ABSTRACT

MCOWEN, DENNIS W. Developing New Electrolytes for Advanced Li-ion Batteries. (Under the direction of Dr. Wesley A. Henderson).

The use of renewable energy sources is on the rise, as new energy generating technologies continue to become more efficient and economical. Furthermore, the advantages of an energy infrastructure which relies more on sustainable and renewable energy sources are becoming increasingly apparent. The most readily available of these renewable energy sources, wind and solar energy in particular, are naturally intermittent. Thus, to enable the continued expansion and widespread adoption of renewable energy generating technology, a cost-effective energy storage system is essential. Additionally, the market for electric/hybrid electric vehicles, which both require efficient energy storage, continues to grow as more consumers seek to reduce their consumption of gasoline. These vehicles, however, remain quite expensive, due primarily to costs associated with storing the electrical energy.

High-voltage and thermally stable Li-ion battery technology is a promising solution for both grid-level and electric vehicle energy storage. Current limitations in materials, however, limit the energy density and safe operating temperature window of the battery. Specifically, the state-of-the-art electrolyte used in Li-ion batteries is not compatible with recently developed high-voltage positive electrodes, which are one of the most effectual ways of increasing the energy density. The electrolyte is also thermally unstable above 50 °C, and prone to thermal runaway reaction if exposed to prolonged heating. The lithium salt used in such electrolytes, LiPF₆, is a primary contributor to both of these issues. Unfortunately, an improved lithium salt which meets the myriad property requirements for Li-ion battery electrolytes has eluded researchers for decades.
In this study, a renewed effort to find such a lithium salt was begun, using a recently developed methodology to rapidly screen for desirable properties. Four new lithium salts and one relatively new but uncharacterized lithium salt were synthesized for this investigation: dilithium 1,2,5-thiadiazolidine-3,4-dione-1,1-dioxide (Li₂TDD), lithium ethyl N-trifluoroacetylcarbamate (LiETAC), lithium hexafluoroisopropoxide (LiHFI), lithium pentafluorophenolate (LiPFPO), and lithium 2-trifluoromethyl-4,5-dicyanoimidazolide (LiTDI). Using crystalline solvate structure analysis and electrolyte solvation numbers, each of these lithium salts were compared to more well-characterized lithium salts, such as LiPF₆ and LiBF₄. From this study, links between anion structural characteristics and the anion⋯Li⁺ cation interactions (i.e., ionic association strength) were made.

From the screening of the five lithium salts that were synthesized, LiTDI was determined to be a promising candidate for Li-ion battery electrolytes. Further characterization of carbonate- and mixed carbonate-LiTDI electrolytes (e.g., ionic conductivity) confirmed this to be the case. Coin cells containing LiTDI or LiPF₆ electrolytes showed that cells with either electrolyte could deliver nearly identical power density at 25 °C. Additionally, thermogravimetric analysis (TGA) and NMR suggested that the LiTDI salt and carbonate-LiTDI electrolytes are thermally stable up to at least 60 °C. Further supporting this finding, coin cells cycled at 60 °C with LiPF₆ lost significantly more capacity than those with LiTDI. Therefore, LiTDI is a prime candidate for the complete replacement of LiPF₆ to significantly increase Li-ion battery tolerance to heat, improving the safety characteristics.

In addition to searching for new lithium salts, the effect of lithium salt concentration on electrolyte physicochemical properties was investigated. This radically different approach to modifying electrolyte properties determined that amorphous, highly concentrated carbonate-
lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) electrolytes have drastically different behavior than more dilute electrolytes. For example, the thermal stability and anodic stability vs. a Pt electrode of the concentrated electrolytes are significantly higher. Most striking, however, was the suppression of Al corrosion by the concentrated carbonate-LiTFSI electrolytes, despite the fact that Al corrosion of more dilute carbonate-LiTFSI electrolytes has consistently been attributed to the TFSI⁻ anion in the literature. These results, explained by crystalline solvate analysis, Raman spectroscopy, and molecular dynamics simulations, could change the way Li-ion battery electrolytes are designed.
Developing New Electrolytes for Advanced Li-ion Batteries

by
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BIOGRAPHY

Dennis McOwen was born in Toledo, OH in 1988, the younger of two sons of Ken and Hélène. In 2006, Dennis graduated from Ottawa Hills High School. Dennis then started his undergraduate education at The Ohio State University and earned his B.S. in Chemical and Biomolecular Engineering in 2010. From there, Dennis moved to North Carolina to start his graduate work in Chemical and Biomolecular Engineering at North Carolina State University in the ILEET group.
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First and foremost, I want to express my deepest appreciation to my parents for doing everything they could to make sure I had the best opportunities. They let me pursue all of my interests and curiosities without reservation, and for that I am sincerely grateful. I am grateful to my older brother, David, for not only encouraging and believing in me, but also understanding me.

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CHAPTER 1: Background

1.1 U.S. Energy Economy and Future

The U.S. Energy Information Administration (EIA) reports that in 2012 the United States consumed 95.0 quadrillion BTUs (100.5 eJ) of primary energy from all energy resources (coal, petroleum, nuclear energy, etc.). Of this, 8.8 quadrillion BTUs, or 9.3% of total energy consumption, were from renewable resources such as hydroelectric power, biomass combustion, and electric wind turbines (Figure 1.1). This represents a significant increase from the year 2000, when renewable resources accounted for 6.2% of energy consumption. This growth is primarily due to a massive expansion in wind turbine electricity generation capacity, as well as smaller but significant increases in solar photovoltaic and biomass combustion capacity. In fact, wind alone accounted for 3.5% of the electricity generated in 2012, up from 0.15% in 2000. In the near future, the EIA projects that from now until 2040, wind and solar will lead renewable energy capacity growth, representing a total renewable energy capacity increase from 9.3% to 13% in 2040 (total demand increases to 107.6 quadrillion BTUs), depending on the political scenario (e.g., carbon taxes or cap-and-trade). These renewables are extremely important to the future energy infrastructure, not only because they help to diminish the U.S. dependence on fossil fuels, but also because they can reduce emissions of CO₂, a primary cause of climate change. Indeed, the electricity generation sector is the number one source of CO₂ emissions in the U.S. (38% or 2.06 billion metric tons of CO₂ equivalent).
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Following close behind, the transportation sector is the number two emitter of CO$_2$ in the U.S. (34% of CO$_2$ emissions), mainly as a result of the pervasive internal combustion engine.$^2$ The EIA outlook report, however, predicts increases in sales of electric and plug-in hybrid electric vehicles as consumer opinion improves and emissions standards and CO$_2$ regulations become more rigorous over the coming decades.$^2$ Electric vehicles use an electric motor to replace the internal combustion engine, while hybrid electric vehicles use an assisting internal combustion engine to recharge the battery pack for the electric motor when the charge is low. Because electric/hybrid electric vehicles use little or no combustible fuel, their use can help to considerably decrease the use of petroleum. One study has shown that if
the average vehicle fuel economy was doubled to 60 mpg instead of 30 mpg (the 2011 Chevrolet Volt plug-in hybrid has a combined composite fuel economy of 60 mpg equivalent),\textsuperscript{4} a cumulative reduction of 25 billion metric tons of CO\textsubscript{2} emissions could be achieved over 50 years.\textsuperscript{5}

\textit{1.2 The Need for Advanced Li-ion Batteries}

While renewable resources and electric vehicles can both significantly reduce the level of CO\textsubscript{2} emissions and reduce the dependence on fossil fuels, using them together may provide an even greater benefit. A central issue with some of the most promising renewable energy sources, wind and solar in particular, is that they are naturally intermittent. For example, solar is mainly dependent on the time of day and cloud coverage, while wind energy is predominantly affected by weather conditions. In essence, the generating capacities of these energy sources cannot be strictly controlled, which presents a problem as demand fluctuates throughout the day, week, and year, and may exceed available supply. These intermittent energy sources, therefore, while abundant and readily available, cannot be used independently without backup generating capabilities from nuclear or fossil fuels, and/or without an energy storage system to buffer between times of excess supply and high demand (i.e., “peak-shaving”).\textsuperscript{6-8} While fossil fuel plants already exist to provide this extra generation, they have significant startup times and must already be running prior to when they are needed, wasting fuel. On the other hand, energy storage in the form of a battery or mechanical system can store energy from times of excess supply and act as a “spinning reserve,” providing energy almost instantaneously to meet sudden changes in supply and
demand, and only when needed. An efficient and economical energy storage solution to aid in peak-shaving is therefore strongly sought after to enable the continued growth of intermittent renewable energy sources while displacing much of the need for fossil fuels.

When the energy supply from renewables exceeds demand, the excess energy can be stored in one of several different ways: electrochemically in batteries, or mechanically in flywheels or liquid piston compressed air. Other methods are possible, such as underground compressed air and pumped hydro energy storage, but these are usually highly location dependent.7 Flywheels and liquid piston compressed air are both attractive candidates for peak-shaving applications because they can be relatively safe and simple to employ. However, both of these systems lose a significant fraction of their stored energy within a matter of hours (20% per hour for flywheel energy storage) and are therefore not effective for storage longer than this timeframe.7,9 In contrast, batteries can store energy for days or weeks with virtually no loss.7,9

Another advantage of using batteries is the prospect of a Vehicle-to-Grid (V2G) system. Because batteries inside electric vehicles are already connected to the grid when charging, they can potentially be used as a distributed energy storage system, reducing the required size and therefore cost of a central energy storage station. Numerous reports have shown that V2G can help to drastically reduce carbon emissions while improving the large-scale feasibility of intermittent energy sources.6,10-14

Of all of the battery chemistries available, Li-ion batteries have garnered strong interest for grid-level energy storage for a number of reasons. First and foremost, Li-ion batteries have a high energy density, principally as a result of the high operating voltage which ranges
from 3.3 to 4.7 V, depending on the specific electrodes used (Figure 1.2). By comparison, lead-acid batteries operate around 2.0 V. Thus, Li-ion batteries can store more energy per unit charge (1 V = 1 Joule Coulomb\(^{-1}\)). Additionally, Li-ion batteries have higher power density than other battery chemistries,\(^9\)\(^,\)\(^15\) and can retain 80% of their capacity over thousands of cycles.\(^9\)\(^,\)\(^16\) Due to these advantageous properties, Li-ion batteries have become ubiquitous in portable electronics and have begun to penetrate the electric and hybrid electric vehicle market. Several projects are currently investigating the deployment of Li-ion batteries as central energy storage for the grid.\(^7\)\(^,\)\(^17\) However, while Li-ion battery technology has permeated and dominated a number of markets related to energy storage in the last two decades, significant advancements must be first be made in order to improve their safety.

![Figure 1.2 Comparison of volumetric and gravimetric energy density for different battery chemistries.\(^{15}\)](image)
stability, and performance characteristics to make large-scale energy storage safe and economical.

1.3 How Li-ion Batteries Work

A Li-ion cell is composed of a metal oxide positive electrode (e.g., LiCoO$_2$ or LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$—"NMC") with an Al current collector, and a graphite negative electrode with a Cu current collector (Figure 1.3). Between the electrodes is a porous polyolefin separator material wetted with an electrolyte consisting of organic aprotic solvent and a lithium salt. Although different electrode combinations can be used, cell voltages from 3.0 to 4.5 V can typically be achieved, resulting in the high energy density for which Li-ion

![Figure 1.3 Li-ion battery schematic in charging mode.](image)
batteries are known.\textsuperscript{16} This high voltage, however, requires the use of a non-aqueous electrolyte, as water readily dissociates above 1.5 V. The state-of-the-art electrolyte for commercial cells is thus composed of ethylene carbonate (EC) with one or more linear carbonates (e.g., dimethyl carbonate or ethyl methyl carbonate) and lithium hexafluorophosphate (LiPF\textsubscript{6}) at a concentration around 1 M (Chart 1.1).\textsuperscript{16} The combination of EC, which solvates Li\textsuperscript{+} cations exceedingly well, with LiPF\textsubscript{6}, whose anion does not compete well for Li\textsuperscript{+} cation coordination, results in electrolytes with high ionic conductivity (> 1 mS cm\textsuperscript{-1}).\textsuperscript{18-20} EC, however, freezes above room temperature and with LiPF\textsubscript{6} can form high-melting solvates. The presence of linear carbonates in quantities equal to or exceeding the EC content decreases the tendency of the electrolyte to crystallize, reduces the viscosity, and increases the conductivity at low temperatures.\textsuperscript{16,19,21}

When a Li-ion battery is in the discharged state, Li\textsuperscript{+} cations are present in the metal oxide positive electrode and in the electrolyte. When the cell is charged, electrons are pulled from the positive electrode through the external circuit and Li\textsuperscript{+} cations move into solution, reducing the Li\textsuperscript{+} content of the positive electrode (Figure 1.3). At the same time, electrons migrate into the graphite negative electrode from the external circuit and Li\textsuperscript{+} cations from the
electrolyte solution intercalate into the negative electrode, forming LiC₆.¹⁶,²²,²³ During discharge, the reverse occurs spontaneously. As the cell charges/discharges, the cell potential (the voltage difference between the two electrodes) increases/decreases as the composition of each electrodes changes, which can be used to determine the state of charge for some batteries (depending on the electrodes in use).

There are a number of metal oxide positive electrodes, each having varying characteristics, which can be used in Li-ion batteries. LiCoO₂ (3.9 V vs. Li/Li⁺) has historically been the most common, but it is expensive since Co is a rare material. Some electrodes are composed of other metals, such as Ni (LiNiO₂, 3.6 V vs. Li/Li⁺), or Mn (LiMn₂O₄, 4.1 V vs. Li/Li⁺). While LiNiO₂ is cheaper than LiCoO₂, it also has a lower operating voltage. LiMnO₄ is a higher voltage material, but this electrode does not cycle well for prolonged periods due to Mn dissolution in the electrolyte.²⁴ This is an issue because of active material loss from the positive electrode and the dissolved Mn can deposit on the graphite, resulting in the poisoning of the negative electrode. LiMn₁.₅Ni₀.₅O₄ is a highly desirable electrode due to its high voltage (4.7 V vs. Li/Li⁺), but it suffers from Mn dissolution as well. The incorporation of small amounts of Co to form LiNiₓMnᵧCoₚO₂ electrodes, where z < 0.35, lowers the voltage to 3.8-4.3 V vs. Li/Li⁺, but stabilizes the Mn and results in a lower cost electrode compared to LiCoO₂.²⁵ Another electrode, LiFePO₄, excludes these three metals altogether. This electrode has fast kinetics which improves the power capability of the battery as compared to the above electrode materials. On the other hand, it has a much lower voltage (3.4 V vs. Li/Li⁺), which decreases the energy density.²⁶,²⁷
Unlike the metal oxide positive electrode, the graphite negative electrode is composed of layers of graphene sheets, with significant spacing between the sheets. It is therefore possible to intercalate other components into the graphite besides the Li$^+$ cations, such as the anions or solvent molecules.\textsuperscript{28-30} These larger molecules can push apart and exfoliate the graphite, irreversibly destroying the negative electrode. In state-of-the-art Li-ion batteries, a solid electrolyte interface (SEI) protects the graphite electrode from this damage.\textsuperscript{16,31,32} During the first several charge cycles, EC, along with contributions from LiPF$_6$, decomposes on the graphite surface forming the SEI film that is conductive to Li$^+$ cations, but prevents the contact of larger molecules with the graphite surface. Thus the structure of the graphite is protected from exfoliation and the electrolyte is protected from continuous degradation. The SEI, and by association, the incorporation of EC in the solvent blend, is thus critical to Li-ion battery performance.

While the SEI formed from EC is satisfactory, it is also possible to form a more stable or lower impedance SEI using additives as sacrificial agents that preferentially decompose on the graphite surface. Examples of these additives include vinylene carbonate (VC), lithium bis(oxalato)borate (LiBOB), and lithium difluoro(oxalato)borate (LiDFOB, Chart 1.2).\textsuperscript{33-38} Each of these additives will decompose on the graphite surface before EC (although it is unclear if EC degradation is completely eliminated) forming an SEI of different composition and thus different properties. There is also evidence to suggest that some additives can form a passivation layer on high-voltage positive electrodes, which serves to reduce Mn dissolution and protect the electrolyte from excessive oxidation.\textsuperscript{35} Recently, some of these additives
Chart 1.2 Structure of additives commonly used in Li-ion batteries.

or others have been incorporated into commercial Li-ion batteries, typically around 1-5 wt% of the electrolyte, improving the cell stability, lifetime, and low temperature performance.

1.4 Barriers to the Next Generation of Li-ion Batteries

Although Li-ion battery technology has improved tremendously since the first cell was sold in 1990, advancements in design and performance have seemingly hit a near standstill in recent years. Efforts over the last decade have been focused primarily on two areas: increasing the energy density (volumetric and gravimetric) of electrode materials to reduce the battery volume/mass, and improving the high temperature and safety characteristics of Li-ion batteries. There are two ways to improve the energy density. The first is to redesign existing electrode materials with new structures, usually with nanotechnology to improve the surface area and structure properties, to increase the electrode capacity (measured in $C \, g^{-1}$ or $mAh \, g^{-1}$ active electrode material). The second is to increase the cell potential to the highest value possible, around 5.1 V, by replacing the positive electrode with a high-voltage positive electrode. A number of high-voltage electrodes already exist, such as $LiNi_{0.5}Mn_{1.5}O_2$ (NMO, 4.7 V vs. Li/Li$^+$) and $LiNiPO_4$ (5.1 V vs. Li/Li$^+$). With these electrodes, each Coulomb of
capacity is transferred at a higher energy, dramatically increasing the energy density (mWh g\(^{-1}\)) relative to conventional electrodes, even though the charge capacity (mAh g\(^{-1}\)) may be similar. The state-of-the-art electrolyte, however, oxidizes on these high-voltage electrodes, leading to poor stability and cycle life. Unfortunately, no other electrolytes have been discovered to date that are compatible with both the high-voltage electrodes and the rest of the cell components at the same time.

The other major focus to improve Li-ion batteries has been in regards to safety/thermal stability. A great deal of energy is stored electrochemically in a Li-ion battery, and this inherent danger is exacerbated by the use of volatile and flammable organic solvents. Additionally, LiPF\(_6\) is in equilibrium with PF\(_5\), an extremely reactive Lewis acid (Eq. 1).\(^{39,40}\)

\[
\text{LiPF}_6 \leftrightarrow \text{PF}_5 + \text{LiF} \quad \text{(Eq. 1)}
\]

At room temperature, the equilibrium heavily favors LiPF\(_6\). However, at elevated temperatures (> 50 °C), PF\(_5\) exists in appreciable amounts, and reacts with any residual moisture or acidic protons to form POF\(_3\), another reactive molecule (Scheme 1.1). In the mechanism shown below, POF\(_3\) reacts with solvent components and additional PF\(_5\) to form CO\(_2\) and more POF\(_3\) in an exothermic reaction. This heat then shifts the equilibrium of Eq. 1 to the right, resulting in increasing amounts of PF\(_5\), and thus POF\(_3\). Current Li-ion batteries are therefore prone to runaway reactions if the cell temperature is not carefully maintained and monitored, leading to cell venting, fire, or explosion.

Due to the possibility of a runaway reaction and consequential cell overpressure/explosion, it would be highly beneficial to completely replace LiPF\(_6\) with a more thermally robust lithium salt. However, the identification of a lithium salt which can withstand higher
temperatures without severely limiting the cell performance has proven elusive—each proposed lithium salt has come with its own disadvantages, and LiPF$_6$ retains the best balance between all properties (Table 1.1). For example, lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI) is much more thermally stable as compared to LiPF$_6$ with a similar conductivity in solution,$^{41-43}$ but LiTFSI-based electrolytes are reported to severely corrode the Al current collector.$^{43,44}$ Therefore, to increase battery safety and thermal stability, a new lithium salt must be identified.

Li-ion battery technology has made great strides since its inception, with significant advancements made in cycle life and energy density. These batteries are perhaps the most promising means of storing large amounts of energy in a small space—a vital need for electric and plug-in hybrid electric vehicles. It may also be that Li-ion batteries enable the widespread use of abundant and renewable energy resources through high-capacity, efficient,
Table 1.1 Selected properties of lithium salts commonly studied in Li-ion battery electrolytes.

<table>
<thead>
<tr>
<th>Li Salt</th>
<th>Al Corrosion*</th>
<th>Stable SEI Formation*</th>
<th>Ionic Conductivity*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPF$_6$</td>
<td>no</td>
<td>yes</td>
<td>high</td>
<td>thermally unstable readily hydrolyzes used in commercial Li-ion batteries</td>
</tr>
<tr>
<td>LiAsF$_6$</td>
<td>no</td>
<td>yes</td>
<td>high</td>
<td>not used commercially due to As</td>
</tr>
<tr>
<td>LiN(SO$_2$C$_2$F$_5$)$_2$ (LiBETI)</td>
<td>yes**</td>
<td>no</td>
<td>high</td>
<td>exceptionally high thermal/electrochemical stability less Al corrosion than LiTFSI</td>
</tr>
<tr>
<td>LiN(SO$_2$CF$_3$)$_2$ (LiTFSI)</td>
<td>yes**</td>
<td>no</td>
<td>high</td>
<td>exceptionally high thermal/electrochemical stability</td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>no</td>
<td>no</td>
<td>high</td>
<td>potentially explosive perchlorate anion</td>
</tr>
<tr>
<td>LiBC$_2$O$_4$F$_2$ (LiDFOB)</td>
<td>no</td>
<td>yes</td>
<td>moderate</td>
<td>more conductive SEI than LiBOB slowly hydrolyzes thermally dissociates to LiBOB and LiBF$_4$</td>
</tr>
<tr>
<td>LiBF$_4$</td>
<td>no</td>
<td>no</td>
<td>moderate</td>
<td>maintains conductivity at low temperature slowly hydrolyzes</td>
</tr>
<tr>
<td>LiCF$_3$SO$_3$</td>
<td>yes**</td>
<td>no</td>
<td>low</td>
<td>thermally stable</td>
</tr>
<tr>
<td>Li(C$_2$O$_4$)$_2$ (LiBOB)</td>
<td>no</td>
<td>yes</td>
<td>low</td>
<td>improves high and low temperature performance when used as an additive</td>
</tr>
<tr>
<td>LiCF$_3$CO$_2$</td>
<td>N/A</td>
<td>no</td>
<td>low</td>
<td>high ionic association tendency</td>
</tr>
</tbody>
</table>

*in EC/DEC or similar carbonate-based electrolyte.

**see Ch. 6.
and economical grid-level energy storage. For these ideas to come to fruition, however, it is clear that new Li-ion battery materials must be developed to further improve the energy density, lifetime, and safety of the battery packs. Specifically, new electrolyte formulations and lithium salts must be explored and studied to determine how next generation Li-ion battery electrolytes may be tuned for use in the demanding applications of the future. If these goals can be met, the energy infrastructure will be able to use more renewable resources, such as wind and solar, and electrified cars will help to both displace the use of petroleum and reduce overall CO₂ emissions.

