ABSTRACT

ZHOU, QIAN. Thermophysical and Transport Properties of Ionic Liquid–LiX Mixtures. (Under the direction of Wesley A. Henderson.)

Ionic liquids (ILs) have attracted strong interest due to their high chemical, thermal and electrochemical stability; wide liquid range; high ionic conductivity and low volatility. The research objective of this project has been to explore the thermophysical and transport properties of ILs and their mixtures with lithium salts (LiX). These mixtures may become the electrolyte materials essential for the success of safer, high-voltage next-generation lithium batteries targeted for plug-in hybrid electric vehicles (PHEVs) and/or electric vehicles (EVs). At present, there is only a limited amount of data available in the literature regarding the properties of IL-LiX electrolytes. Such information, however, is crucial for determining the electrolyte safety characteristics and useful operating temperature range, as well as for clarifying the composition-temperature relationship for other properties such as ionic conductivity. The thermal phase behavior, thermal stability and transport properties (viscosity, density and conductivity) are reported here for the neat ILs, as well as their mixtures with LiTFSI salts. Ternary (three component) electrolytes have also been examined. Further, aprotic solvent additives with varying structures and concentration have been added to IL-LiX mixtures. This study significantly advances the knowledge of how IL ion structure and the influence of additives determine critical electrolyte physical properties.
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Thermophysical and Transport Properties of Ionic Liquid-LiX Mixtures

by
Qian Zhou

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North Carolina State University
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DEDICATION

To my advisor

Prof. Wesley A. Henderson
BIOGRAPHY

After graduating from high school, Qian Zhou attended Harbin Institute of Technology for her undergraduate studies (2001). She graduated with a Bachelors of Science degree in Applied Chemistry in 2005 and then enrolled in a two year Master's degree Materials and Business Program at Queen Mary, University of London. She joined the Department of Chemical and Biomolecular Engineering at North Carolina State University as a graduate student in 2007.
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Chapter 1. Introduction

1.1 Electrical Energy Storage (EES)

The world's oil supply is a finite resource. World oil production has peaked.\(^1\) The easily accessible supplies of oil have been tapped and depleted. Future oil production therefore requires drilling in inhospitable environments such as deep in the Gulf of Mexico and on the North Slope of Alaska. Restrictions on gasoline supplies and growing demand have led to a gasoline price increases of over 200% over the last 8 years.\(^2\) Alternatively, unconventional sources of oil such as tar sands and oil shale may be used, but this is expensive, energy intensive, and environmentally destructive.\(^1\) In addition, the burning of fossil fuels has led to the rapid increase in greenhouse gases in the atmosphere. The resulting climate change has become a global concern as the possible transformation of the world's environment may be catastrophic for mankind.

Electrical energy storage is the key to the success of future alternative energy technologies. Such storage systems provide three basic services: supplying peak electricity demand by using electricity stored during periods of lower demand; balancing electricity supply and demand fluctuations (for example, from wind and/or solar power generation) over a period of seconds and minutes; and deferring expansions of electric grid capacity.\(^3\) There are several methods of storing electrical energy include the following:\(^3\)

- rechargeable batteries
- electrochemical capacitors
- pumped hydro
• compressed air
• thermal energy storage
• hydrogen
• flywheels
• superconducting magnetic energy storage (SMES)

The most efficient devices, which minimize losses, are batteries and electrochemical capacitors. This dissertation will mainly focus on electrolyte materials for Li-ion batteries, with an emphasis on ionic liquid (IL)-based electrolytes. Such materials may become the essential component for the success of safer, high-voltage next-generation Li-ion batteries targeted for plug-in hybrid electric vehicles (PHEVs) and/or electric vehicles (EVs).

