ due to the formation of a contact ion-pair [46]. In contrast, the crystal structure of LiDFOB has carbonyl oxygen atoms coordinated to
three Li\(^+\) cations, one of which is coordinated by both carbonyl groups (Figure 3.6). This coordination within the LiDFOB crystal structure may result in the single Raman peak at 1404 cm\(^{-1}\) (Figure 3.9). In LiBOB, multiple peaks are present in the 1300–1450 cm\(^{-1}\) range. These peaks likely result from the coordination of the anion to multiple Li\(^+\) cations in various ways (Figure 3.6), causing distinct C–C stretching bands to form as a function of the type of cation coordination. *Ab initio* calculations initially suggested that the best peak for analyzing the ionic association interactions (i.e., Li\(^+\) cation coordination) may be the Raman band at \(~1400\) cm\(^{-1}\) [46]. A study of the crystalline solvate coordination behavior, however, has identified the bands at \(~707-725\) cm\(^{-1}\) as a means for identifying specific solvates present in electrolyte mixtures with LiDFOB [47].

![Figure 3.9 Raman spectra of LiBF\(_4\), LiDFOB and LiBOB.](image_url)
3.6. Conclusions

The structural determination of the crystal structure of LiDFOB has shown that the Li\(^+\) cations are coordinated by both fluorine and oxygen atoms. The DFOB\(^-\) anions are coordinated to five Li\(^+\) cations with the anion's oxalate group coordinated to three cations through the carbonyl oxygen atoms, with one of the Li\(^+\) cations coordinated by both carbonyl oxygen atoms. Each anion fluorine atom is coordinated to a single Li\(^+\) cation. In contrast, in LiDFOB\(\cdot\)2H\(_2\)O, the Li\(^+\) cations are coordinated by a total of six oxygen atoms. The H\(_2\)O molecules are coordinated to two Li\(^+\) cations. Each Li\(^+\) cation is coordinated by two DFOB\(^-\) anions through their carbonyl oxygen atoms and four H\(_2\)O molecules. Each DFOB\(^-\) anion is coordinated to two Li\(^+\) cations, resulting in ionic polymeric chains. The thermal decomposition of LiDFOB displays similarities to both LiBF\(_4\) and LiBOB. Although the decomposition products of both LiBF\(_4\) and LiBOB are well studied, and it appears that the decomposition of LiDFOB is a combination of these pathways, the actual decomposition products of LiDFOB are yet to be determined. Based upon the DSC and TGA analysis of all three salts, vapor pressure appears to play a significant role in the thermal decomposition, leading to a much higher thermal stability in a sealed system. The similarities of DFOB\(^-\) and BOB\(^-\) coordination to Li\(^+\) cations results in similar Raman spectra for the two lithium salts. Thus, calculated vibrational band assignments for the BOB\(^-\) anion are similar with calculated band assignments for the DFOB\(^-\) anion.
3.7. References


CHAPTER 4: Raman and DFT Analysis of Li\(^+\) Cation Solvation: Cyclic Carbonate Solvents—EC and PC

Abstract

Experimental and computational analysis of EC and PC mixtures with varying lithium salts is reported. Previously reported Raman analyses of (EC)\(_n\)-LiX mixtures have been flawed due to a lack of accounting for varying intensity ratios of the uncomplexed and Li\(^+\) complexed solvent vibrational bands. Therefore, analysis of the two perturbed vibrational bands yields differing solvation numbers in these analyses. These issues have been resolved in the present work by incorporating a DFT analysis of the solvent-Li\(^+\) cation coordination to determine the scaling factors for the intensity differences. By scaling the uncomplexed and complexed vibrational bands accordingly, the solvation numbers calculated from the two different solvent Raman bands are in excellent agreement. In contrast to EC mixtures, PC is difficult to analyze both experimentally and computationally. Commercially available PC is a racemic mixture of (S)- and (R)-PC isomers. Based on quantum chemistry calculations, however, each of these isomers may exist as multiple conformers due to a low energy barrier for ring inversion, making deconvolution of the Raman bands daunting and inherently prone to errors. Thus, an analysis of (EC)\(_n\)-LiX mixtures by Raman spectroscopy may be able to accurately predict the EC...Li\(^+\) solvation interactions, while a similar analysis of (PC)\(_n\)-LiX mixtures significantly underestimates the PC...Li\(^+\) solvation interactions.
4.1. Introduction

Electrolytes have become the limiting component for next-generation Li-ion batteries with regard to implementing alternative electrodes, improving safety, operation at high and/or low-temperature, etc. Many electrolyte properties directly depend upon the solvation interactions. In particular, in order to achieve a high rate performance (power), the ionic conductivity of electrolyte solutions is of utmost importance. As this is a direct reflection of the transport properties of the ions, it is highly dependent upon the ionic association tendency of the anions. One reason that LiPF₆ is predominantly used as the electrolyte salt for commercial Li-ion batteries is that the salt dissociates into fully solvated Li⁺ cations and uncoordinated PF₆⁻ anions, resulting in exceptionally high ionic conductivity values. Anion...Li⁺ cation interactions are minimized by the weakly coordinating PF₆⁻ anions, thus reducing or eliminating contact ion pair and aggregated solvate formation. The molecular interactions present within an electrolyte, however, are dictated not only by ionic association (cation-anion) interactions, but also by the strength of ion solvation (cation-solvent) interactions; thus the anions and solvent molecules directly compete with one another for coordination to the Li⁺ cations. Scrutinizing the solvation interactions present within electrolyte mixtures is therefore imperative for understanding the origin of electrolyte properties and facilitating the tuning of these properties for particular battery applications/requirements.

A number of experimental studies have been performed on Li⁺ cation solvation by EC and/or PC with varying lithium salts [1-21]. These studies relied solely on experimental procedures to determine Li⁺ cation solvation numbers from Raman, IR and NMR
spectroscopy, or through volumetric studies. Additionally, DFT calculations and molecular dynamics (MD) simulations have long contributed to the understanding of the various species present in electrolytes, as well as the theoretical solvation numbers of specific solvent-Li\(^+\) cation complexes [22-37]. Such studies, however, have generally failed to obtain consistent solvation numbers, which suggests that an inherent flaw exists in the various analysis techniques used. A joint experimental/computational analysis has therefore been conducted in the present study to rigorously scrutinize the procedure for obtaining solvation numbers with EC and PC. The DFT calculations determine the vibrational bands present and their corresponding Raman activity. This information can then be utilized to tune the analysis of the experimental data for a more in-depth understanding of the electrolyte interactions. More explicitly, the evaluation of the experimental data is dependent upon the consideration of both band overlap and the intensities of the uncomplexed and Li\(^+\) complexed solvent bands. Previously reported experimental analyses of the Raman band variation relied heavily on assumptions. But, using the reported methodology/evaluation, consistent solvation numbers are obtained when analyzing two different EC solvent bands and a detailed explanation is provided for why the analysis of PC solvation numbers using Raman spectroscopy is inherently full of error, which results in highly misleading solvation numbers.

4.2. Raman Band Analysis

4.2.1. (EC)\(_n\)-LiX Mixtures

The experimental Raman spectra of EC at 60°C (liquid) and -80°C (crystalline) are shown in Figure 4.1. Numerous vibrational spectroscopic investigations have been performed on
(EC)$_n$-LiX mixtures in which two Raman EC solvent bands have been reported to shift upon solvent coordination to a Li$^+$ cation—i.e., the ring breathing and ring bending modes [1,2,13,18,38-43]. Some controversy exists, however, as to the assignment of these bands. Durig et al. attributed the band at ca 717 cm$^{-1}$ to a skeletal bending mode with A$_1$ symmetry after concluding that this bending mode could not be due to a C=O-ring bending vibrations because of its polarized nature [42]. This is also consistent with a study performed by Dorris et al. on vinylene carbonate [43]. Fortunato et al. also reported a ring bending mode at ca 717 cm$^{-1}$ and a ring breathing mode at ca 894 cm$^{-1}$ [41]. Conversely, Hyodo et al. and Klassen et al. have more recently associated the ca 714 cm$^{-1}$ Raman band to an out-of-plane C=O–ring bending vibration (whereas the ca 891 cm$^{-1}$ band shares a similar assignment with the previous reports) [1,13].

**Figure 4.1** Comparison of the Raman spectra of EC at 60°C (liquid) and -80°C (crystalline).
DFT calculations in the present work examined the vibrational modes of EC, EC$_n$/Li$^+$ and EC$_n$/LiX complexes with high Raman activity in the 700-900 cm$^{-1}$ region and the C=O vibrational mode near 1800 cm$^{-1}$. Figure 4.2 shows the Raman spectrum of an EC molecule calculated at the B3LYP/Tz and B3LYP/6-31+G(d,p) levels with PCM(EC). The spectra indicate that the ca 713 cm$^{-1}$ and 902 cm$^{-1}$ peaks each have contributions from two vibrational modes. These vibrational modes are shown in Figure 4.3. The peak at ca 713 cm$^{-1}$ is dominated by a vibration consisting of ring breathing with O–C–O symmetric stretch and a minor contribution from the ring distortion with a –CH$_2$– rocking mode that is red shifted to ca 704 cm$^{-1}$. The ring breathing mode at ca 902 cm$^{-1}$ also contains a minor left shoulder due to –CH$_2$– twisting motion (ca 885 cm$^{-1}$), as shown in Figure 4.2. A comparison of the spectra from the B3LYP/Tz and B3LYP/6-31+G(d,p) calculations indicates that usage of the smaller 6-31+G(d,p) basis set, as compared to Tz, results in no appreciable difference in the spectra. Therefore, the 6-31+G(d,p) basis set was used for a majority of the calculations.
Figure 4.2 Calculated Raman spectra for EC from (top) B3LYP/Tz and (bottom) B3LYP/6-31+G(d,p) calculations with PCM(EC).
Figure 4.3 Vibrational modes of EC from B3LYP/6-31+G(d,p) with PCM(EC) calculations for (a) ring distortion with –CH₂– rocking at ca 704 cm⁻¹, (b) ring breathing with O–C–O symmetric stretch at ca 713 cm⁻¹, (c) –CH₂– twisting symmetric with respect to C₂ᵥ symmetry plane at ca 885 cm⁻¹, and (d) ring breathing symmetric with respect to C₂ᵥ at ca 902 cm⁻¹.

Although the carbonyl oxygen atoms are widely accepted to dominate the coordination of EC to Li⁺ cations, the complexity of the overlapping carbonyl Raman bands makes their deconvolution impractical. The C=O stretching vibration, calculated to be a single band at ca 1808 cm⁻¹, is natively split into two peaks (Figure 4.1). These peaks exist primarily as a consequence of Fermi resonance of the C=O stretching mode with an overtone of the ring breathing mode [44,45]. Once coordinated to a Li⁺ cation, these bands are each shifted, further increasing the complexity of the analysis. Due to the difficulties of deconvoluting these bands, and the compounding error associated with such an analysis, the evaluation of the carbonyl stretching bands has not been performed in the present study.

Most quantum chemical studies to date have focused on examining the Raman spectra of gas-phase solvent and solvent/Li⁺ clusters, while largely neglecting condensed phase effects.
The influence of including the implicit (PCM) and explicit interactions between solvent molecules, the latter by comparing EC1 and EC4, on the Raman spectra was examined in the present study with the results reported in Table 4.1. Inclusion of PCM results in a significant frequency shift of up to 11 cm\(^{-1}\) for bands below 940 cm\(^{-1}\) and 80-100 cm\(^{-1}\) for the C=O vibration. The PCM inclusion also increased the Raman activities, but, importantly, the increase was not uniform for all of the bands—i.e., the increase ranged from a factor of 1.6 to 2.2. A comparison of the EC4 vs. EC1 Raman spectra predictions indicates smaller shifts of the average band positions as compared to the initial inclusion of the PCM model for EC. Interestingly, explicit consideration of EC4 changed the Raman activity by factors ranging from 0.8 to 1.4. A comparison of the predicted spectra for EC4 and EC1 with the experimental data for EC shown in Figure 4.1 indicates a slightly better agreement for the EC4 spectrum with experiments (see Appendix C). Experimental deconvolution is able to adequately model the shoulder present at \textit{ca} 704 cm\(^{-1}\), but a shoulder is not observed in the experimental EC spectrum for the \textit{ca} 885 cm\(^{-1}\) band. Given the difficulty in deconvoluting the multiple bands calculated for EC4, however, the experimental analysis was instead performed based upon the frequency shifts and activity ratios relative to EC1 (rather than EC4).
Table 4.1 EC Raman band frequency (cm\(^{-1}\)) and activities (\(S\)) from calculations using the 6-31+G(d,p) basis set. Activity weighted averages are given for EC\(_4\).

<table>
<thead>
<tr>
<th></th>
<th>freq(_1)</th>
<th>freq(_2)</th>
<th>freq(_3)</th>
<th>freq(_4)</th>
<th>freq(_5)</th>
<th>freq(_1)</th>
<th>freq(_2)</th>
<th>freq(_3)</th>
<th>freq(_4)</th>
<th>freq(_5)</th>
</tr>
</thead>
<tbody>
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<td>EC(_1)</td>
<td>B3LYP no PCM, (\varepsilon = 1)</td>
<td>693</td>
<td>715</td>
<td>890</td>
<td>892</td>
<td>1898</td>
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<td>6.0</td>
<td>1.6</td>
<td>15.0</td>
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<tr>
<td>EC(_1)</td>
<td>B3LYP PCM(EC)</td>
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<td>713</td>
<td>885</td>
<td>902</td>
<td>1808</td>
<td>4.5</td>
<td>12.6</td>
<td>2.5</td>
<td>33.5</td>
</tr>
<tr>
<td>EC(_1)</td>
<td>M05-2X no PCM, (\varepsilon = 1)</td>
<td>691</td>
<td>730</td>
<td>908</td>
<td>929</td>
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</tr>
<tr>
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<td>729</td>
<td>904</td>
<td>938</td>
<td>1862</td>
<td>3.6</td>
<td>9.6</td>
<td>2.5</td>
<td>31.4</td>
</tr>
<tr>
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<td>M06L no PCM, (\varepsilon = 1)</td>
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<td>721</td>
<td>893</td>
<td>901</td>
<td>1930</td>
<td>2.6</td>
<td>6.0</td>
<td>1.9</td>
<td>14.1</td>
</tr>
<tr>
<td>EC(_1)</td>
<td>M06L PCM(EC)</td>
<td>703</td>
<td>721</td>
<td>889</td>
<td>910</td>
<td>1851</td>
<td>4.7</td>
<td>12.2</td>
<td>3.2</td>
<td>31.4</td>
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<td>B3LYP PCM(EC)</td>
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<td>715</td>
<td>884</td>
<td>902</td>
<td>1804</td>
<td>4.3</td>
<td>16.0</td>
<td>2.2</td>
<td>36.7</td>
</tr>
<tr>
<td>EC(_4)</td>
<td>M05-2X PCM(EC)</td>
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<td>732</td>
<td>903</td>
<td>939</td>
<td>1849</td>
<td>3.0</td>
<td>11.5</td>
<td>2.2</td>
<td>32.7</td>
</tr>
</tbody>
</table>

When an EC molecule coordinates a Li\(^+\) cation, the vibrational bands mentioned previously are shifted. The calculated frequency shift of these coordinated solvent bands is highly dependent upon the functional used in the DFT calculation. While previous DFT calculations of EC\(_1\) and EC\(_1\)/Li\(^+\) were performed for the isolated solvent and complex in vacuum [24,46], the present calculations were performed with PCM(EC) to implicitly account for solvent effects. When PCM is not included, the EC polarization by the Li\(^+\) cation is dramatically overestimated for EC\(_1\)/Li\(^+\) and much larger clusters are needed to correct for this artifact [24]. For example, gas phase calculations for the ring breathing mode (ca 719 cm\(^{-1}\) for neat EC\(_1\) with the B3LYP/Tz functional) yielded shifts of 41-102 cm\(^{-1}\) for EC\(_2\)/Li\(^+\), 33.5-47.5 cm\(^{-1}\) for EC\(_3\)/Li\(^+\), and 22.1-26.7 cm\(^{-1}\) for EC\(_4\)/Li\(^+\); these shifts are clearly decreasing with increasing cluster size [24]. Our calculations for EC\(_1\)/Li\(^+\) with PCM(EC), however, yield a shift of only 19-24 cm\(^{-1}\), which is more representative of the experimental shifts observed in (EC\(_n\)-LiX mixtures. Various functionals were surveyed to determine the most suitable analysis technique for comparison with the experimental data. The calculated frequency shifts and activities of the EC\(_1\)/Li\(^+\) complex, and their relationship with EC, using multiple
functionals is reported in Appendix C. Upon Li$^+$ cation complexation, the present calculations indicated that the EC ring breathing modes at ca 713 cm$^{-1}$ and ca 902 cm$^{-1}$ are blue shifted ~19-25 cm$^{-1}$ and 7-11 cm$^{-1}$, respectively. The ring distortion mode (shoulder) at ca 704 cm$^{-1}$, however, is blue shifted only ~5-10 cm$^{-1}$ and the ca 885 cm$^{-1}$ band is red shifted only ~3-5 cm$^{-1}$. Since the Raman activity of the ca 885 cm$^{-1}$ twisting band is quite small relative to the ring breathing (902 cm$^{-1}$) band activity (Figure 4.2), the former was neglected in the analysis of Li$^+$ cation complexation.