1.5 Methods to Study and Screen for New Electrolytes

To rationally design a new electrolyte to replace the state-of-the-art electrolyte, it is imperative to be able to understand how the characteristics of different lithium salts and solvents ultimately affect cell performance. That is, the ways in which the molecular interactions between the lithium salt ions and solvent give to rise to varying electrolyte properties and how these properties, in turn, change how the cell operates must be studied. The ionic conductivity, viscosity, phase behavior, thermal stability, and electrochemical stability are the physicochemical properties that are of utmost importance to Li-ion battery performance. The ionic conductivity impacts the maximum charge/discharge rate and thus the power capability of the battery, as a low ionic conductivity results in high total cell impedance. A high viscosity electrolyte can negatively affect the wetting of the electrodes or separator and also makes handling the electrolyte difficult. The phase behavior of the electrolyte is important because consumers require that Li-ion batteries work at temperatures
at least as low as -20 °C, and thus the electrolyte must remain a liquid at this temperature. At higher temperatures, the thermal stability of the electrolyte comes into play. The electrolyte must not decompose during prolonged exposure to temperatures at least as high as 60 °C, or the lifetime of the battery will suffer. Decomposition of the electrolyte can also compromise the safety of the battery, as is the case for electrolytes based on LiPF₆. Lastly, the electrochemical stability of the electrolyte is of particular importance for next generation Li-ion batteries which incorporate high-voltage cathode materials. Any redox reactions outside of the desired electrode reactions or passivation film formation will eventually lead to decreased capacity and possible safety hazards. The relationships between electrolyte physicochemical properties and cell performance have therefore been established.

While it is relatively straightforward to link electrolyte properties to cell properties, it is much more complex but equally beneficial to be able to understand how the molecular interactions are linked to electrolyte properties and thus cell properties. Understanding such a connection would make the design and tailoring of electrolytes for specific Li-ion battery applications possible, rather than using the traditional empirical approach where varying electrolytes are simply screened for desirable properties with little regard towards the source of such properties. In recent years, a methodology has been developed to rapidly characterize and compare a new lithium salt to conventional lithium salts. This approach has accurately linked the molecular interactions of known lithium salts to electrolyte physicochemical properties and can therefore be used to predict the same properties of electrolytes with a new lithium salt. The methodology relies on the determination of the ionic association strength of the anion and average solvation number. The ionic association strength is a qualitative
measure which describes how strongly the anion coordinates Li⁺ cations relative to other lithium salt anions. The solvation number quantifies how many solvent molecules are coordinated to each Li⁺ cation on average in solution, and is heavily influenced by the ionic association strength of the anion, as well as the salt concentration and solvent being used. By comparing the ionic association strength and solvation number of an uncharacterized lithium salt to well-known lithium salts, the electrolyte and some cell properties can be accurately predicted. Additionally, the methodology allows for the quick screening of a number of lithium salts without ever assembling a battery cell, significantly improving throughput.

1.5.1 Crystalline Solvate Structure Analysis

The ionic association strength of a lithium salt anion can be assessed in several ways. The first method, analysis of crystalline solvate structures, offers insight into the anion and solvent interactions with the Li⁺ cations. Typically, there are only minimal interactions between the solvent and anions. Instead, competition between the anion and solvent molecules to coordinate the Li⁺ cations is what largely determines the crystalline solvate structure. To compare different crystalline solvates, it is useful to first classify the varying levels of ionic association of the solvates using the following terms: solvent separated ion pair (SSIP, anion uncoordinated to a Li⁺ cation), contact ion pair (CIP, anion coordinated to one Li⁺ cation), and aggregate (AGG, anion coordinated to more than one Li⁺ cation) (Figure 1.4). The AGG solvates can be further distinguished as AGG-I, AGG-II, or AGG-III, with the anion coordinated to two, three, or four or more Li⁺ cations, respectively. Thus, an AGG
Figure 1.4 Diagram of different types of coordination commonly found in solvates of lithium salts (X is the anion, Li is the Li\(^+\) cation, and tetrahydrofuran (THF) is the solvent) (from known crystal structures).

A solvate would indicate that the anions compete well for occupancy within the Li\(^+\) cation coordination spheres (suggesting high ionic association strength), while an SSIP would indicate that the solvent competes better than the anion (low ionic association strength).

There are more factors at play, however, than the ionic association strength of the anion that determine what type of solvate will form, including the size and flexibility of the solvent and anion. Because of these other factors, crystalline solvates of lithium salts with aprotic solvents like acetonitrile (AN), EC, or tetrahydrofuran (THF), are not always predictable or indicative of the ionic association strength of the anion. In contrast, several reports have shown that comparisons of solvates of different lithium salts with glyme solvents (e.g., G1, G2, or G3, Chart 1.3) are much better indicators of ionic association strength (although still not entirely definitive).\(^49,50\) For example, Table 1.2 shows that LiAsF\(_6\) and LiTFSI form SSIP (G1)\(_3\):LiAsF\(_6\) and (G1)\(_3\):LiTFSI solvates, respectively, while LiBF\(_4\) forms a CIP (G1)\(_2\):LiBF\(_4\)
solvate, and LiCF$_3$CO$_2$ forms an AGG (G1)$_1$:LiCF$_3$CO$_2$ solvate (the first crystalline solvates to form from dilute solutions). This would suggest that these salts would be arranged in order of increasing ionic association strength as follows: LiAsF$_6$ ~ LiTFSI, LiBF$_4$, and LiCF$_3$CO$_2$. Similar trends are noted for the solvates formed from G2-LiX and G3-LiX mixtures. A number of other reports using different methodologies have found the same order in ionic association strength for these lithium salts. For example, when measuring the conductivity of AN-LiX electrolytes, the conductivity decreases with increasing ionic association strength as indicated in Table 1.2.\textsuperscript{47,48} It should be noted that while no glyme-LiPF$_6$ solvates are known, the behavior of glyme-LiAsF$_6$ mixtures is likely quite similar, as these anions are quite similar in shape and size, and poly(ethylene oxide)-LiPF$_6$ and -LiAsF$_6$ mixtures have comparable phase behavior.\textsuperscript{51}

Overall, the solvate structural analysis is quite useful as a fast screening technique. However, it is not precise enough to differentiate between lithium salts which have somewhat similar ionic association strength, such as LiClO$_4$ and LiCF$_3$SO$_3$, two salts which have quite different electrolyte properties. Thus, further characterization of promising lithium salts is essential.
Table 1.2 Comparison of the first crystalline solvate phases (glyme-LiX) to form from dilute mixtures (*speculative assignment).\textsuperscript{50,52}

<table>
<thead>
<tr>
<th></th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3-1 (SSIP)</td>
<td>2-1 (CIP)</td>
<td>1-1 (AGG)</td>
</tr>
<tr>
<td>LiBETI</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>LiAsF\textsubscript{6}</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>LiClO\textsubscript{4}</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>LiDFOB</td>
<td>X</td>
<td>X*</td>
<td></td>
</tr>
<tr>
<td>LiBF\textsubscript{4}</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>LiCF\textsubscript{3}SO\textsubscript{3}</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>LiBOB</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCF\textsubscript{3}CO\textsubscript{2}</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

1.5.2 Characterization of Liquid AN-LiX Electrolytes

Just as glyme solvates are a useful way to quickly probe the ionic association strength in the solid state, AN-LiX electrolytes are proven to be a valuable vehicle to examine the same property in the liquid state. Specifically, the solvation numbers of AN-LiX electrolytes, determined by Raman spectroscopy, are used to compare the ionic association strength of different lithium salts. The solvation number is a measure of the average number of solvent molecules to which each Li\textsuperscript{+} cation is coordinated. A higher solvation number (at a particular concentration) indicates that the anion has a lower ionic association strength, since the solvent competes well with the anions for coordination of the Li\textsuperscript{+} cations. Conversely, a low solvation number is usually measured for anions which compete much better than the solvent for Li\textsuperscript{+} cation coordination and are said to be of high ionic association strength. If this
analysis is performed for different salts using the same solvent and temperature, the ionic association strength of different lithium salts can be directly compared as a function of salt concentration. This study has already been performed, and the most common lithium salts were arranged in order from lowest ionic association strength to highest. This is found to agree well with the glyme-LiX solvate data in Table 1.2:\textsuperscript{45-48}

\[
\text{LiPF}_6 < \text{LiTFSI} \sim \text{LiClO}_4 < \text{LiBF}_4 < \text{LiCF}_3\text{SO}_3 < \text{LiCF}_3\text{CO}_2
\]

In order to identify the degree of solvation in a particular electrolyte using Raman spectroscopy, one or more Raman bands must shift upon coordination to a Li\textsuperscript{+} cation. The spectra can then be fit with Gaussian-Lorentzian curves (i.e., deconvolution) and each curve integrated. However, this deconvolution becomes much less accurate and precise when there is significant overlap with other vibrational bands in the spectra. The Raman-active C-C (918 cm\textsuperscript{-1} and 922 cm\textsuperscript{-1} hot band) and C≡N (2254 cm\textsuperscript{-1} and 2251 cm\textsuperscript{-1} hot band) vibrational modes of AN both shift upon coordination to a Li\textsuperscript{+} cation (930 cm\textsuperscript{-1} and 2277 cm\textsuperscript{-1}, respectively, Figure 1.5), and these bands usually have little or no overlap with the vibrational bands of common lithium salt anions, making the deconvolution of the Raman spectra more simplistic and accurate (other solvents, such as EC, can be used but comparisons can only be made between electrolytes of the same solvent). To measure the degree of solvation, the two vibrational band regions are analyzed separately. The area under each coordinated and uncoordinated peak from one vibrational mode is then used in the following equation to determine the fraction of coordinated solvent. This fraction is then multiplied by the number of solvent molecules per Li\textsuperscript{+} cation (n) to give the solvation number, N (Eq. 2).

\[
\frac{A_{\text{coordinated peaks}}}{A_{\text{coordinated peaks}} + A_{\text{uncoordinated peaks}}} * n = N
\]

Eq. 2
Figure 1.5 Raman spectra of the AN vibrational modes at 918 and 2254 cm$^{-1}$, and the corresponding shifts to 930 and 2277 cm$^{-1}$ upon Li$^+$ coordination.

An underlying assumption of this analysis is that the size/shape of the coordinated and uncoordinated solvent bands are equivalent (i.e., they have equivalent Raman scattering activities). While this has been shown to be a valid assumption for AN, other solvents, such as EC, require correction factors determined from quantum chemical calculations to take into account the differences between the coordinated/uncoordinated bands.$^{53}$

By comparing the solvation numbers of different AN-LiX electrolytes, the ionic association strength of a new lithium salt can be assessed and compared with the results from the glyme-LiX crystalline solvate analysis. In doing so, the relation of a new lithium salt to known lithium salts can be established and the need for further study determined.

1.5.3 Physicochemical Properties of Electrolytes

If the methodology described above concludes that a lithium salt may be a promising Li-ion battery electrolyte salt, then the physicochemical properties of the electrolyte must be studied before actual battery testing. The properties of interest include the phase behavior in
carbonate solvents, ionic conductivity, thermal stability, and electrochemical stability. The phase behavior can be studied by differential scanning calorimetry (DSC) to analyze the EC-LiX electrolytes to determine if a carbonate solvate could crystallize within a battery cell. Using electrochemical impedance spectroscopy and an environmental chamber (temperature control), the ionic conductivity can be measured as a function of lithium salt concentration and temperature. It is generally accepted that the ionic conductivity must exceed 1.0 mS cm\(^{-1}\) in the battery’s operating temperature window. Thermal stability can be studied using DSC, as well as thermogravimetric analysis (TGA) to measure mass loss as a function of temperature and nuclear magnetic resonance (NMR) to search for byproducts of decomposition. Ultimately, to determine the thermal stability of an electrolyte within a cell, cells must be cycled at high temperature because, although an electrolyte may or may not decompose on its own at high temperature, it may react with the electrode materials in a battery cell at elevated temperature, as is the case with LiPF\(_6\).\(^{16,54,55}\)

The electrochemical stability of an electrolyte is dependent on several factors, mainly the solvent, lithium salt, electrode, concentration (see Ch. 6), and temperature. For a given electrolyte, the electrochemical stability must be studied on passive and active electrode materials, before examining the stability with actual battery electrodes. In this way, the cause(s) of instability can be separated and identified. A passive electrode material, such as Pt, reflects the intrinsic electrochemical stability of an electrolyte where film formation is unlikely. An active electrode material, such as Al, can participate in the redox reactions and reveal if the electrolyte components either react with the electrode, passivate the surface, or do not react at all. The stability towards an Al electrode is particularly important for Li-ion
batteries, as this is used as the current collector for the positive electrode and is prone to corrosion (Figure 1.3).

For Li-ion battery electrolytes, the cathodic (reductive) stability is usually more dependent on the solvent, since it is unlikely the anion will undergo reduction. The anodic (oxidative) stability is dependent on the both the solvent and the anion and it is critical that the electrolyte has a high anodic stability to allow the use of high-voltage positive electrode materials. The electrochemical stability can be studied using linear sweep (LSV) or cyclic (CV) voltammetry, where the potential of the cell is swept at a slow but constant rate starting from open circuit voltage up to a specified limit while the current density is measured.

1.5.4 Half-Cell and Full-Cell Li-ion Battery Testing

Understanding the electrochemical and cycling stability of electrolytes towards Li-ion battery electrodes is more complex, partly because the redox reactions due to Li\(^+\) cation intercalation/deintercalation are supposed to occur. Therefore, current passed across the cell must be carefully analyzed to determine if it is from Li\(^+\) cation transfer, or another reversible or irreversible side reaction. Additionally, Li metal or a Li containing electrode must be used since a Li source is needed to maintain the electrolyte charge balance as Li\(^+\) cations intercalate/deintercalate from the electrodes. These measurements can be done by CV or galvanostatic cycling. In galvanostatic cycling, instead of sweeping the potential, the current is held constant while the voltage of the cell is measured. At first, the current is kept low so the SEI can form evenly on the electrode surface. When the desired vertex potential is reached (e.g., 4.3 V for a NMC half-cell), the current is reversed until the potential reaches
the second vertex (3.0 V for a NMC half-cell). This process is repeated for 5-20 cycles at low C rates, typically from C/24 to C/10 (1C = theoretical current required to fully charge or discharge the cell in 1 h). This is called the SEI formation period and it is critical to determining if the electrolyte can passivate the electrode surfaces adequately while maintaining the ability to transfer Li\(^+\) cations.

An important value that can be determined from galvanostatic cycling is the capacity of the cell, measured in mAh g\(^{-1}\) of active material of the limiting electrode. This is easily calculated by multiplying the current by the time it took for the cell to charge or discharge between the vertex potentials. Both the charge and discharge capacity can be determined and, from these, a Coulombic efficiency can be calculated. The discharge capacity and efficiency of the cell as a function of cycle number are what is used to measure the cycling stability of the cell. Furthermore, the cell voltage can be plotted against time or the cell capacity (capacity is related to time only by the current, which is constant in any given cycle). This provides crucial information about the voltages that different reactions occur at, and during which cycles.

After the formation period, the cells are cycled at faster rates more typical of regular battery use, usually C/5 to 1C. Here, several different protocols can be used to study the cell performance. A study of the rate capability of the cell measures the capacity of the cell as a function of C rate up to 5C or higher, and is a direct indicator of how much power the cell can deliver. The lifetime can be measured by cycling the cell at a moderate rate of C/5 for long periods (100-500 cycles). The thermal stability of the cell can also be studied by first cycling the cell at 25 °C and then increasing the temperature to 60 °C for a predetermined
number of cycles. The efficiency and charge/discharge capacity are then monitored for changes. Each of these tests can be done using half-cells or full-cells. Half-cells are useful for looking at electrolyte interactions with only one electrode (ideally), but cannot be cycled for long periods due to dendrite formation on the Li metal surface. Full cells are more challenging to analyze, as it is difficult to separate the interactions on one electrode from the other, but they are ultimately a more realistic model for cell performance.

**1.6 Motivation and Objectives**

Developing a high-energy and intrinsically safe Li-ion battery necessitates the improvement of the electrolyte. Incremental improvements to the state-of-the-art electrolyte using various additives and slightly modified solvent blends, as has been the model for the last two decades, will likely not be sufficient to meet the substantial demands of the next-generation Li-ion battery applications (e.g., electric vehicles). Instead, the discovery of new electrolytes which are more electrochemically and thermally stable is critical to the future of Li-ion batteries.

This study focuses on the development of new electrolyte formulations for Li-ion batteries that are intrinsically more thermally and/or electrochemically stable. The first approach was to synthesize new lithium salts or relatively new lithium salts which had not been adequately characterized. Then, a methodology that has been recently developed to rapidly characterize lithium salts was used to screen these lithium salts for desirable properties. Lithium salts which passed the screening were more fully characterized in carbonate electrolytes and tested in battery cells.
The second approach was to study the properties of highly concentrated electrolytes to determine how salt concentration could affect electrolyte physicochemical properties and electrochemical stability. Several of the physicochemical properties described above are strongly dependent on lithium salt concentration (e.g., solvation number, conductivity, etc.), however, most research generally only uses the electrolyte concentration at which the conductivity is maximized. Here, the relationship between electrolyte molecular interactions, electrode interactions, and physicochemical properties with salt concentration are scrutinized. Startling new observations are found and an entirely new mechanism for the corrosion of Al in Li-ion batteries is proposed, which could cause a paradigm shift in the design of non-aqueous electrolytes for next generation Li-ion batteries.
1.7 References

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2.1 Materials

2.1.1 Solvents

Acetonitrile (AN, anhydrous, 99.9%), ethyl acetate (EA, anhydrous, 99.9%), ethylene carbonate (EC, 99%, < 0.005% H₂O), propylene carbonate (PC, > 99.0%, < 0.01% H₂O), dimethyl carbonate (DMC, anhydrous, ≥ 99%), diethyl carbonate (DEC, anhydrous, ≥ 99%), tetrahydrofuran (THF, anhydrous, ≥ 99.9%), methanol (MeOH, anhydrous, 99.8%), ethanol (EtOH, denatured, reagent grade), diethyl ether (Et₂O, anhydrous), and hexanes (≥ 98.5%) were purchased from either Sigma-Aldrich, Novolyte, and/or Fisher Scientific. AN, PC, DMC, and DEC, were dried over 3 Å molecular sieves. THF was distilled over Na metal and benzophenone indicator, while the hexanes, EC, EtOH, and Et₂O were used as-received. The H₂O content of each solvent (excluding MeOH and EtOH) was verified to be negligible (< 30 ppm) using a Mettler Toledo DL39 Karl Fischer coulometer.

2.1.2 Reagents

Dilithium oxalate (Li₂Ox, Sigma-Aldrich, > 99%) and activated alumina (Fisher Scientific) were vacuum dried at 120 °C for 24 h. Activated carbon (Fisher Scientific, neutral decolorizing), lithium hydride (LiH, Fisher Scientific, 97%), lithium carbonate (Li₂CO₃, Fisher Scientific, > 99%), lithium methoxide (LiMeO, Fisher-Scientific, 99%), trifluoroacetic anhydride (Fisher Scientific, > 99%), diaminomaleonitrile (Fisher Scientific, 98%), boron trifluoride diethyl etherate (BF₃-Et₂O, Sigma-Aldrich, > 46.5% BF₃), sulfamide (Atomole Scientific, 99%), trifluoromethanesulfonic anhydride (Sigma-Aldrich, > 99%), urea (Fisher
Scientific, > 99%), urethane (Sigma-Aldrich, > 99%), diethyl oxalate (Fisher Scientific, 99%), N-methylpyrrolidine (Acros Organics, 98%), 1-iodopentane (Acros Organics, 97%), 1-iodobutane (Acros Organics, 98%), trifluoroacetamide (Sigma-Aldrich, 97%), hexafluoroisopropanol (HFI, Sigma-Aldrich, 99+%), pentafluorophenol (PFPO, Sigma-Aldrich, > 99%) and sulfamic acid (Sigma-Aldrich, 99.3%) were used as-received. Silver trifluoromethanesulfonate (AgCF$_3$SO$_3$, Sigma-Aldrich, > 99%) was used as-received and stored in a dark area. Sulfuric acid (H$_2$SO$_4$, Fisher Scientific, 95-98%) was diluted to 0.5 M with deionized H$_2$O.

2.1.3 Lithium Salts

The purchased lithium salts that were used in this study and their acronyms are shown in Chart 2.1. LiBF$_4$ (electrolyte grade), LiClO$_4$ (electrolyte-grade), and LiPF$_6$ (battery-grade) were purchased from Novolyte and used as-received. LiTFSI (3M, electrolyte grade) was vacuum dried at 120 °C for 24 h. LiBOB (Chemetal, > 99.9 %,) was recrystallized from AN and vacuum dried at 105 °C for 24 h.

2.1.4 Preparation of PY$_{15}$TFSI and PY$_{14}$TFSI Ionic Liquids

N-methylpyrrolidine was reacted with 1-iodopentane or 1-iodobutane in EA at a molar ratio of 1.00:0.95 to ensure complete reaction of the haloalkane. The solid iodide salts (PY$_{15}$I or PY$_{14}$I) generated were washed and filtered with EA until the salts were white. The PY$_{15}$I or PY$_{14}$I salts were then reacted with LiTFSI in H$_2$O at a molar ratio of 1.00:1.05 to ensure complete reaction of the iodide salts to form the N-methyl-N-pentylpyrrolidinium or N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PY$_{15}$TFSI or PY$_{14}$TFSI,
Chart 2.1 Purchased lithium salts.

respectively) ionic liquids (ILs). The resulting PY$_{15}$TFSI or PY$_{14}$TFSI ILs were allowed to separate from the aqueous layer and the aqueous layer was decanted. The ILs were washed several times with deionized H$_2$O to remove excess LiTFSI and LiI until the addition of AgNO$_3$ to the wash solutions did not form a precipitate. The ILs were then treated with activated carbon until colorless and dried under vacuum at 100 °C for 48 h. The water content of the ILs was checked with Karl Fischer coulometry and was found to be less than 30 ppm. The purity of the ILs was then verified by $^1$H NMR spectroscopy.