1.1.1 Electrical Grid Load Leveling

The current U.S. electrical grid is a complex system. Features of this grid include:

• 30,000 transmission paths
• 14,000 transmission substations
• 3 major interconnections
• 3,170 traditional electric utilities
• operated in a decentralized manner
• demand is uncontrolled

Most generating stations were built in the 1960s and thus the grid now operates with very low efficiency. 70% of transmission lines and transformers are 30 years or older. 60% of
circuit breakers are 33 years or older. The electric power industry spends less on R&D than virtually any other industry in the world (Fig. 1-1).\textsuperscript{5} There have been 5 major blackouts in the last 40 years. The Northeast Blackout of 2003 was the second most widespread electrical blackout in history (the largest was the 1999 Southern Brazil blackout), which affected an estimated 10 million people in Ontario and 45 million people in eight U.S. states. In addition, the demand for electricity is uncontrolled. Electricity must be used as soon as it is generated. During the summer months, additional electricity must be generated for the grid to meet the increasing demand. Climate change and environmental concerns, new entrants and disruptive technologies, increasing desire by consumers for a role in energy management and conservation, growth in renewable generation and distributed resources, aging asset performance with increased expectations on reliability and increased pressure on operational efficiency and workforce productivity are the main driving forces to develop the Smart Grid.\textsuperscript{6} The Smart Grid, which moves renewable energy where needed and balances demand and supply, is thus urgently needed. There are five fundamental technologies required for the Smart Grid, including integrated communication, sensing and measuring technology, advanced components, advanced control methods, and improved interface and decision support.\textsuperscript{4} These systems can be treated as a single huge resource serving multiple applications that offer vast benefits, such as high temperature superconductivity (wires and cables), visualization and controls (real-time monitoring and smart meters), distributed energy resources, plug-in hybrids, vehicle-to-grid (V2G) technology, etc. (Fig. 1-2).\textsuperscript{4} The Smart Grid permits consumers to buy and store low cost energy during off-peak periods to
displace the much higher cost of generation during peak periods. Currently, approximately $120 million in annual funding from the U.S. Federal Government is used for the development of the Smart Grid.

Fig. 1-1. R&D as a % of revenue.⁵
1.1.2 Vehicle-to-Grid (V2G) Charging and Plug-in Hybrid Electric Vehicles (PHEVs)

Vehicle-to-Grid (V2G) charging and PHEVs are two key technologies for the Smart Grid. A PHEV is composed of an electric motor, battery and an internal combustion engine. The combustion engine uses gasoline now; it may use natural gas, ethanol or biofuels in the future. In addition, there is a plug to connect the battery to the electrical grid. Fig. 1-3 shows the concept for V2G technology with a PHEV in which electrical power can be supplied from the car to the grid during peak demand periods. Batteries could provide back-up energy to critical customers during a power outage. The PHEV battery systems will “talk” to the electrical grid. The owner can choose when the vehicle should recharge, for how long, at what utility rate and whether or not electricity should be supplied to the grid upon demand. The owner may choose to charge the vehicle during off-peak hours with lower electricity
rates. The ability to store large amounts of electricity (in millions of PHEVs) will be particularly beneficial for adding intermittent electrical generating sources such as solar and wind power. PHEV technology can provide fewer fill-ups, home recharging convenience and cleaner, quieter cars without performance changes. In addition, these vehicles will reduce greenhouse emissions/pollution, decrease the dependency on imported oil, and increase national security.\(^7\)

Fig. 1-3. V2G communications with a PHEV.

The U.S. department of Energy's (DOE's) goals are to develop PHEVs batteries in the near-term and batteries for EVs for the long term.\(^8,9\) Cost, calendar life and safety are major impediments currently for batteries for transportation applications. For the PHEVs, the
battery target range for driving is between 10-40 miles and over 5,000 deep-discharge cycles during the lifetime of the battery. The calendar life for these batteries should be more than 10 years. For EV batteries, the battery range target is 100+ miles with over 10,000+ deep-discharge cycles. Fig. 1-4 is the current HEV and EV battery status, which is far behind the DOE target.