The extent to which the vibrational bands shift upon cation coordination was found to be slightly dependent upon the number of EC molecules and/or the presence of an anion in the coordination shell that surrounds the Li$^+$ cation, as shown in Figure 4.4 (only the average activity weighted frequencies are shown for clarity). The calculated EC frequency shifts upon Li$^+$ cation complexation indicate a weak dependence on the number of EC molecules coordinating a Li$^+$ cation for the 704, 713, 885 and 902 cm$^{-1}$ bands. In contrast to these results, previously reported gas-phase calculations (without a PCM model) indicated a dramatic dependence of the EC shifts upon Li$^+$ cation complexation with varying number of EC molecules in the EC$_n$/Li$^+$ cluster for n = 1-4 [24]. The presence of an anion as a solvent-separated ion pair (SSIP) or contact ion pair (CIP) (i.e., EC$_4$/LiBF$_4$ or EC$_3$/LiBF$_4$, respectively, in Figure 4.4) had a relatively minor influence on the frequency shifts and activity ratios for the EC$_n$/Li$^+$ complexation (vs. the EC$_1$ solvent vibrational bands). This is an important conclusion as it supports the assumption that the frequency shifts and activity differences will be negligible upon increasing salt concentration. Thus, the frequency shifts and activity values are assumed to be independent of the salt concentration, the state of ion
aggregation (i.e., SSIP vs. CIP), and the nature of the anion used in the analysis (i.e., PF$_6^-$ vs. BF$_4^-$). Table 4.2 was therefore generated from B3LYP/6-31+G(d,p) calculations with PCM(EC) for EC$_1$/Li$^+$ and EC$_3$/Li$^+$ complexes (see Appendix C). Using experimental data in conjunction with the calculated Raman shifts of the complexed EC$_3$/Li$^+$ species, along with the fact that other four coordinated Li$^+$ solvates yield very similar values, it was determined that the EC$_3$/Li$^+$ complex reasonably represented the influence of Li$^+$ cations on the EC Raman spectrum. In order to properly interpret the experimental results, it is necessary to scale the intensities of the Raman bands to account for less/more Raman active species. Table 4.2 displays the calculated Raman frequency and relative activity for EC$_3$/Li$^+$ as compared with EC$_1$. The Raman activity for the ca 902 cm$^{-1}$ band (shifted to ca 911 cm$^{-1}$) is largely unchanged upon Li$^+$ cation complexation, while the activity of the ca 713 cm$^{-1}$ band (shifted to ca 738 cm$^{-1}$) is decreased approximately 22 or 31% when compared with EC$_1$ or EC$_4$, respectively.
Figure 4.4 Frequency shifts (cm\(^{-1}\)) and activity ratios of EC\(_n\)/Li\(^{+}\) and EC\(_n\)/LiX complexes vs. EC\(_1\) from B3LYP/6-31+G(d,p) calculations with PCM(EC) and the corresponding coordination for (a) EC\(_1\)/Li\(^{+}\), (b) EC\(_2\)/Li\(^{+}\), (c) EC\(_3\)/Li\(^{+}\), (d) (CIP) EC\(_3\)/LiPF\(_6\), (e) (CIP) EC\(_3\)/LiBF\(_4\), (f) (CIP) EC\(_3\)/LiTFSI, (g) EC\(_4\)/Li\(^{+}\) and (h) (SSIP) EC\(_4\)/LiBF\(_4\).

Table 4.2 EC\(_3\)/Li\(^{+}\) Raman band frequency (cm\(^{-1}\)) and activities (\(S\)) from calculations using B3LYP/6-31+G(d,p) with PCM(EC) (average weighted by Raman activities). Bold values were used for the corrected solvation numbers in Table 4.3

<table>
<thead>
<tr>
<th></th>
<th>freq(_1)</th>
<th>freq(_2)</th>
<th>freq(_3)</th>
<th>freq(_4)</th>
<th>freq(_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC(_1)/Li(^{+}) freq</td>
<td>712</td>
<td>738</td>
<td>882</td>
<td>911</td>
<td>1790</td>
</tr>
<tr>
<td>EC(_1)/Li(^{+}) freq shift (vs. EC(_1))</td>
<td>8</td>
<td>24</td>
<td>-3</td>
<td>9</td>
<td>-18</td>
</tr>
<tr>
<td>EC(_3)/Li(^{+}) freq (avg)</td>
<td>713</td>
<td>730</td>
<td>885</td>
<td>911</td>
<td>1788</td>
</tr>
<tr>
<td>EC(_3)/Li(^{+}) shift (EC-1)</td>
<td>8</td>
<td>14</td>
<td>-2</td>
<td>9</td>
<td>-26</td>
</tr>
<tr>
<td>EC(_3)/Li(^{+}) shift (EC-2)</td>
<td>9</td>
<td>19</td>
<td>0</td>
<td>10</td>
<td>-25</td>
</tr>
<tr>
<td>EC(_3)/Li(^{+}) shift (EC-3)</td>
<td>10</td>
<td>21</td>
<td>1</td>
<td>10</td>
<td>-17</td>
</tr>
<tr>
<td>EC(_3)/Li(^{+}) shift (avg.) (vs. EC(_1))</td>
<td>9</td>
<td>17</td>
<td>0</td>
<td>9</td>
<td>-20</td>
</tr>
<tr>
<td>(S(\text{EC}_3/\text{Li}^+)))</td>
<td>4.95</td>
<td>11.08</td>
<td>2.44</td>
<td>35.40</td>
<td>23.63</td>
</tr>
<tr>
<td>(S(\text{EC}_3/\text{Li}^+)/S(\text{EC}_1)))</td>
<td>\textbf{1.09}</td>
<td>extbf{0.88}</td>
<td>extbf{0.96}</td>
<td>\textbf{1.06}</td>
<td>\textbf{0.75}</td>
</tr>
</tbody>
</table>
The Raman spectra of (EC)$_n$-LiX mixtures were deconvoluted by accounting for each peak calculated from the DFT analysis of the EC$_3$/Li$^+$ complex. A representative Raman band deconvolution of an (EC)$_n$-LiClO$_4$ ($n = 10$) mixture is shown in Figure 5. The blue peaks represent the uncomplexed EC vibrational bands (as calculated from the DFT analysis of EC$_1$). Upon coordination to Li$^+$ cations, these bands shift to a higher frequency, which is modeled as the red peaks. It is noteworthy that the shoulder at 697 cm$^{-1}$ (ca 704 cm$^{-1}$) is calculated to shift ~8.5 cm$^{-1}$, which overlaps extensively with the ring breathing mode at 717 cm$^{-1}$ (ca 713 cm$^{-1}$). Fitting this band, however, was fairly easy as the 697 cm$^{-1}$ band appeared as a secondary shoulder that was necessary to properly fit the spectra. The ratio of the uncoordinated and coordinated bands was used to calculate the average solvation numbers via the following formula:

$$\frac{A_C}{A_C + A_U} = N \frac{c_{LiX}}{c_S}$$

where $A_C$ and $A_U$ are the integrated area intensities of the vibrational bands for Li$^+$ coordinated (729 cm$^{-1}$ or 905 cm$^{-1}$) and uncoordinated (717 cm$^{-1}$ or 894 cm$^{-1}$) solvent, respectively, $c_{LiX}$ and $c_S$ are the concentration of the lithium salt and solvent, respectively, and $N$ is the average solvation number.
Figure 4.5 (a) Deconvoluted Raman spectra of the (EC)<sub>n</sub>-LiClO<sub>4</sub> (n = 10) mixture displaying uncomplexed (blue) and Li<sup>+</sup> complexed (red) vibrational bands and (b) Raman band analysis of (EC)<sub>n</sub>-LiX (n = 10 and X = PF<sub>6</sub><sup>-</sup>, TFSI<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>) mixtures displaying solvation trends observed due to varying lithium salt (i.e., Li<sup>+</sup>...anion) ionic association strengths (note that the additional bands are due to anion vibrational bands).

The uncorrected solvation numbers in Table 4.3 for (EC)<sub>n</sub>-LiX mixtures calculated from both solvent bands display significant discrepancies. The difference in the solvation numbers obtained from the 729 cm<sup>-1</sup> and 905 cm<sup>-1</sup> bands suggest that the analysis performed in other reports is insufficient for the accurate evaluation of Li<sup>+</sup> cation solvation by EC. By including the second smaller band for the 729 cm<sup>-1</sup> band analysis and scaling the bands by the activity...
ratios listed in Table 4.2, however, the calculated solvation numbers converge nearly perfectly for the mixtures tested. In addition, the anion association strengths have previously been shown to increase in the order [47-49]:

\[
\text{CF}_3\text{CO}_2^- > \text{CF}_3\text{SO}_3^- > \text{BF}_4^- > \text{ClO}_4^- > \text{TFSI}^- > \text{PF}_6^- 
\]

The solvation numbers obtained are in excellent agreement with this association trend (increasing solvation results in less ionic association). Additionally, the BOB\(^-\) and DFOB\(^-\) anion association strengths were determined and the following trend was obtained:

\[
\text{CF}_3\text{CO}_2^- > \text{CF}_3\text{SO}_3^- > \text{DFOB}^- \approx \text{BF}_4^- > \text{ClO}_4^- > \text{BOB}^- > \text{TFSI}^- > \text{PF}_6^- 
\]

This trend is evident by normalizing the intensity of the uncoordinated bands of the (EC)\(_n\)-LiX mixtures (Figure 4.5). The Raman band deconvolution for all of the (EC)\(_n\)-LiX mixtures is provided in Appendix C.

| Table 4.3 Uncorrected and corrected solvation numbers (N) for (EC)\(_n\)-LiX mixtures (n = 20, 10 and X = PF\(_6\)^-, TFSI\(^-\), ClO\(_4\)^-, BF\(_4\)^-, LiCF\(_3\)SO\(_3\)^- and LiCF\(_3\)CO\(_2\)^-) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| EC/Li           | 728 cm\(^{-1}\) | 905 cm\(^{-1}\) | difference      |
| LiPF\(_6\)      | 3.75 3.62       | 4.36 4.03       | 0.62 0.41       |
| LiTFSI          | 3.30 3.33       | 3.84 3.76       | 0.55 0.43       |
| LiBOB           | --   --          | 3.61 3.51       | --   --          |
| LiClO\(_4\)     | 3.01 3.03       | 3.50 3.41       | 0.49 0.37       |
| LiBF\(_4\)      | 2.73 2.75       | 3.19 3.14       | 0.46 0.38       |
| LiDFOB          | --   --          | 3.17 3.13       | --   --          |
| LiCF\(_3\)SO\(_3\) | 2.31 2.06   | 2.73 2.37       | 0.41 0.32       |
| LiCF\(_3\)CO\(_2\) | 1.16 1.15 | 1.35 1.32       | 0.19 0.17       |
| **corrected**   |                 |                 |                 |
| LiPF\(_6\)      | 4.15 3.92       | 4.17 3.89       | 0.02 0.03       |
| LiTFSI          | 3.66 3.62       | 3.66 3.62       | 0.00 0.00       |
| LiBOB           | --   --          | 3.44 3.38       | --   --          |
| LiClO\(_4\)     | 3.35 3.31       | 3.33 3.28       | 0.02 0.03       |
| LiBF\(_4\)      | 3.05 3.01       | 3.04 3.01       | 0.01 0.00       |
| LiDFOB          | --   --          | 3.02 3.01       | --   --          |
| LiCF\(_3\)SO\(_3\) | 2.59 2.27   | 2.59 2.27       | 0.01 0.01       |
| LiCF\(_3\)CO\(_2\) | 1.30 1.28 | 1.28 1.25       | 0.03 0.03       |
4.2.2. (PC)\textsubscript{n}-LiX Mixtures

Due to its similarity in structure to EC, PC also contains a vibrational band at 712 cm\textsuperscript{-1} which is commonly attributed to a symmetric ring deformation mode [6,14,18,50]. Analysis of the experimental and calculated data indicates that no other bands are significantly perturbed by the addition of a lithium salt in a manner suitable to accurately deconvolute the peaks; thus, only the 712 cm\textsuperscript{-1} band was analyzed. PC contains a chiral center and commercial sources of the solvent are actually racemic mixtures of its isomers. A DSC analysis of the isomeric mixtures suggested that such mixtures contain a eutectic point near or at the equimolar composition with a eutectic melt temperature well below the $T_m$ of each isomer (Figure 4.6). Preliminary calculations yielded a Raman spectrum that was in disagreement with the experimentally obtained results. These conflicting spectra were originally thought to be attributed to the fact that only the $(S)$-PC conformer was used in the calculations. Experimental analysis of the $(S)$-PC isomer in the liquid phase (-20$^\circ$C to 100$^\circ$C), however, yielded a spectrum identical to that for the $(R)$-PC isomer and the racemic PC. Analysis of the crystalline $(S)$-PC and $(R)$-PC isomers at -80$^\circ$C, in contrast, yielded spectra that differ from the crystalline commercial PC (Figure 4.7). The variations in these spectra at low temperature indicate that different vibrations are obtained depending upon the conformations of the individual isomers in the solid-state.
Figure 4.6 DSC heating traces (5°C min⁻¹) of (1-\(x\)) (\(S\))-PC-(\(x\)) (\(R\))-PC isomer mixtures (\(x\) is mol fraction), as well as commercial PC (a racemic mixture of the isomers).

Figure 4.7 Comparison of the Raman spectra of the liquid (top, 60°C) and crystalline (bottom, -80°C) (\(S\))-PC and (\(R\))-PC isomers, as well as commercial PC (a racemic mixture of the isomers).
Quantum chemical calculations were therefore performed to further investigate the relative conformational energies of PC and their contribution to the overall Raman spectra. Møller–Plesset perturbation theory (MP2), composite G4MP2 and B3LYP functionals were used in conjunction with PCM(PC). Table 4.4 summarizes the relationship between the O–C–C–O dihedral angle and relative conformational energies for the varying PC conformers. The most accurate geometry is expected from the MP2/Tz calculations. Two low energy conformers were identified, as shown in Figure 4.8, for the (S)-PC isomer. The cis$^+$ conformer has an O–C–C–O dihedral angle of 24.7°, while the cis$^-$ conformer has an angle of -25.0° (Table 4.4). The B3LYP functional and G4MP2 composite level calculation, which also uses a DFT-based geometry, predicted smaller magnitudes for the dihedral angle (Table 4.4). The G4MP2 and MP2/Tz levels are expected to provide the best estimate of the conformational energy difference between the cis$^+$ and cis$^-$ conformers. At 0 K, the cis$^+$ conformer is calculated to be more stable by 0.10-0.23 kcal mol$^{-1}$, while the cis$^-$ conformer becomes more stable (by 0.06 kcal mol$^{-1}$) when entropic vibrational contributions are included in the calculations using a temperature of 298 K. Applying the vibrational energy and entropy correction from B3LYP/Tz calculations ($\Delta G - \Delta E$) to the MP2/Tz energy results gives a $\Delta G^{cis^-} - \Delta G^{cis^+}$ value of -0.26 kcal mol$^{-1}$, indicating that at room temperature one would expect ~40% of the cis$^+$ and ~60% of the cis$^-$ conformers to be present in the liquid.
Table 4.4 PC calculated relative conformational energies (∆E) and free energies (∆G at 298 K) for the cis+ and cis− conformers with the indicated O-C-C-O dihedral angle (ϕ)

<table>
<thead>
<tr>
<th>ϕO-C-C-O (°)</th>
<th>∆E (kcal mol⁻¹)</th>
<th>∆G (kcal mol⁻¹)</th>
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<td>19.3</td>
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<td>0</td>
</tr>
<tr>
<td>-12.9</td>
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<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>17.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-13.2</td>
<td>0.23</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

Figure 4.8 Low energy cis⁺ and cis⁻ conformers of the (S)-PC isomer.