2.2 Lithium Salt Synthesis and Purification

Chart 2.2 shows the lithium salts that were successfully synthesized and purified. A complete list of the attempted reaction schemes is available in Appendix A. Some of the reagents used were particularly sensitive to moisture contamination. In order to exclude moisture, some solid reagents were vacuum dried and the solvents were either used as-received, distilled, or dried using 3 Å molecular sieves. Schlenk flasks and sealed addition funnels for the reactions were dried in a glassware oven (110 °C), assembled and sealed in a N$_2$(g) or Ar(g) glovebox (< 5 ppm O$_2$, < 1 ppm H$_2$O) and then transferred to a fume hood. The reaction flasks were then connected to a N$_2$(g) Schlenk line and a bubbler to prevent
moisture contamination, vessel pressurization, and buildup of evolved H₂ (in the case of LiH reactions). LiDFOB synthesis and crystallization, however, were both performed exclusively in the Ar(g) glovebox. Unsuccessful reactions were identified when either a solid compound could not be separated from the reaction mixtures after repeated attempts at drying or precipitation/crystallization, or if the obtained solid was identified as a reagent by comparison of the crystal structures, TGA, DSC, and/or Raman spectral data with the corresponding analysis of the reagents. Purification of reaction products was done through crystallization by vapor diffusion or supersaturation. Single crystals of the products were analyzed by X-ray crystallography.
2.2.1 Dilithium 1,2,5-Thiadiazolidine-3,4-dione-1,1-dioxide (Li₂TDD)

Li₂TDD was synthesized by procedures previously reported in the literature for the sodium and potassium salts, as well as the acid (Scheme 2.1).

Sulfamide (1.00 eq.) was dissolved in methanol and slowly added to a MeOH solution of LiMeO (2.10 eq.) at room temperature, yielding a white, cloudy solution. Addition of 1.05 eq. of Li₂Ox yielded a clear solution. The solution was gently refluxed for 20 h to ensure complete reaction, after which the MeOH solvent was removed by vacuum leaving a clear, viscous solution. After 24-48 h, a white solid precipitated from solution. This solid was filtered and vacuum dried at 75 °C for 24 h.

Scheme 2.1 Li₂TDD reaction sequence.

2.2.2 Lithium Ethyl N-Trifluoroacetylcarbamate (LiETAC)

Urethane (1.00 eq.) dissolved in Et₂O was reacted with trifluoroacetic anhydride (1.10 eq.) at 0 °C to form the protonated ETAC⁻ anion (Scheme 2.2, HETAC). To reduce the sublimation of the acid, the Et₂O was removed under vacuum while maintaining a temperature of 0 °C, yielding a white precipitate. The precipitate was filtered to separate the CF₃COOH liquid byproduct, and then recrystallized from benzene. The purified HETAC was dissolved in THF and reacted with LiH (1.05 eq.) at 0 °C to form the lithium salt. After the
excess LiH was filtered off, the THF solvent was removed and the LiETAC was vacuum dried at 80 °C for 24 h.

Scheme 2.2 HETAC reaction sequence.

2.2.3 Lithium Hexafluoroisopropoxide (LiHFI)

Hexafluoroisopropanol (1.00 eq.) was reacted with LiH (1.05 eq.) in Et₂O at 0 °C, instead of a reaction with Li metal or butyl lithium as reported in the literature. After warming to room temperature, the mixture was filtered to remove the excess LiH. The Et₂O was removed under vacuum leaving a white solid. The LiHFI was sublimed once under vacuum at 60 °C before transferring the solid into the glovebox.

2.2.4 Lithium Pentafluorophenolate (LiPFPO)

In a previous report, LiPFPO was synthesized by the reaction of pentafluorophenol with lithium hydroxide hydrate. To eliminate water contamination, the pentafluorophenol (1.00 eq.) was instead reacted with LiH (1.05 eq.) in THF at 0 °C. After warming to room temperature, the mixture was filtered to remove the excess LiH. The solution was concentrated by removing some of the THF under vacuum while heating the solution. Upon cooling, crystals formed (identified as the (THF)₃/₄:LiPFPO solvate), which were dried at 80 °C for 24 h, yielding neat LiPFPO.
2.2.5 Lithium 2-Trifluoromethyl-4,5-dicyanoimidazolide (LiTDI)

Following methods reported in the literature, DAMN (1.00 eq.) was reacted with trifluoroacetic anhydride (1.10 eq.) using THF instead of 1,4-dioxane (Scheme 2.3). The anhydride was added dropwise at 0 °C. After the addition was complete, the mixture was stirred overnight at room temperature, followed by refluxing for 6 h. The mixture was partially dried using a rotary evaporator to remove most of the THF solvent, H₂O and CF₃COOH reaction byproducts. The resulting viscous brown solution was dissolved in EtOH. Li₂CO₃ was added until gas evolution terminated. The mixture was stirred overnight, filtered, and carbon treated at 60 °C overnight. The solution was then dried to an orange-brown solid on a rotary evaporator. Rinsing the solid with Et₂O yielded an off-white LiTDI product. The LiTDI was then recrystallized twice in minimal AN (forming the (AN)₂:LiTDI solvate) and then brought into the N₂(g) glovebox. The solvate was dissolved in anhydrous AN and treated with activated alumina to remove residual moisture. The AN was removed under vacuum yielding the white LiTDI powder. The LiTDI was then vacuum dried for 24 h at 110 °C and for 2 h at 150 °C.

Scheme 2.3 HTDI reaction sequence.
2.2.6 Lithium Difluoro(oxalato)borate (LiDFOB)

LiDFOB was synthesized by the reaction of BF$_3$-$\text{Et}_2$O with 1.05 eq. of Li$_2$Ox in Et$_2$O (Scheme 2.4). After filtration to remove the Et$_2$O, the solids were stirred with anhydrous DMC at 80 °C for 2-4 h, dissolving the LiDFOB. The LiF and remaining Li$_2$Ox were filtered off and the filtrate was partially reduced by vacuum to crystallize the (DMC)$_{3/2}$:LiDFOB solvate. The crude LiDFOB was then recrystallized 2-3 times in minimal DMC, while ensuring that the heating temperature remained below 80 °C to prevent the DFOB$^-$ anion disproportionation to BOB$^-$ and BF$_4^-$.

The solvate was then dried at 80 °C for 24 h to yield dry LiDFOB. The LiBOB and LiBF$_4$ contents were verified to be < 0.1% by $^{11}$B NMR.

Scheme 2.4 LiDFOB reaction sequence.

2.3 Sample Preparation

Electrolytes were prepared in the N$_2$(g) or Ar(g) gloveboxes in hermetically-sealed glass vials. If necessary, electrolytes were heated/stirred on a hot plate to dissolve the salt. The LiPF$_6$ electrolytes were not heated beyond 40 °C to minimize LiPF$_6$ decomposition. The LiPF$_6$ electrolytes that were to be used for the coin cell testing were stored in HDPE bottles instead of glass vials, as small amounts of HF (formed from the reaction of the anion with glass) are known to negatively affect cell performance.$^{11-13}$
In general, single crystals for X-ray analysis were grown by slowly cooling saturated solutions of the solvent-lithium salt mixtures. For low melting solvates, the solutions were cooled further in a refrigerator (5 °C), freezer (-5 °C), or environmental chamber (-5 °C to -35 °C). In some cases, crystals were grown by vapor diffusion of a volatile, nonpolar solvent (e.g., n-pentane) into the solvent-lithium salt solutions. Lastly, several single crystals were grown by slow evaporation of the solvent from the solutions, thus concentrating the mixtures until the salt precipitated or a solvate crystallized.

2.4 Experimental Methods

2.4.1 Differential Scanning Calorimetry (DSC)

DSC experiments were performed using a TA Instruments Q2000 differential scanning calorimeter with a liquid N₂ cooling unit. The instrument was calibrated with indium (T\text{m} at 156.60 °C) and cyclohexane (solid-solid phase transition at -87.06 °C, T\text{m} at 6.54 °C). The Al sample pans were loaded with the samples and hermetically-sealed in the glovebox. The pans were cooled to -150 °C at 5 °C min⁻¹ and cycled/annealed repeatedly to fully crystallize the samples when possible. The samples were then equilibrated at -150 °C and heated until the samples were fully melted. The final heating traces were used to identify thermal events for the phase diagram.

2.4.2 Thermogravimetric Analysis (TGA)

TGA experiments were performed using a TA Instruments Q5000 thermogravimetric analyzer and Pt sample pans. Contact of the sample to ambient air during sample loading was
approximately 15 s to minimize moisture absorption. The samples were heated from room temperature to 600 °C at 5 °C min\(^{-1}\) under \(\text{N}_2(\text{g})\) flow.

2.4.3 Raman Spectral Analysis

A Horiba Jobin-Yvon LabRAM HR VIS high-resolution confocal Raman microscope with a 632 nm\(^{-1}\) He-Ne laser excitation source and 50X objective was used to collect Raman spectra. The instrument was calibrated with a monocrystalline Si wafer at 520.7 cm\(^{-1}\). A hermetically-sealed Linkam stage was used for temperature control. Raman spectra were obtained using a 10-60 s exposure time and 5-10 accumulations. Labspec v5.45.09 software was used to fit Gaussian-Lorentzian functions to the spectra to deconvolute the Raman spectra.

2.4.4 X-Ray Diffraction (XRD)

Crystal structures were determined by Drs. Paul Boyle and Roger Sommer in the Department of Chemistry at North Carolina State University. X-ray measurements were made on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer. Crystals were mounted on either a quartz fiber or nylon loops with a small amount of Paratone N oil. The unit cell dimensions were determined from symmetry constrained fits of the reflections. The frame integrations were performed using SAINT.\(^{14}\) The resulting raw data were then scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.\(^{14}\) The structures were solved by direct methods using either SIR92 or XS.\(^{15,16}\) All non-hydrogen atoms were obtained from the initial solution. 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 structure factors included corrections for anomalous dispersion from the usual tabulation. The structures were refined using the XL program from SHELXTL. Structures were drawn using Mercury 3.0 software.

2.4.5 Nuclear Magnetic Resonance (NMR)

$^1$H and $^{19}$F NMR were used to monitor the thermal decomposition of LiTDI electrolytes. $^{11}$B NMR was used to verify the LiDFOB purity. The electrolytes were inserted into glass NMR tubes with deuterated AN which were then sealed. All measurements were taken at 21 °C. ACD Labs v12.01 software was used to analyze the data. Standard solutions of 0.1% LiBOB and LiBF$_4$ were used to verify that the detection limits of the $^{11}$B NMR were at least 0.1% LiBOB or LiBF$_4$.

2.4.6 Electrochemical Impedance Spectroscopy (EIS)

EIS was used to measure the ionic conductivity of the electrolytes. 0.7 mL of the electrolyte samples was loaded into hermetically-sealed AMEL Instruments two-electrode dip cells with Pt electrodes while in the glovebox. The vials were transferred to either a Binder or Tenney environmental chamber where the temperature was varied from -40 °C to 100 °C in 10 °C increments, allowing at least 45 min for equilibration. Measurements were performed with a BioLogic VMP3 potentiostat/impedance analyzer using a 10.0 mV perturbation from 1 MHz to 20 Hz (no DC bias). The conductivity cell constants (C, cm$^{-1}$) were determined using aqueous KCl standard solutions (100 mS cm$^{-1}$ at 25 °C). The ionic
conductivity ($\sigma$, mS cm$^{-1}$) was determined using Eq. 3, where $Z_{\text{Re}}$ (mS$^{-1}$) is the real component of the impedance when the phase angle is equal to 0.

$$\sigma = C/Z_{\text{Re}}$$  
Eq. 3

2.4.7 Voltammetry and Galvanostatic Cell Cycling

A ceramic-patterned cell with inert Pt counter and working electrodes from Pine Instruments was used to determine the anodic stability of the electrolytes (Figure 2.1). The reference electrode was a Ag wire immersed in a solution of 10.0 mM AgCF$_3$SO$_3$ in PY$_{14}$TFSI (i.e., Ag/Ag$^+$), separated from the electrolyte by a fine glass frit. This reference electrode has been shown to have a potential of 3.4 V vs. Li/Li$^+$ and to be stable within 5 mV for a period of 3 weeks.$^{17}$ The patterned cell and reference electrode were immersed in the electrolytes in the Ar(g) glovebox and connected to a BioLogic VMP3 potentiostat to conduct the LSV experiments. The potential was swept from the open circuit voltage (OCV)
to 2.45 V vs. Ag/Ag$^+$ at 5.0 mV s$^{-1}$. After use, the patterned electrode was cycled from -0.8 to 0.8 V at 50 mV s$^{-1}$ in 0.5 M H$_2$SO$_4$ until the current response no longer changed (~40 cycles) to remove deposits. The Pt patterned cell was dried at 110 °C for 2 h prior to use and the reference electrode was immersed in a vial of the reference solution for storage.

Li metal was provided by the U.S. Army Research Laboratory (ARL), LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$ (NMC) and A-A003 graphite electrodes were provided by Argonne National Laboratory, and CGP-A8 graphite electrodes were provided by Lawrence Berkeley National Laboratory. The Li metal was polished with a nylon brush and punched into 1.27 cm$^2$ discs just prior to use. NMC and graphite electrodes were punched into 0.97 and 1.27 cm$^2$ discs, respectively, so that all of the full-cells were limited by the NMC in capacity and cross-sectional area (electrodes were vacuum dried at 105 °C overnight). Coin cells were assembled in the Ar(g) glovebox using size 2032 Al-clad bottom cans, stainless steel top cans with polypropylene sealing rings, and stainless steel spacers and springs from MTI Corporation. Celgard 2500 polypropylene separators were used in most of the coin cells, with the exception of the concentrated EC-LiTFSI and PY$_{15}$TFSI-EC-LiTFSI electrolytes, where Celgard 3501 surfactant-coated separators were used to improve the wetting. For these electrolytes, Whatman GF/D glass fiber separators were also used with similar results to ensure that there was no effect from the surfactant coating of the 3501 separator. Each cell was loaded with approximately 0.05-0.10 mL of the electrolytes. The cells were crimped with an electric crimping machine from MTI Corporation and sealed with epoxy. Coin cells were assembled as shown in Figure 2.2.
Coin cells for the Al corrosion studies were assembled using 0.97 cm$^2$ Al foil working electrodes with Li metal counter electrodes. The cells were kept at 25 °C in a Binder or Tenney environmental chamber and were swept from 2.0 to 6.0 V at 5 mV s$^{-1}$ for three cycles with a Biologic VMP3 potentiostat. The cells containing the concentrated electrolytes were stored at 50 °C for 1 h prior to testing to ensure full separator wetting.
Half-cells with Li metal and NMC electrodes were cycled at constant current from 3.0 V (discharged) to 4.3 V (charged). Full cells with A-A003 graphite and NMC electrodes were cycled at constant current from 3.0-4.2 V. The C rates (the current required to fully charge/discharge the limiting electrode in 1 h) were determined using the theoretical capacity of the NMC (172 mAh g\(^{-1}\) active material) and the total mass of the NMC electrode (90% active, average Al current collector mass: 5.46 mg cm\(^{-2}\)). Each cell test began with an SEI formation period consisting of two charge/discharge cycles at C/24, and ten cycles at C/10. Unless otherwise indicated, all measurements were taken at 25 °C and cycling after the formation period was done at C/5. For the high temperature testing, 30 min was allowed for equilibration between temperatures before cycling was started. For rate testing, all charging steps after the initial C/24 cycles during formation were constant current at C/10, and then held at constant voltage until the current fell below C/20 to ensure the same capacity was reached for each charge cycle. The various discharge steps during rate testing were constant current only (no constant voltage step).

2.4.8 Molecular Dynamics (MD) Simulations

MD simulations were performed by Dr. Oleg Borodin at ARL. The simulations on EC-LiTFSI electrolytes employed a many-body polarizable force field (APPLE&P) that was previously developed for EC,\(^{18}\) [EC-Li\(^+\)],\(^{18}\) TFSI\(^{-}\)\(^{19}\) and [Li\(^+\)-TFSI]\(^{20}\) with one modification: the polarizability of the TFSI\(^-\) anion oxygen atom was reduced from 1.36 Å\(^3\) to 1.00 Å\(^3\). This modification was performed in order to decrease the [Li\(^+\)-TFSI] binding energy from 140.4 to 134.0 kcal mol\(^{-1}\) for the geometry shown in Figure A1. Density functional theory (DFT)
calculations performed at M05-2X/6-31+G** and B3LYP/aug-cc-pvTz levels yielded the
[Li⁺-TFSI⁻] binding energy of -140.0 and -141.3 kcal mol⁻¹, respectively, in good agreement
with the prediction from the previous version of the force field. A more accurate G4MP2
calculation resulted in a significantly lower [Li⁺-TFSI⁻] binding energy of -135.6 kcal mol⁻¹
indicating a need to modify the force field to reduce the [Li⁺-TFSI⁻] binding energy.
Quantum chemical calculations were performed using Gaussian g09.32. The revised force
field predicted the geometry of the [Li⁺-TFSI⁻] complex in good agreement with the
geometry obtained from G4MP2 calculations.

MD simulations were performed for four different EC-LiTFSI concentrations (20-1, 10-1,
5-1, and 2-1) at 60 °C. The MD simulation package Lucretius, which includes many-body
polarization, was used for all of the MD simulations. The Ewald method was used for
calculating charge-charge and charge induced dipole interactions with k = 73 vectors used.
The Thole screening parameter of 0.2 was used. The interaction between an induced dipole
and a partial charge separated by three bonds was scaled by 0.8, providing an improved
description of the electrostatic potential around the molecules. Multiple timestep integration
was used, as well as for the reciprocal part of Ewald, with an inner timestep of 0.5 fs (bonded
interactions), a central time step of 1.5 fs for all nonbonded interactions within a truncation
of 7.0 Å and an outer timestep of 3.0 fs for all nonbonded between 7.0 Å and the nonbonded
truncation distance of 14 Å. A Nose-Hoover thermostat and a barostat were used to control
the temperature and pressure with the associated frequencies of 10⁻² and 10⁻⁵ fs. Equilibration
runs were performed in NPT ensemble, while production runs were performed in NVT
ensemble. The length of the MD runs and composition of the 60 simulation cells are given in
Table A1. The diffusion coefficient, viscosity, conductivity and enthalpy of vaporization values (Table A1) were determined as previously described.\textsuperscript{18,19}
2.5 References


CHAPTER 3: New Lithium Salts

3.1 Introduction

Developing a high-energy and intrinsically safe Li-ion battery necessitates improvement of the electrolyte. Incremental improvements to the state-of-the-art electrolyte using various additives and slightly modified solvent blends will likely not be sufficient to meet the requirements of next-generation Li-ion batteries. Instead, the discovery of new materials which are more electrochemically and thermally stable is imperative. The use of appropriately chosen dianions, that is, anions with two negative charges, could be the basis for these improved electrolytes. Dianions which are based upon a parent anion with desirable properties could, in theory, provide lithium salts with properties similar to their single charge counterparts, while supplying two Li\(^+\) cations with minimal structural modification of the anion. One possible parent anion is TFSI\(^-\), which has many desirable qualities for a lithium salt in a Li-ion battery, including high electrochemical/thermal stability and high conductivity with organic solvents. Unfortunately, many electrolytes with LiTFSI corrode the Al current collector, which, in part, has largely prevented the commercial use of LiTFSI thus far. A dianion based on the structure of the TFSI\(^-\) anion may have similar favorable properties, but perhaps without the corrosive behavior towards Al.\(^{1,2}\) Notably, it has been shown that increasing the size of perfluoroalkylsulfonyl imide anions increases the potential at which the electrolyte begins to corrode the Al current collector.\(^3\) Thus, a dilithium salt based on but larger than LiTFSI may reduce or eliminate the corrosion of Al. At the same time, a dilithium salt would also provide more Li\(^+\) cations to the electrolyte solution than a
comparable amount of LiTFSI, potentially decreasing the amount of salt required. On the other hand, it may be that dianions are much more strongly coordinated to the Li\(^+\) cations making solvation of Li\(^+\) cations difficult and thereby reducing the salt’s solubility (e.g., Li\(_2\)CO\(_3\), which has very low solubility in organic solvents).\(^4\)

In addition to dilithium salts, other new lithium salts with potentially favorable structural characteristics were explored. For example, Table 1.1 shows a number of lithium salts that have some favorable and unfavorable properties for Li-ion batteries. The anions with the lowest ionic association strength all have extensive charge delocalization, often due to extensive fluorination. Therefore, a number of lithium salts with varying degrees of fluorination, charge delocalization, and/or structural flexibility were investigated—Chart 3.1 shows the structures of the lithium salts whose syntheses were attempted. Of these, LiETAC,

Chart 3.1 Structures of some of the lithium salts whose syntheses were attempted.

\[
\begin{align*}
\text{LiETAC} & \quad \text{LiHFI} & \quad \text{Li}_2\text{TDD} & \quad \text{LiPFPO} \\
\end{align*}
\]
LiHFI, and LiPFPO were successfully synthesized and purified, along with the dilithium salt, Li$_2$TDD. For some, little characterization was possible or necessary beyond solvate structural analysis, as it was clear the lithium salt would not be suitable for a battery electrolyte. For others, solvate crystal structure analysis, DSC, and Raman spectral analysis were all used to scrutinize the properties of the lithium salts and their viability for use in battery electrolytes.

3.2 Li$_2$TDD

Crystals of the dilithium salt, Li$_2$TDD, were grown in deionized H$_2$O, forming a dihydrate. The crystal structure for this solvate is shown in Figure 3.1.\textsuperscript{5} The dihydrate consists of an infinite three-dimensional structure with a high degree of aggregation. There are both five- and six-coordinate Li$^+$ cations. The five-coordinate Li$^+$ cation is coordinated by three H$_2$O molecules, one carbonyl O atom and one sulfonyl O atom, while the six-
coordinate Li\(^+\) cation is coordinated by one H\(_2\)O molecule, three carbonyl O atoms and two sulfonyl O atoms. Each anion is coordinated to six Li\(^+\) cations (AGG-III).

The high level of aggregation found in the (H\(_2\)O\(_2\))\(_2\)Li\(_2\)TDD dihydrate structure may explain why Li\(_2\)TDD has a very low solubility in aprotic solvents (although it is slightly soluble in MeOH). Thus while Li\(_2\)TDD was successfully synthesized and crystallized, its low solubility prevents its use as a bulk salt in Li-ion battery electrolytes and a further comparison to more conventional lithium salts was not possible.

3.3 LiETAC

The structure of the ETAC\(^-\) anion allows for delocalization of the negative charge across the two carbonyl O atoms and the N atom. Additionally, the –CF\(_3\) electron withdrawing group further distributes the negative charge. Because of the chain-like structure of ETAC\(^-\), it should be expected to have some rotational flexibility around the C-N bonds. However, in each of the crystal structures which were determined containing the ETAC\(^-\) anion, only one conformation was found (Figures 3.2-3.4) as this favors the coordination of the anion to multiple cations or protons.