Fig. 1-4. A battery technology chart for: (a) HEVs and (b) EVs. The 100% line equals the DOE target for HEVs and USABC target for EVs; the gray area and line represent technological achievements.
1.1.3 Battery Choices for PHEVs

The battery is a key component for PHEVs. Lead acid, NiMH and Li-ion batteries are all potential candidates for PHEV propulsion (Fig. 1-5). Lead acid batteries have the advantages of high power, low cost and safety. However, their low specific energy, poor low temperature performance and short battery life limit their use for PHEVs. NiMH batteries can be designed to have high specific energy and power, long cycle life and high reliability. Challenges for their use, however, include their high cost, high self-discharge rate and the need for hydrogen gas loss control. Li-ion batteries are therefore likely to be the dominate future transportation batteries in the near term due to their high voltage, high specific energy (> 150 Wh kg\(^{-1}\)), high energy density (> 400 Wh L\(^{-1}\)), low self-discharge rate (2-8% per month), long cycle life (> 1000 cycles), wide temperature operational range (-10 °C to 50 °C), and lack of memory effect from different charging/discharging procedures.\(^{11}\) Most battery companies, such as Johnson Controls/SAFT, A123 Systems, LG Chem, and EnerDel have focused their efforts on developing advanced Li-ion batteries for PHEV applications.
### 1.2 Lithium Batteries — Chemistry and Applications

#### 1.2.1 Lithium Batteries

Li metal is perhaps the optimal anode material for a battery as it combines a very high specific capacity (3.86 Ah g⁻¹, 7.23 Ah cm⁻³ due to its light weight) with a very favorable thermodynamic electrode potential enabling the formation of single-cell batteries (Fig. 1-6) with a potential in excess of 4 V.¹³,¹⁴ Due to its electropositive nature, however, Li metal rapidly reduces water forming hydrogen gas. In the 1950s, Li metal was found to be stable in nonaqueous solvents due to the formation of a passivation film on the Li surface.¹⁵ This crucial discovery resulted in extensive research in the use of Li as a battery electrode in the following years.¹⁶-¹⁹ Primary (non-rechargeable) cells which use Li metal as an anode are found to have numerous advantages as compared with other conventional batteries, such as a

<table>
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<th>Volume (Li)</th>
<th>Capacity (Energy kWh)</th>
<th>Discharge Power (kW)</th>
<th>Regen Power (kW)</th>
<th>Low Temp (°C)</th>
<th>Cycle Life (#)</th>
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<td></td>
<td></td>
</tr>
<tr>
<td>Li-Ion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1-5. Qualitative comparison of existing energy battery technologies for PHEVs (red: poor, yellow: fair and green: good).¹²
high voltage, high specific energy and energy density, a wide operating temperature range, good power density, flat voltage discharge characteristics, superior shelf life, etc.\textsuperscript{13,14}

Fig. 1-6. Schematic of the components of a Li metal battery.

For secondary (rechargeable) battery applications, however, a critical problem hindered the use of Li metal. A “dendritic” structure (needle-like Li crystals) was found to form on the Li anode when recharging the batteries (replating the Li metal).\textsuperscript{20,21} This isolates the Li metal in the dendrites from the Li metal substrate during the subsequent discharge period (Fig. 1-7).\textsuperscript{22} The nickname “dead lithium” was given to this phenomenon,\textsuperscript{23} because this electrochemically inactive electrode material results in a significant energy density loss. A further complication is the possibility of the dendrites piercing the separator/electrolyte, thus contacting the cathode to create an internal short-circuit which may lead to thermal runaway (rapid heating produced from an uncontrolled battery reaction) resulting in flaming of the battery or a battery explosion. SEM images of dendrites are shown in Fig. 1-8.\textsuperscript{24} Due to such
high risks, several producers of early commercial Li batteries recalled their batteries and research related to batteries which used Li metal as an anode was largely terminated in 1989.\textsuperscript{25}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1-7}
\caption{(a) Schematic description for the growth of dendrite crystals on a Li surface during recharging resulting in the formation of tree-like dendrites and (b) schematic description for the formation of isolated Li particles from Li dendrites.\textsuperscript{23}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1-8}
\caption{Typical SEM micrographs of single dendrites formed by Li deposition: (a) LiClO\textsubscript{4} 0.5M/propylene carbonate (PC) solution and (b) LiClO\textsubscript{4} 0.5M/\textgreek{b}-butyrolactone (BL) solution.\textsuperscript{24}}
\end{figure}
1.2.2 Lithium-Ion Batteries