The calculated Raman spectra were found to be quite different for the cis⁺ and cis⁻ conformers in the region of ~600-760 cm⁻¹, as shown in Figure 4.9. The ca 645 cm⁻¹ peak present for the cis⁺ conformer completely disappears for the cis⁻ conformer, while a new peak appears at ca 740 cm⁻¹ for the cis⁻ conformer. Clearly, the Raman spectra of neither conformer corresponds well to the experimental data, while a combination of the cis⁺ and cis⁻ spectra describes the experimentally observed peak positions adequately. Specifically, a spectral mixture of 25% cis⁺ and 75% cis⁻ fits the relative magnitudes of the experimentally observable peaks at ~645 cm⁻¹ and 712 cm⁻¹ quite well. Calculations on the cluster containing one cis⁺ and three cis⁻ conformers yielded a Raman spectrum with a ratio of ~0.25 between
the 640 cm\(^{-1}\) and 700 cm\(^{-1}\) bands. This ratio is in good agreement with the intensity values obtained experimentally. Additionally, the estimated population of cis\(^{+}\) and cis\(^{-}\) conformers agrees reasonably well with the composition of 40% cis\(^{+}\) and 60% of cis\(^{-}\) obtained from the above discussed estimation for \(\Delta E_{cis^{+}-cis^{-}}(MP2/Tz) + (\Delta G_{cis^{+}-cis^{-}}(B3LYP/Tz) - \Delta E_{cis^{+}-cis^{-}}(B3LYP/Tz))\), further supporting the picture that at room temperature the isomeric PC molecules consist of a mixture of cis\(^{+}\) and cis\(^{-}\) conformers.

![Raman Spectrum](image)

**Figure 4.9** Raman spectrum for the cis\(^{+}\) (top) and cis\(^{-}\) (bottom) conformers of PC from B3LYP/Tz calculations with PCM(PC).
Similar dihedral conformational variability is expected for EC. Various researchers, however, have found that EC tends to adopt the cis\(^{+}\) conformation with a dihedral angle between 24.8\(^{\circ}\)-29.5\(^{\circ}\) [22,51,52]. Other experimental results suggest the ring inversion of EC must overcome a barrier of 0.67 kcal mol\(^{-1}\) [53]. Based upon the present calculations of the energy requirements for PC to undergo ring inversion, almost all of the conformers with an O–C–C–O dihedral angle between -25\(^{\circ}\) and 25\(^{\circ}\) require less than 0.5 kcal mol\(^{-1}\) to undergo conformational transformations (Figure 4.10). Due to the low barrier between the cis\(^{+}\) and cis\(^{-}\) conformers (as compared to \(k_B T\) which is 0.6 kcal mol\(^{-1}\) at room temperature), a fast exchange is expected at room temperature. The EC Raman structure is much less complex than for PC, as there are vibrational contributions principally from a single stable conformer rather than multiple conformers (the cis\(^{+}\) and cis\(^{-}\) conformers of EC are equivalent). Furthermore, an analysis (B3LYP/Tz level with PCM(PC)) of PC as a function of the O–C–C–O dihedral angle suggests that the frequency of the \(\sim 650\) cm\(^{-1}\) vibration is highly dependent upon the dihedral angle of the conformer. As the dihedral angle changes between the stable conformations (between -25\(^{\circ}\) and 25\(^{\circ}\)), the frequency of the vibrational band changes markedly from \(ca\) 720 cm\(^{-1}\) to 630 cm\(^{-1}\), respectively (Figure 4.10). Although the PC spectra is quite complex due to the existence of its two isomers and the varying conformations for each, an analysis of PC\(_4\) (one cis\(^{+}\), three cis\(^{-}\)) does result in reasonably good agreement with experimental data with the exception of a small peak \(ca\) 735 cm\(^{-1}\) (see Appendix C).
As noted above, the experimental deconvolution of the spectrum of bulk PC is quite difficult due to the complexity of the Raman signature from the isomers and conformers, and the varying vibrational frequencies of each. Thus, multiple peaks are necessary to properly fit the uncoordinated PC bands. Upon Li⁺ complexation, a new band is observed at ~722 cm⁻¹, but no major perturbation of the 850 cm⁻¹ band occurs (Figure 4.11). Solvation numbers were calculated for all the (PC)ₙ-LiX mixtures. These solvation numbers, although in good agreement with reported literature values,⁴ were implausibly low. For example, the solvation
number calculated for the \((\text{PC})_n\)-LiBF$_4$ \((n = 10)\) mixture was ~1.35, which is consistent with the literature values of 1.2-1.5 for similar concentrations [4]. When the dielectric constant \((\varepsilon)\) and donor number \((\text{DN})\) of PC (64.95 and 16.4, respectively) are compared to those for EC (90.36 and 15.1, respectively), such a dramatic difference in solvation behavior between the two solvents is unreasonable [54]. Similarly, the \((\text{EC})_n\)-LiPF$_6$ \((n = 20)\) data analysis provides a solvation number of 4.15-4.17, as expected since LiPF$_6$ is a highly dissociated salt. The data for a \((\text{PC})_n\)-LiPF$_6$ \((n = 20)\) mixture, in contrast, provide a solvation number of ~1.67. A solvation number this low implies that the Li$^+$ cation (in order to maintain a 4- or 5-fold coordination) must be highly coordinated by PF$_6^-$ anions. With the dissociated PF$_6^-$ anion, it is unrealistic to expect a high population of CIP and aggregated (AGG) solvates in dilute concentrations (i.e., the \(n = 20\) mixture corresponds to ~0.6 mol L$^{-1}$). Thus, it is unlikely that the experimentally calculated solvation numbers for the \((\text{PC})_n\)-LiX mixtures are representative of the actual solution structure. These numbers also contradicts MD simulation predictions of roughly similar Li$^+$ coordination in EC:PC/LiPF$_6$ mixture with a slight preference for Li$^+$-PC coordination and the preference for PC$_n$/Li$^+$ over EC$_n$/Li$^+$ coordination in the gas-phase [29].
Figure 4.11 Deconvoluted Raman spectra of (PC)$_n$-LiClO$_4$ (n = 10) displaying uncomplexed (blue) and Li$^+$ complexed (red) vibrational bands.

Quantum chemical calculations can provide additional insight into the problems associated with extracting the Li$^+$ cation coordination numbers in PC mixtures. Shifts of the PC bands upon Li$^+$ cation complexation are shown in Table 4.5. According to the calculations, the ca 704 cm$^{-1}$ band of the cis$^-$ conformer is shifted to ca 720 cm$^{-1}$ upon Li$^+$ cation complexation. Therefore, the PC(cis$^-$)$_1$/Li$^+$ complex is expected to overlap with the cis$^+$ band observed at ca 715 cm$^{-1}$. Due to this overlap, the only observable band would be the upshifted PC(cis$^+$)$_1$/Li$^+$ band at ca 736 cm$^{-1}$, which agrees with the experimentally deconvoluted bands in Figure 4.11. Based upon the calculations for neat PC, the population of the PC(cis$^+$) conformer is expected to be only 25-40% of the total conformations; thus the calculated coordination numbers for the (PC)$_n$-LiX mixtures may only be 25-40% of the actual value. This conclusion assumes that the populations of cis$^-$ and cis$^+$ conformers bound to the Li$^+$ cation is similar to the populations of the uncomplexed cis$^-$ and cis$^+$ conformers. Conformational energies for PC and PC/Li$^+$, shown in Figure 4.10, indicate that there is no
appreciable change in populations as the PC molecules coordinate a Li\(^+\) cation. Due to the minor perturbation of the PC(cis\(^+\))\(_1\)/Li\(^+\) complex band (723 cm\(^{-1}\)), and the expected overlap of the PC(cis\(^-\))\(_1\)/Li\(^+\) complex band with the uncomplexed PC(cis\(^+\)) solvent band, analysis of the (PC)\(_n\)-LiX mixtures is extremely difficult and inherently full of error. Thus, it is likely not possible to accurately measure the solvation numbers of (PC)\(_n\)-LiX mixtures from a Raman vibrational analysis of the vibrational band of PC.

Table 4.5  Shifts of the PC Raman frequencies and activities (S) upon Li\(^+\) cation complexation from calculations using B3LYP/Tz calculations with PCM(PC)

<table>
<thead>
<tr>
<th></th>
<th>PC freq(_1)</th>
<th>PC freq(_2)</th>
<th>PC freq(_3)</th>
<th>shift(_1)</th>
<th>shift(_2)</th>
<th>shift(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis(^+)</td>
<td>643 653</td>
<td>715 736</td>
<td>856 856</td>
<td>10 21</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>cis(^-)</td>
<td>704 720</td>
<td>733 741</td>
<td>841 840</td>
<td>16 9</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>cis(^+)</td>
<td>S(freq(_1))</td>
<td>S(freq(_2))</td>
<td>S(freq(_3))</td>
<td>S(PC/Li(^+))/S(PC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis(^-)</td>
<td>9.8 8.1</td>
<td>11.7 10.2</td>
<td>21.7 19.9</td>
<td>0.82 0.87 0.92</td>
<td></td>
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</tr>
</tbody>
</table>

4.3. Conclusions

Understanding the solvation characteristics of electrolyte mixtures is crucial for correlating the electrolyte properties with solvent/ion structures and electrolyte formulations. Although numerous studies have been reported for the determination of the average solvation numbers of Li\(^+\) cations coordinated by cyclic carbonate solvents, these studies have, in general, not taken into account the scaling of the Raman intensities for the coordinated solvent bands or the possibility of overlapping Raman bands. Thus, considerable inconsistencies have been found for the solvation number values reported in the literature from the evaluation of different EC solvent bands. Using a more rigorous analysis for the
reported data in the present study, however, results in solvation numbers that are in exceptional agreement with one another. The solvation trends determined from this analysis of EC are also in excellent agreement with the known ionic association trends of varying anions. These results, when combined with the analysis of the BOB\(^{-}\) and DFOB\(^{-}\) anions (previously unreported), suggest the following ionic association trends:

\[ \text{CF}_3\text{CO}_2^- > \text{CF}_3\text{SO}_3^- > \text{DFOB}^- \approx \text{BF}_4^- > \text{ClO}_4^- > \text{BOB}^- > \text{TFSI}^- > \text{PF}_6^- \]

In contrast to EC, PC is difficult to analyze both experimentally and computationally. Commercially available PC is a racemic mixture of \((S)-\) and \((R)-\)PC isomers. Each of these isomers, however, exists as multiple conformers (cis\(^{+}\) and cis\(^{-}\)) due to an energetically favorable ring inversion and these conformers result in notable differences in the Raman spectral signature. This confluence of spectral features makes the deconvolution of the bands daunting and inherently full of error. Nevertheless, a combined quantum chemistry and experimental analysis indicates a slight preference for the PC(cis\(^{-}\)) conformer over the PC(cis\(^{+}\)) conformer at room temperature. Thus, using the bands and scaling factors reported, the average solvation numbers of \((\text{EC})_n\)-LiX mixtures can be accurately determined from a Raman spectroscopic analysis, whereas those for \((\text{PC})_n\)-LiX mixtures cannot.
4.4. References


CHAPTER 5: Ion Solvation and Physicochemical Properties in Cyclic Carbonates and Lactones with LiBF₄, LiDFOB and LiBOB

Abstract

Carbonate solvents are almost exclusively used in commercial Li-ion battery electrolytes due largely to their favorable electrode passivation properties and the sufficiently high conductivity of the electrolytes formed when the solvents are mixed with a lithium salt. When higher potential anodes are used, however, the passivation requirements of the solvent are reduced or eliminated due to decreased electrolyte decomposition. Thus, solvents that provide electrolytes with an even higher conductivity may be desirable (i.e., lactone-based solvents) that otherwise are unusable due to the lack of SEI formation. This study examines the ion solvation and physicochemical properties of carbonate and lactone-based solvents with the three salts: LiBF₄, LiDFOB and LiBOB. Mixtures with LiBOB have the highest solvation numbers and thus LiBOB is the most dissociated salt (in dilute solutions), followed by LiDFOB and LiBF₄, respectively. Surprisingly, however, despite the lower solvation numbers of the LiDFOB mixtures (relative to those with LiBOB), the LiDFOB mixtures have a significantly higher ionic and molar conductivity. Surprising results were also obtained from the comparison of electrolytes with different solvents. For example, the (GBL)ₙ-LiDFOB (n = 10) electrolyte has an ionic conductivity of ~18 mS cm⁻¹ compared to ~12 mS cm⁻¹ for (EC)ₙ-LiDFOB (n = 10) at 60°C. Although solvation data from the Raman
vibrational modes of the solvent cannot be directly compared, Raman analysis of the BF$_4^-$ anion suggests that GBL is a superior solvent to EC, despite having a lower dielectric constant. Of the lithium salts tested, LiDFOB is most attractive as an electrolyte component due largely to the formation of amorphous samples when mixed with the carbonate and lactone solvents tested. Such mixtures also yield higher solvation numbers than mixtures with LiBF$_4$, sufficiently low viscosity, and exceptional ionic and molar conductivity values.

5.1. Introduction

Secondary lithium ion batteries have matured significantly since their initial utilization in small consumer electronics in the 1990’s. Attempts to understand the molecular-level interactions that exist in state-of-the-art electrolytes, however, have remained largely underdeveloped. Molecular interactions within an electrolyte directly govern the physical and electrochemical properties (i.e. viscosity, volatility, ionic conductivity, etc.) of the mixture. Numerous reports have investigated common lithium salts (i.e., LiPF$_6$, LiBF$_4$, LiClO$_4$, etc.) in single solvent or multiple solvent systems [1–16]. The various techniques utilized in these studies, however, make it difficult to compare the ionic association strength of the anions, solvate species present and their distribution, and the average solvation numbers ($N$). Furthermore, significant challenges are associated with studying the liquid electrolytes due to the dynamic coordination that exists. By studying the solid-liquid phase behavior of electrolyte mixtures using phase diagrams, solvate crystal structures (to determine the ion coordination) and solvent/ionic coordination information obtained from the Raman
characterization of single crystal structures, it is possible to obtain significant insight regarding the liquid structure of the electrolytes mixtures.

In a previous study, it was demonstrated that the ionic conductivity is strongly dependent on the ionic association strength of the anions in a given lithium salt [17]. This study focused on the investigation of various anions with a single solvent (acetonitrile) and the influence that this solvent has on the ion pair/aggregate formation tendency of the anions. Thus, the complementary in-depth study of lithium salts performed here with various structurally similar solvents provides a robust understanding of how competitive solvent/anion coordination can influence the physical/electrochemical properties of electrolytes.

In the present study, the cyclic carbonates EC and PC and the cyclic esters GBL and GVL have been studied with LiBF$_4$, LiDFOB and LiBOB. To date, the scientific literature provides no clear indication as to how small structural changes of the solvent and/or lithium salt can affect the physical/electrochemical properties of bulk electrolytes. The present study utilizes a systematic approach to investigate how such structural variations can influence the molecular-level interactions present in electrolyte solutions, which ultimately govern the physicochemical properties of electrolytes.