In the crystal structure of the acid, HETAC, the acidic proton is coordinated to the N atom and is hydrogen-bonded to a carbonyl O atom on another ETAC\(^-\) anion (Figure 3.2). However, in the lithium salt crystal structure (Figure 3.3), there is dual bidentate coordination of one Li\(^+\) cation on one side of the anion through the ester O atom and the N atom, and another Li\(^+\) cation on the other side of the anion through both carbonyl O atoms. In addition, the carbonyl O atom near the CF\(_3\) group also coordinates another Li\(^+\) cation. Thus, each
anion coordinates three Li$^+$ cations (AGG-II) and each Li$^+$ cation is coordinated to four O atoms and one N atom. This coordination leads to the polymeric sheets found in the structure.

The (THF)$_1$:LiETAC solvate structure is an AGG-I solvate with similar dual bidentate coordination found, but the THF O atom forms the fifth coordination bond to the Li$^+$ cation, replacing the coordination bond from the carbonyl O atom near the CF$_3$ group. In this solvate, a polymeric chain structure is formed. The ability to form bidentate coordination on both sides of the ETAC$^-$ anion seems to be quite favorable and this may be why only one anion conformation has been found in each of the solvates.

As discussed above, glyme-LiX solvates can be used to gauge the ionic association strength of different lithium salts relative to each other. Unfortunately, G2-LiETAC and G3-LiETAC mixtures are amorphous and crystalline solvates could not be formed, despite repeated attempts. A (G1)$_1$:LiETAC crystalline solvate was able to be isolated and solved, however, and, once again, the ETAC$^-$ anion has bidentate coordination, but only to a single

Figure 3.2 Ion coordination in the HETAC crystal structure (O-red, N-blue, F-light green).
Figure 3.3 Ion coordination in the (a) LiETAC and (b) (THF)$_2$:LiETAC crystal structures (Li-purple, O-red, N-blue, F-light green).

Li$^+$ cation (Figure 3.4). In this crystalline solvate structure, each Li$^+$ cation is coordinated to two O atoms from a G1 molecule and three carbonyl O atoms from two ETAC$^-$ anions. Each anion is coordinated to two Li$^+$ cations (AGG-I). Table 3.1 compares the first glyme-LiX solvates to form from dilute mixtures, with the previously known and characterized lithium salts arranged in order of ionic association strength (weakest at the top), and the new lithium salts at the bottom. While the lithium salts of low and intermediate ionic association strength form SSIP or CIP solvates with G1, the only lithium salts besides LiETAC to form (G1)$_2$:LiX AGG solvates are LiBOB and LiCF$_3$CO$_2$, both of which have a relatively high ionic association strength, suggesting that LiETAC also has a high ionic association tendency, perhaps similar to LiCF$_3$CO$_2$.

To further assess the degree of ionic association for LiETAC relative to other commonly used lithium salts, AN-LiETAC solutions were prepared for characterization in varying concentrations from 40-1 to the solubility limit. Crystals formed in the 5-1, 4-1 and 3-1 AN-
Figure 3.4 Ion coordination in the (G1)$_1$:LiETAC AGG-I crystalline solvate structure (Li-purple, O-red, N-blue, F-light green).

Table 3.1 Comparison of the first crystalline solvate phases (glyme-LiX) to form from dilute mixtures (*speculative assignment).\textsuperscript{6,7}

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LiETAC solutions upon standing at room temperature, and these were determined by X-ray diffraction to be the pure LiETAC salt and not a solvate (Figure 3.3). This suggests again that LiETAC is a more associated lithium salt than other commonly used lithium salts. DSC measurements for the AN-LiETAC solutions are shown in Figure 3.5. As the salt concentration increases, the peaks near the $T_m$ of AN do not shift to higher or lower temperature, but do decrease in intensity. Thus, these peaks are attributed to the melting of the pure AN solvent. This leaves two possibilities: the pure salt is precipitating out of solution or it is remaining in an amorphous (liquid or glassy) phase. An amorphous phase would have a glass transition and none is observed for the concentrated samples, which is strong evidence that (much of) the salt is precipitating out of solution, further confirming that this is a highly associated salt.

To gauge the relative degree of ionic association another way, the conductivity of an 8-1 AN-LiETAC solution was measured as function of temperature. The results are compared to

![Figure 3.5 DSC heating traces (5 °C min^{-1}) of (AN)$_n$-LiETAC mixtures.](image)
other 8-1 AN-LiX electrolytes in Figure 3.6. The conductivity values are just above those for AN-LiCF$_3$CO$_2$, and well below those for other lithium salts, further demonstrating the similarity in high ionic association strength of LiETAC and LiCF$_3$CO$_2$.

A Raman spectroscopic analysis of the AN-LiETAC electrolytes was also used to examine the ionic association strength by measuring the solvation number. The 2254 cm$^{-1}$ C≡N vibrational band was analyzed for concentrations ranging from 30-1 to 4-1 AN-LiETAC at 60 °C and compared to other AN-LiX electrolytes from previous studies (Figure 3.7).$^{6-8}$ Across the concentration range studied, the solvation number of the AN-LiETAC electrolytes is slightly greater than 1.0, and just above the curve for comparable AN-LiCF$_3$CO$_2$ mixtures. Since the solvation number remains close to 1.0, the Li$^+$ cations must remain highly aggregated to the anions, even for dilute concentrations. Furthermore, these

![Figure 3.6 Variable temperature ionic conductivity of 8-1 AN-LiX electrolytes (the sharp increase in the conductivity for the LiPF$_6$ mixtures is due to the melting of crystalline solvates, whereas the other mixtures did not crystallize during the measurements).](image)
results partly explain why lithium salts with anions having a higher ionic association strength typically have lower conductivity values. If a large fraction of the Li$^+$ cations in solution are coordinated to anions instead of being fully solvated, thus forming charge-neutral CIPs and AGGs, then the local charge neutrality decreases the response to an electric field (although charged AGGs in solution are also possible). Additionally, AGG structures are expected to have reduced mobility due to their larger size compared to CIP and SSIP solvates. As a result, the measured ionic conductivity is lower. This explanation, however, does not take into account the dynamics of solvate formation in solution.$^9$

The results of the crystalline solvate analysis, spectroscopic solvation study, and conductivity measurements all imply that the ETAC$^-$ anion has a high ionic association tendency. Thus, no further characterization of LiETAC was completed and battery tests were not performed (although a carbonate-LiETAC electrolyte was shown to corrode Al below 4.0 V—see Figure D1).
3.4 LiHFI

Unlike the other lithium salts that were synthesized, the structure of HFI does not have any resonance structures. Furthermore, LiHFI is an alkoxide salt (i.e., the conjugate base of the alcohol, hexafluoroisopropanol, or CH(CF₃)₂OH). Alkoxide salts of small metal ions are usually strongly associated, and as such, LiHFI was anticipated to have a relatively high ionic association tendency, despite the two electron withdrawing CF₃ groups.

The previously reported (Et₂O)₁/₂:LiHFI solvate (Figure 3.8) has a cubic structure that resembles several other common lithium alkoxide solvate structures.¹⁰ In this structure, four O atoms from four HFI anions bond to four Li⁺ cations to form the cubic structure. Thus, each HFI anion coordinates three Li⁺ cations through the anion O atom, making the structure an AGG-II solvate. Additionally, two of the Li⁺ cations in the cube are coordinated to an Et₂O O atom. The other two Li⁺ cations are each coordinated by two F atoms from neighboring HFI anions. This is a unique feature, as F atoms usually do not participate in Li⁺ cation coordination when other functional groups are present.

A THF AGG-II solvate was determined in the present study, and its structure is strikingly similar to the (Et₂O)₁/₂:LiHFI solvate. In the (THF)₃/₄:LiHFI solvate (Figure 3.8), an analogous cubic structure arises, except that a third THF solvent molecule coordinates one of the Li⁺ cations that, in the (Et₂O)₁/₂:LiHFI solvate structure, was coordinated instead by two F atoms. THF is more polar than Et₂O and causes less steric hindrance due to its cyclic structure, which may explain its ability to increase the Li⁺ cation solvation in this solvate structure.
Figure 3.8 Ion coordination in the (a) (Et_2O)_{1/2}:LiHFI and (b) (THF)_{3/4}:LiHFI crystalline solvate structures (Li-purple, O-red, F-light green).^{10}

AN-LiHFI and G2-LiHFI mixtures both turned yellow within 24 h. Metal alkoxides, including LiHFI, are used in a number of organic and inorganic synthesis procedures, and it is possible the LiHFI reacted with these solvents. Additionally, LiHFI was only slightly soluble in EC, and two distinct liquid phases formed, one cloudy and one clear. Because of this, further Raman and DSC analysis was not possible and LiHFI was eliminated as a candidate for use as a primary lithium salt for battery electrolytes.

3.5 LiPFPO

LiPFPO is another lithium alkoxide like LiHFI, but due to the perfluorophenyl ring, the negative charge is able to delocalize more extensively, perhaps reducing the ionic association strength to some degree. The first indication that this could be the case was the structure of the (Et_2O)_{3/4}:LiPFPO AGG-II solvate determined in the present study (Figure 3.9a), which is comparable to the (THF)_{3/4}:LiHFI solvate structure in that the solvent molecules reside in the
same locations and the unsolvated Li$^+$ cation is coordinated to two nearby F atoms from two anions. When THF was used, however, a square structured AGG-I (THF)$_2$:LiPFPO solvate formed (Figure 3.9b), in contrast to the AGG-II (THF)$_{3/4}$:LiHFI solvate. Thus both Et$_2$O and THF are able to solvate the Li$^+$ cations to a greater extent for LiPFPO than for LiHFI in the crystalline solvates, suggesting a lower ionic association tendency for LiPFPO than for LiHFI (although still high, relative to other lithium salts). Also, in contrast to LiHFI, an AGG-II solvate with AN was formed with LiPFPO (Figure 3.10). This solvate, (AN)$_1$:LiPFPO, contains the cubic structure once again. However, there is no Li$^+$ cation coordination by any F atoms. Instead, each Li$^+$ cation is solvated by one AN molecule.

G1, G2, and G3 solvates of LiPFPO were grown, however the G2 solvate structure was unable to be solved by crystallography. This may have been caused by shattering of the crystal due to a solid-solid phase transition near 25 °C (Figure 3.12). The (G1)$_1$:LiPFPO and
Figure 3.10 Ion coordination in the (AN)$_1$:LiPFPO crystalline solvate structure (Li-purple, O-red, N-blue, F-light green).

Figure 3.11 Ion coordination in the (a) (G1)$_1$:LiPFPO and (b) (G3)$_{1/2}$:LiPFPO crystalline solvate structures (Li-purple, O-red, F-light green).

(G3)$_{1/2}$:LiPFPO solvates are both AGG-I solvates and are shown in Figure 3.11. As shown in Table 3.1, LiPFPO tends to form AGG solvates with glymes, similar to LiETAC and other
Figure 3.12 DSC heating traces (5 °C min⁻¹) of glymes and glyme-LiPFPO mixtures. Note: For the 3-1 G1-LiPFPO DSC, a liquidus peak is observed at 50 °C. The larger peak at 75 °C may be due to pan rupture or electrolyte decomposition.

highly associated lithium salts. These comparisons indicate that while LiPFPO may not be as highly associated as LiHFI, its ionic association strength is high relative to most lithium salts. Additionally, the DSC of G1-LiPFPO (3-1, and 1-1), G2-LiPFPO (3-1, 2-1, and 1-1), and G3-LiPFPO (2-1, and 1/2-1) mixtures and crystalline solvates does not suggest the formation of any other solvate phases (Figure 3.12).
To compare the Li\textsuperscript{+} cation solvation by AN for AN-LiPFPO mixtures to similar mixtures with other lithium salts, Raman spectroscopy was used in a similar fashion to LiETAC (Figure 3.7). Similar to LiETAC and LiCF\textsubscript{3}CO\textsubscript{2}, the solvation number is just greater than 1.0 across the concentration range studied. From the solvate structural analysis and Raman spectroscopic results, it can be concluded that LiPFPO has a comparable ionic association strength to LiCF\textsubscript{3}CO\textsubscript{2} and is therefore not likely to be appropriate for advanced Li-ion battery electrolytes.

### 3.6 Conclusions

Each of the four new lithium salts described above has a relatively high ionic association strength compared to the lithium salts commonly studied in Li-ion battery electrolytes—all four are either as associated as LiCF\textsubscript{3}CO\textsubscript{2} or more so. Therefore, these lithium salts are not appropriate for use as the primary lithium salt in battery electrolytes. However, the results described here offer more than the characterization of individual lithium salts. Taken together with the properties of other lithium salts, several conclusions can be drawn concerning how structural characteristics give rise to a lithium salt of high, low, or intermediate ionic association strength. For example, all of the lithium salts of low and intermediate ionic association strength are fluorinated, except LiClO\textsubscript{4}, suggesting the need for strong electron-withdrawing groups. Resonance delocalization of the negative charge is also a factor. Additionally, it may be that C-O and C=O bonds result in strong anion…Li\textsuperscript{+} cation coordination interactions as suggested by Table 3.1 and the crystalline solvate structures of
LiETAC, LiHFI, LiPFPO, and Li$_2$TDD, as well as LiBOB and LiDFOB. This knowledge can be carried forward in the search for new lithium salts to replace LiPF$_6$ in Li-ion batteries.
3.7 References


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CHAPTER 4: Crystalline Solvates of LiDCTA and LiTDI

4.1 Introduction

In addition to the new lithium salts discussed in Ch. 3, a relatively new lithium salt with a potentially advantageous anion chemical structure was synthesized and studied. This lithium salt, lithium 2-trifluoromethyl-4,5-dicyanoimidazolide (LiTDI), is structurally similar to lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA), and both salts have been proposed as candidates for use in next-generation Li-ion battery electrolytes. Both salts have an aromatic five-membered ring with two electron-withdrawing cyano groups, but the TDI\textsuperscript{−} anion replaces the center N atom on the azole ring of the DCTA\textsuperscript{−} anion with an electron-withdrawing C-CF\textsubscript{3} group (Chart 4.1). Additionally, neither anion contains any C-O bonds. Despite the structural similarities, however, electrolytes with LiTDI are shown to have remarkably improved electrolyte properties as compared to those with LiDCTA.

LiDCTA was first prepared by Michot in 1995\textsuperscript{1} and reported in two publications in 2003.\textsuperscript{2,3} Although LiDCTA was found to be highly soluble in polyethylene oxide (PEO), the ionic conductivity of the resulting polymer electrolytes was found to be relatively low (comparable to those with LiCF\textsubscript{3}SO\textsubscript{3}).\textsuperscript{3} Furthermore, 1 M PC electrolytes with LiDCTA are...
also much less conductive than the corresponding electrolytes with LiPF$_6$.\textsuperscript{4} When paired with organic cations, the DCTA$^-$ anion readily forms low melting salts (i.e., ionic liquids) with a low viscosity,\textsuperscript{5,6} perhaps suggesting that this anion may be weakly coordinating, possibly due to the extensive negative charge delocalization across the anion’s structure. The relatively low conductivity of electrolytes with LiDCTA, however, contradicts this notion. In addition, the 1 M PC-LiDCTA electrolyte is highly reactive with an Al electrode at $< 4.0 \text{ V vs. Li/Li}^+$ indicating that the DCTA$^-$ anion is unable to passivate the Al current collector to prevent corrosion.\textsuperscript{4} Thus, LiDCTA is unlikely to be useful for electrolyte formulations.

LiTDI was first reported by Bukowska \textit{et al.} in 2004.\textsuperscript{7} Only a few publications are, as yet, available exploring the properties of this salt.\textsuperscript{8-14} In contrast with many other lithium salts (e.g., LiPF$_6$), LiTDI is stable in water.\textsuperscript{9} In terms of electrolyte properties, a 1 M EC/DMC (1/1 w/w)-LiTDI electrolyte has a conductivity of 6.7 mS cm$^{-1}$ at 20 °C (the value for the corresponding LiPF$_6$ electrolyte is 10.8 mS cm$^{-1}$) and cycles well in Li$\mid$LiMn$_2$O$_4$ half-cells (comparable to cells with a similar LiPF$_6$-based electrolyte up to a 2C rate).\textsuperscript{8} In addition, this LiTDI electrolyte is electrochemically stable with an Al electrode up to 4.8 V vs. Li/Li$^+$.\textsuperscript{11} Thus, LiTDI, in contrast with the structurally similar LiDCTA salt, holds promise as a practical electrolyte salt for batteries with high-voltage cathode materials.

While computational studies have been used to predict the ion interactions within electrolytes to explain properties,\textsuperscript{2,9,13,15} only limited experimental information is available regarding the specific manner in which the DCTA$^-$ and TDI anions interact with Li$^+$ cations.\textsuperscript{2,9,14} A knowledge of the ion and solvent coordination interactions which are possible, however, provides a key foundation for explaining/predicting the observed macroscale
physicochemical properties of electrolytes and, in turn, the performance of the batteries employing such electrolytes. Solvate crystal structures impart such insight which is unavailable from other experimental methods. Crystal structures for solvates with both LiDCTA and LiTDI are therefore reported here to aid in understanding the molecular-level properties of electrolytes with these salts.

4.2 HDCTA and HTDI Acid Crystal Structures

The DCTA$^-$/anion has five possible donor atoms for cation coordination, including three ring and two cyano N atoms. The numerous resonance structures for the DCTA$^-$ anion indicate that the negative charge can be delocalized on all five N atoms. The HDCTA acid crystal structure has been previously reported,\textsuperscript{16} but this was also determined as part of the present investigation (the crystal structure of LiDCTA is also known\textsuperscript{17}). In this structure (Figure 4.1a), each DCTA$^-$ anion is coordinated to three protons (H$^+$ cations) using two ring and one cyano N atoms. Each proton is therefore coordinated by three N atoms from three anions.

The TDI$^-$ anion has four possible donor atoms for cation coordination, including two ring and two cyano N atoms. The solvates reported herein indicate that the anion F atoms do not participate in cation coordination, as is typical for anion F atoms when O atoms are available. In the HTDI crystal structure, each TDI$^-$ anion is coordinated to two protons using one ring and one cyano N atoms. The TDI$^-$ ring N atoms shown as uncoordinated in Figure 4.1b are actually located near another neighboring proton (not shown) and thus may be considered to
be very weakly coordinated to a third proton. Each proton is therefore coordinated by two N atoms from two anions with a third N atom (from a third anion) located in close proximity.

4.3 Lithium Salt Crystalline Solvates and Ionic Association

4.3.1 Glyme-LiDCTA and -LiTDI Crystalline Solvate Structures

As noted above, aprotic solvent-based electrolytes with LiDCTA tend to have a low conductivity, as compared to similar electrolytes with LiPF$_6$. This suggests that instead of the ions being fully dissociated (i.e., the Li$^+$ cations being fully solvated) extensive ionic
association (anion...Li$^+$ cation coordination) is present in such electrolytes.$^{18}$ As discussed in Section 1.5.1, the ionic association tendency of lithium salts can be gauged by scrutinizing which crystalline solvates form from glyme-LiX mixtures.$^{19}$ Utilizing this methodology to explore the ionic association tendency of the salts, crystalline solvates with LiDCTA or LiTDI were grown from G1 and G2 solutions. The LiDCTA solutions with excess solvent did not result in SSIP (G1)$_3$:LiDCTA or SSIP (G2)$_2$:LiDCTA crystalline solvate phases with uncoordinated DCTA$^{-}$ anions, nor was a CIP (G1)$_2$:LiDCTA phase formed. Instead, the obtained crystals consist of AGG-I (G1)$_1$:LiDCTA and AGG-I (G2)$_1$:LiDCTA solvate phases in which the DCTA$^{-}$ anions are coordinated to two Li$^+$ cations using two of the ring N atoms (Figure 4.2, and Table 4.1). Each cation, in turn, is coordinated to two anions thereby creating similar dimers of two ion pairs.

The glyme mixtures with LiTDI, however, have a quite different phase behavior (Figure 4.3). A 3-1 G1-LiTDI mixture forms a (G1)$_2$:LiTDI crystalline phase when stored in the freezer. The ion coordination within this phase is shown in Figure 4.4a. Each anion is coordinated to a single Li$^+$ cation using one of the ring N atoms. Each Li$^+$ cation has five-fold coordination to a single TDI$^{-}$ anion and four O atoms from two G1 molecules. DSC performed on a 3-1 G1-LiTDI mixture displays an endothermic peak near 6 $^\circ$C (the temperature is lowered relative to the 2-1 sample due to the liquidus curve$^{19}$) which is attributed to this phase. Additional peaks at -66 and -36 $^\circ$C are due to crystalline G1 and another crystalline phase which is likely a SSIP (G1)$_3$:LiTDI phase, as is found with many other lithium salts.$^{19}$ Note that it was not possible to fully crystallize the sample into this phase. Instead, depending upon the thermal history of the sample, some amount of the CIP-I
Figure 4.2 Ion coordination in the (a) AGG-I (G1):LiDCTA and (b) AGG-I (G2):LiDCTA solvate crystal structures (Li-purple, O-red, N-blue).

Table 4.1 Comparison of the first crystalline solvate phases (glyme-LiX) to form from dilute mixtures (*speculative assignment).

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<td>LiETAC</td>
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<td>LiPFPO</td>
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<td>LiDCTA</td>
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<td>LiTDI</td>
<td>X*</td>
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</tbody>
</table>
Figure 4.3 DSC heating traces (5 °C min⁻¹) of glyme and glyme-LiTDI mixtures.

Figure 4.4 Ion coordination in the (a) CIP-I (G1)_2:LiTDI, (b) SSIP (G2)_2:LiTDI and (c) CIP-I (G3)_1:LiTDI solvate crystal structures (Li-purple, O-red, N-blue, F-light green).
(G1)$_2$:LiTDI solvate always crystallized (which resulted in excess G1 when the remainder of the sample crystallized as the SSIP (G1)$_3$:LiTDI phase)—this variation in the phase behavior is shown in Figure 4.3 for two different sample pans prepared from the same 3-1 G1-LiTDI mixture. Note that the DSC peaks near 120 °C for these samples are due to the rupture of the hermetically sealed DSC pan due to the pressure from the vaporized G1 solvent.

A 2-1 G2-LiTDI mixture forms a (G2)$_2$:LiTDI crystalline phase which melts at 104 °C. A common motif in (G2)$_2$:LiX solvates,\textsuperscript{19} which is present in the SSIP (G2)$_2$:LiTDI crystalline solvate (Figure 4.4b), is for two G2 molecules to coordinate the Li$^+$ cations thereby shielding them from the anions. Thus, the Li$^+$ cations are six-fold coordinated by six O atoms and the TDI anions are uncoordinated.