Due to the serious problems with rechargeable Li metal batteries, an alternative battery design based upon Li chemistry was proposed which was alternatively named “rocking-chair”, “shuttle-cock” or “swing” batteries. The term “lithium-ion or Li-ion” was finally adopted, however, and this battery was introduced to the public in the late 1980s. In 1990, both Sony and Moli commercialized their first Li-ion battery which rapidly became popular for consumer electronics applications, such as cell phones, laptop computers, and personal data assistants, as well as military electronics, such as radios, mine detectors and thermal weapon sights. Large Li-ion batteries have also been increasingly used in space vehicles, satellites, and electric or hybrid electric vehicles.

The typical Li-ion battery consists of a carbonaceous (instead of Li metal) anode (typically graphite), a separator/electrolyte, a composite cathode containing a metal oxide active material (such as LiCoO$_2$, LiMn$_2$O$_4$, or LiNiO$_2$), and current collectors (Fig. 1-6 with the anode material replaced). No Li metal is ever present in the battery. Rather, Li$^+$ cations are transported back and forth through the electrolyte between the intercalation electrodes, thus avoiding the formation of dendrites during the recharging of the anode leading to a significant improvement in safety. Fig. 1-9 shows the charge/discharge reactions in a typical Li-ion battery. When the battery is being charged, the metal oxide cathode (positive material) is oxidized and the carbon anode (negative material) is reduced. The Li$^+$ cations are thus deintercalated from the cathode and intercalated into the anode during recharging.
Positive: \[ \text{LiMO}_2 \xrightarrow{\text{charge}} \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \xleftarrow{\text{discharge}} \]

Negative: \[ \text{C} + x\text{Li}^+ + xe^- \xrightarrow{\text{charge}} \text{Li}_x\text{C} \xleftarrow{\text{discharge}} \]

Overall: \[ \text{LiMO}_2 + \text{C} \xrightarrow{\text{charge}} \text{Li}_x\text{C} + \text{Li}_{1-x}\text{MO}_2 \xleftarrow{\text{discharge}} \]

Fig. 1-9. Electrode and cell reactions in a Li-ion cell.

The general merits and drawbacks of Li-ion batteries are summarized in Table 1-1. Such batteries have both high specific energy (~150 Wh kg\(^{-1}\)) and energy density (~400 Wh L\(^{-1}\)), as well as a low self-discharge rate (2-8% per month), long cycle life (more than 1000 cycles), a broad temperature range of operation (-10 °C to 50 °C) and a large electrochemical window, making the Li-ion battery suitable for numerous applications. The main disadvantage of these batteries, as for Li metal batteries, is their safety hazard. Under standard usage conditions, the batteries perform well. But mechanical short circuits or internal short circuits (as occurred for the Dell computer batteries recalled in 2006) may result in localized heating. If the Li-ion battery is heated above a certain temperature (usually above 130-150 °C), exothermic chemical reactions begin to occur between the electrodes and electrolyte, causing the temperature to rapidly increase, eventually resulting in thermal runaway.\(^{36-39}\) Heating above 50 °C tends to degrade the battery, but does not necessarily lead to thermal runaway. Several techniques to improve safety have been utilized including device safety features as well as inherently safer battery materials. Examples of the former include safety vents and positive temperature coefficient (PTC) elements.\(^{36}\) Example of safer
materials include shutdown separators,\textsuperscript{40} redox shuttle mechanisms and more oxidation-tolerant and less volatile/flammable electrolyte constituents.