5.2. Thermal Phase Behavior

5.2.1. (EC)$_n$-LiX Phase Behavior

(EC)$_n$-LiBF$_4$: Neat EC has a $T_m$ of ~38°C (Figure 5.1). (EC)$_n$-LiBF$_4$ mixtures form two crystalline phases (i.e., 2/1 and 1/1 (EC/Li) crystalline solvates). A eutectic exists between the neat EC and the 2/1 crystalline phase, with the eutectic point present at approximately $n =$
6. A detailed explanation of the \((EC)_n\)-LiBF\(_4\) phase diagram is provided in Appendix A. The structure of the AGG-I 2/1 solvate (i.e., \((EC)_2\):LiBF\(_4\)) was determined by single crystal X-ray diffraction and is reported in Figure 5.2. In this solvate structure, the Li\(^+\) cations are coordinated by two carbonyl oxygen atoms from two EC solvent molecules and two fluorine atoms from two BF\(_4^-\) anions. Each BF\(_4^-\) anion is coordinated to two Li\(^+\) cations through two different fluorine atoms (i.e., AGG-I). The structure is held together by Li\(^+\) cations that form a polymeric network. No single crystals were obtained for the 1/1 solvate so the structure remains unknown. It is probable that the 1/1 solvate has a higher degree of aggregation (i.e., AGG-II) than the 2/1 solvate and may, perhaps, be similar to the (GBL):LiBF\(_4\) solvate (see Section 5.2.2).

\((EC)_n\)-LiDFOB: The phase behavior of the \((EC)_n\)-LiDFOB mixtures is markedly different from that for the \((EC)_n\)-LiBF\(_4\) mixtures, with only a portion of the pure EC crystallizing in the dilute region (Figure 5.1). Concentrated mixtures up to 2/1 were not able to be crystalized under the testing conditions. This is highly advantageous as it is necessary for battery electrolytes to remain liquid over the entire operating temperature range of the battery.

\((EC)_n\)-LiBOB: Similar to the mixtures with LiBF\(_4\), both pure EC and a solvate crystallizes from the dilute \((EC)_n\)-LiBOB mixtures. The data for the \((EC)_n\)-LiBOB mixtures, however, is more difficult to interpret than for those with LiBF\(_4\). The phase diagram suggests that there are multiple phases that can form, but their formation is strongly dependent upon nucleation kinetics. Analysis of the same sample in some cases yielded two very different thermograms. The dilute mixtures were expected to form a \((EC)_4\):LiBOB crystalline solvate, as reported by Zavalij \textit{et al.} [18]. Isolated single crystals, however, formed a \((EC)_{3/2}\)-LiBOB solvate instead,
even in dilute mixtures. Thus, (EC)$_n$-LiBOB mixtures are able to form either the (EC)$_4$:LiBOB or the (EC)$_{3/2}$:LiBOB crystalline solvate, depending upon which phase nucleates. The ion coordination within the (EC)$_4$:LiBOB and (EC)$_{3/2}$:LiBOB crystalline solvates can be seen in Figure 5.2. Only a small portion of the (EC)$_n$-LiBOB phase diagram was examined due to the limited solubility of this salt in EC.

![Image](image_url)

**Figure 5.1** Phase diagrams of (1-x) EC-(x) LiX mixtures ($T_g$ indicated with an x symbol).

![Image](image_url)

**Figure 5.2** Ion coordination in the (a) (EC)$_2$:LiBF$_4$, (b) (EC)$_4$:LiBOB and (c) (EC)$_{3/2}$:LiBOB crystalline solvates.
5.2.2. (PC)$_n$-LiX Phase Behavior

*(PC)$_n$-LiBF$_4$:* Neat PC was difficult to crystallize (requiring multiple thermal cycles to fully crystallize), but yields a $T_m$ of $-54^\circ$C. LiBF$_4$ dissolved easily in PC, forming concentrated solutions up to $n = 1.5$. No crystalline solvates formed in these mixtures. Interestingly, the very dilute LiBF$_4$ mixture ($n = 19$) resulted in no crystallization of the neat PC solvent (Figure 5.3). Thus, completely amorphous mixtures were obtained across the entire concentration range tested. To determine if isomeric variations within commercial PC may be preventing crystallization, the individual enantiomers (i.e., (S)-PC and (R)-PC) were used to make samples with a concentration of $\sim n = 3.8$ (Appendix D). Upon testing these mixtures, no crystallization was observed, thus suggesting that the isomeric variation in the commercial PC solvent does not directly result in the amorphous behavior.

*(PC)$_n$-LiDFOB:* Mixtures of (PC)$_n$-LiDFOB behave similarly to both (PC)$_n$-LiBF$_4$ and (PC)$_n$-LiBOB. Upon sitting at room temperature for over a month, however, the concentrated ($n = 3$) solution of (PC)$_n$-LiDFOB did form single crystals. The crystals were determined to be an 1/1 crystalline solvate (i.e., (PC)$_1$:LiDFOB) [19]. In this complex, the Li$^+$ cations are coordinated by two carbonyl oxygen atoms from two different DFOB$^-$ anions, one carbonyl oxygen atom from a single PC solvent molecule and two fluorine atoms from two different DFOB$^-$ anions. Each DFOB$^-$ anion is coordinated to four Li$^+$ cations through two different carbonyl oxygen atoms and two different fluorine atoms (i.e., AGG-III). The ion coordination within the (PC)$_1$:LiDFOB complex can be seen in Figure 5.4.
(PC)$_n$-LiBOB: LiBOB was much less soluble in mixtures with PC, with a maximum concentration of $n = 10$. Similar to both the (PC)$_n$-LiBF$_4$ and (PC)$_n$-LiDFOB mixtures, neat PC was unable to crystallize in the dilute LiBOB mixtures.

![Phase diagrams of (1-x) PC-(x) LiX mixtures ($T_g$ indicated with an x symbol).](image)

**Figure 5.3** Phase diagrams of (1-x) PC-(x) LiX mixtures ($T_g$ indicated with an x symbol).

![Ion coordination in the (PC)$_1$:LiDFOB crystalline solvate.](image)

**Figure 5.4** Ion coordination in the (PC)$_1$:LiDFOB crystalline solvate.

5.2.3. (GBL)$_n$-LiX Phase Behavior

(GBL)$_n$-LiBF$_4$: Neat GBL has a $T_m$ of -42°C. (GBL)$_n$-LiBF$_4$ mixtures, like (EC)$_n$-LiBF$_4$, form two crystalline phases, a 2/1 and 1/1 (GBL/Li) solvate. For dilute concentrations, the phase diagram indicates that much of the excess (uncoordinated) GBL crystallizes, leaving a
concentrated amorphous GBL-LiBF₄ phase that does not crystallize (Figure 5.5). The crystallinity gap in the (GBL)ₙ-LiBF₄ mixtures (2.3 < n < 9.0) likely consists of both coordinated and uncoordinated GBL molecules. The uncoordinated GBL molecules, however, are unable to crystallize as neat solvent due to weak interactions with the solvates in the amorphous phase. The structure of the 2/1 solvate could not be solved due to an apparent solid-solid phase transition at lower temperatures (−59°C) and complications associated with analyzing a sample with a low T_m. The structure of the AGG-II 1/1 crystalline solvate (i.e., (GBL)_1:LiBF₄), however, was determined by single crystal X-ray diffraction (Figure 5.6). In this solvate structure, the Li⁺ cations are coordinated by a carbonyl oxygen atom from a single GBL solvent molecule and three fluorine atoms from three different BF₄⁻ anions. Each BF₄⁻ anion is coordinated to three Li⁺ cations through three different fluorine atoms (i.e., AGG-II). The crystal structure is held together by Li⁺ cations thus forming a polymeric network.

(GBL)_ₙ-LiDFOB & (GBL)_ₙ-LiBOB: GBL mixtures with LiDFOB and LiBOB behave similarly. The (GBL)_ₙ-LiDFOB mixtures crystalized only neat GBL in the dilute region (up to n = 8), while concentrations greater than n = 8 remained amorphous. The (GBL)_ₙ-LiBOB mixtures were also able to crystallize only neat GBL in the dilute region. The amorphous region for the (GBL)_ₙ-LiBOB mixtures, however, begins at concentrations greater than n = 15. (GBL)_ₙ-LiBOB mixtures with concentrations greater than n = 8 were not able to be tested due to the limited solubility of the salt.
Figure 5.5 Phase diagrams of (1-x) GBL-(x) LiX mixtures ($T_g$ indicated with an x symbol).

Figure 5.6 Ion coordination in the (GBL)$_1$:LiBF$_4$ crystalline solvate.

5.2.4. (GVL)$_n$-LiX Phase Behavior

(GVL)$_n$-LiBF$_4$: Neat GVL, despite being a racemic mixture of enantiomers (similar to PC), was readily crystallized and had a $T_m$ of -31°C (Figure 5.7). The (GVL)$_n$-LiBF$_4$ mixtures formed no crystalline solvates across the entire concentration range tested. Unlike PC, uncoordinated (neat) GVL is able to be crystallized in the dilute region. DSC data indicates that the composition of the amorphous phase is (GVL)$_n$-LiBF$_4$ ($n < 4$). It is presumed, as is the case with the (PC)$_n$-LiBF$_4$ mixtures, that the uncoordinated GVL is weakly interacting with the solvated ions and thus is not crystallized as bulk solvent at concentrations higher than (GVL)$_n$-LiBF$_4$ ($n < 4$). There remains the possibility that isomeric
variations in the solvent may be preventing crystallization of the solvates; however, this was not tested due to the unavailability of enantiopure GVL.

(GVL)\textsubscript{n}-LiDFOB & (GVL)\textsubscript{n}-LiBOB: GVL mixtures with LiDFOB and LiBOB have similar phase behavior. Neat GVL crystallizes from the (GVL)\textsubscript{n}-LiDFOB mixtures in the dilute region (up to n = 8), while concentrations greater than n = 8 are amorphous (similar to mixtures with GBL). The (GVL)\textsubscript{n}-LiBOB mixtures are also able to crystallize neat GVL in the dilute region. The amorphous region for (GVL)\textsubscript{n}-LiBOB mixtures begins at concentrations greater than n = 9. (GVL)\textsubscript{n}-LiBOB mixtures at concentrations greater than n = 8 were not able to be tested due to the limited solubility of the salt.

Figure 5.7 Phase diagrams of (1-x) GVL-(x) LiX mixtures ($T_g$ indicated with an x symbol).

5.3. Raman Band Analysis

5.3.1. (EC)\textsubscript{n}-LiX Mixtures

Vibrational dynamics investigations have been performed on EC in which the ring breathing and ring bending Raman vibrational modes have been reported to shift upon coordination to the Li\textsuperscript{+} cation [12,13,20–24]. The bands at 695 cm\textsuperscript{-1} (in-plane ring distortion,
shoulder), 717 cm\(^{-1}\) (ring bending, very strong), and 894 cm\(^{-1}\) (ring breathing, very strong) were deconvoluted. Upon addition of a lithium salt, the 695 cm\(^{-1}\), 717 cm\(^{-1}\) and 894 cm\(^{-1}\) bands upshift \(\sim 10\) cm\(^{-1}\) to yield perturbed solvent bands as a consequence of coordination to the Li\(^{+}\) cation. The proper band fitting of Raman spectra for (EC)\(_n\)-LiX mixtures has been previously discussed in Chapter 4. The concentration dependent Raman spectra of the (EC)\(_n\)-LiX mixtures are displayed in Figure 5.8. The fraction of coordinated solvent molecules was calculated for each plot and the average solvation numbers \((N)\) were calculated, as will be further discussed in Section 5.3.5.
Figure 5.8 Raman spectra of EC ring bending (left) and ring breathing (right) modes as a function of LiX concentration.
5.3.2. (PC)$_n$-LiX Mixtures

Neat PC has a vibrational band at 712 cm$^{-1}$ which is commonly attributed to a symmetric ring deformation mode [15,21,25,26]. No other bands were perturbed by the addition of a lithium salt in a manner suitable to accurately deconvolute the peaks and thus only the 712 cm$^{-1}$ band was analyzed. The difficulties associated with deconvoluting (PC)$_n$-LiX mixtures, however, has been thoroughly discussed in Chapter 4. Nevertheless, the fraction of coordinated solvent molecules and $N$ of (PC)$_n$-LiX mixtures has been calculated based upon an approximate fit of the data. All peaks in close proximity to the 712 cm$^{-1}$ band were deconvoluted to ensure only the areas associated with the perturbed/unperturbed solvent peaks were used. The bands at 635 cm$^{-1}$ (calculated but unassigned by Janz et al.), 712 cm$^{-1}$ (ring deformation, very strong), and bands associated with the anions (760-780 cm$^{-1}$) were modeled [26]. Upon addition of a lithium salt, the 712 cm$^{-1}$ band upshifts yielding a perturbed solvent band at 723 cm$^{-1}$. Additionally, other peaks were deconvoluted, as necessary, to ensure a proper fit was obtained. The unperturbed/perturbed solvent bands in the 712-723 cm$^{-1}$ region (Figure 5.9) were used to calculate the fraction of coordinated solvent and the corresponding solvation numbers are reported in Section 5.3.5.
5.3.3. (GBL)$_n$-LiX Mixtures

GBL is very similar to EC in structure, lacking only one ring oxygen atom. However, the presence of one ring oxygen atom yields only a single plane of symmetry, thus all ring
bending vibrations are Raman active [23]. Consequently, two C-C ring vibrations were observed to perturb upon addition of a LiX salt. The Raman bands at 676 cm\(^{-1}\) and 871 cm\(^{-1}\) are attributed to C-C ring stretching bands and upshift to 688 cm\(^{-1}\) and 880 cm\(^{-1}\) upon coordinating with a Li\(^+\) cation, respectively [14,27,28]. Due to the broad peaks and narrow upshift in the 871-880 cm\(^{-1}\) region, these peaks were unable to be analyzed without significant error. Thus, only the 676-688 cm\(^{-1}\) bands were evaluated. The bands deconvoluted for the (GBL)\(_n\)-LiX analysis include the bands at 638 cm\(^{-1}\) (C-C stretching, medium), 676 cm\(^{-1}\) (C-C stretching, strong), 805 cm\(^{-1}\) (C-C stretching, medium) and bands associated with the anion (760-780 cm\(^{-1}\)) [14,28]. The unperturbed/perturbed bands in the 676-688 cm\(^{-1}\) region (Figure 5.10) were used to calculate the fraction of coordinated solvent and the corresponding solvation numbers are reported in Section 5.3.5.
Figure 5.10 Raman spectra of GBL C-C ring stretching bands as a function of LiX concentration.
5.3.4. (GVL)$_n$-LiX Mixtures

GVL has multiple ring stretching vibrations, as well as methyl stretching vibrations, that are Raman active. Most notable of the vibrations are the ring bending mode at 652 cm$^{-1}$ and the C-CH$_3$ stretching vibration at 941 cm$^{-1}$ [29,30]. The band deconvolution for (GVL)$_n$-LiX mixtures includes the bands at 609 cm$^{-1}$ and 652 cm$^{-1}$ (ring bending, strong), 706 cm$^{-1}$ (CH$_2$ rocking, weak), 805 cm$^{-1}$, 812 cm$^{-1}$ and 826 cm$^{-1}$ (ring stretching modes, very strong), 896 cm$^{-1}$ (CH bending, very weak), 941 cm$^{-1}$ (C-CH$_3$ stretching, strong), 965 cm$^{-1}$ (CH$_2$ rocking, weak), and 1000 cm$^{-1}$ (ring breathing, strong) [29,30]. Upon coordinating a Li$^+$ cation, the 652 cm$^{-1}$ and 941 cm$^{-1}$ bands upshift $\sim$10 cm$^{-1}$, yielding peaks at 661 cm$^{-1}$ and 951 cm$^{-1}$, respectively. The unperturbed/perturbed bands in the 652-661 cm$^{-1}$ and 941-951 cm$^{-1}$ regions (Figure 5.11) were used to calculate the fraction of coordinated solvent and the corresponding solvation numbers are reported in Section 5.3.5.
Figure 5.11 Raman spectra of GVL ring bending mode (left) and the C-CH$_3$ stretching vibration (right) as a function of LiX concentration.
5.3.5. Average Solvation Numbers