A 1.5-1 G3-LiTDI mixture forms a (G3)$_1$:LiTDI crystalline phase which melts at 48 °C. DSC of the 1.5-1 mixture has a broad peak at a slightly lower temperature (34 °C) due to the liquidus and, instead of an endothermic peak for the excess G3 or a SSIP (G3)$_2$:LiTDI phase, a glass transition ($T_g$) is noted at -95 °C indicating that the remainder of the sample did not crystallize. The Li$^+$ cations are five-fold coordinated by one TDI anion through one ring N atom and four O atoms from a single G3 molecule (Figure 4.4c). The cation coordination therefore also closely resembles that of the CIP-I (G1)$_2$:LiTDI solvate (Figure 4.4a). In these two solvates, the solvated ion pairs are isolated from one another.

The CIP-I (G3)$_1$:LiTDI crystalline solvate phase resembles the coordination found for the (G3)$_1$:LiBETI (i.e., LiN(SO$_2$C$_2$F$_5$)$_2$) solvate, in that isolated CIPs are formed.\textsuperscript{20} CIP (G3)$_1$:LiX crystalline solvates with smaller anions (e.g., LiBF$_4$, LiClO$_4$, LiCF$_3$SO$_3$ and LiAsF$_6$), however, have a linear polymeric structure in which the G3 molecules coordinates
two Li\(^+\) cations using two O atoms for each.\(^{21}\) Each Li\(^+\) cation is therefore five-fold coordinated to four O atoms from two G3 molecules (two O atoms from each G3 molecule) and a single donor atom from an anion. The larger size of the TDI\(^-\) (or BETI\(^-\)) anion, however, precludes this form of ion and solvent coordination/packing thus resulting in the coordination of the G3 molecules to a single Li\(^+\) cation.

Taken together, the glyme-LiTDI phase behavior suggests that the TDI\(^-\) anion has intermediate ionic association strength (comparable to ClO\(_4^-\) or BF\(_4^-\)) (Table 4.1). The DCTA\(^-\) anion, in contrast, has a much greater ionic association strength (comparable to CF\(_3\)SO\(_3^-\) or more so). Such an analysis is not definitive or quantitative in nature, but it readily explains the relatively low conductivity of LiDCTA electrolytes with aprotic solvents and the much higher values noted for LiTDI electrolytes.\(^{18}\)

4.3.2 Other LiTDI Crystalline Solvate Structures

The AGG-I (AN)\(_2\):LiTDI crystalline solvate (Figure 4.5a) has been previously reported, but was also determined as part of this study.\(^{14}\) This solvate consists of isolated dimers of two ion pairs with the two coplanar TDI\(^-\) anions aligned parallel to one other, each coordinating two Li\(^+\) cations. Each Li\(^+\) cation has four-fold coordination to two AN molecules and two anions (one ring and one cyano N atom). The AGG-I (AN)\(_2\):LiTDI solvate crystallizes from dilute AN-LiTDI solutions (e.g., 20-1, Figure 4.6) at room temperature, rather than forming SSIP (AN)\(_4\):LiTDI or perhaps CIP (AN)\(_3\):LiTDI phases,\(^{18,22,23}\) suggesting that this aggregate dimer structure is particularly stable.
A similar TDI anion dimer arrangement persists when larger, cyclic solvents are used (i.e., THF, EC and PC), although the overall coordination behavior of each structure is more aggregated than for the (AN)$_2$:LiTDI solvate (Figure 4.5b, 4.5c and 4.5d). Specifically, for the (THF)$_1$:LiTDI and (EC)$_1$:LiTDI solvates, one AN...Li$^+$ cation coordination bond is replaced with a TDI...Li$^+$ cation coordination bond in an adjacent dimer pair. Each dimer is thus linked to two neighboring parallel (although not coplanar) dimers on opposite sides.

Figure 4.5 Ion coordination in the (a) AGG-I (AN)$_2$:LiTDI, (b) AGG-II (THF)$_1$:LiTDI, (c) AGG-II (EC)$_1$:LiTDI and (d) AGG-II (PC)$_1$:LiTDI solvate crystal structures (Li-purple, O-red, N-blue, F-light green).
Figure 4.6 DSC heating traces (5 °C min\(^{-1}\)) of AN-LiTDI mixtures and the \((AN)_2\):LiTDI solvate.

The resulting structures are AGG-II solvates consisting of nearly flat, polymeric chains of the dimer arrangement with the solvent molecules above and below the plane of the TDI\(^-\) anions (Figure B24). The THF and EC molecules share similar positions in the \((THF)_1\):LiTDI and \((EC)_1\):LiTDI solvate structures, but the EC molecules are rotated slightly closer to the plane of the anion to accommodate for its larger size. Similarly, the PC molecules in the \((PC)_1\):LiTDI solvate are rotated still closer to the plane of the TDI\(^-\) anions to include the additional length of the methyl group present on the PC ring. This rotation, however, significantly changes the angle of the TDI\(...\)Li\(^+\) cation coordination bond relative to the plane of the dimer, resulting in each dimer pair being coordinated to four neighboring dimers rather than two. This AGG-II solvate thus contains jagged polymeric sheets, with the PC molecules above and below the sheets, rather than polymeric chains (Figures B22 and B23). The
inclusion of the base dimer units in each of these three polymeric crystalline solvate structures again suggests that the \([\text{TDI}...\text{Li}^+]_2\) dimer arrangement easily forms and can accommodate a variety of solvent molecules.

In the AGG-III (DMC)$_{1/2}$:LiTDI crystalline solvate, all four of the TDI anion N atoms are coordinated to Li$^+$ cations (Figure 4.7). In contrast to the solvent molecules in the previously noted solvate structures which coordinate a single Li$^+$ cation, each DMC molecule is coordinated to two Li$^+$ cations. Additionally, instead of the base dimer structure of two oppositely aligned TDI anions, an infinite three-dimensional network is formed. Two Li$^+$ cations are coordinated by the TDI anion ring and cyano N atoms, as in the dimer structure, but the two anions are nearly orthogonal to each other instead of sharing a plane. Since each anion is coordinated to four Li$^+$ cations through all of the N atoms, a stairstep structure forms. In each “step,” two anions are aligned and share coordination to two Li$^+$ cations.

![Figure 4.7](image.png)

**Figure 4.7** Ion coordination in the AGG-III (DMC)$_{1/2}$:LiTDI crystalline solvate structure. Solvent disorder in the DMC position has been omitted for clarity (Li-purple, O-red, N-blue, F-light green).
through the two cyano N atoms of each anion. The Li$^+$ cations have five-fold coordination by one O atom from the DMC molecules and four N atoms from four different TDI$^-$ anions.

### 4.4 Conclusions

The reported HTDI and seven new LiTDI solvate structures demonstrate a disparate range of coordination modes with the TDI$^-$ anions either uncoordinated or coordinated to one to four Li$^+$ cations (or two H$^+$ cations in the case of HTDI) through the ring and cyano N atoms. The ring N atoms appear to have the greatest Lewis basicity, since no solvates were identified with H$^+$ or Li$^+$ cation coordination through only the cyano N atoms. This may, however, also be related to differences in the energetics for the favorable packing of the ions and solvent molecules in the solid state. Additionally, no Li$^+$ cation coordination was found through the F atoms. A [TDI$^-...$Li$^+ ]_2$ ionic dimer arrangement appears to be prevalent in the aggregated solvates that were identified, but it is not yet clear if this type of coordination persists in the liquid phase for electrolyte solutions with aprotic solvents.

The replacement of a ring N atom in the DCTA$^-$ anion with a C-CF$_3$ group to form the TDI$^-$ anion significantly reduces the Li$^+$ cation ionic association tendency of the anion. This is evident from the LiDCTA and LiTDI glyme solvates formed. The low ionic association strength of the TDI$^-$ anion, as compared to DCTA$^-$ and other lithium salt anions, indicates that LiTDI electrolytes may be well-suited for Li-ion battery applications, although further physicochemical characterization of such electrolytes is needed.
4.5 References


CHAPTER 5: LiTDI Electrolyte Characterization and Cell Cycling

5.1 Introduction

The analysis of various crystalline solvate structures of LiTDI indicates that the TDI anion has a low ionic association strength, which partially explains the high conductivity values reported for carbonate-LiTDI electrolytes.\textsuperscript{1} To more fully characterize the ion and solvent interactions of LiTDI in electrolytes, the solvation and electrolyte physical properties need to be studied. Solvation studies with AN, however, are precluded by the tendency of the (AN)\textsubscript{2}:LiTDI solvate to crystallize in dilute solutions. At 60 °C, the temperature at which this solvation study is usually performed, the (AN)\textsubscript{2}:LiTDI solvate crystallizes in 17-1 AN-LiTDI electrolytes. The solvation and electrolyte characterization were therefore completed with EC, as the EC-LiTDI electrolytes remain in the liquid state for up to 6-1 at 60 °C (Figure D2).

The favorable properties previously reported for LiTDI electrolytes\textsuperscript{1-7} and the indication that the TDI anion has a low ionic association strength makes further study of this salt imperative. To completely replace LiPF\textsubscript{6} as the primary lithium salt in Li-ion battery electrolytes, however, LiTDI electrolytes must be more thermally robust and must not produce reactive decomposition products at temperatures at least as high 60 °C. Thus, the thermal stability of the LiTDI salt and carbonate-LiTDI electrolytes was studied by TGA and NMR, respectively. Furthermore, the cycling behavior of LiTDI and LiPF\textsubscript{6} electrolytes with mixed carbonate solvents were analyzed in both half-cells and full-cells, at room temperature
and at 60 °C, and at variable discharge rates to determine the feasibility of using LiTDI electrolytes in next-generation Li-ion batteries.

5.2 EC-LiTDI Electrolyte Characterization

5.2.1 Solvation

The solvation of EC-LiX electrolytes can be analyzed in a similar manner to AN-LiX electrolytes. Specifically, the 717 and 895 cm⁻¹ Raman bands of neat EC, which correspond to two different ring breathing vibrational modes, shift to 729 and 905 cm⁻¹, respectively, upon Li⁺ cation coordination.⁸⁻¹⁰ The fraction of uncoordinated solvent may be determined in the same way as the AN-LiX mixtures—by dividing the peak area of the uncoordinated band by the total peak area of the coordinated and uncoordinated bands for each vibrational mode. However, the Raman scattering activities of the two EC vibrational modes both change to different extents when the EC coordinates a Li⁺ cation. This difference can be taken into account, using scaling factors obtained from quantum chemical calculations (0.88 for the 717 cm⁻¹ band, and 1.06 for the 895 cm⁻¹ band).⁸ The 717-729 cm⁻¹ region can be difficult to deconvolute, however, as it often has significant overlap with the anion bands (see Ch. 6). Therefore, it is expected that the results from this region are less accurate and the 895-905 cm⁻¹ region is used for discussion instead (see Figure D3 for analysis of both regions).

Figure 5.1 shows the solvation number (N) of EC-LiX electrolytes at 60 °C. Table 4.1 indicates that the TDI⁻ anion may have a similar ionic association strength to BF₄⁻ and DFOB⁻, but a higher ionic association strength than TFSI⁻. This same trend is observed in Figure 5.1, where the solvation number of EC-LiTDI electrolytes is slightly higher than
corresponding EC-LiBF$_4$ and EC–LiDFOB electrolytes, but lower than for the EC-LiTFSI electrolytes. The ionic conductivity of the EC-LiTDI electrolytes at 60 °C (Figure 5.2), however, is lower than for the EC-LiBF$_4$ and EC-LiDFOB electrolytes. Instead, the conductivity is similar to EC-LiBOB electrolytes. This contradicts the expectation that a higher solvation number results in higher electrolyte conductivity.
To explore this result further, the conductivity was normalized by the salt concentration (mol L\(^{-1}\)) to give the molar conductivity (Figure 5.3). The molar conductivity removes the effect of the variations in the density between the electrolytes (as the conductivity is proportional to the number of charge carriers), and can be described as the efficiency with which the ions (or sum of the solvates) conduct in solution. Thus, the peak molar conductivity is at infinite dilution, in contrast to the conductivity, where the peak is at an intermediate concentration (usually near 1 M for Li-ion battery electrolytes) due to a balance between the optimum number of charge carriers and Li\(^+\) cation-anion interactions.

Here, the molar conductivity of the EC-LiTDI and EC-LiBOB electrolytes are nearly the same, but lower than for EC-LiDFOB and higher than for EC-LiBF\(_4\) electrolytes. The differences between these latter electrolytes are readily explained by a previous more thorough AN-LiX electrolyte characterization of the salts which indicated that LiBF\(_4\) is more

![Figure 5.3 Molar conductivity of EC-LiX electrolytes at 60 °C.](image)
associated than LiDFOB. Furthermore, although LiBOB has slightly higher solvation numbers in EC than LiBF$_4$ and LiDFOB, implying it should have the highest conductivity, it has been suggested that this is not the case, perhaps due to the reduced mobility of the larger BOB$^-$ anion—i.e., conductivity is dependent on charge carrier mobility, while Raman spectroscopy is not. Since the TDI$^-$ and BOB$^-$ anions are large anions and similar in size, the TDI$^-$ anion may also have reduced mobility in solution, while still being less associated than BF$_4^-$ and DFOB$^-$.  

5.3 EC/DEC-LiTDI Electrolyte Characterization

5.3.1 Conductivity

Instead of EC-LiX electrolytes, commercial Li-ion cells typically use a mixture of EC with one or more linear carbonates, such as DEC, and a lithium salt. This usually improves the conductivity and reduces the tendency to crystallize at sub-ambient temperatures. Thus, a mixture of 3/7 v/v EC/DEC was used with LiTDI for the cell cycling tests. Figure 5.4 shows the variable temperature ionic conductivity of the EC-LiTDI and EC/DEC-LiTDI electrolytes. At room temperature, the incorporation of DEC has little effect on the conductivity. However, at high temperatures, the conductivity is significantly decreased. This can likely be explained by the decreased ability of DEC to coordinated Li$^+$ cations and an aggregation effect. It has been shown that aggregation typically increases to a small extent with increasing temperature for liquid electrolytes—that is, the distribution of ionic species in solution shifts from more SSIP type structures toward more AGG type structures. While this should also be expected of the EC-LiTDI electrolyte, the effect would be greater in the
Figure 5.4 Variable temperature ionic conductivity of (a) EC-LiTDI and (b) EC/DEC-LiTDI electrolytes (3/7 v/v EC/DEC). Isotherms shown in 10 °C increments from -40 °C to 100 °C.

EC/DEC-LiTDI electrolyte because of the weaker solvating capacity of DEC. Therefore, the aggregation in an EC/DEC-LiTDI electrolyte likely increases more at high temperature as compared to an EC-LiTDI electrolyte, thus reducing the conductivity.

At low temperature, however, the DEC proves to be beneficial. The addition of this solvent inhibits the formation of the (EC)$_1$:LiTDI solvate and/or crystalline EC. For example, most of the electrolytes within the concentration range studied remain liquid to -20 °C for the EC/DEC-LiTDI electrolytes, in contrast to the EC-LiTDI electrolytes, for which many of the samples crystallized at 0 °C (no data is recorded in the figure if the samples crystallized).

At 20 °C, the EC/DEC-LiTDI electrolytes have a conductivity maximum of 4.0 mS cm$^{-1}$ at a LiTDI mole fraction near $x = 0.070$. The maximum conductivity of the EC/DEC-LiPF$_6$ electrolytes at 20 °C is 7.0 mS cm$^{-1}$ at a higher mole fraction of $x = 0.078$ (Figure D4). It is
generally accepted that a minimum electrolyte conductivity of 1.0 mS cm\(^{-1}\) is required for a high-performance Li-ion battery, and thus, the EC/DEC-LiTDI is acceptable for such applications.

### 5.3.2 Thermal Stability

The thermal stability of the pure LiTDI salt was investigated first by TGA to determine if LiTDI decomposes and volatilizes like LiPF\(_6\) (Figure 5.5). Due to safety hazards associated with exposing LiPF\(_6\) to ambient moisture (i.e., hydrolysis and subsequent HF formation), the TGA thermogram of pure LiTDI is compared to a 1M LiPF\(_6\) EC/DEC electrolyte. The first section of the LiPF\(_6\) electrolyte curve is attributed to DEC volatilization, while the second portion is due to EC and PF\(_6\) volatilization to PF\(_5\). The mass loss begins as soon as the measurement is started (25 °C) and the mass remaining near 150 °C is mainly LiF. In stark

![Figure 5.5 TGA thermograms of dry LiTDI powder and 1 M EC/DEC-LiPF\(_6\) electrolyte.](image-url)
contrast, no significant mass loss is observed for LiTDI below 200 °C, attesting to the high intrinsic thermal stability of this salt.

While LiTDI appears to be quite thermally stable on its own, solvent-LiTDI reactions are possible in an actual electrolyte at higher temperature. A 1 M LiTDI EC/DEC (3/7 v/v) electrolyte was stored at 25 °C, 60 °C, and 100 °C for one week to assess the stability of the dissolved LiTDI (Figure D5). The sample stored at 25 °C is clear, colorless solution, and remains so after one week (and much longer). After one week, the electrolyte stored at 60 °C is slightly yellow in color, but remains clear and no precipitate is observed. After one week at 100 °C, however, a white solid precipitated out of solution, and the electrolyte was brown in color. The significant discoloration and precipitate formation at 100 °C are both suggestive of electrolyte degradation.

Because color is not a definitive indication of decomposition, the contents of these electrolytes were examined by $^{19}$F and $^1$H NMR spectroscopy (Figures 5.6 and 5.7). The $^{19}$F spectra for the electrolyte stored at 25 °C contains one peak at -62 ppm for the one unique F atom of the TDI$-$ anion. The spectra for the electrolyte stored at 60 °C is identical, despite the mild discoloration—no new peaks are observed, and the TDI$-$ anion peak has not shifted, indicating no measurable amount of decomposition has occurred. For the electrolyte stored at 100 °C, several new peaks are observed close to -61 and -63 ppm, indicating reaction of the TDI$-$ anion occurred.

The $^1$H NMR spectra indicate complementary results. The electrolytes stored at 25 °C and 60 °C show identical peaks characteristic of EC (4.46 ppm) and DEC (4.12 and 1.22 ppm). The electrolyte stored at 100 °C has a new, small peak in the $^1$H spectra at 4.28 ppm,
Figure 5.6 $^{19}$F NMR spectra for 1 M EC/DEC-LiTDI electrolytes stored at 25 °C, 60 °C, and 100 °C for one week.

Figure 5.7 $^1$H NMR spectra for 1 M EC/DEC-LiTDI electrolytes stored at 25 °C, 60 °C, and 100 °C for one week.
suggesting a reaction of one or both of the solvents with LiTDI. Although decomposition is
evident at 100 °C, the carbonate-LiTDI electrolyte seems to be stable for at least one week at
60 °C, whereas LiPF$_6$ electrolytes are known to be unstable at this temperature.

5.4 Coin Cell Cycling with LiTDI Electrolyte

Coin cells are a useful and low cost model for studying battery performance without
using a large amount of active material. Each coin cell contains approximately 100 μL of
electrolyte and 11 mg of active positive electrode material (e.g., NMC). In half-cells, the
NMC positive electrode is used with a polished Li metal counter electrode (the same
configuration is used in primary lithium batteries). Ideally, cycling half-cells provides
information about the electrolyte’s interactions with only the positive electrode, as the Li$^+$
plating/stripping from the Li metal should be fast and thus not limit the performance of the
cell. Although a passivation film usually forms on the Li metal surface, this typically has
very low impedance and does not limit cell performance, unless the electrolyte reacts
significantly with the Li metal surface.$^{15,16}$

In full-cells, the NMC positive electrode is used with a graphite negative electrode, and
ultimately, these cells are a better indicator of the electrolyte’s capability to be used in Li-ion
batteries. Because a graphite negative electrode is employed in full-cells, an SEI must form
to protect the graphite from exfoliation and the electrolyte from extensive decomposition.
Therefore, there are significant electrolyte interactions with both electrodes. By studying
half-cells and full-cells together, information about the electrolyte’s interactions with each
electrode can be evaluated, while also assessing the overall performance of the electrolyte in an actual Li-ion battery configuration.

5.4.1 Half-Cell Cycling

Cell cycling tests using the carbonate-LiTDI and –LiPF₆ electrolytes began with half-cells to gauge the compatibility of the electrolyte with the NMC positive electrode. The first two cycles were run at very slow charge/discharge rates of C/24 (i.e., 24 h to each fully charge/discharge the cell). Afterwards, the charge rate was maintained at C/10 with a constant voltage step to ensure the cell was charged to the same point after every cycle. The discharge rate was increased every ten cycles from C/10 to 5C (i.e., maximum 12 min to fully discharge the cell). By varying the discharge rate in this manner, the power capability of the half-cells can be measured. Figure 5.8 shows the discharge capacity and Coulombic efficiency for each charge/discharge cycle of two half-cells: one half-cell containing a 1 M EC/DEC-LiTDI electrolyte and one half-cell containing a 1 M EC/DEC-LiPF₆ electrolyte. During the first 12 cycles (formation period), both cells have nearly identical discharge capacity. The efficiency, however, of the cell containing LiTDI is significantly lower than that containing LiPF₆, which indicates that irreversible reactions are taking place when the LiTDI half-cell is being charged. These irreversible reactions are likely the generation of a passivation film on the positive electrode (or the Li metal surface) which requires many more cycles and perhaps much more charge to form than the half-cell containing LiPF₆. The low efficiency, however, does not seem to impact the cycling performance of the cell in terms of discharge capacity. Instead, the discharge capacity of the half-cell with LiTDI is nearly the
Figure 5.8 Variable discharge rate testing of NMC|Li metal half-cells with either 1 M EC/DEC-LiPF$_6$ (black circles) or 1 M EC/DEC-LiTDI (red triangles) at 25 °C. Discharge capacity is shown in filled symbols and Coulombic efficiency in open symbols.

same as the half-cell with LiPF$_6$. Furthermore, the rate capability (i.e., the dependence of the discharge capacity on the discharge rate) of the half-cell containing LiTDI is nearly the same as the half-cell containing LiPF$_6$ up to a 5C rate, in spite of the decreased initial efficiency and lower ionic conductivity of the LiTDI electrolyte. Any passivation films that are formed do not seem to be increasing the impedance of the LiTDI half-cells.

As indicated by Figure 5.8, the LiTDI half-cell performs as well as the half-cell with LiPF$_6$ at room temperature. To stress the electrolytes further, half-cells were charged and discharged at a faster than normal rate of C/2 (after the formation period) first at 25 °C, then 60 °C, and then again at 25 °C (Figure 5.9). Throughout the initial cycling at 25 °C, half-cells with either a LiTDI or LiPF$_6$ electrolyte have the same capacity, however the capacity begins
Figure 5.9 Variable temperature NMC|Li metal half-cell cycling of 1 M EC/DEC-LiPF$_6$ (black circles) or 1 M EC/DEC-LiTDI (red triangles). Discharge capacity is shown in filled symbols and Coulombic efficiency in open symbols. Charge/discharge rate: C/2 after 12 cycle formation period.

to diminish when the charge and discharge rates are increased to C/2. This “capacity fade” is a cumulative capacity loss caused by the fast charge rate.\textsuperscript{17,18} Both half-cells are affected by this equally and thus the capacity fade may be related to electrode kinetics rather than the electrolytes.