### Table 1-1. Advantages and Disadvantages of Li-ion Batteries\textsuperscript{13}

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sealed cells; no maintenance required</td>
<td>Moderate initial cost</td>
</tr>
<tr>
<td>Long cycle life</td>
<td>Degrades at high temperature</td>
</tr>
<tr>
<td>Broad temperature range of operation</td>
<td>Need for protective circuitry</td>
</tr>
<tr>
<td>Long shelf life</td>
<td>Capacity loss or thermal runaway when overcharged</td>
</tr>
<tr>
<td>Rapid charge capability</td>
<td>Venting and possible thermal when crushed</td>
</tr>
<tr>
<td>High rate and high power discharge capability</td>
<td>Cylindrical designs typically offer lower power density than NiCd or NiMH</td>
</tr>
<tr>
<td>High coulombic and energy efficiency</td>
<td>High specific energy and energy density</td>
</tr>
<tr>
<td>High specific energy and energy density</td>
<td>No memory effect</td>
</tr>
</tbody>
</table>

1.3 Electrolyte Materials

Electrolytes in current use for Li-ion battery include four principal types: liquid, gel, polymer and ceramic electrolytes.\textsuperscript{13} Liquid electrolytes consist of a lithium salt and one or more organic solvents. The conductive portion of gel electrolytes are solutions of salts and solvents which are mixed with a high molecular weight polymer, but for polymer electrolytes the ionic conductivity originates from directly dissolving the salt in a high molecular weight
polymer such as poly(ethylene oxide) (the polymer serves as the solvent). Polymer electrolytes are therefore liquid-free materials, whereas a liquid can be separated from a gel electrolyte upon the application of pressure to the material. Both such electrolytes tend to form flexible membranes. Ceramic electrolytes, in contrast, are rigid inorganic solid-state materials. No matter which type of electrolyte is used, however, the function of the electrolyte is the same – it serves as the medium to transfer Li\(^+\) cations (but not electrons) between the cell electrodes.\(^{22}\)

1.3.1 Current State-of-the-Art Liquid Electrolytes

The state-of-the-art liquid electrolytes used in most commercial Li-ion batteries consists of LiPF\(_6\) dissolved in a mixture of ethylene carbonate (EC) and a linear carbonate (i.e., diethyl carbonate (DEC)).\(^{22}\) Such electrolytes have a high ionic conductivity (>10\(^{-3}\) S cm\(^{-1}\)) and relatively high lithium ion transference number (~0.35) (the fraction of the total current due to Li\(^+\) cations).\(^{13}\) The LiPF\(_6\) and EC react with the graphite anode surface to form a stable interface (a solid electrolyte interface or SEI) which prevents further electrolyte decomposition, but permits rapid Li\(^+\) cation transport. In addition, LiPF\(_6\) reacts with Al at high potentials to form a stable, insoluble layer. This is vital since Al is used almost universally as the cathode current collector in Li-ion batteries. The stable layer prevents further corrosion of the current collector. All of these properties are essential for a Li-ion battery to have excellent performance and a reasonable longevity.
These electrolyte compositions are not without their drawbacks. LiPF₆ is hygroscopic and produces hydrofluoric acid (HF) when exposed to water, thus requiring a very strict working and storage environment. Further, LiPF₆ has a relatively low thermal stability⁴¹,⁴² and the reaction of LiPF₆ with the aprotic solvents at elevated temperature produces fluorinated toxic compounds.⁴³ In addition, the EC solvent is believed to lead to a rapid increase in the viscosity at subambient temperatures resulting in an effective operating temperature lower limit of about -10 °C. The upper operating temperature limit is about 50 °C due to the degradation of the SEI layer and reactivity of the LiPF₆.

1.3.2 Lithium Salts

Other lithium salts (LiX), such as LiBF₄, LiClO₄, LiAsF₆, LiCF₃SO₂ and LiN(SO₂CF₃)₂ (or LiTFSI), have been examined as possible replacements for LiPF₆ in Li-ion battery applications. Each of these suffers from problems which have precluded their use in rechargeable Li-ion batteries thus far. The TFSI⁻ anion (as HTFSI) was first reported by Foropoulos and DesMarteau in 1984.⁴⁴ In the early 1990s, 3M commercialized LiTFSI.²² The negative charge on the TFSI⁻ anion is extensively delocalized due to resonance (Fig. 1-10) and the strong electron-withdrawing triflic groups. The melting point (Tₘ) of LiTFSI is 236 °C, but the salt has been reported to not decompose until 360 °C.⁴⁵ Thermogravimetric studies of anhydrous LiTFSI indicate that the onset point for mass loss (1 wt%) is around 327 °C. Approximately 7 wt% of the original mass of LiTFSI is left after heated under an N₂ atmosphere to 600 °C (Fig. 1-11). An isothermal TGA study (not shown) indicates that LiTFSI looses approximately 1 wt% of its mass after heating at 250 °C for 900 min. The
main disadvantage associated with LiTFSI is its corrosion of Al. LiTFSI reacts with Al at high potentials to form Al(TFSI)$_3$, which is soluble in the aprotic solvents.$^{46}$ This solubility results in a fresh Al surface constantly exposed for continued corrosion reactions (in contrast with LiPF$_6$). Several methods have been suggested to solve this problem,$^{46-48}$ but this has not yet led to the use of LiTFSI in commercial Li-ion batteries.