The average solvation numbers of the various mixtures have been calculated from the data in Figures 5.8-5.11 using Eq. 1.8. The results from the Raman analysis, however, are somewhat misleading; to compare the uncoordinated and coordinated vibrational modes directly requires the assumption that the vibrational bands either have identical intensities or that the scaling factors are known. In other words, for the former case, a Raman band from the uncoordinated solvent would have an intensity that is identical in shape/size to the corresponding Raman band for the Li\(^+\) coordinated solvent. Although this assumption has proven valid for some solvents (such as AN), this may not be the case for carbonate or lactone-based solvents. The scaling of EC solvent bands has been discussed in detail in Chapter 4. Such scaling factors, however, were only investigated in the dilute region for various salts. In order for these calculated scaling factors to be valid, they must apply to the entire concentration range. Figure 5.12 displays the variable concentration solvation numbers of \((\text{EC})_n\)-LiBF\(_4\) mixtures. By scaling the data appropriately, the average solvation numbers for the two bands are identical. Additionally, the average solvation number of \(-3\) in the dilute region agrees well with previous results that indicate LiBF\(_4\) is a fairly associated salt (since Li\(^+\) cations typically have a coordination number of four); EC is unable to fully dissociate the ions and thus the BF\(_4^-\) anion remains coordinated to many of the Li\(^+\) cations, even in dilute concentrations where there are approximately 20 solvent molecules for each ion.
Analysis of the 728 cm\(^{-1}\) band of EC was not possible in the LiDFOB and LiBOB mixtures due to severe overlap with a strong O–B–O deformation mode at 710-722 cm\(^{-1}\) [31]. These bands can be seen in Figures 5.10 and 5.11. The ring breathing mode at 905 cm\(^{-1}\), however, does not overlap with any of the lithium salts tested. Surprisingly, the solvation numbers calculated for (EC)\(_n\)-LiBF\(_4\) and (EC)\(_n\)-LiDFOB mixtures are nearly identical. The (EC)\(_n\)-LiBOB mixture have a higher solvation number in the dilute region, but quickly decreased to the same approximate value as LiBF\(_4\) and LiDFOB mixtures by a concentration of \(n = 8\). The slope of the (EC)\(_n\)-LiBOB mixtures seems to indicate that the salt is highly dissociated in the dilute region, but quickly becomes more associated as the concentration increases. This is somewhat expected, as LiBF\(_4\) contains F atoms of high electronegativity and has only four potential coordination sights, while LiBOB contains the less electronegative O atoms and is much more delocalized, containing up to eight coordination sights. This data is also also supported by the fact that both (EC)\(_4\):LiBOB and (EC)\(_{3/2}\):LiBOB crystalline solvates can form in dilute regions, depending upon crystallization kinetics.
Therefore, the (EC)$_n$-LiBOB mixtures seems to be more dissociated in the dilute region than both LiBF$_4$ and LiDFOB mixtures, but easily form aggregated complexes upon concentration or temperature increase. The solvation numbers of (EC)$_n$-LiX mixtures, as well as the fraction of un/coordinated bands, can be seen in Figure 5.13.

![Figure 5.13](image.png)

**Figure 5.13** Calculated $N$ (top) and fraction of uncoordinated and coordinated bands (bottom) of (EC)$_n$-LiX mixtures (left) and (PC)$_n$-LiX mixture (right).

Similar to the (EC)$_n$-LiDFOB and (EC)$_n$-LiBOB mixtures, analysis of the 728 cm$^{-1}$ band of PC was not possible due to anion band overlap [31]. Furthermore, the $\sim$850 cm$^{-1}$ band of
PC does not shift upon Li$^+$ complexation (see Appendix C). In light of these complications, (PC)$_n$-LiBF$_4$ mixtures were the only samples able to be analyzed. The solvation numbers of (PC)$_n$-LiBF$_4$ mixtures, as well as the fraction of un/coordinated bands, can be seen in Figure 5.13. The solvation numbers reported, however, may be significantly underestimated. As discussed in Chapter 4, quantum chemistry (QC) calculations indicate that there may be overlap of coordinated vibrational bands with the neat (uncoordinated) PC bands. The fraction of uncoordinated solvent molecules, therefore, may be significantly overestimated and, thus low solvation numbers are obtained. Since PC has $D_N$ and $\varepsilon$ values similar to EC, it is unreasonable to expect solvation numbers for (EC)$_n$-LiBF$_4$ mixtures to be double (or more) the solvation numbers for (PC)$_n$-LiBF$_4$ mixtures. Based upon the previous analysis, it is believed that accurate solvation numbers for (PC)$_n$-LiX mixtures are unobtainable due to complications from solvent band overlap.

(GBL)$_n$-LiX mixtures were analyzed to confirm the previous conclusion that LiBF$_4$ and LiDFOB are similarly aggregated, while LiBOB forms more dissociated mixtures (in dilute concentrations). Solvation numbers were calculated from the GBL C-C stretching mode (675 cm$^{-1}$) that shifts to 690 cm$^{-1}$ upon coordination with the Li$^+$ cation [14]. The data generated from the 871 cm$^{-1}$ band are difficult to accurately deconvolute due to broad peaks that were not well separated, thus these data were not used to calculate $N$ due to significant error. Nonetheless, the $N$ values for the (GBL)$_n$-LiX mixtures suggest that GBL is able to coordinate with the Li$^+$ cation to a greater extent than for EC. Additionally, the $N$ values suggest that LiBOB is the least associated, followed by LiDFOB and LiBF$_4$. This trend is indirectly supported by the fact that LiBOB is able to form a SSIP (EC)$_4$:LiBOB crystalline
solvate, while LiBF$_4$ instead forms the more aggregated (EC)$_2$:LiBF$_4$ and (EC)$_1$:LiBF$_4$ crystalline solvates. The fact that the solvent-LiBF$_4$ solvation numbers are less affected by varying the solvent also supports the conclusion that LiBF$_4$ is the more associated salt, i.e., LiBF$_4$ mixtures had the lowest solvation numbers in both EC and GBL. Thus, the BF$_4^-$ anions are able to competitively coordinate the Li$^+$ cations in both solvents. The average solvation numbers of (GBL)$_n$-LiX mixtures, as well as the fraction of un/coordinated bands, can be seen in Figure 5.14.

![Figure 5.14](image_url)

**Figure 5.14** Calculated $N$ (top) and fraction of uncoordinated and coordinated bands (bottom) of (GBL)$_n$-LiX mixtures (left) and (GVL)$_n$-LiX mixture (right).
Unlike the (EC)$_n$-LiX Raman analysis, the relative intensities of the GBL vibrational bands have not been computed and are not reported in the literature. This solvation data, therefore, is subject to change depending upon the necessity of a correction factor from QC calculations for the relative intensities of the bands for the uncomplexed and Li$^+$ complexed solvent. A comparison of the solvation numbers calculated (as seen in Figure 5.14), however, tells us a great deal of information about the association behavior of the lithium salts tested. Such a comparison does not require a correction factor to draw conclusions as to the solvation tendencies of the solvent/salt mixtures. A similar analysis was therefore performed on (GVL)-LiX mixtures to confirm the previously established association strengths of the lithium salts. When GVL is complexed to a Li$^+$ cation, the 652 cm$^{-1}$ and 941 cm$^{-1}$ bands shift. The ring bending mode at 652 cm$^{-1}$ was very broad and difficult to accurately deconvolute; analysis of this band was not possible due to severe error. The C-CH$_3$ stretching vibration at 941 cm$^{-1}$, however, was perturbed ~9 cm$^{-1}$ and it was possible to accurately deconvolute this band. Although the relative intensities of the uncoordinated and coordinated bands have not been calculated via QC analysis, comparison of the (GVL)$_n$-LiX mixtures agrees markedly with the results obtained from the (GBL)$_n$-LiX mixtures. The (GVL)$_n$-LiBF$_4$ mixtures have the lowest solvation numbers, followed by the LiDFOB and LiBOB mixtures. These results again suggest that LiBF$_4$ is the most associated salt, followed by LiDFOB and LiBOB.

5.3.6. (Solvent)$_n$-LiBF$_4$ Anion Band Analysis

Another means for determining a solvent’s coordination strength (ion solvation) is by measuring the effects the coordinated solvent molecules have on the lithium salt’s anion
vibrational bands. Due to anion/solvent band overlap with all of the mixtures containing LiDFOB and LiBOB, these salts were unable to be analyzed by Raman spectroscopy. The anion bands for the BF$_4^-$ anion, however, are mostly separated from the solvent vibrational bands and can therefore be analyzed. Neat LiBF$_4$ has a B-F stretching vibration at ~800 cm$^{-1}$ (see Chapter 3). In the neat lithium salt, each fluorine atom is coordinated to a Li$^+$ cation (AGG-III). As solvent molecules preferentially coordinate with the Li$^+$ cations, and thus the ion aggregation decreases, the Raman vibrational bands are red shifted. These shifts may be directly correlated with specific forms of BF$_4^-$...Li$^+$ cation coordination. The LiBF$_4$-containing solvates reported in this work were included in such a complementary study. From this analysis, it was determined that the BF$_4^-$ anion has band positions at 764-767 cm$^{-1}$, 766-770 cm$^{-1}$, 777-778 cm$^{-1}$ and 782-786 cm$^{-1}$ for crystalline solvates with SSIP, CIP-I, AGG-I and AGG-II coordination, respectively [32]. Based upon this analysis, the Raman spectra of the (solvent)$_n$-LiBF$_4$ mixtures was obtained and deconvoluted to determine the approximate ratio of solvates. The Raman spectra of the (solvent)$_n$-LiBF$_4$ mixtures can be seen in Figure 5.15.
Figure 5.15 Raman spectra of the B-F stretching vibration in (solvent)$_n$-LiBF$_4$ mixtures at 60°C.

The anion band distribution of the (solvent)$_n$-LiBF$_4$ mixtures is shown in Figure 5.16. The (GBL)$_n$-LiBF$_4$ mixtures have the largest fraction of SSIP solvates, followed by GVL, EC and PC, respectively. This data suggests that GBL is better able to solvate the Li$^+$ cation, leaving the BF$_4^-$ anion uncoordinated. Although the data suggest that GBL and GVL have a relatively small fraction of AGG-II solvates, even in higher concentrations, this is likely due to solvent band overlap that prevents the proper deconvolution of such bands. EC and PC initially have
a moderate fraction of SSIP solvates. As the concentration increases, however, the fraction of SSIP solvates quickly decreases as the more aggregated solvates begin to form. It is also noteworthy that PC mixtures initially have a large fraction of SSIP solvates ($x < 0.1$), approximately the same as GVL mixtures ($\sim 38\%$). As the salt concentration increases to $\sim x = 0.15$, however, the SSIP solvates present in PC decrease below 10%, while GBL and GVL mixtures contain over 20%. Anion band deconvolution plots are shown in Appendix D.

Figure 5.16 Distribution of anion modes of Li$^+$ cation coordination present in the (solvent)$_n$-LiBF$_4$ mixtures at 60°C.
5.4. Transport Properties

5.4.1. Concentration/Density

When discussing the interactions of the solvent and ions, it is helpful to discuss the ratio of solvent molecules to Li\(^+\) cations. Most of the work reported in the literature, especially with respect to transport properties, report concentrations in terms of molarity or molality (mol L\(^{-1}\) or mol kg\(^{-1}\), respectively). In order to demonstrate the relationship between molarity and the ratio of solvent/Li\(^+\), the variable concentration density of solvent-LiX mixtures was obtained. From this data, the link between the concentrations expressed in molarity vs. mole fraction was determined. Figures 5.17-5.19 display the density and concentration relationship of solvent-LiBF\(_4\), -LiDFOB and -LiBOB mixtures, respectively. It is important to note that a 1.0 M solution is roughly equivalent to a concentration of \(n = 9-17\) for all mixtures tested. The molecular weights (g mol\(^{-1}\)) of the salts are: LiBF\(_4\) (93.75), LiDFOB (143.77) and LiBOB (193.79).

![Figure 5.17](image)

**Figure 5.17** Density of \((\text{solvent})_n\)-LiBF\(_4\) mixtures (left) and relationship between molarity and solvent/LiBF\(_4\) ratio (right) at 60°C.
5.4.2. Viscosity

The variable temperature viscosity of the (solvent)$_n$-LiX mixtures was obtained and the isothermal (60°C) viscosity is reported in Figures 5.20 and 5.21. In the dilute liquids, one
would expect these mixtures to contain primarily uncoordinated solvent molecules with dispersed solvates (similar to Figures 5.2, 5.4 & 5.6). The quantity of these solvates, however, is a function of both the solvent and anions coordination strengths (ion solvation and ionic association, respectively). The most dissociated salts will therefore have a greater amount of solvent molecules coordinated to the Li$^+$ cations, while associated salts will have a greater amount of uncoordinated solvent molecules. Viscosity can be correlated with association strength as an increase in uncoordinated solvent molecules led to a decrease in viscosity for electrolytes with acetonitrile [32]. If a large amount of uncoordinated solvent is present, a mixture is more fluid and thus serves as a medium through which the solvates can easily flow (reduced internal resistance to flow). Therefore, viscosity analysis may serve as an indirect measurement of association strength by comparing different lithium salts with a constant solvent.
Based upon the initial viscosity comparison (Figure 5.20), however, there was no clear trend between the various solvents and/or lithium salts. It was observed that the viscosity trends of the mixtures were dominated by the viscosity of the neat solvent. The viscosity (mPa s) of the pure solvents at 60°C are: EC (1.44), PC (1.23), GBL (1.09), GVL (1.10). For a more direct comparison, each lithium salt was compared in the same solvents (Figure 5.21). The order of association strengths determined from the Raman analysis is LiBOB < LiDFOB < LiBF₄. From the data in Figure 5.21, it is apparent that (solvent)ₙ-LiBOB mixtures have a higher viscosity than similar mixtures with LiBF₄ and LiDFOB. This is consistent with the
results obtained from the Raman analysis in which (solvent)$_n$-LiBOB mixtures were determined to be the most dissociated. Furthermore, (solvent)$_n$-LiDFOB mixtures have (in most cases) a slightly higher viscosity, especially in the more concentrated region.

5.4.3. Conductivity

It is generally understood that a decrease in viscosity will be accompanied by an increase in ionic conductivity. The explanation that is typically given is that any decrease in viscosity will yield a more fluid solution (fluidity is the inverse of viscosity) and thus more mobile ions. If the ions are more mobile, one would expect a higher ionic conductivity; a measure of the transport of charged ions between two plates of a normalized distance. Based upon the previous viscosity analysis, mixtures with LiBF$_4$ and LiDFOB should have the highest conductivity values, while mixtures with LiBOB should have the lowest. The variable temperature ionic conductivity (60°C) of (solvent)$_n$-LiX mixtures is displayed in Figure 5.22. Interestingly, the conductivity data clearly contradicts conventional wisdom that less viscous
solutions are more conductive; mixtures with LiBF₄ generally have the lowest viscosity and conductivity values at nearly all concentrations. Furthermore, mixtures with LiDFOB have the highest conductivity at all concentrations, despite the fact that these mixtures have lower viscosity values than similar mixtures with LiBOB. When compared to the state-of-the-art salt LiPF₆, however, (EC)ₙ-LiDFOB and (PC)ₙ-LiDFOB mixtures have a lower conductivity. Mixtures of GBL or GVL with LiPF₆, however, could not be tested due to significant decomposition, even at lower temperatures.

Figure 5.22 Conductivity of (solvent)ₙ-LiX mixtures at 60°C.
The conductivity plots of each mixture (Figure 5.22) display similar trends, with each having a maximum conductivity value at $n = \sim 10$. Ionic conductivity is affected by the number of charge carriers present and their mobility in the solution. In the dilute region ($n > 10$), there are an insufficient number of charge carriers, but they are quite mobile. As the concentration increases to $n = \sim 10$, there is an ideal number of charge carriers and they are easily able to move through the solution. As the concentration increases further ($n < 10$), there is an increased number of CIP and AGG solvates and thus the ions are not able to move easily due to the large size of the solvate/complex. A similar analysis may help explain the differences between the three lithium salts. Based upon the Raman analysis, mixtures with LiBOB are expected to be the least associated, followed by LiDFOB and LiBF$_4$, respectively. This trend is also supported by the viscosity analysis in which LiBOB and LiDFOB generally had higher viscosity values than LiBF$_4$ mixtures. It follows that LiBOB and LiDFOB mixtures generally have a higher conductivity than LiBF$_4$ mixtures. One exception to this case is mixtures of (EC)$_n$-LiBF$_4$ and (EC)$_n$-LiBOB; this is the only instance in which the LiBF$_4$ mixtures had a higher conductivity than the LiBOB mixtures.