Upon increasing the temperature to 60 °C, the discharge capacity of both half-cells increases, due to the faster kinetics associated with the lithiation/delithiation of the electrodes and decreased cell impedance. After two cycles, however, the capacity of the half-cell containing LiPF$_6$ begins to drop, and after five cycles, the capacity drops precipitously. At this high temperature, the LiPF$_6$ is decomposing to form PF$_5$ and LiF, and reacting with the NMC and Li metal electrodes. As a result, the electrolyte is likely depositing thick surface
films on the electrodes while the NMC positive electrode is deteriorating due to Mn dissolution.\(^{19}\) When the temperature is returned to 25 °C, the capacity of the LiPF\(_6\) half-cell is much lower than it was before being heated, at approximately 30 mAh g\(^{-1}\).

In stark contrast, the half-cell containing LiTDI maintains a stable capacity over the entire 60 °C period (~7 days). The capacity fade is also reduced at 60 °C as compared to 25 °C, presumably due to improved electrode kinetics. Upon lowering the temperature back to 25 °C, the capacity returns to a level that would be expected if the cell had not been heated to 60 °C. Therefore, there is no memory effect of being exposed to high temperature, further validating the high thermal stability of the LiTDI electrolyte.

5.4.2 Full-Cell Cycling

While the half-cell results have shown the compatibility of the LiTDI electrolyte with an NMC electrode at both room and high temperatures, commercial Li-ion batteries use full-cells, where a graphite negative electrode replaces the Li metal used in the half-cells. As previously discussed, a graphite electrode requires an adequate SEI to form from reactions with the electrolyte for protection from solvent and anion co-intercalation. Full-cells with either the EC/DEC-LiPF\(_6\) or EC/DEC-LiTDI electrolytes were cycled at C/5 (after a 14 cycle SEI formation period) for 20 cycles at 25 °C to assess the SEI formation of the LiTDI electrolyte as compared to the LiPF\(_6\) electrolyte (Figure 5.10). Afterwards, the cells were thermally stressed by cycling at 60 °C for 20 cycles, followed by 20 additional cycles at 25 °C.
Figure 5.10 Discharge capacity (filled symbols) and Coulombic efficiency (open symbols) for NMC|graphite full-cells (a) without additives and (b) with 1 wt% LiBOB or LiDFOB. Cumulative irreversible capacity of full-cells containing 1 M EC/DEC-LiPF$_6$ (black circles) or 1 M EC/DEC-LiTDI (red triangles) (c) without additives and (d) with 1 wt% LiBOB or LiDFOB additives

Within the first 5 cycles of the formation period, the full-cell with LiPF$_6$ achieves high efficiency and stable cycling, while the full-cell with LiTDI has ~20 mAh g$^{-1}$ less discharge capacity. Additionally, the full-cell with LiTDI has significant capacity fade and its
efficiency remains below the full-cell containing LiPF$_6$ for 30 cycles indicating that extensive irreversible reactions occur. The charge/discharge voltage profile for the first cycle of both full-cells (Figure 5.11a) illustrates the large difference in initial irreversible capacity between the two cells (42.5 and 111 mAh g$^{-1}$ for the LiPF$_6$ and LiTDI full-cells, respectively). Furthermore, a plot of the differential charge vs. cell voltage (Figure 5.11b) shows two peaks at low cell voltage for both full-cells. The small peak at 3.0 V for the full-cell containing LiPF$_6$ is attributed to SEI formation (the two much larger peaks near 4.0 V are attributed to Li$^+$ cation transfer between the electrodes). For the full-cell containing LiTDI, there is a much larger peak at 2.8 V, which shows that much more charge is being passed due to a combination of SEI formation and/or possible side reactions that do not contribute to the SEI. While the irreversible capacity losses due to SEI formation typically slow significantly after several cycles (Figure 5.10c and 5.10d), it is possible that the SEI formed from the LiTDI electrolyte takes much longer to form and requires much more charge and thus electrolyte degradation.

When the full-cells are stressed by increasing the temperature to 60 °C, the full-cell with LiPF$_6$ begins to lose capacity, as expected, due to electrolyte decomposition and reaction with the electrode materials. On the other hand, the capacity fade rate associated with the full-cell containing LiTDI does not increase when the temperature is increased. On the contrary, the cell seems to stabilize, and when returning the 25 °C, the capacity fade seems to have stopped altogether. This result would seem to indicate that the LiTDI electrolyte requires a large number of cycles form a suitable SEI, and the formation rate may be
increased at high temperature. However, once the SEI layer is formed, the cell is quite stable, albeit with significantly reduced capacity compared to a full-cell containing LiPF$_6$.

To address this issue, known SEI-forming additives were used. These additives, LiBOB and LiDFOB in particular, preferentially react on the graphite surface to form a stable SEI film.$^{20-25}$ Additionally, these additives have shown evidence of passivating the positive electrode and improving high temperature performance of cells containing LiPF$_6$. Typically, 1-5 wt% additive is used in the electrolyte—1 wt% of either additive was used here in the LiTDI and LiPF$_6$ electrolytes. Figure 5.12 shows the effect of the additives on the first charge/discharge cycle. For LiPF$_6$ and LiTDI electrolytes with LiBOB additive, the first cycle irreversible capacity is reduced to 37.1 and 45.3 mAh g$^{-1}$, respectively. For LiPF$_6$ and LiTDI electrolytes with LiDFOB additive, the same value is reduced to 40.4 and 50.8
Figure 5.12 First cycle charge/discharge voltage profiles and dQ/dE vs. E of NMC|graphite full-cells with 1 M EC/DEC-LiPF₆ (black lines) or 1 M EC/DEC-LiTDI (red dashed lines) with (a and b) 1 wt% LiBOB and (c and d) 1 wt% LiDFOB.

mAh g⁻¹, respectively. The dQ/dE plots have new peaks at 2.0 V and 2.2 V for electrolytes with LiBOB and LiDFOB, respectively, which is indicative of the preferential reaction of the additives on the electrode surface(s).
The results in Figure 5.10b and 5.10d show that for LiTDI and LiPF$_6$ electrolytes, the additives significantly reduce the cumulative irreversible capacity losses and increase the Coulombic efficiency of the cells both during the initial and prolonged cycling. From these measurements, it seems that the LiTDI + additive electrolytes decompose slightly more than the LiPF$_6$ + additive electrolytes, but the additives significantly improve the performance of the full-cells.

At 60 °C, the discharge capacity retention is significantly higher for the full-cells containing the LiTDI electrolyte. Over the entire 60 cycle period after the formation cycles (cycle 13 to 72), the capacity retention of the LiTDI full-cells with LiBOB and LiDFOB are 98.6% and 92.9%, respectively, while the same values for the LiPF$_6$ full-cells with LiBOB and LiDFOB are 91.9% and 85.9%, respectively. Once again, the LiPF$_6$ decomposition is increased by the high temperature and the SEI formed from the additives is not able to completely inhibit the LiPF$_6$ electrolyte reactions with the electrodes. Thus, the discharge capacity suffers. In comparison, the discharge capacity of the full-cells with LiTDI is only marginally affected by high temperature, despite the higher irreversible capacity losses (Figure 5.10b and 5.10d). It may be that these side reactions are slowly increasing the thickness of the SEI and positive electrode passivation layer, gradually increasing the impedance of the cell. Nevertheless, the full-cells with the LiTDI electrolyte are clearly much more stable at high temperature than the LiPF$_6$ electrolyte, provided that an SEI-forming additive is used.

After establishing the effectiveness using SEI-forming additives has on the performance of LiTDI electrolyte in full-cells, the rate capability was tested to ensure LiTDI-containing
full-cells would have comparable power capability to those with LiPF$_6$. As with the half-cells, the full-cells with LiTDI and either LiBOB or LiDFOB additive have similar discharge capacity as the LiPF$_6$ + additive full-cells, up to a 5C rate (Figure 5.13). Thus, the full-cells are not limited by the marginally lower conductivity of the LiTDI electrolyte as compared to LiPF$_6$.

### 5.5 Conclusions

The physicochemical characterization of EC-LiTDI electrolytes has shown that the TDI$^-$ anion behaves somewhat similarly to the BOB$^-$ anion in EC, both in terms of Li$^+$ cation solvation and molar conductivity. These similarities and the comparable sizes of the two anions suggests that both the BOB$^-$ and TDI$^-$ anions may have a lower ionic association strength than DFOB$^-$ and BF$_4^-$ (indicated by the higher solvation number in EC), but are less
mobile, and thus have lower conductivity values. However, the conductivity of EC-LiTDI electrolytes is still well above the minimum required for Li-ion battery electrolytes and a mixed carbonate-LiTDI electrolyte maintains a conductivity above 1.0 mS cm\(^{-1}\) down to -20 °C.

Mixed carbonate-LiTDI electrolytes are also suitable for battery applications. The thermal stability of an EC/DEC-LiTDI electrolyte did not decompose after one week at 60 °C. In half-cells, the LiTDI electrolyte performed as well as the standard LiPF\(_6\) electrolyte at room temperature, but far exceeded the capability of the LiPF\(_6\) electrolyte at 60 °C. Although SEI-forming additives are needed for stable cycling of LiTDI electrolytes in full-cells, LiTDI + additive electrolytes again outperformed LiPF\(_6\) + additive electrolytes at 60 °C, while having the same cycling stability and power capability at room temperature. Although further characterization is needed (low temperature performance, cell impedance, etc.), this relatively new salt may be what is needed to replace the unstable LiPF\(_6\) and take Li-ion batteries to the next level in terms of safety and thermal stability.
5.6 References


CHAPTER 6: Concentrated Electrolytes

6.1 Introduction

The use of different lithium salts results in electrolytes with drastically different properties. Each lithium salt has its inherent advantages and drawbacks, as discussed in Ch. 1. Additionally, new lithium salts, such as LiTDI discussed in Chs. 4 and 5, may be used to tailor the characteristics of Li-ion battery electrolytes for different applications. However, another method to adjust electrolyte properties, which has largely been overlooked by the lithium battery community, is the tuning of the lithium salt concentration. When Li-ion batteries were first produced, it was found that the electrolyte conductivity reaches a maximum near a 1 M lithium salt concentration.\(^1\)\(^-\)\(^3\) Since then, nearly all studies have employed a similar concentration in cell testing. Thus, the effect of increasing the salt concentration on other properties, beyond the ionic conductivity, is largely unknown. It is expected that in a sufficiently concentrated electrolyte, nearly all of the solvent and anions would be coordinated to Li\(^+\) cations. By effectively eliminating any bulk (uncoordinated) solvent in the system, the properties of the electrolyte, such as the thermal and electrochemical stability, would thus be anticipated to shift considerably. Recently, Yoshida \textit{et al.} reported a dramatic increase in the anodic stability of G3 and tetraglyme (G4) electrolytes with LiTFSI through the formation of a [glyme-Li]\(^+\)TFSI\(^-\) complex and the elimination of excess solvent by increasing the salt concentration up to a 1-1 glyme-lithium salt ratio.\(^4\),\(^5\) This remarkably high anodic stability for the [G4-Li]\(^+\)TFSI\(^-\) complex had also been previously reported in an earlier publication.\(^6\) Related electrolytes based upon highly
concentrated liquid complexes of LiTFSI with acetamide, 2-oxazolidinone, ethylene urea, etc. have also been reported.\textsuperscript{7-10}

The improved electrochemical stability (relative to more dilute electrolytes) originates from the formation of coordination bonds between the glyme molecules to the Li\textsuperscript{+} cations, which effectively stabilizes the solvent’s electron lone-pairs, thereby reducing their susceptibility to oxidation. Interestingly, it has also been reported that stable cycling of a graphite anode can be achieved with highly concentrated (> 2.7 M) propylene carbonate (PC) or dimethyl sulfoxide (DMSO)-based electrolytes with lithium salts, whereas solvent decomposition and graphite exfoliation occurred for more dilute PC-based electrolytes.\textsuperscript{11-14}

The cycling of Li metal anodes (i.e., suppression of dendritic lithium formation) has also been greatly improved using concentrated PC-based electrolytes.\textsuperscript{15} Clearly, radically different electrolyte properties may be obtained with highly concentrated solvent-lithium salt electrolytes.

This approach was extended here to the carbonate-based solvents which are commonly used in Li-ion battery electrolytes. LiTFSI was used in place of LiPF\textsubscript{6}, due primarily to favorable phase behavior at high concentrations, as LiPF\textsubscript{6} tends to form high melting solvates. In these highly concentrated LiTFSI electrolytes, nearly 95\% of the solvent molecules are found to be coordinated to the Li\textsuperscript{+} cations. Investigation of the anodic stability of concentrated electrolytes containing LiTFSI with either EC or conventional solvent mixtures—3/7 v/v EC/DEC and EC/PC mixed solvents—results in a marked increase in the onset potential for oxidation on a Pt electrode as the salt concentration is increased. Most notably, however, the oxidative corrosion of Al by the LiTFSI-based electrolytes is
effectively suppressed at high concentrations of LiTFSI. Furthermore, because only about 5% of the solvent is uncoordinated at the highest concentrations, the electrolyte volatility is dramatically decreased, thereby reducing the dangers of cell overpressure and electrolyte flammability. In addition, electrolytes with PY_{15}TFSI (known to not interact with Al) are used to systematically change the solvent and salt concentrations, which, in conjunction with MD simulations of the concentrated electrolytes and of the electrolyte-electrode interface, aid in explaining the how the molecular interactions change at high salt concentrations and how this affects the bulk electrolyte properties.

6.2 Results and Discussion

6.2.1 Phase Behavior

The formation of crystalline solvate phases is a key consideration for concentrated electrolytes. In most cases, when the lithium salt concentration is increased in organic solvents, solvates crystallize from solution severely reducing the ionic conductivity. For example, most concentrated mixtures of aprotic solvents with LiPF_6 readily crystallize with the solvates formed often melting well above ambient temperature (Figure D6). However, for other salts, low melting crystalline solvates or crystallinity gaps (specific concentration ranges over which it is difficult/impossible for crystalline solvates to crystallize) can exist. A knowledge of the phase behavior of solvent-salt mixtures is therefore critical for the determination of viable concentrated electrolyte formulations.

The phase diagram for EC-LiTFSI mixtures is depicted in Figure 6.1a. Two crystalline solvates form—(EC)_3:LiTFSI and (EC)_1:LiTFSI—which melt at 26 °C and 50 °C,
Figure 6.1 (a) Phase diagram for EC-LiTFSI mixtures. Vertical lines indicate the phases present (at $x = 0$, 0.25, and 0.50) corresponding to pure EC and the $(EC)_3$:LiTFSI and $(EC)_1$:LiTFSI solvates, respectively. Triangles and crosses indicate the glass transition temperature ($T_g$) for partially crystalline and fully amorphous samples, respectively. Ion and solvent coordination within the (b) $(EC)_3$:LiTFSI and (c) $(EC)_1$:LiTFSI crystalline solvate structures (Li-purple, O-red, N-blue, S-yellow, F-light green). (d) Summary of Raman spectroscopic analysis of liquid EC-LiTFSI electrolytes at 20 °C indicating the fraction of coordinated (to a Li$^+$ cation) (905 cm$^{-1}$, squares) and uncoordinated (895 cm$^{-1}$, circles) EC.
respectively (note: a 3-1 mixture of EC-LiTFSI remains liquid at room temperature unless subcooled). A crystallinity gap exists between these two compositions from 2.5-1 to 1.7-1 EC-LiTFSI, indicating that electrolytes within this composition range are difficult to crystallize, especially for smaller sample sizes due to slow nucleation kinetics. It was possible to crystallize a larger sample (~5 mL) of a 2-1 EC-LiTFSI electrolyte after holding the sample at -20 °C for 24 h, but this then melted near 0 °C.

The (EC)₃:LiTFSI crystalline solvate structure (Figure 6.1b) consists of one symmetry independent (unique) Li⁺ cation, one TFSI⁻ anion and three EC molecules. The Li⁺ cation has five-fold coordination by two O atoms from two different TFSI⁻ anions and three carbonyl O atoms from three EC molecules. The anion F atoms do not participate in the Li⁺ cation coordination. Two O atoms from the TFSI⁻ anion are coordinated to two different Li⁺ cations (AGG-I). This structure displays positional disorder for the TFSI⁻ anion and one of the EC molecules (not shown in Figure 6.1b). The TFSI⁻ anion has the C₂ conformation.¹⁶ The ions and solvent together form one-dimensional (linear) polymeric chains.

The (EC)₁:LiTFSI crystalline solvate structure (Figure 6.1c), in contrast, consists of one symmetry independent (unique) Li⁺ cation, one TFSI⁻ anion and one EC molecule. The Li⁺ cation has five-fold coordination by four O atoms from three different TFSI⁻ anions and the carbonyl O atom from one EC molecule. Again, the anion F atoms do not participate in the Li⁺ cation coordination. The four O atoms from the TFSI⁻ anion are coordinated to three different Li⁺ cations (AGG-II). The TFSI⁻ anion has the C₂ conformation in the crystal structure.¹⁶ The ions and solvent together form two-dimensional (planar) polymeric sheets.
6.2.2 Anion and Solvent...Li$^+$ Cation Coordination

The two crystalline solvate structures indicate that, in the solid state, all of the EC solvent molecules are coordinated to the Li$^+$ cations. In addition, the TFSI$^-$ anions are each coordinated to two or more Li$^+$ cations resulting in polymeric aggregates. Similar solvate aggregate clusters are expected to persist in the melt state for concentrated salt mixtures. This is confirmed by MD simulations of a concentrated EC-LiTFSI 2-1 mixture (Figure 6.2 and Figure C4) in which aggregate clusters predominate with Li$^+$ cations coordinated by four,

Figure 6.2 Examples of ion and solvent coordination in several aggregate solvates extracted from the MD simulation at 60 °C for a 2-1 EC-LiTFSI mixture (Li-purple, O-red, N-blue, S-yellow, F-light green).
three, two, one and even zero EC molecules. One of the anions in Figure 6.2 is coordinated to a Li\(^+\) cation via the N atom, but this form of coordination is exceptionally rare. Instead, nearly all of the anions are coordinated to the Li\(^+\) cations through the anion O atoms. Li\(^+\) cations in the center of the aggregated solvates tend to be less solvated, whereas those at the ends have greater solvation. In addition to most of the EC solvent molecules being coordinated, the anions also have extensive coordination to the Li\(^+\) cations as most of the Li\(^+\) cations have either four- or five-fold coordination.

Using Raman spectroscopy, the TFSI\(^-\) anion bands in the 740-750 cm\(^{-1}\) region were analyzed as a function of concentration to investigate the relative distribution of uncoordinated and coordinated anions in the electrolytes (Figure 6.3). The bands from 739 to 742 cm\(^{-1}\) have previously been assigned to SSIP coordination, while bands from 745 to 755 cm\(^{-1}\) have previously been assigned to SSIP coordination, while bands from 745 to 755 cm\(^{-1}\).

Figure 6.3 Raman spectra of the TFSI\(^-\) anion expansion-contraction band (740-750 cm\(^{-1}\)) at 20 °C (liquid electrolytes), as well as the coordinated EC solvent band at 729 cm\(^{-1}\) (data normalized to the TFSI\(^-\) anion bands: 735-765 cm\(^{-1}\)).
114 cm\(^{-1}\) have been assigned to CIP and AGG coordination.\(^{17}\) The data in Figure 6.3 show that, as the concentration of LiTFSI increases, the anion bands shift to higher wavenumber with bands evident at 740, 744-745, 747 and 751 cm\(^{-1}\). In reality, there are numerous forms of TFSI\(^{-}\)...Li\(^+\) cation coordination which may exist for the aggregate species which result in closely positioned, overlapping bands and, in addition, the band at 740 cm\(^{-1}\) may also include CIP anion coordination.\(^{17,18}\) The results do clearly indicate, however, that a change occurs from numerous SSIP (uncoordinated) anions to CIP and then AGG anion coordination with increasing salt concentration, as expected. For the 2-1 EC-LiTFSI concentration, the anion band is centered at 747 cm\(^{-1}\) with shoulders evident at 742 and 751 cm\(^{-1}\). While the 751 cm\(^{-1}\) shoulder signifies AGG anion coordination, the 742 cm\(^{-1}\) shoulder could represent a small amount of SSIP anion coordination or more likely CIP anion coordination from anions at the end of aggregate clusters (e.g., the top right cluster in Figure 6.2).\(^{18}\) The Raman spectra demonstrate that the aggregate clusters do indeed persist in the melt state for the concentrated electrolytes with few, if any, uncoordinated anions present. The MD simulations also support this conclusion as they indicate that for the 2-1 concentration 99% of the anions are coordinated to one or more Li\(^+\) cations (Table C1 and Figure C4).

For liquid mixtures, even with aggregate cluster formation, some of the solvent may be uncoordinated, thus affecting the electrolyte’s anodic stability and volatility. The fraction of coordinated/uncoordinated EC was studied using Raman spectroscopy (Figure 6.4) and the correction factors previously discussed. Figure 6.5 shows the effect of these correction factors and the improved agreement of the values for the fraction of the coordinated EC between the 717-729 and 895-905 cm\(^{-1}\) regions for EC-LiTFSI electrolytes. At high
Figure 6.4 Raman spectra of EC ring breathing modes at (left) 717 cm\(^{-1}\) and (right) 895 cm\(^{-1}\) for the EC-LiTFSI electrolytes (EC-Li ratio indicated). Peaks above 735 cm\(^{-1}\) are due to TFSI vibrational modes (data for both regions normalized to the EC solvent band: 850-950 cm\(^{-1}\)).

Concentrations of LiTFSI (x > 0.15), however, there remains some disagreement between these two regions. The 717-729 cm\(^{-1}\) region is expected to be less accurate than the 895-905 cm\(^{-1}\) region, however, due to the overlap of the numerous anion bands, which become much more intense at high LiTFSI concentration (Figure 6.3 and 6.4). Thus, while there is qualitative agreement between the two regions, the 895-905 cm\(^{-1}\) region is anticipated to be more accurate and has therefore been used for the remainder of the discussion.