Another way to examine the ionic conductivity trends is to normalize the data by the concentration of the mixture to give the molar conductivity. The molar conductivity of the mixtures can be seen in Figure 5.23. Due to the molecular weight differences of the three salts, a variety of new trends are observed. Most notably, none of the mixtures have a maximum conductivity value at $n = 10$; the most dilute solutions have the highest molar conductivity because the ionic conductivity is divided by a low concentration value. If the ions were fully dissociated, then the molar conductivity would be the conductivity
normalized in terms of the number of available charge carriers. But since the ions are not fully dissociated, this is not the case. All solvent mixtures with LiDFOB have molar conductivity values larger than those for the mixtures with LiBF₄ and LiBOB, although these values are still lower than similar mixtures with the state-of-the-art salt LiPF₆. In contrast with the ionic conductivity results, all of the mixtures with LiBOB have higher molar conductivity values than the mixtures with LiBF₄ (except at temperatures < 10°C in some cases).

The ionic and molar conductivity plots display one common trend that is difficult to explain. The Raman and viscosity analyses indicate that LiBOB is much more dissociated than LiDFOB. The conductivity values of LiBOB mixtures, however, are less than those for mixtures with LiDFOB in nearly every case. One possible explanation is the size of the BOB⁻ anion in comparison with the DFOB⁻ anion; the increased size of the BOB⁻ anion could limit the mobility of charged complexes. The size of the BOB⁻ anion would have no impact on the Raman or viscosity analyses as these results are affected primarily by the coordination of the solvent to the Li⁺ cation (or lack thereof).
Figure 5.23 Molar conductivity of (a,e) (EC)$_n$-LiX, (b,f) (PC)$_n$-LiX, (c,g) (GBL)$_n$-LiX, and (d,h) (GVL)$_n$-LiX. (a)-(d) variable temperature data for 20/1 mixtures and (e)-(h) variable concentration data for 60°C.
5.5. Conclusions

This study focused on the differences between the lithium salts LiBF$_4$, LiDFOB and LiBOB with the solvents EC, PC, GBL and GVL. Phase diagrams of the solvent-LiX mixtures were prepared and the phase behavior was compared. Most of the mixtures tested have amorphous behavior, aside from bulk solvent crystallization/melting. Mixtures of (EC)$_n$-LiBF$_4$, (EC)$_n$-LiBOB, (PC)$_n$-LiDFOB and (GBL)$_n$-LiBF$_4$ formed crystalline solvates. Solvate crystal structures were determined for most of these compositions that add insight into the phase behavior of both the solid and liquid phases. Raman analyses were used to examine the solvation behavior of the mixtures in the liquid phase. An average solvation number was determined as a function of the lithium salt concentration. Although the (EC)$_n$-LiX mixtures have similar solvation numbers, analysis of the (GBL)$_n$-LiX and (GVL)$_n$-LiX mixtures indicate that LiBOB is the most dissociated salt, followed by LiDFOB and LiBF$_4$, respectively. This trend is further supported by the viscosity analysis. Although LiDFOB is more associated than LiBOB, mixtures with LiDFOB have higher ionic and molar conductivity values than mixtures with LiBOB and LiBF$_4$. LiDFOB is a highly attractive lithium salt that is largely amorphous when mixed with the carbonate and lactone-based solvents tested. The (solvent)$_n$-LiDFOB mixtures have high solvation numbers, sufficiently low viscosity and exceptional ionic and molar conductivity values (although lower than for mixtures with LiPF$_6$). It follows that carbonate and lactone-based mixtures that contain the LiDFOB salt may be utilized as next-generation Li-ion battery electrolytes.
5.6. References


CHAPTER 6: Properties of DFOB-Based Ionic Liquids

Abstract

The synthesis and physical properties of difluoro(oxalato)borate (DFOB⁻)-based ionic liquids (ILs) are reported with N-alkyl-N-methylpyrrolidinium (PY₁ᵣ⁺) cations with butyl, pentyl and hexyl alkyl chains. The PY₁₄DFOB and PY₁₆DFOB salts have a melting point ($T_m$) of -5°C and 31°C, respectively, whereas the PY₁₅DFOB salt does not crystallize. Instead, this salt has a glass transition temperature ($T_g$) of -74°C. Electrolytes composed of these ILs are noncorrosive towards Al when mixed with LiTFSI and LiFSI, as well as with LiPF₆ or LiDFOB. The exceptional oxidative stability of the ILs suggests that they may be suitable for battery electrolyte applications.
6.1. Introduction

As Li-ion batteries are used in more demanding applications, the need for safer, more electrochemically/thermally stable, and more conductive electrolytes grows tremendously. This is especially true for new cell chemistries with high-voltage cathodes and/or alloy anodes. In particular, electrolytes are often considered a bottleneck in the development of the high-voltage cathode materials, as the current state-of-the-art electrolyte used in commercial Li-ion batteries, with mixed carbonate solvents and LiPF$_6$, does not enable stable long-term cycling of cells with such cathodes. The principal means of addressing this challenge thus far has been through the use of electrolyte additives [1–8]. One such additive that has gained significant attention is lithium difluoro(oxalato)borate with the DFOB$^-$ anion:

\[
\begin{array}{c}
\text{F}^- \quad \text{O} \\
\text{B} \quad \text{O} \\
\text{F}^- \\
\end{array}
\]

LiDFOB has been shown to stabilize various cathode materials, including (but not limited to) LiCoPO$_4$, LiMn$_2$O$_4$, LiFePO$_4$, and Li$_{1.1}[\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}]_{0.9}\text{O}_2$ [7–11], yielding an increased performance when used as both a primary electrolyte salt (replacing LiPF$_6$) and in low (additive) concentrations (with LiPF$_6$). LiDFOB possesses the intrinsic ability to form an SEI layer on graphite anodes, even in high concentrations of propylene carbonate (PC), a solvent known to exfoliate graphene layers [11–14]. Furthermore, LiDFOB has also been shown to passivate the aluminum (Al) current collector, protecting it from corrosion [15,16]. Only a trace amount (i.e., 0.5-2.0 wt%) of an additive, such as LiDFOB, is generally used as a sacrificial agent to preferentially react on the electrode surface(s) within the first few cycles,
producing stabilizing interfacial layer(s). The additives thus do little to influence the electrolyte volatility, flammability and bulk electrolyte stability (should the passivation layer become disrupted).

Despite the increased performance of the industry-standard electrolyte with additives, significant attention has recently shifted to ionic liquids (ILs) as a viable alternative to traditional carbonate-based electrolytes. ILs possess many favorable properties including low volatility, low flammability, high electrochemical stability window, etc. [17–19]. However, Li-ion batteries that utilize IL-based electrolytes (without additives) suffer from poor charge-discharge performance due to the lack of SEI formation and thus increased irreversible capacity loss when cycled with a graphitic anode (due to the intercalation of the organic cations) [20–23]. Therefore, IL-based electrolytes require additives (perhaps in high concentration) such as lithium bis(fluorosulfonyl)imide (LiN(SO$_2$F)$_2$ or LiFSI) or FSI$^-$-based ILs to form a suitable SEI layer [22–25]. It may be desirable, however, to utilize ILs containing other anions, such as the DFOB$^-$ anion, to optimize properties for specific cell designs and applications. Thus far, 1-alkyl-3-methylimidazolium difluoro(oxalato)borate (C$_R$nimDFOB) ILs have been synthesized via a bidentate trimethylsilyl oxalate reaction with C$_R$nimBF$_4$ ILs [26]. ILs with these cations, however, are expected to display a significantly lower degree of stability towards oxidation and reduction than those with N-alkyl-N-methylpiperidinium (PI$_{1R}^+$) and N-alkyl-N-methylpyrrolidinium (PY$_{1R}^+$) cations [27,28].

The synthesis of N-alkyl-N-methylpyrrolidinium difluoro(oxalato)borate (PY$_{1R}$DFOB) ILs using a different (metathesis) procedure is reported here. The thermal properties of these ILs have been investigated, as well as their oxidation/reduction stability limits. Additionally, the
Al corrosion properties of these ILs were tested with common lithium salts, including LiFSI and lithium bis(trifluoromethanesulfonyl)imide (LiN(SO$_2$CF$_3$)$_2$ or LiTFSI)—both of which are highly corrosive towards Al when used with carbonate solvents at higher potentials. These ILs show promise as battery electrolyte materials, as they combine the exceptional thermal stability and nonvolatility properties of many ILs with the graphite SEI forming and cathode stabilization properties of the DFOB$^-$ anion and the increased oxidative/reductive properties of PY$_{1R}^+$ cations.

### 6.2. Synthesis of PY$_{1R}$DFOB ILs

**Materials:** Sodium oxalate (Sigma-Aldrich, ≥ 99%) was dried at 105°C for 48 h, while boron trifluoride diethyl etherate (Sigma-Aldrich, ≥ 46.5% BF$_3$ basis), 1-methylpyrrolidine (Sigma-Aldrich, ≥ 98.0%) and bromoalkanes (Sigma-Aldrich—1-bromobutane 99%, 1-bromopentane 99%, 1-bromohexane 98%) were used as-received. LiDFOB was synthesized as previously reported (≥ 99.9%) [29]. LiPF$_6$ and LiBF$_4$ (Novolyte, electrolyte-grade) were used as-received. Lithium bis(oxalato)borate (LiBOB, gratis, Chemetal) was purified by extraction/recrystallization in AN and then dried at 105°C for 24 h prior to use. The LiBF$_4$ and LiBOB were used only for the peak identification and detection limit determination for the $^{11}$B-NMR and $^{19}$F-NMR measurements. Al electrodes were provided gratis from Argonne National Laboratory and represent the standard foil used as a current collector in state-of-the-art cathode fabrication. The materials were stored in sealed containers in a Vacuum Atmospheres glovebox with an N$_2$ atmosphere (< 5 ppm O$_2$ and < 1 ppm H$_2$O).
**Synthesis of NaDFOB:** 101.29 g (0.756 mol) of sodium oxalate was reacted with 109.78 g (0.773 mol) of boron trifluoride diethyl etherate in Et₂O. The slurry was stirred at 80°C in a sealed container and allowed to react for 24 h. The excess BF₃ and Et₂O were then removed via vacuum filtration. The resulting sodium difluoro(oxalato)borate (NaDFOB) was extracted with AN and filtered to remove the unreacted sodium oxalate and NaF byproduct. The solution was concentrated, recrystallized (as an (AN)₂:NaDFOB solvate) and dried at 105°C for 24 h to yield a highly pure NaDFOB powder. The structure of the solvate, obtained from the recrystallized solids, was determined [30].

**Synthesis of PY₁RBr:** N-Alkyl-N-methylpyrrolidinium bromide (PY₁RBr) salts were prepared by combining 1-methylpyrrolidine with an equimolar amount of the appropriate bromoalkane in EA. Upon stirring overnight at 60°C, the previously homogeneous solutions formed slurries, confirming that reactions occurred. The resulting solid PY₁RBr salts were filtered with a fine-frit glass filter and rinsed with excess amounts of EA. The recovered salts were then dried at 90°C for 24 h and stored in sealed containers in the glovebox.

**Synthesis of PY₁₄TFSI and PY₁₄DFOB ILs:** PY₁₄TFSI was synthesized as previously reported [31]. N-Alkyl-N-methylpyrrolidinium difluoro(oxalato)borate (PY₁₄DFOB) ILs were synthesized by reacting NaDFOB with the appropriate PY₁RBr salt (0.95:1.00 ratio), each dissolved in AN. The PY₁RBr was used in excess such that the rinse solution could be monitored with silver nitrate (to ensure PY₁RBr was fully removed). Br was also measured via elemental analysis as a means to ensure high purity (see Appendix E). Upon adding the NaDFOB solutions to the PY₁RBr solutions, a precipitate (i.e., NaBr) was instantly noted. The NaBr byproduct was filtered off. The resulting ILs (once the AN was removed from the
filtrate via roto-evaporation) were then purified using the same procedure as for PY$_{14}$TFSI [31]. The resulting ILs were vacuum dried at 60°C for 48 h and stored in hermetically-sealed containers in the glovebox.

### 6.3. Purity Evaluation

Purity is a critical criterion for battery electrolytes. NMR spectra were therefore obtained to fully characterize the ILs. $^1$H-NMR spectra of the PY$_{1R}$DFOB ILs (with CD$_3$CN) were used to determine if any proton-containing impurities were present. A small amount of a proton-containing impurity was observed at 4.46 ppm in the PY$_{15}$DFOB and PY$_{16}$DFOB ILs, but identification of this impurity was unsuccessful and further attempts to purify the ILs lead to no noticeable decrease in the impurity concentration.

The $^{19}$F-NMR spectra of the ILs (with CD$_3$CN) have two clusters of peaks separated by ~2 ppm (see Appendix E). The separated $^{19}$F peaks are due to the natural isotopic distribution of $^{10}$B (19.9%) and $^{11}$B (80.1%), as noted by Zhou et al. [32], as the fluorine atoms are bonded to the boron atom. Additional $^{19}$F NMR spectra were also acquired for PY$_{16}$DFOB in dimethyl sulfoxide-$d_6$, acetone-$d_6$, and chloroform-$d_3$—solvents with dielectric constants of 47.0, 20.56, and 4.7218, respectively (as compared to 35.95 for acetonitrile) [33]. The $^{19}$F-NMR spectra of PY$_{16}$DFOB in dimethyl sulfoxide-$d_6$ and acetone-$d_6$ are similar to the spectrum in acetonitrile-$d_3$ with the separation of the peaks varying slightly. The $^{19}$F-NMR spectra of PY$_{16}$DFOB in chloroform-$d_3$ (CDCl$_3$), however, contains (at least) four peaks for each cluster (see Appendix E). Since the $^{11}$B-NMR spectra of these ILs show only trace amounts of BF$_4^-$ and BOB$^-$ anions (see below), the extra pair of peaks in the $^{19}$F-NMR
spectra are thus not due (principally) to the BF$_4^-$ anion impurity. Another explanation for these peaks is that they originate from the DFOB$^-$ anion, but the fluorine atoms of the DFOB$^-$ anion are in different coordination environments and therefore are magnetically inequivalent. The DFOB$^-$ anion is able to coordinate cations through the fluorine atoms, as well as the oxygen atoms. Such variability in the anion...cation coordination would lead to different chemical shifts in the $^{19}$F-NMR spectra. Then the question to ask is what are the anions coordinated to...? One possibility is that there is a residual amount of Na$^+$ cations remaining in the ILs following the synthesis procedure. If this is the case, however, these Na$^+$ cations would be expected to be principally coordinated by the carbonyl oxygen atoms of the anion instead of the fluorine atoms [34]. Such anion coordination far removed from the fluorine atoms is not expected to significantly influence the peak positions of the $^{19}$F-NMR spectra. Further, the $^{19}$F-NMR spectra closely resemble one another (for the three ILs) and this would also not be expected with differing amounts of a Na$^+$ cation impurity. ICP-MS analysis of the samples verified a negligible Na$^+$ cation content (Appendix E). The most likely explanation is the dynamic interactions of the anions with the organic cations. The anions are not expected to form strong coordinate bonds to the PY$_{1R}^+$ cations (as occurs for Li$^+$ and Na$^+$ cations) due to the steric bulk from the alkyl groups around the positively charged nitrogen atom of the cations. The $^{19}$F-NMR peak shifts are relatively small, however, so perhaps longer range interactions account for the peak variability noted in the chloroform $^{19}$F-NMR spectrum. In particular, the cation–anion interactions are expected to be relatively strong in the poor CDCl$_3$ solvent (i.e., resulting in significant association/clustering of the
ions—ion aggregation), while in the other, more polar, solvents the cation–anion interactions are attenuated by the ability of the solvents to more fully disperse the ions [35].

$^{11}$B-NMR spectra were used to analyze the concentration of BF$_4^-$ and BOB$^-$ anions present in the ILs, as the DFOB$^-$ anion is known to disproportionate into these anions (due to thermodynamic equilibrium) [32]. To determine the detection limit of this technique, LiDFOB was dissolved in CD$_3$CN and spiked with 0.1 mol% LiBF$_4$ and LiBOB. This test confirmed, by integrating the resulting spectra, that levels of $\geq$ 0.1 mol% BF$_4^-$ and BOB$^-$ could be observed through $^{11}$B-NMR analysis. Schreiner et al. also report the use of this technique with a limit of detection of $\sim$0.05-0.10 mol% [26]. The purity of the ILs (in terms of the anions) was thus determined to be approximately 96.9%, 97.0% and 96.2% for PY$_{14}$DFOB, PY$_{15}$DFOB and PY$_{16}$DFOB, respectively. Due to the disproportionation reaction, the purity limits of the ILs actually represent the intrinsic equilibrium of the DFOB$^-$ anions with small amounts of BF$_4^-$ and BOB$^-$ anions, which will always be present in these ILs.

6.4. Thermal Analysis

Thermal phase behavior: DSC measurements were conducted to determine the $T_m$ and/or $T_g$ of the ILs (Figure 6.1). The PY$_{14}$DFOB salt initially displayed a $T_g$ at -77°C. Upon multiple cooling/heating scans below/above the $T_g$, the sample crystallized into a solid phase with a $T_m$ at -5°C. For comparison, PY$_{14}$BF$_4$ has a $T_m$ at 142°C and PY$_{14}$BOB does not crystallize, but instead has a $T_g$ at -38°C [36,37]. The $T_m$ for the PY$_{14}$DFOB salt is similar to that of PY$_{14}$TFSI (i.e., -3°C) [38]. The PY$_{15}$DFOB salt exhibits a $T_g$ at -74°C and it was not
possible to crystallize the salt with the thermal cycling/annealing conditions used, despite extensive efforts to do so. The PY$_{16}$DFOB salt, similar to PY$_{14}$DFOB, did not crystallize during the initial cooling scan. Subsequent heating indicated a $T_g$ at -74°C followed by crystallization (thermal cycling). The resulting crystalline phase has a $T_m$ at 31°C. Despite the $T_m$ above ambient temperature, the PY$_{16}$DFOB salt remained a liquid throughout all of the testing. This salt could only be crystallized upon cycling multiple times at low temperature (crystallization onset at -27°C) indicating that the nucleation kinetics for the crystalline phase are quite slow.

![Figure 6.1](image) DSC heating traces (5°C min$^{-1}$) of the PY$_{14}$DFOB, PY$_{15}$DFOB and PY$_{16}$DFOB ILs.

**Thermal stability:** Figure 6.2 shows the TGA heating traces for the ILs which indicate their approximate decomposition temperature ($T_d$). The ILs all display a similar two-step decomposition pathway with an onset temperature of about 290°C. This onset temperature is
somewhat higher than that noted for LiDFOB, which also undergoes a multi-step decomposition pathway [29].

![TGA heating traces](image)

**Figure 6.2** TGA heating traces (5°C min⁻¹) of the PY₁₄DFOB, PY₁₅DFOB and PY₁₆DFOB ILs.

### 6.5. Electrochemical Stability

#### 6.5.1. Aluminum Corrosion Stability

In order to be utilized as an additive or in lieu of a primary electrolyte solvent, the ILs must be non-corrosive towards the Al current collector widely used with cathode materials. Mixtures with either common carbonate solvents or ILs and various lithium salts were
therefore tested. Current state-of-the-art electrolytes are typically composed of 1M LiPF$_6$ dissolved in EC/linear carbonate (DMC, EMC or diethyl carbonate (DEC)) in a 3/7 volume ratio, which sufficiently passivates the Al current collector and prevents corrosion through the formation of an AlF$_3$ interfacial layer [39-41]. Similar mixtures with LiDFOB have also been shown to passivate Al [15,16]. LiTFSI and LiFSI, however, are known to corrode Al in such solvent mixtures at higher potentials, limiting the usefulness of these salts for commercial cells [41-44]. This is evident in Figure 6.3, which indicates that a significant corrosive current is present for the carbonate-LiTFSI and LiFSI mixtures, but not for the LiPF$_6$ and LiDFOB mixtures (passivation occurs during the first cycle for the latter salts). A summary of the corrosive and non-corrosive properties of the carbonate- and IL-based electrolytes is shown in Table 6.1. It is noteworthy that corrosion only occurs at potentials $>$ 4 V for carbonate-LiFSI mixtures, which suggests these electrolytes are suitable for standard (commercial) electrode materials operating at $\sim$3.7 V. Microscope images of the Al electrodes after the CV scans are shown in Figures 6.4 and 6.5. These images confirm that there is extensive pitting-corrosion only for the carbonate-LiTFSI and LiFSI mixtures.

**Table 6.1.** Summary of corrosive/non-corrosive (NA) properties of carbonate- and IL-based electrolytes.

<table>
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<tr>
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<th>LiTFSI</th>
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<th>LiDFOB</th>
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<td>Corrodes</td>
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<td>NA</td>
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</tr>
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</table>
Figure 6.3 Cyclic voltammograms (Al working electrode) of (a-d) EC/DMC-LiX and (e-h) PY_{14}DFOB-LiX mixtures with (a,e) LiTFSI, (b,f) LiFSI, (c,g) LiPF_6 and (d,h) LiDFOB. Full scale plots are shown in the insets (mA cm^{-2} units used for clarity). Scans were performed at 1 mV s^{-1}. 
Figure 6.4 Surface images of the (a) pristine Al electrode and Al electrodes cycled with the (b) EC/DMC-LiTFSI, (c) EC/DMC-LiFSI, (d) PY$_{14}$DFOB-LiTFSI and (e) PY$_{14}$DFOB-LiFSI electrolytes.
ILs such as PY$_{1R}$TFSI, in contrast to the carbonate solvents, have been reported to prevent Al corrosion, even for mixtures containing LiTFSI [45,46]. The mechanism of corrosion inhibition for ILs is thought to be due to the insolubility of the Al-TFSI or Al-FSI complexes formed from the initial reaction of the salts with the Al at high potential [45]. The complexes effectively passivate the Al surface. The PY$_{1R}$DFOB ILs also resist Al corrosion, as found for the PY$_{1R}$TFSI ILs, even when mixed with LiTFSI or LiFSI (Figure 6.3). IL-LiFSI mixtures, however, display some unexpected results. PY$_{14}$TFSI-LiFSI exhibits a CV curve indicative of corrosion, although the current passed is significantly less than for carbonate-LiFSI mixtures (see Appendix E). This suggests that if an Al(FSI)$_3$ complex is formed, it may be
marginally soluble in PY\textsubscript{14}TFSI. The PY\textsubscript{14}DFOB-LiFSI mixture, on the contrary, shows CV curves indicative of passivation. Thus, PY\textsubscript{14}DFOB is evidently able to passivate the Al working electrode and prevent corrosion, even in circumstances where PY\textsubscript{14}TFSI cannot. It is unclear which mechanism results in the non-corrosive properties of the PY\textsubscript{1R}DFOB-based electrolytes—i.e., the decomposition of the DFOB\textsuperscript{−} anion to form AlF\textsubscript{3} (similar to the PF\textsubscript{6}\textsuperscript{−} anion) or the formation of an Al(DFOB)\textsubscript{3} complex (similar to PY\textsubscript{1R}TFSI). A summary of the results with the different electrolytes is given in Table 6.1. The complete CVs and corresponding pictures for all of the mixtures tested can be found in Appendix E.

### 6.5.2. Oxidation/Reduction Stability

Voltammograms for each IL (with a Pt working electrode) are shown in Figures 6.6 and 6.7. The oxidation stability limit of the ILs is approximately 5.0 V (vs. Li/Li\textsuperscript{+}) (Figure 6.6). This limit is much higher than might be expected, as the anion contains an oxalate group. The stability of the PY\textsubscript{1R}DFOB ILs is close to the reported 5.2 V anodic stability limit of PY\textsubscript{14}TFSI, which is attributed to the irreversible oxidization of the TFSI\textsuperscript{−} anion [47]. The cathodic stability limit, however, is inherently more difficult to determine for these ILs. Surprisingly, the neat PY\textsubscript{1R}DFOB ILs exhibit partially reversible oxidation/reduction behavior at potentials between 0 to 1 V (Figure 6.6). It was initially thought that dissolved gases might be a source of contamination, as it has been reported that a significantly different reduction stability limit is obtained for PY\textsubscript{14}TFSI with and without dissolved N\textsubscript{2} or O\textsubscript{2} gases [48]. Yet, degassing the ILs (with Ar) at 80°C for 24 h lead to negligible differences in subsequent voltammetry tests. It was also thought that trace Na\textsuperscript{+} cation impurities (if present)
might lead to the reversible behavior, as Na plating is known to occur around this potential. However, an ICP-MS analysis of the PY$_{16}$DFOB IL indicated that only $\sim$2 ppm Na was present. Further, the elemental analysis of the three ILs found a negligible Br$^-$ anion content which indicates that the ILs are free of NaBr (see Appendix E). These analyses, and the amount of current passed, suggest instead that this electrochemical behavior is inherent to the PY$_{18}$DFOB salts. The origin of this redox behavior is not yet known. It may be that the DFOB$^-$ anions are the reactive species (as this redox behavior is not noted for the PY$_{14}$TFSI salt - Figure 6.7) and that upon reduction, some of the resulting product (from the cathodic scan) diffuses away from the electrode and is thus unavailable for subsequent oxidation (during the anodic scan to higher potential).

![Voltammograms of the PY$_{14}$DFOB, PY$_{15}$DFOB and PY$_{16}$DFOB ILs on a Pt electrode.](image)

**Figure 6.6** Voltammograms of the PY$_{14}$DFOB, PY$_{15}$DFOB and PY$_{16}$DFOB ILs on a Pt electrode.
Figure 6.7 Cyclic Voltammograms of the ILs and IL-LiX electrolytes on a Pt electrode.

To further examine the electrochemical properties of the ILs, the PY\textsubscript{14}DFOB and PY\textsubscript{14}TFSI salts were mixed with either LiDFOB or LiTFSI, as it has been previously noted that the addition of lithium salts can improve the cathodic stability of ILs [49-51]. Interestingly, the addition of the lithium salts to the PY\textsubscript{14}DFOB IL eliminates the partially reversible redox peaks and consequently enables largely reversible Li/Li\textsuperscript{+} plating/stripping (with a coulombic efficiency of 90% or greater after the initial cycle), similar to that found for the PY\textsubscript{14}TFSI ILs (Figure 6.7). It is notable that the voltammograms displayed multiple peaks, including peaks above 1.0 V vs. Li/Li\textsuperscript{+} during the anodic scans. These are due to Pt\textsubscript{x}Li alloy formation, as well as Li plating. During the cathodic scan, the Pt\textsubscript{x}Li alloys are formed with subsequent Li plated on top of the alloys. In the reverse (anodic) scan, the plated Li
metal is oxidized first, then the Pt₃Li alloys are oxidized as multiple peaks, depending upon which alloy was formed [52,53]. A comparison of the PY₁₄TFSI and PY₁₄DFOB voltammograms indicates that the cation is likely not responsible for the (partially) reversible behavior at low potentials, given that these ILs share a common cation. This suggests that the partially reversible redox peak for the PY₁ᵣDFOB ILs (in the absence of Li⁺ cations) may instead be attributed to chemistry associated with the DFOB⁻ anions.

6.6. Conclusions

PY₁ᵣDFOB ILs are difficult to purify due to the presence of an equilibrium concentration of BF₄⁻ and BOB⁻ anions formed from the thermodynamic disproportionation reaction of the DFOB⁻ anions. A DSC analysis of the ILs indicated Tₘ values of -5°C and 31°C, respectively, for the PY₁₄DFOB and PY₁₆DFOB salts, while the PY₁₅DFOB salt did not crystallize (instead a Tₕ at -74°C was noted). All three ILs possess a high thermal stability, displaying a two-step thermal decomposition pathway with an onset temperature of ~290°C for each IL. Similar to TFSI⁻-based IL electrolytes, the PY₁ᵣDFOB-LiX mixtures do not corrode Al, even in mixtures with LiTFSI and LiFSI (salts known to corrode Al in carbonate-based electrolytes at higher potentials). Electrochemical stability testing of the neat PY₁ᵣDFOB ILs suggests that they are stable up to 5.0 V (vs. Li/Li⁺). The addition of lithium salts (i.e., LiDFOB or LiTFSI) results in an improvement in the cathodic stability of the mixtures (relative to the neat ILs) with reversible Li/Li⁺ plating/stripping observed. The thermal and electrochemical properties of the PY₁ᵣDFOB ILs suggest they are potentially well-suited for battery electrolyte applications.
6.7. References


CHAPTER 7: Conclusions

The goals of this research project were to investigate the molecular-level interactions that are present within electrolyte mixtures that contain a relatively new lithium salt (LiDFOB), link these molecular interactions to the physicochemical properties of such mixtures, and explore alternative applications for the DFOB$^-$ anion, such as its use as a counter ion in ILs.

High purity LiDFOB was synthesized as part of the present study. Single crystal X-ray structural determination of the neat salt suggests that the Li$^+$ cations are able to be coordinated by each of the anion’s fluorine and oxygen atoms, resulting in an AGG-III ion coordination for the neat salt. When LiDFOB is mixed with carbonate or lactone-based solvents (EC, PC, GBL or GVL), largely amorphous mixtures are obtained with only a single crystalline solvate obtained, i.e., (PC)$_1$:LiDFOB.

Raman analyses of (solvent)$_n$:LiDFOB mixtures were somewhat difficult. Although numerous studies have been reported for the determination of the average solvation numbers of Li$^+$ cations coordinated by cyclic carbonate solvents, these studies have, in general, not taken into account the scaling of the Raman intensities for the coordinated solvent bands or the possibility of overlapped Raman bands. Utilizing quantum chemical and experimental techniques, a more rigorous analysis method has been reported that allows for an accurate determination of solvation numbers for EC. The association trends determined with this technique are in excellent agreement with previously reported trends. Combining these trends with the analysis of the BOB$^-$ and DFOB$^-$ anions, for which the solution behavior is largely unknown, the following ionic association trends are obtained:
The solvation behavior of electrolyte mixtures was further scrutinized through a comparative study of the carbonate and lactone-based solvents with the lithium salts LiBF₄, LiDFOB and LiBOB. Phase diagrams were prepared for the various mixtures and the phase behavior was compared. Most of the LiDFOB and LiBOB-based electrolytes were amorphous, aside from bulk solvent crystallization/melting, while mixtures of (EC)ₙ-LiBF₄ and (GBL)ₙ-LiBF₄ contained multiple crystalline solvate phases. Of the mixtures tested, the following crystalline solvates were observed: (EC)₂:LiBF₄, (EC)₁:LiBF₄, (GBL)₂:LiBF₄, (GBL)₁:LiBF₄, (PC)₁:LiDFOB, (EC)₄:LiBOB (literature) and (EC)₃/₂:LiBOB. Although Raman analysis of the (EC)ₙ-LiX mixtures indicated that the three lithium salts have similar solvation numbers, analysis of the (GBL)ₙ-LiX and (GVL)ₙ-LiX mixtures suggested that the ion association strength increases in the order:

$$\text{BOB}^- < \text{DFOB}^- < \text{BF}_4^-$$

This solvation trend is further supported by the viscosity analysis; electrolyte mixtures with LiBOB have the highest viscosity, followed by LiDFOB and LiBF₄, respectively. Although LiDFOB is more associated than LiBOB, mixtures with LiDFOB have higher ionic and molar conductivity values than the corresponding mixtures with LiBOB and LiBF₄, suggesting that the size of the anion plays a significant role in the ionic conductivity. Thus, (solvent)ₙ-LiDFOB mixtures have relatively high solvation numbers, sufficiently low viscosity and exceptional ionic and molar conductivity values (although less than mixtures with LiPF₆).
Analysis of the LiBF₄ anion vibrational bands also yields an interesting trend with respect to ion solvation interactions. EC is traditionally thought to be an exceptional solvent that dominates Li⁺ cation solvation due to its large dielectric constant. Analysis of the B-F stretching mode, however, indicates that the $DN$ of the solvent may play a more important role in defining the ability of the solvent to preferentially coordinate the Li⁺ cation (instead of the anion). The data indicates the ion solvation strength increases in the following order (which roughly correlates with increasing $DN$ values):

$$PC < EC < GVL < GBL$$

ILs were synthesized with the $N$-alkyl-$N$-methylpyrrolidinium ($PY_{1R}^+$) cation and DFOB⁻ anion (i.e., $PY_{1R}DFOB$ where $R =$ butyl, pentyl and hexyl). These ILs either have melting points at or below room temperature (i.e., $PY_{16}DFOB$ and $PY_{14}DFOB$) or do not crystallize (i.e., $PY_{15}DFOB$). Electrolytes composed of $PY_{1R}DFOB$ ILs are noncorrosive towards Al current collectors when mixed with LiTFSI and LiFSI, salts known to corrode Al in traditional carbonate-based electrolytes. The exceptional oxidative stability of the ILs suggests that they may be suitable for high-voltage battery electrolyte applications.