Evaluation of the 895 and 905 cm\(^{-1}\) EC solvent Raman bands at 20 °C indicates that, for the 2-1 EC-LiTFSI concentration, approximately 95% of the EC is coordinated to the Li\(^+\) cations. Overall, the experimental solvation data is in very good agreement with the MD simulation results (Figure 6.1d), although the MD simulations for the more concentrated 5-1 and 2-1 mixtures give a somewhat higher value for the fraction of uncoordinated EC than is
Figure 6.5 Raman spectroscopic analysis of liquid EC-LiTFSI electrolytes at 20 °C indicating the fraction of coordinated (729 and 905 cm$^{-1}$) and uncoordinated (717 and 895 cm$^{-1}$) EC before (left) and after (right) applying the correction factors obtained from previous quantum chemical calculations for changes in Raman scattering intensity. 717-729 cm$^{-1}$: filled symbols, 895-905 cm$^{-1}$: open symbols.

obtained from the experimental Raman evaluation. There are two probable explanations for this. The MD simulations were run at 60 °C, while the Raman analysis was performed at 20 °C. Raman data for the mixtures at higher temperature (Figure 6.6) reveal that the solvation decreases (and the ionic association correspondingly increases) upon increasing the temperature from 20 °C to 60 °C, but this occurs only to a limited extent for a given sample concentration. An additional explanation for this discrepancy is that a small fraction of the EC solvent molecules in the most concentrated simulation mixtures may be coordinated to the Li$^+$ cations by the ring O atoms instead of the carbonyl O atoms (Table C1). This is likely not accounted for in the fraction of coordinated solvent calculated from the simulations. It is
Figure 6.6 Raman spectroscopic analysis of the 895 and 905 cm\(^{-1}\) bands of EC in liquid EC-LiTFSI electrolytes at 20 °C (open symbols) and 60 °C (filled symbols) indicating the fraction of coordinated (905 cm\(^{-1}\), squares) and uncoordinated (895 cm\(^{-1}\), circles) EC.

unclear, however, if this coordination would be accounted for by the experimental methodology as the perturbation effect of such coordination on the solvent band positions/intensities is unknown.\(^{19}\)

The experimental/computational work indicates that the solution structure differs markedly between the relatively dilute (i.e., 10-1) and concentrated (i.e., 2-1) EC-LiTFSI electrolytes. For the more dilute electrolytes, the MD simulation (Figure C3) consists of a relatively large fraction of uncoordinated TFSI\(^-\) anions and fully solvated Li\(^+\) cations. In addition, a significant fraction of the ions are present as CIP and AGG solvate clusters. This differs somewhat from the model of complete solvation of the Li\(^+\) cations which is often used for carbonate solvent mixtures with LiPF\(_6\), but then this latter salt is expected to have a lower
ionic association strength than LiTFSI. Furthermore, the typical electrolyte concentration of 1 M corresponds to an EC-LiTFSI mole ratio of about 14-1 and thus is more dilute than the 10-1 concentration, and therefore likely has a higher degree of solvation. In contrast to the dilute electrolytes, the MD simulations indicate that for the concentrated electrolyte, most of the Li\(^+\) cations are coordinated to one or more TFSI\(^-\) anions resulting in much more extensive ionic association as CIP and AGG solvates (Figure C4). This difference in solution structure is expected to strongly influence the kinetics of the Li\(^+\) cation transfer at the electrolyte-electrode interfaces. Notably, the anions may have a much longer residence time in the coordination shell of the Li\(^+\) cations than the solvent molecules (thus shedding anions may be more difficult than desolvation), but the much higher concentration of Li\(^+\) cations at the interphases (higher availability for transfer) should not be overlooked.

6.2.3 Solvent Volatility/Thermal Stability

The extensive solvent coordination for the concentrated electrolytes has a dramatic influence on the volatility of the electrolytes. Figure 6.7 shows the TGA results for each of the EC-LiTFSI electrolytes, as compared to a 1 M EC/DEC-LiPF\(_6\) electrolyte. The state-of-the-art electrolyte begins to lose mass immediately after the heating begins at 25 °C, attesting to its high volatility. Nearly half of this electrolyte has volatilized upon heating to 50 °C and only nonvolatile decomposition products remain at 150 °C due to solvent vaporization and LiPF\(_6\) conversion to PF\(_5\)(g) and LiF(s). In contrast, all of the EC-LiTFSI electrolytes are significantly more thermally robust due, in part, to the absence of the volatile DEC, but also
Figure 6.7 TGA heating thermograms (5 °C min⁻¹) of 1 M EC/DEC-LiPF₆, pure EC and EC-LiTFSI mixtures.

due to the increased thermal stability of LiTFSI as compared to LiPF₆. Perhaps the most intriguing aspect of these measurements, however, is the trend with respect to LiTFSI concentration—as the concentration of LiTFSI increases, the volatility of the EC significantly decreases. For example, the 10-1 electrolyte loses approximately 5 wt% upon heating to 100 °C, whereas the 2-1 EC-LiTFSI electrolyte loses negligible mass at this temperature. This is attributed to the coordination of the solvent molecules to the Li⁺ cations making them less susceptible to volatilization. The MD simulations for the EC-LiTFSI mixtures support this as the computed enthalpy of vaporization rises precipitously as the salt concentration increases (Table C1). A decrease in volatility would be beneficial for Li-ion batteries, as lower cells pressures would result from cell heating, perhaps decreasing the probability of cell venting.
6.2.4 Anodic Stability

The extensive coordination found in the concentrated electrolytes takes place through the electron lone-pairs on the solvent molecules and anions which form coordination bonds to Li\(^{+}\) cations. This bonding stabilizes the electron lone-pairs, making the solvent and anions less prone to oxidation. To demonstrate this effect, the anodic stability of the EC-LiTFSI electrolytes was investigated on both Pt (Figure 6.8) and Al electrodes (Figure 6.9). When an inert Pt electrode was used, the onset potential for oxidation of the electrolyte increases with increasing LiTFSI concentration, while the oxidation current is reduced. It must be noted, however, that the oxidation of the electrolytes is occurring near 5.4 V vs. Li/Li\(^{+}\) where the TFSI\(^{-}\) anion itself is known to oxidize.\(^{35}\) A possible oxidation mechanism for the EC solvent molecules reacting with the TFSI\(^{-}\) anions is given in Figure C5 and the calculated oxidation potential is in good agreement with the results in Figure 6.8. The effect of solvent coordination may therefore not play a prominent role in the results due to the inherent high oxidative stability of EC (with the Pt electrode), but this effect is much more dramatic on an active electrode such as Al.

![Figure 6.8 Anodic stability (25 °C, 5.0 mV s\(^{-1}\)) of EC-LiTFSI electrolytes vs. Pt electrode with a Ag/Ag\(^{+}\) reference electrode (3.4 V vs. Li/Li\(^{+}\)).](image)

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Numerous studies show that LiTFSI, when mixed with organic aprotic solvents such as EC, extensively corrodes Al electrodes near 4.0 V vs. Li/Li$^+$.\textsuperscript{36-46} This is of particular importance because, as noted previously, Al is used as the current collector for most Li-ion battery cathode materials and is thus a nearly indispensable component of commercial Li-ion batteries. In fact, the corrosive behavior of LiTFSI towards Al has been one key factor in largely excluding its use from such batteries. To explore the corrosion characteristics of the concentrated electrolytes, half-cells containing Al working electrodes were cycled (5 mV s$^{-1}$) between 2.0-6.0 V vs. Li/Li$^+$ for three cycles at 25 °C. The third cycle of the CVs are presented in Figure 6.9 (during the first two cycles, the native oxide layer of the aluminum foil is removed—see Figure D7). The sudden increase in current density near 4.0 V for the half-cells containing the 10-1 and 6-1 EC-LiTFSI electrolytes results from the corrosive

![Figure 6.9 CVs](image)

Figure 6.9 CVs (25 °C, 5.0 mV s$^{-1}$, third cycle) vs. Al foil electrode of EC-LiTFSI electrolytes.
reaction of the electrolyte with the Al electrode. Remarkably, for the highest concentrations (3-1 and 2-1), only a negligible current density is observed beyond 4.0 V for all three cycles, indicating that the corrosion of Al has effectively been suppressed, despite the exceptionally high concentration of LiTFSI present.

This suppression of Al corrosion for a concentrated EC/DEC-LiTFSI electrolyte was also noted in a recent report. The notion that Al corrosion by LiTFSI electrolytes can be inhibited by increasing the concentration of LiTFSI may, at first, seem counterintuitive. The authors of this work found that significant pitting corrosion occurred when an 3/7 v/v EC/DEC-LiTFSI electrolyte with a 1 M concentration (approximately 9-1 EC/DEC-LiTFSI, Figure D8) was cycled to high potential with an Al electrode, but much less pitting was found for a 1.8 M (4.5-1 EC/DEC-LiTFSI) electrolyte, in agreement with the results presented here. X-ray photoelectron spectroscopy (XPS) analysis afterwards found that the Al surface in contact with the 1.0 M electrolyte (polarized at 4.3 V vs. Li/Li+ for 3 h) consisted principally of Al and O, along with small amounts of Li and F. In sharp contrast, the surface layer which resulted from contact with the 1.8 M electrolyte had a relatively large amount of Li and F, with lesser amounts of Al and O. It was suggested that, for the more dilute concentration, the thin surface film was principally composed of AlF3 and Al2O3, whereas for the 1.8 M electrolyte, the surface instead consisted of a large amount of LiF, in addition to AlF3 and Al2O3. The proposed explanation for this was linked to the dissociation tendency (ionic association) of the LiTFSI salt. For the lower concentration, the salt was postulated to be separated into solvated Li+ cations and uncoordinated anions. Thus, at high potential, the TFSI- anions decompose (oxidize) on the Al surface producing fluoride...
anions (F) which reacted with the Al to form AlF₃. For the more concentrated mixture, however, it was suggested that the Li⁺ cations and TFSI⁻ anions were associated with one another and this ion proximity resulted in the formation of the LiF following TFSI⁻ reaction on the Al electrode surface, and the LiF is what inhibits the Al corrosion. This explanation is problematic, however, as very little F was actually noted on the Al surface for the 1 M LiTFSI electrolyte.

An alternative explanation is provided below for the variability in the Al corrosion using the concentrated electrolyte data from the present work and a discussion about uncoordinated solvent and anion stability. Figure 6.10 shows the interfacial interactions obtained from previous computational MD simulations of a graphite surface in contact with an EC/DMC-LiPF₆ electrolyte (with approximately a 1/2 EC/DMC mole ratio and 12-1 solvent-LiPF₆ concentration) upon increasing polarization. At the unpolarized (0 V) graphite surface, a mixture of both EC and DMC molecules is found, with no significant preferential orientation, and a low anion concentration which is representative of the overall bulk electrolyte concentration. As the graphite surface is positively polarized, however, the PF₆⁻ anion concentration at the surface progressively increases. In addition, the EC molecules displace the DMC molecules, despite the larger concentration of the latter in the bulk electrolyte, and the EC molecules tend to orient themselves so that the electron lone-pairs from both the carbonyl and one ring O atoms are directed at the surface. This occurs because the EC molecules are more readily polarizable than the DMC molecules, as reflected in the disparity in the dielectric constants of the solvents (ε: 90.4 for EC, 3.1 for DMC). Thus, both the
Figure 6.10 (a) MD simulation snapshots (spaceview) of a graphite-electrolyte (EC/DMC-LiPF₆) interface as the electrode potential between two graphite electrodes is progressively increased. Only the positively polarized electrode is shown, and the boundaries are periodic (Li-purple, C-gray, O-red, F-green with two views—rotated 90°—shown for each potential).④₈ (b) Size comparison for the PF₆⁻, TFSI⁻, BETI⁻ and N(SO₂CF₂)(SO₂C₄F₉)⁻ anions.

anions and EC molecules stabilize the positive charge dispersed on the C surface atoms at high potential.

As part of the present work it was proposed that the reason that electrolytes with LiTFSI and LiCF₃SO₃ strongly corrode Al, in sharp contrast to those with LiPF₆ and LiBF₄, is because these anions with C-F bonds are essentially too stable (rather than being overly
reactive). All four anions display a similar oxidative stability on inert glassy carbon or Pt electrodes, whereas TFSI is found to be more stable than PF$_6^-$ on a W electrode. However, an Al surface is much more active than Pt (once the native, dense Al$_2$O$_3$ layer formed from the reaction with O$_2$ is removed). Thus, it is proposed that as the potential increases, the solvent molecules at the surface react to form Al$_2$O$_3$, while the PF$_6^-$ (or BF$_4^-$) anions react either with the Al to form AlF$_3$, or with the neighboring solvent molecules to form HF. The HF then reacts with the Al$_2$O$_3$ to form AlF$_3$ and AlOF, or with the Li$^+$ cations to form LiF, all of which serve to passivate the surface. These reactions occur at a much lower potential than is noted for the PF$_6^-$ (or BF$_4^-$) anion or uncoordinated solvent oxidation on a Pt surface. In contrast, the TFSI anions do not degrade significantly until a much higher potential. Thus, the surface reactions involve principally the oxidation of the uncoordinated solvent with the Al to form Al$_2$O$_3$ and this does not effectively passivate the surface from further reactions (perhaps including the formation of Al-TFSI complexes which disperse in the electrolyte solution as part of the surface pitting).

In contrast to the extensive corrosion noted for dilute LiTFSI and LiCF$_3$SO$_3$ electrolytes with aprotic solvents, a reduction in Al corrosion has been noted for lithium salts with bulkier imide anions, such as BETI or N(SO$_2$CF$_3$)(SO$_2$C$_4$F$_9$)$^-$, despite the fact that the Al surfaces after polarization to high potentials for all of these electrolytes have nearly the same composition. This can be explained by a solvent exclusion effect. If the PF$_6^-$ anions in Figure 6.10a are replaced with these bulky anions (Figure 6.10b), then the surface would be effectively covered almost exclusively with the anions, thus effectively suppressing the continuous oxidation of the solvent. XPS data does indicate that anions are strongly absorbed
on the oxidized Al surface, even after washing the electrodes.\textsuperscript{40} The solvent used has also been found to influence the Al corrosion, with LiTFSI-based electrolytes with ethers or fluorinated solvents having less corrosion than those with cyclic carbonate (EC and PC) solvents,\textsuperscript{39,43} even though carbonate solvents have been found to be more stable than ether solvents when using a Pt electrode.\textsuperscript{53} The lower dielectric constants of the ethers and fluorinated solvents, relative to the cyclic carbonates, will result in a lower concentration of these solvent molecules at the polarized surface (replaced by a greater number of anions), thus reducing the solvent oxidation.

The high oxidative stability of the TFSI\textsuperscript{−} anion with Al is further confirmed by the lack of Al oxidation until very high potentials for ILs with TFSI\textsuperscript{−} anions, even when mixed with LiTFSI, despite the very high concentration of TFSI\textsuperscript{−} anions present.\textsuperscript{54-56} In fact, MD simulations suggest that upon positively polarizing an electrode surface, the electrode is effectively covered solely by the anions for such electrolytes.\textsuperscript{57} Similarly, for the concentrated electrolytes, the high concentration of TFSI\textsuperscript{−} anions at the electrode-electrolyte interface (similar to the interface with ILs) will also serve as a barrier which hinders the access of solvent to the electrode and loss of material (dissolution) from the electrode surface. Furthermore, it is expected that the solubility of Al-TFSI complexes will be much lower than for dilute electrolytes, as the solvent molecules and anions are already extensively coordinated. The absence of uncoordinated solvent, relatively low amount of solvent present in general and extensive coordination of both the solvent molecules and anions to Li\textsuperscript{+} cations (which increases their oxidative stability) further combine to inhibit the oxidation reactions at
the Al electrode surface until much higher potentials than is found for dilute electrolytes (Figure 6.9).

To further support this argument, the PY$_{15}$TFSI IL was mixed with EC and LiTFSI and the Al corrosion was investigated by CV. Because PY$_{15}$TFSI-EC interactions are known to be quite weak, this IL provides a way to remove the Li$^+$ cations (and thus also removing the possibility of having large amounts of EC or TFSI$^-$ coordinated to the Li$^+$ cations) while maintaining a conductive electrolyte.$^{58,59}$ For these PY$_{15}$TFSI-EC-LiTFSI mixtures, the PY$_{15}$TFSI mole ratio was maintained at 9, the EC mole ratio was either 0, 2, 3, 6, or 10 to be consistent with the concentrated EC-LiTFSI electrolytes, and the LiTFSI mole ratio was either 0 or 1 (e.g., 9-10-0 and 9-2-1 PY$_{15}$TFSI-EC-LiTFSI). In this way, the effect of changing the EC content with and without the effect of EC…Li$^+$ or TFSI$^-$…Li$^+$ coordination could be elucidated.

Figure 6.11 shows the results from these CVs. The mixtures with and without LiTFSI behave similarly to the concentrated EC-LiTFSI electrolytes, in that the degree of corrosion increases with increasing EC content. Little, if any, corrosion is observed for the 9-3-1 and 9-2-1 PY$_{15}$TFSI-EC-LiTFSI mixtures, because most of the EC remains coordinated to Li$^+$ cations, as in the IL-free electrolytes. The overall current density is lower (with or without the LiTFSI) than for the EC-LiTFSI electrolytes because the additional TFSI$^-$ anions from the IL cover a fraction of the Al surface area, and this increases with increasing IL mole fraction. When the LiTFSI is removed, however, and thus no Li$^+$ cation coordinated EC is present, corrosion is observed for all of the mixtures from 9-10-0 to 9-2-0, with the current density
increasing as the EC content increases. When no EC is present, and LiTFSI is present (i.e., 9-0-1 PY$_{15}$TFSI-EC-LiTFSI), no corrosion is observed. Additionally, it is well-established that ILs, including PY$_{15}$TFSI, with and without LiTFSI do not corrode Al, so the effect described here cannot be due to the changing coordination environment of the TFSI$^-$ anions. Therefore, the corrosion must be due to the EC, and not the TFSI$^-$ anion, contradicting the conventional wisdom within the battery community.

6.2.5 Ionic Conductivity

One particular limitation for the concentrated EC-LiTFSI electrolytes is the effect of the high level of coordination on the ionic conductivity (Figure 6.12a). Concentrations of 3-1 and 2-1 EC-LiTFSI have conductivity values at 20 °C of 0.7 and 0.1 mS cm$^{-1}$, respectively, while
Figure 6.12 Variable-temperature ionic conductivity of (a) EC-LiTFSI, (b) EC/DEC-LiTFSI, and (c) EC/PC-LiTFSI electrolytes.

carbonate-LiPF₆ electrolytes commonly used in batteries have conductivity values at 20 °C near 8-10 mS cm⁻¹ (Figure D4). These low conductivity values for the concentrated EC-LiTFSI electrolytes would be expected to negatively affect the power capability of a Li-ion battery. However, state-of-the-art electrolyte formulations use a mixed solvent blend, such as EC/DEC, to both inhibit solvate formation and significantly increase the conductivity. For
the concentrated electrolytes, if the EC is substituted with a 3/7 v/v EC/PC mixture (i.e., a 2-1 EC/PC-LiTFSI mixture represents a 2-1 total solvent-LiTFSI (molar basis) composition in which the solvent ratio is 3/7 v/v), little effect is noted for the electrolyte conductivity (Figure 6.12c). In contrast, a similar ratio of EC/DEC increased the conductivity of the most concentrated electrolytes, especially at low temperature (Figure 6.12b). For example, at 20 °C, the conductivity of the 3-1 and 2-1 EC/DEC-LiTFSI electrolytes is 1.5 and 0.5 mS cm⁻¹, respectively. While the inclusion of DEC increases the volatility of the concentrated electrolytes (Figure 6.13), the most concentrated EC/DEC electrolytes are still much less volatile than the dilute mixtures. Furthermore, the corrosion of Al continues to be suppressed in concentrated electrolytes using either EC/PC or EC/DEC solvent mixtures (Figure 6.14). A mixed solvent approach is therefore a promising strategy for further tuning the properties of concentrated electrolytes.

![Figure 6.13 TGA heating thermograms (5 °C min⁻¹) of 1 M EC/DEC-LiPF₆, compared to EC/DEC-LiTFSI mixtures.](image)
Figure 6.14 CVs (25 °C, 5.0 mV s\(^{-1}\), third cycle) vs. Al foil electrode of (a) EC/DEC-LiTFSI and (b) EC/PC-LiTFSI electrolytes.

6.3 Conclusions

Concentrated EC-LiTFSI electrolytes have a dramatically improved thermal and anodic stability relative to more dilute mixtures. In particular, the electrolytes with a high concentration of LiTFSI effectively suppress the corrosion of Al. An explanation for the stabilization behavior of concentrated electrolytes is obtained from crystalline solvate structures, MD simulation/QC calculation results and the Raman spectroscopic analysis of the mixtures. From these results, it was determined that in the liquid state, nearly all of the EC molecules are coordinated to the Li\(^+\) cations through their carbonyl O atoms and the anions are coordinated to multiple Li\(^+\) cations. The anodic stability arises from this extensive coordination—electron lone-pairs on the solvent and anions are stabilized by extensive
coordination to the positively-charged Li$^+$ cations. A dramatic reduction in the volatility of the coordinated solvent, as compared to the uncoordinated solvent, is also found. The main drawback of the concentrated EC-LiTFSI electrolytes is the relatively low ionic conductivity ($< 1.0$ mS cm$^{-1}$) at ambient temperature. A mixture of EC/DEC with LiTFSI, however, did significantly increase the conductivity of the concentrated electrolytes, especially at low temperatures. Concentrated electrolytes are thus a promising approach for tailoring electrolyte properties for demanding electrochemical applications.
6.4 References


CHAPTER 7: Conclusions

The objective of this project was to develop electrolytes for next-generation Li-ion batteries. These batteries, to be used for demanding applications like electric vehicles and grid-level storage, must be safer and thus more thermally and electrochemically stable than current technology, necessitating the discovery of new electrolyte materials or deviating substantially from common electrolyte formulations. Four new lithium salts were synthesized and screened for their potential use in these advanced electrolytes: Li$_2$TDD, LiETAC, LiHFI, and LiPFPO. Using crystalline solvate structural analysis in tandem with Raman spectroscopy to determine the solvation numbers of AN-LiX electrolytes, each of these lithium salts was found to be strongly associated—a property which is generally not desirable for Li-ion battery electrolytes. However, close scrutiny of the anion chemical structures and comparison to the structures of more conventional lithium salt anions with more advantageous properties revealed new insight into the connections between anion chemical structure and ionic association strength. This knowledge revealed that another lithium salt, LiTDI, has a more beneficial anion structure, and was thus anticipated to have improved properties.