As demonstrated throughout this study, the transport properties of electrolyte mixtures are directly governed by the ionic association and ion solvation interactions present within the mixture. Furthermore, the relatively new DFOB⁻ anion has many favorable properties, both as a lithium salt and a counter anion in an IL. This research demonstrates a methodology for investigating new electrolyte materials from initial synthesis to exploration of alternative applications, and a means for benchmarking their performance against state-of-the-art materials.
APPENDICES
Appendix A

Understanding Phase Diagrams

Phase diagrams are constructed by plotting the maximum peak value(s) of the $T_m$, as well as the $T_g$ when present for amorphous phases, as determined from DSC analysis of the samples. By varying the concentration of species ($x$), the formation of new phases can be directly visualized. Figure A1 displays a typical phase diagram that exhibits many of the characteristics that may or may not be present. Thus, an in depth explanation of how to understand this phase diagram should enable the reader to understand the variation in the phase behavior seen in this study.

Figure A.1 DSC thermograms (left) and phase diagram (right) of $(1-x)$ EC-(x) LiBF$_4$ mixtures with possible phases indicated (grey indicates phase contamination due to limitations of cycling).
DSC testing typically begins with analysis of the pure solvent, which is present at $x = 0$. Pure EC has a $T_m$ of 38°C. As the concentration of lithium salt is increased (as $x$ increases), a eutectic composition begins to form (horizontal line at ~20°C). A eutectic is a mixture of two compounds (or phases) that has a single composition for which they will solidify at a lower temperature than either of the single components. In the case of region (1), the neat EC$_{(s)}$ is present with a liquid (eutectic composition). As the concentration further increases to region (2), a eutectic point is reached. This point represents the composition of the eutectic, which consists of EC$_{(s)}$ and the 2/1 (EC/LiBF$_4$) phase. Upon further increasing the concentration to region (3), a mixture of the 2/1 phase and a liquid phase is observed. The region below the eutectic line (4) consists of solids with varying amounts of EC$_{(s)}$ and the 2/1 phase. Section (5) is composed entirely of liquid. As the concentration of lithium salt is increased above 0.333 ($x$), a new crystalline solvate phase begins to form. At low temperature ($< -40°C$), the 2/1 phase exists as well as a 1/1 phase. Upon increasing the temperature, a small peak is observed in the DSC thermograms at these concentrations, which is indicative of a solid-solid phase transition. Thus, region (6) is due to a 2/1 solvate and a 1/1 solvate (phase III or 1/1$_{III}$). Once this solid-solid phase transition occurs (upon increasing temperature), the 1/1$_{III}$ phase transitions into a 1/1$_{II}$ phase that has a different crystal structure (region 7). Upon increasing temperature further, another solid-solid phase transition occurs as the 1/1$_{II}$ phase transforms into a 1/1$_{I}$ phase. Thus, in region (9) a mixture of the 2/1 and 1/1$_{I}$ phase exists. It is possible, based upon the DSC analysis, that the 2/1 phase may also have a solid-solid phase transition in region (8). However, it is most likely phase contamination from the eutectic phase as the $T_m$ of this possible solid-solid phase transition is identical to the $T_m$ of eutectic point. As the
temperature is increased further, the $T_m$ of the 2/1 phase is reached and the phase is melted into a liquid. Region (10), therefore, is a mixture of liquid and the 1/1$_1$ phase. As the temperature is increased further, the $T_m$ of the 1/1$_1$ phase is reached, and the entire mixture is melted into the liquid phase. Although most phase diagrams consisting of simple solvent-lithium salt mixtures are not as complex as the example given, understanding phase diagrams in general is important for determining the crystalline phases which may form in electrolyte mixtures.
Appendix B

Figure B.1 ORTEP drawing of LiDFOB asymmetric unit showing naming and numbering scheme. Ellipsoids are at the 50% probability level.

Table B.1 Bond angles for LiDFOB

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<th>Bonds</th>
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<td>116.27(12)</td>
<td>C1-O2-B1</td>
<td>109.26(6)</td>
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Symmetry transformations used to generate equivalent atoms:
1) 1-x, y, z
2) -x+1/2, -y+1/2, 1+z
3) x+1/2, -y+1/2, 1-z
4) -x+1/2, y+1/2, -z+1/2
5) x+1/2, y+1/2, z
6) 1-x, 1+y, 2+z
7) 1-x, 1+y, -1+z
8) -x, y, z
9) -x, 1+y, -1+z+1/2
10) -1+x+1/2, -1+y+1/2, z

Table B.2 Bond lengths for LiDFOB

<table>
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<th>Length, Å</th>
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<tr>
<td>Li1-Li1^7</td>
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<td>B1-F1</td>
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<td>B1-O2</td>
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Figure B.2 ORTEP drawing of LiDFOB·2H₂O asymmetric unit showing naming and numbering scheme. Ellipsoids are at the 50% probability level and hydrogen atoms are drawn with arbitrary radii for clarity.

Table B.3 Bond angles for LiDFOB·2H₂O

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<th>Angle, °</th>
<th>Bonds</th>
<th>Angle, °</th>
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<tr>
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<tr>
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<td>O1-C1-C2</td>
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<td>O₅₁-Li₁-Li₁²</td>
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<td>129.51(5)</td>
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<td>107.6(8)</td>
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Symmetry transformations used to generate equivalent atoms:
1) x,1+ -y-1/2,1+ z-1/2  2) x,1+ -y-1/2, z-1/2

Table B.4 Bond lengths for LiDFOB·2H₂O

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Length, Å</th>
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<td>Li₁-O₃</td>
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Appendix C

Table C.1 EC$_1$ and EC$_1$/Li$^+$ Raman vibrational mode frequencies (cm$^{-1}$) and activities (all calculations were done with PCM(EC)) and the ratios of the frequency shift/activity for EC/Li$^+$ vs. EC.

<table>
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<th>B3LYP/ aug-cc-pvTz</th>
<th>B3LYP/Tz// B3LYP/cc-pvTz</th>
<th>B3LYP/cc-pvTz</th>
<th>M06L/aug-cc-pvTz</th>
<th>M06-6-31+G(d,p)</th>
<th>M05-2X/6-31+G(d,p)</th>
<th>B3LYP/6-31+G(d,p)</th>
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<td>activ 3.7</td>
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<td>freq 745</td>
<td>freq 744</td>
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<td>activ 34.9</td>
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<td>activ 26.8</td>
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Table C.2 Comparison of EC$_4$ (avg) vs. EC$_1$ shift using 6-31+G(d,p) with PCM(EC) and EC$_1$ PCM(EC) vs. EC$_1$ no PCM ($\varepsilon = 1$)

<table>
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<th>freq3</th>
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<td>0.88</td>
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<td>1.61</td>
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Comparing EC$_1$ PCM (EC) vs. EC$_1$ no PCM ($\varepsilon = 1$)

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Figure C.1 Frequency shifts and intensity ratios of ECₙ/Li⁺ and ECₙ/LiX complexes vs. (a) EC₁ or (b) EC₄ from B3LYP functional with 6-31+G(d,p) basis set (unless noted otherwise) with PCM(EC).

Figure C.2 EC₄ from B3LYP/6-31+G(d,p) with PCM(EC) calculations.
Figure C.3 Raman spectra calculated for (top) EC$_1$ and (bottom) EC$_4$ from B3LYP/6-31+G(d,p) with PCM(EC) calculations.
Figure C.4 PC$_4$ from B3LYP/6-31+G(d,p) with PCM(PC) calculations. All isomers are in the cis$^+$ conformation.

Figure C.5 Raman spectrum calculated for PC$_4$ from B3LYP/6-31+G(d,p) with PCM(PC) calculations.
Figure C.6 Band deconvolution of the experimental spectrum of neat EC at 60°C.
(EC)$_n$-LiPF$_6$:

Figure C.7 Band deconvolution of the experimental spectra of (EC)$_n$-LiPF$_6$ ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
Figure C.8 Band deconvolution of the experimental spectra of $(EC)_n$-LiTFSI ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
Figure C.9 Band deconvolution of the experimental spectra of (EC)_n-LiBOB ((top) n = 20 and (bottom) n = 10) mixtures. The ~720 cm⁻¹ band of EC overlaps with the BOB⁻ anion bands.
Figure C.10 Band deconvolution of the experimental spectra of \((\text{EC})_n\)-LiClO$_4$ ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
Figure C.11 Band deconvolution of the experimental spectra of (EC)$_n$-LiBF$_4$ ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
Figure C.12 Band deconvolution of the experimental spectra of (EC)$_n$-LiDFOB ((top) $n = 20$ and (bottom) $n = 10$) mixtures. The $\sim 720$ cm$^{-1}$ band of EC overlaps with the DFOB$^-$ anion bands.
Figure C.13 Band deconvolution of the experimental spectra of (EC)$_n$-LiCF$_3$SO$_3$ (top) $n = 20$ and (bottom) $n = 10$ mixtures.
Figure C.14 Band deconvolution of the experimental spectra of (EC)$_n$-LiCF$_3$CO$_2$ ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
Figure C.15 Raman spectra of the experimental spectra of (EC)$_n$-LiX ((top) $n = 20$ and (bottom) $n = 10$) mixtures. The $\sim 720$ cm$^{-1}$ band of EC overlaps with the BOB$^-$ and DFOB$^-$ anion bands.
Figure C.16 Raman spectra of the experimental spectrum of neat PC at 60°C.
(PC)$_n$-LiPF$_6$.

**Figure C.17** Band deconvolution of the experimental spectra of (PC)$_n$-LiPF$_6$ ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
Figure C.18 Band deconvolution of the experimental spectra of (PC)$_n$-LiTFSI ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
(PC)\textsubscript{\textit{n}}-LiClO\textsubscript{4}:

**Figure C.19** Band deconvolution of the experimental spectra of (PC)\textsubscript{\textit{n}}-LiClO\textsubscript{4} ((top) \textit{n} = 20 and (bottom) \textit{n} = 10) mixtures.
Figure C.20 Band deconvolution of the experimental spectra of (PC)$_n$-LiBF$_4$ ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
(PC)$_n$-LiCF$_3$SO$_3$:

Figure C.21 Band deconvolution of the experimental spectra of (PC)$_n$-LiCF$_3$SO$_3$ ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
(PC)$_n$-LiCF$_3$CO$_2$:

Figure C.22 Band deconvolution of the experimental spectra of (PC)$_n$-LiCF$_3$CO$_2$ ((top) $n = 20$ and (bottom) $n = 10$) mixtures.
Appendix D

Figure D.1 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) EC-(x) LiBF₄ mixtures.

Figure D.2 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) PC-(x) LiBF₄ mixtures.
Figure D.3 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) GBL-(x) LiBF₄ mixtures.

Figure D.4 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) GVL-(x) LiBF₄ mixtures.
Figure D.5 DSC heating traces ($5^\circ$C min$^{-1}$) and phase diagram of (1-x) EC-(x) LiDFOB mixtures.

Figure D.6 DSC heating traces ($5^\circ$C min$^{-1}$) and phase diagram of (1-x) PC-(x) LiDFOB mixtures.
Figure D.7 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) GBL-(x) LiDFOB mixtures.

Figure D.8 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) GVL-(x) LiDFOB mixtures.
Figure D.9 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) EC-(x) LiBOB mixtures.

Figure D.10 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) PC-(x) LiBOB mixtures.
Figure D.11 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) GBL-(x) LiBOB mixtures.

Figure D.12 DSC heating traces (5°C min⁻¹) and phase diagram of (1-x) GVL-(x) LiBOB mixtures.
Figure D.13 Anion band deconvolution of (solvent)$_n$-LiBF$_4$ ($n = 5$) at 60°C.

Figure D.14 Raman spectra at -40°C of anion B-F stretching mode (763 cm$^{-1}$) for EC-LiBF$_4$ mixtures indicating the AGG-I (EC)$_2$:LiBF$_4$ phase is present in crystallized samples and not SSIP or CIP phases.
Figure D.15 Viscosity plots of (left) \((EC)_n\)-LiX mixtures and (right) \((PC)_n\)-LiX mixtures.
Figure D.16 Viscosity plots of (left) (GBL)$_n$-LiX mixtures and (right) (GVL)$_n$-LiX mixtures.
Figure D.17 Conductivity plots of (left) (EC)$_n$-LiX mixtures and (right) (PC)$_n$-LiX mixtures.
Figure D.18 Conductivity plots of (left) (GBL)_n-LiX mixtures and (right) (GVL)_n-LiX mixtures.
Appendix E

Elemental Analysis of PYIRDFOB ionic liquids:

PY14DFOB:  
Theory: C 47.34; H 7.22; F 13.61; N 5.02; Br 0.0; B 3.87; O 22.93  
Actual: C 47.07; H 7.44; F 13.35; N 4.97, Br 0.0

PY15DFOB:  
Theory: C 49.17; H 7.57; F 12.96; N 4.78; Br 0.0; B 3.69; O 21.83  
Actual: C 49.39; H 7.81; F 12.68; N 4.80, Br 0.0

PY16DFOB:  
Theory: C 50.84; H 7.88; F 12.37; N 4.56; Br 0.0; B 3.52; O 20.84  
Actual: C 50.21; H 7.81; F 11.48; N 4.26, Br 0.0

Analysis of Na⁺ Cation Content in PY16DFOB by ICP-MS:

Performed by Kim Hutchison, Department of Soil Science, North Carolina State University, Raleigh, NC.

Procedure: PY16DFOB was tested via ICP-MS to rule out the possibility of Na⁺ cation contamination. This IL was chosen because it contains the largest amount of H-containing impurities and elemental analysis results suggest that it is the least pure. 2 mL of PY16DFOB was pipetted into an acid-washed Teflon 50 mL tube. 0.50 mL of optima pure nitric acid was added and the mixture was stored at room temperature for 10 d. The sample was diluted (along with a blank acid solution) ~25x with an addition of 0.5 mL concentrated optima pure HCl and the remainder DI water. The sample and blank were measured on a Perkin Elmer ICP-optical emission spectrometer. The concentrations of Na⁺ cations are as follows:

- DI water/acid blank: 0.017 mg L⁻¹
- PY16DFOB: 2.06 mg L⁻¹
PY$_{14}$DFOB: $^1$H-NMR (299.8 MHz, CD$_3$CN, CH$_3$CN ref. at 1.94 ppm)

PY$_{14}$DFOB: $^{11}$B-NMR (160.5 MHz, CD$_3$CN, LiBOB ext. ref. at 6.60 ppm)

**Figure E.1** NMR spectra of the PY$_{14}$DFOB IL (in CD$_3$CN).
PY$_{15}$DFOB: $^1$H-NMR (299.8 MHz, CD$_3$CN, CH$_3$CN ref. at 1.94 ppm)

PY$_{15}$DFOB: $^{11}$B-NMR (160.5 MHz, CD$_3$CN, LiBOB ext. ref. at 6.60 ppm)

**Figure E.2** NMR spectra of the PY$_{15}$DFOB IL (in CD$_3$CN).
Figure E.3 NMR spectra of the PY$_{16}$DFOB IL (in CD$_3$CN).
Figure E.4 CV scans of solvent-LiX electrolytes with an Al working electrode. Note: The scale varies to ensure full scans are observable.
Figure E.5 Microscope images of Al working electrodes after the CV scans displayed in Figure E.4. Darker contrast spots correspond to increased pitting corrosion.