LiTDI, along with the structurally similar but nonfluorinated LiDCTA, was synthesized and analyzed by crystalline solvate structural analysis and compared to the four previous lithium salts synthesized in this study, as well as other lithium salts commonly studied for electrolyte applications. The incorporation of a delocalized triazole ring and the electron-withdrawing cyano groups in the DCTA$^-$ anion was alone not enough to make an anion of low ionic association strength. Instead, the substitution of an N atom on the DCTA$^-$ anion
with an electron withdrawing C-CF₃ group to form the TDI anion drastically alters the anion’s properties and significantly reduces the ionic association tendency as compared to LiDCTA, as well as the four new lithium salts described previously. Furthermore, Raman spectroscopic analysis and conductivity measurements of EC-LiTDI electrolytes concluded that the LiTDI ionic association strength is in-between that of LiTFSI and LiBF₄. These findings indicated that LiTDI was a promising lithium salt for Li-ion battery electrolyte applications.

A mixed carbonate-LiTDI electrolyte was cycled in half-cells and was found to be comparable to a mixed carbonate-LiPF₆ electrolyte, in terms of discharge capacity and power capability. At 60 °C, however, the LiTDI electrolyte proved to be advantageous. While the half-cell with LiPF₆ lost over half of its discharge capacity over cycling for one week at 60 °C, the half-cell containing LiTDI was stable and showed no signs of degradation. NMR analysis of the LiTDI electrolyte stored for a similar amount of time at 60 °C complemented these results, and found that no significant decomposition had occurred, signifying LiTDI is more thermally stable than LiPF₆.

Full-cells with LiTDI, however, have significantly reduced discharge capacity and Coulombic efficiency as compared to those with LiPF₆. This was attributed to inadequate SEI formation on the surface of the graphite electrode. To resolve this, the SEI-forming lithium salts, LiBOB and LiDFOB, were used in additive quantities of 1 wt% in both the LiPF₆ and LiTDI electrolyte. The full-cell performance improved accordingly, as full-cells with either the LiTDI or LiPF₆ electrolytes with 1 wt% of either additive had similar discharge capacities and power capabilities at room temperature. When cycled at 60 °C, on the other hand, the
full-cells containing LiPF$_6$ had a significantly higher capacity fade rate than at 25 °C, with or without additives. In stark contrast, full-cells containing the LiTDI electrolyte with either additive had very little capacity fade at high temperature, once again demonstrating the stability of the LiTDI electrolyte. Although further study of this salt and its electrolytes is imperative (e.g., full-cell impedance measurements, low temperature cycling, etc.) to reveal to the full spectrum of its benefits and any disadvantages, LiTDI shows encouraging potential to replace LiPF$_6$ in Li-ion battery electrolytes.

Another method was found to dramatically shift the properties of lithium battery electrolytes, instead of using different lithium salts. By utilizing highly concentrated EC-LiTFSI electrolytes, nearly all of the uncoordinated solvent was eliminated, as was proven by a Raman spectroscopic analysis and MD simulations. These highly concentrated electrolytes were found to have unique properties, including a significantly reduced volatility and higher anodic stability on a Pt electrode, as compared to more dilute electrolytes. Perhaps most striking, though, was the suppression of Al corrosion by the concentrated electrolytes. This new finding suggests a different mechanism of Al corrosion than is currently accepted by the battery community—one that concludes it is actually the solvent that is reacting with the Al surface due to the inability of LiTFSI to passivate the Al, while other salts, such as LiPF$_6$ and LiBF$_4$, do passivate the Al surface and prevent excessive Al corrosion. This new interpretation could change the manner with which Li-ion battery electrolytes are currently formulated and perhaps pave the way to the advanced Li-ion batteries that are needed for the demanding applications of the future.
APPENDICES
Appendix A: Li Salt Synthesis

Figure A1 Attempted syntheses of dianions. Most reactions were tried in multiple ways—for example, by first lithiating a reagent (e.g., Li$_2$(NH)$_2$CO) using LiH or LiMeO, or using a reagent with another leaving group (e.g., (Me$_3$SiNH)$_2$CO).
Figure A2 Attempted syntheses of various anions.
Appendix B: Crystalline Solvates with LiTDI

Figure B1 DSC heating traces of the AGG LiTDI crystalline solvates—AGG-I: (AN)$_2$:LiTDI, AGG-IIa: (EC)$_1$:LiTDI, (THF)$_1$:LiTDI, AGG-IIb: (PC)$_1$:LiTDI and AGG-III: (DMC)$_{0.5}$:LiTDI.

Single Crystal Preparation:
HDCTA: Crystals were grown by sublimation of crude HDCTA from the initial reaction of DAMN and tert-butyl-nitrite.
(G1)$_1$:LiDCTA: Crystals were grown from a 3-1 G1-LiDCTA mixture that was heated until the solid dissolved and allowed to slowly cool.
(G2)$_1$:LiDCTA: Crystals were grown from a 4-1 G2-LiDCTA mixture that was heated until the solid dissolved and allowed to slowly cool.
HTDI: LiTDI was mixed with two equivalents of boron trifluoride diethyl etherate in diethyl ether at 0 °C in an attempt to form a (BF$_3$)$_2$:LiTDI complex. After addition, the mixture was refluxed overnight forming a yellow solution. The ether solvent was removed by evaporation, and the resulting yellow paste was dissolved in DMC. Slow addition of dichloromethane yielded crystals of HTDI overnight.
(G1)$_2$:LiTDI: Crystals were grown from a 3-1 G1-LiTDI mixture after storage overnight in the freezer.
(G2)$_2$:LiTDI: Crystals were grown from a 2-1 G2-LiTDI mixture that was heated until the solid dissolved and allowed to slowly cool.
(G3)$_1$:LiTDI: Crystals were grown by slow cooling of a hot solution of 1.5-1 G3-LiTDI to -5 °C, yielding a solid mixture. Upon warming to room temperature, crystals were observed within a liquid solution.

(AN)$_1$:LiTDI: Crystals were grown by slow cooling a hot saturated solution of 15-1 AN-LiTDI.

(EC)$_1$:LiTDI: Crystals were grown by slow cooling a hot saturated solution of 6-1 EC-LiTDI.

(THF)$_1$:LiTDI: Crystals were grown by vapor diffusion of n-pentane into a solution of 20-1 THF-LiTDI and allowing slow diffusion of the two solvents.

(PC)$_1$:LiTDI: Crystals were grown by slow cooling of a hot saturated solution of 10-1 PC-LiTDI.

(DMC)$_{1/2}$:LiTDI: Crystals were grown by vapor diffusion of DCM into a solution of 6-1 DMC-LiTDI and allowing slow diffusion of the two solvents.
Figure B2 $H^+$ cation and TDI$^-$ anion coordination within the crystal structure of HDCTA (N-blue).

Figure B3 Ion packing within the crystal structure of HDCTA (two views) (N-blue).
Figure B4 Li$^+$ cation and DCTA$^-$ anion coordination within the crystal structure of the AGG-I (G1)$_1$:LiDCTA solvate (Li-purple, O-red, N-blue).

Figure B5 Ion packing within the crystal structure of the AGG-I (G1)$_1$:LiDCTA solvate (two views) (Li-purple, O-red, N-blue).
Figure B6 Li$^+$ cation and DCTA$^-$ anion coordination within the crystal structure of the AGG-I (G2)$_1$:LiDCTA solvate (Li-purple, O-red, N-blue).

Figure B7 Ion packing within the crystal structure of the AGG-I (G2)$_1$:LiDCTA solvate (two views) (Li-purple, O-red, N-blue).
Figure B8 H+ cation and TDI anion coordination within the crystal structure of HTDI (N-blue, F- light green).

Figure B9 Ion packing within the crystal structure of HTDI (two views) (N-blue, F- light green).
Figure B10 Li⁺ cation and TDI⁻ anion coordination within the crystal structure of the SSIP (G2)₂:LiTDI solvate (Li-purple, O-red, N-blue, F- light green).

Figure B11 Ion packing within the crystal structure of the SSIP (G2)₂:LiTDI solvate (two views) (Li-purple, O-red, N-blue, F- light green).
Figure B12 Li$^+$ cation and TDI$^-$ anion coordination within the crystal structure of the CIP (G1)$_2$:LiTDI solvate (Li-purple, O-red, N-blue, F-light green).

Figure B13 Ion packing within the crystal structure of the CIP (G1)$_2$:LiTDI solvate (two views) (Li-purple, O-red, N-blue, F-light green).
Figure B14 Li$^+$ cation and TDI$^-$ anion coordination within the crystal structure of the CIP (G3)$_1$:LiTDI solvate (Li-purple, O-red, N-blue, F-light green).

Figure B15 Ion packing within the crystal structure of the CIP (G3)$_1$:LiTDI solvate (two views) (Li-purple, O-red, N-blue, F-light green).
Figure B16 Li$^+$ cation and TDI$^-$ anion coordination within the crystal structure of the AGG-I (AN)$_2$:LiTDI solvate (Li-purple, O-red, N-blue, F-light green).

Figure B17 Ion packing within the crystal structure of the AGG-I (AN)$_2$:LiTDI solvate (two views) (Li-purple, O-red, N-blue, F-light green).
Figure B18 Li$^+$ cation and TDI$^-$ anion coordination within the crystal structure of the AGG-IIa (EC)$_1$:LiTDI solvate (Li-purple, O-red, N-blue, F-light green).

Figure B19 Ion packing within the crystal structure of the AGG-IIa (EC)$_1$:LiTDI solvate (two views) (Li-purple, O-red, N-blue, F-light green).
Figure B20 Li$^+$ cation and TDI$^-$ anion coordination within the crystal structure of the AGG-IIa (THF)$_1$:LiTDI solvate (Li-purple, O-red, N-blue, F- light green).

Figure B21 Ion packing within the crystal structure of the AGG-IIa (THF)$_1$:LiTDI solvate (two views) (Li-purple, O-red, N-blue, F- light green).
Figure B22. Li$^+$ cation and TDI$^-$ anion coordination within the crystal structure of the AGG-IIb (PC)$_1$:LiTDI solvate (Li-purple, O-red, N-blue, F-light green).
Figure B23 Ion packing within the crystal structure of the AGG-IIb (PC)$_1$:LiTDI solvate (two views) (Li-purple, O-red, N-blue, F-light green).
Figure B24 Side view of the (a) (THF)$_1$:LiTDI (b) (EC)$_1$:LiTDI and (c) (PC)$_1$:LiTDI crystalline solvates, showing the changing angle of the solvent-Li$^+$ coordination bond.
Figure B25 Li$^+$ cation and TDI$^-$ anion coordination within the crystal structure of the AGG-III (DMC)$_{1/2}$:LiTDI solvate (Li-purple, O-red, N-blue, F- light green).

Figure B26 Ion packing within the crystal structure of the AGG-III (DMC)$_{1/2}$:LiTDI solvate (two views) (Li-purple, O-red, N-blue, F- light green).
Appendix C: Quantum Chemical Calculations and MD Simulations

Figure C1 Geometry of the [Li⁺-TFSI⁻] complex from G4MP2 calculations. The G4MP2 distances are shown in black, while distances obtained from molecular mechanics optimization using APPLE&P force field are shown in blue parentheses and italicized.
Molecular Dynamics (MD) Simulations of EC-LiTFSI Electrolytes

Table C1  **MD simulations results at 333 K and specification of simulated systems**

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<th>5</th>
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<td>64</td>
<td>128</td>
<td>192</td>
</tr>
<tr>
<td>concentration (M)</td>
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<td>2.03</td>
<td>3.48</td>
</tr>
<tr>
<td>length of equilibration runs (ns)</td>
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<td>10</td>
</tr>
<tr>
<td>length of production run (ns)</td>
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<td>9</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
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<td>1399</td>
<td>1478</td>
<td>1614</td>
</tr>
<tr>
<td>( \rho ) (density), experimental (kg m(^{-3}))</td>
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<td>1415</td>
<td>1495</td>
<td></td>
</tr>
<tr>
<td>( \rho ) (density), error %</td>
<td>-1.3</td>
<td>-1.1</td>
<td>-1.1</td>
<td></td>
</tr>
</tbody>
</table>

**Transport Properties**

| \( D_{\text{solvent}} \), MD \((10^{-10} \text{ m}^2 \text{ s}^{-1})\) | 7.4 | 5.5 | 2.8 | 0.450 |
| \( D_{-} \), MD \((10^{-10} \text{ m}^2 \text{ s}^{-1})\) | 4.4 | 2.7 | 1.4 | 0.144 |
| \( D_{+} \), MD \((10^{-10} \text{ m}^2 \text{ s}^{-1})\) | 3.5 | 2.7 | 1.4 | 0.166 |
| \( \kappa \) (conductivity), MD (mS cm\(^{-1}\)) | 13.4| 11.4| 7.8 | 1.45 |
| \( \kappa \) (conductivity), experimental (mS cm\(^{-1}\)) | 11.5| 12.3| 8.1 | 1.3 |
| viscosity, MD (mPa s) | 1.9 | 2.6 | 5.0 | 37.3 |

**Ion Coordination**

| fraction of free Li\(^+\) (SSIP) | 0.62| 0.44| 0.23| 0.05 |
| fraction of free N(TFSI) (SSIP) | 0.61| 0.38| 0.15| 0.01 |
| fraction of free EC (not coordinated by Li\(^+\)) | 0.81| 0.66| 0.44| 0.14 |
| Li\(^+\) coordination numbers | | | | |
| number O (EC) \((r(\text{O-Li}) < 2.5 \text{ Å})\) | 3.69| 3.3 | 2.78| 1.72 |
| number O(TFSI) \((r(\text{O-Li}) < 2.5 \text{ Å})\) | 0.59| 0.98| 1.52| 2.55 |
| number N(TFSI) \((r(\text{N-Li}) < 4.74 \text{ Å})\) | 0.42| 0.70| 1.10| 1.99 |
| fraction of bidentate O(TFSI)/Li\(^+\) coordination* | 0.44| 0.46| 0.42| 0.30 |
| enthalpy of vaporization (kJ mol\(^{-1}\))** | 81 | 104| 144| 220 |

* NOTE: The fraction of free EC (not coordinated by Li\(^+\)) (Table S1) is determined by calculating the fraction of EC carbonyl oxygen atoms with an O-Li\(^+\) distance > 2.8 Å. But approximately 4.4% of the EC molecules are coordinated to Li\(^+\) cations in the 2-1 EC-LiTFSI simulation via the ring oxygen atoms (instead of the carbonyl oxygen atoms). For more dilute compositions, this percentage is much lower. This coordination is not reflected in the calculated fraction of coordinated and free EC molecules. Thus, the 14% value of uncoordinated EC molecules for the 2-1 composition in Table A1 is too high. It is unclear if the experimental analysis of the solvation numbers (Figure 6.1) would capture such
coordination, however, as it is not known how this ring oxygen coordination would affect the EC solvent Raman vibrational bands.

** The experimental molar enthalpy of vaporization for pure EC at 298.15 K is 60.81 kJ mol\(^{-1}\) and at 333.6 K is 59.13 kJ mol\(^{-1}\).\(^1\)
Figure C2 (top) Full MD simulation snapshot at 60°C for the EC-LiTFSI 10-1 mixture and (bottom) the same MD simulation snapshot with the uncoordinated EC molecules removed and the solvates grown across the periodic boundaries (Li-purple, O-red, N-blue, S-yellow, F-light green).
Figure C3 Visual list of individual anions and solvates extracted from the MD simulation at 60°C for the EC-LiTFSI 10-1 mixture (shown in Figure S9)—uncoordinated EC molecules not shown (Li-purple, O-red, N-blue, S-yellow, F-light green).
Figure C3 (cont). Visual list of individual anions and solvates extracted from the MD simulation at 60°C for the EC-LiTFSI 10-1 mixture (shown in Figure S9)—uncoordinated EC molecules not shown (Li-purple, O-red, N-blue, S-yellow, F-light green).
Figure C4 Visual list of individual anions and solvates extracted from the MD simulation at 60°C for the EC-LiTFSI 2-1 mixture—uncoordinated EC molecules not shown (Li-purple, O-red, N-blue, S-yellow, F-light green).
Figure C4 (cont). Visual list of individual anions and solvates extracted from the MD simulation at 60°C for the EC-LiTFSI 2-1 mixture—uncoordinated EC molecules not shown (Li-purple, O-red, N-blue, S-yellow, F-light green).
Figure C4 (cont). Visual list of individual anions and solvates extracted from the MD simulation at 60°C for the EC-LiTFSI 2-1 mixture—uncoordinated EC molecules not shown (Li-purple, O-red, N-blue, S-yellow, F-light green).
Quantum Chemistry Study of EC/TFSI\(^-\) and EC/LiTFSI Oxidation

The initial stages of the oxidation induced reactions of [EC-TFSI\(^-\)] and [EC-Li\(^+\)-TFSI\(^-\)] complexes were studied using density functional calculations employing the M05-2X/6-31+G** level in order to understand the influence of a Li\(^+\) cation on the oxidation stability of these complexes. The Gaussian g09 package was used with the SMD implicit solvent model developed by Marenich et al.\(^{2,3}\) The absolute oxidation potential of a complex M relative to an electron at rest in vacuum \((E_{\text{abs}}^0(M))\) was calculated using Eq. 1:

\[
E_{\text{abs}}^0 = \frac{\Delta G_e + \Delta G_{S}^0(M^+) - \Delta G_{S}^0(M)}{F}
\]  

1

where \(\Delta G_e\) is the ionization free energy in the gas-phase at 298.15 K; \(\Delta G_{S}^0(M^+)\) and \(\Delta G_{S}^0(M)\) are the free energies of solvation of the oxidized and initial complexes \(M^+\) and \(M\), respectively, and \(F\) is Faraday’s constant. Using the Li/Li\(^+\) standard electrode potential of -3.05 V vs. SHE for aqueous solutions,\(^4\) a value of 4.42 - 3.05 = 1.37 V is obtained to convert the absolute potential scale \(E_{\text{abs}}^0\) to the Li/Li\(^+\) scale in aqueous solutions from IUPAC recommendations as expressed by Eq. 2:

\[
\Delta G_{\text{ox}}^0 (\text{vs. Li}/\text{Li}) = E_{\text{abs}}^0 + E_{\text{abs}}^0 (\text{Li}/\text{Li}) = E_{\text{abs}}^0 - 4.42 + 3.05 = E_{\text{abs}}^0 - 1.37 \approx E_{\text{abs}}^0 - 1.4 V
\]  

2

where \(E^0\) is the potential vs. Li\(^+\)/Li.

The initial oxidation of the [EC-TFSI\(^-\)] complex (M0 in Figure S12) resulted in a M1 complex with an oxidation potential of 6.33 V vs. Li\(^+\)/Li, which is significantly higher than the measured oxidation potential ~5.4 V for the 10-1 EC-LiTFSI concentration. Further investigation, however, revealed that there is a low barrier (~0.10 V, see TS1 - Figure S12) for the H-transfer reaction from EC to TFSI\(^-\) for the oxidized [EC-TFSI\(^-\)] complex M2. Such H-transfer significantly reduces the oxidation stability of the [EC-TFSI\(^-\)] complex from 6.3 V to 5.3 V in agreement with previous studies of EC complexed with PF\(_6\)^-, BF\(_4\)^- and FSI\(^-\) anions.\(^5,6\) A similar H-transfer reaction was found in EC\(_n\) (n = 2 and 4) clusters resulting in a slightly higher oxidation potential around 5.8 to 6.0 V as compared to the [EC-TFSI\(^-\)] reaction.\(^6,7\)

The oxidative stability of the [EC-Li\(^+\)-TFSI\(^-\)] cluster was also calculated for two complexes with EC coordinated by a Li\(^+\) cation (M4) and the TFSI\(^-\) anion coordinating a Li\(^+\) cation (M5) (relative to the M3 complex). EC polarization by a Li\(^+\) cation increases the oxidative stability by 0.3 V. Interestingly, the TFSI\(^-\) anion complexation to a Li\(^+\) cation also increases the oxidative stability by a similar amount (~0.5 V). These calculations indicate that polarization of either the TFSI\(^-\) anion or EC solvent molecule involved in the oxidation reaction increases the oxidation stability of the corresponding complex by 0.3 to 0.5 V.
Figure C5 Oxidation-induced decomposition reactions of [EC-TFSI] and [EC-Li^+TFSI^-] calculated at the M05-2X/6-31+G** level with SMD (EC, ε = 89.7, ε_{inf} = 2.05). Oxidation free energy (ΔG^{ox}) is given vs. Li^+/Li.
References


Appendix D: Supplemental Electrolyte Characterization

Figure D1 CVs (25 °C, 5.0 mV s⁻¹, three cycles) vs. Al foil electrode of 1 M EC/DEC-LiPF₆ (black line) and 1 M EC/DEC-LiETAC (red line) electrolytes.
Figure D2 DSC of EC-LiTDI electrolytes and (EC)$_1$:LiTDI crystalline solvate.

Figure D3 Solvation number ($N$) of EC-LiX electrolytes comparing the 717-728 and 895-905 cm$^{-1}$ regions. The 717-728 cm$^{-1}$ region was not analyzed for the EC-LiBOB and EC-LiDFOB electrolytes due to significant anion band overlap, and therefore they are excluded from this plot.
Figure D4 Variable temperature conductivity of EC/DEC-LiPF$_6$ electrolytes.

Figure D5 1 M EC/DEC-LiTDI electrolytes stored for one week at (left) 25 °C, (middle) 60 °C, and (right) 100 °C.
Figure D6 DSC for two high melting crystalline LiPF₆ solvates with EC and γ-butyrolactone (GBL): (EC)₄LiPF₆ and (GBL)₄LiPF₆.

Figure D7 CVs (25 °C, 5.0 mV s⁻¹) vs. Al foil electrode of EC-LiTFSI electrolytes: (left) first cycle, (right) third cycle.
Figure D8 (a) Variable-temperature density of EC/DEC 3/7 (v/v)-LiTFSI electrolytes and (b) the corresponding link between the solvent-LiTFSI molar ratio and electrolyte molarity.
Appendix E: Concentrated Electrolytes

Figure E1 Ionic conductivity PY$_{15}$-EC-LiTFSI electrolytes.

Figure E2 Anodic stability vs. Pt electrode of PY$_{15}$-EC-LiTFSI electrolytes.
Figure E3 Anodic stability vs. Pt electrolyte of γ-butyrolactone (GBL), γ-valerolactone (GVL), and PC with LiTFSI, LiClO₄, and LiBF₄.
Appendix F: Competitive Solvation

Mixtures of 15-1 EC/XN-LiPF$_6$ (XN = AN, PN, BN) were studied using Raman spectroscopy to explore competitive solvation of Li$^+$ cations between two solvents. LiPF$_6$ was used to reduce competition for Li$^+$ cation coordination from the anion.

Figure F1 Solvation number of EC, XN, and the total solvation number of 15-1 EC/XN-LiPF$_6$ electrolytes (XN = AN, PN, BN). The Raman analysis used both of the 717-728 and 895-905 cm$^{-1}$ regions for EC, as well as the 2251-2277 cm$^{-1}$ region for the nitriles. For AN, the 918-930 cm$^{-1}$ region was used as well.