![Resonance structures of the TFSI$^-$ anion.](image)

**Fig. 1-10.** Resonance structures of the TFSI$^-$ anion.$^{22}$
1.3.3 Solvent Selection

Commercial liquid electrolytes utilize two (or more) solvents. Important properties of the electrolyte solvents include:\(^1\)

- they must be aprotic (i.e., have no reactive protons);
- they must have low reactivity with graphite or other anode materials (or form a protective coating on the graphite surface to prevent further reaction) and the cathode;
- they must be capable of forming an electrolyte with a high ionic conductivity;
- they should form electrolyte solutions which are liquid over a broad temperature range;
- they should have favorable physical characteristics, such as low vapor pressure, high stability, nontoxicity, and low flammability;
• they must be able to dissolve sufficient amounts of the lithium salt (typically a 1 M concentration) and therefore contain polar functional groups such as one or more carbonyl, nitrile, sulfonyle, and/or ether groups.22

Table 1-2 shows the structures of some solvents of potential use for battery electrolytes. Carbonate solvents, such as EC, propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and DEC, are currently the most widely used. Battery performance is enhanced by mixing two or more solvents together.22 Single solvent-LiX mixtures tend not to have the properties necessary to meet the needs for battery applications. For example, EC has a high permittivity (and thus solvates Li⁺ cations well), but the solvent is a solid at room temperature ($T_m = 36 ^\circ C$).22 Thus, a linear carbonate such as DEC with a lower permittivity, but also with a low viscosity, is added to form a concentrated electrolyte solution with the LiX with low viscosity and high conductivity. Table 1-3 shows the physical property of select solvents. Most aprotic organic solvents, however, have a relatively low boiling point ($T_b$) and are thus volatile as well as flammable.
Table 1-2. Structure of aprotic solvents of potential interest for Li-ion batteries.\textsuperscript{49}
Table 1-3. Physical property data of select solvents.\textsuperscript{49}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>l.p./m.p. (°C)</th>
<th>b.p. (°C)</th>
<th>flash pt. temp. (°C)</th>
<th>density\textsuperscript{a} (g/mL)</th>
<th>viscosity\textsuperscript{a} (cP)</th>
<th>vap. pres.\textsuperscript{a} (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile</td>
<td>-45</td>
<td>82</td>
<td>2</td>
<td>524</td>
<td>0.786</td>
<td>0.34</td>
</tr>
<tr>
<td>propionitrile</td>
<td>-93</td>
<td>97</td>
<td>6</td>
<td>0.722</td>
<td></td>
<td></td>
</tr>
<tr>
<td>butyronitrile</td>
<td>112</td>
<td>117</td>
<td>18</td>
<td>0.79</td>
<td></td>
<td>23</td>
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<tr>
<td>valeronitrile</td>
<td>96</td>
<td>140</td>
<td>40</td>
<td>520</td>
<td>0.795</td>
<td>5.3</td>
</tr>
<tr>
<td>hexanenitrile</td>
<td>-80</td>
<td>165</td>
<td>43</td>
<td>0.809</td>
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<td></td>
</tr>
<tr>
<td>malononitrile</td>
<td>30</td>
<td>220</td>
<td>86</td>
<td>1.049</td>
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<td></td>
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<td>succinonitrile</td>
<td>53</td>
<td>266</td>
<td>113</td>
<td>0.985</td>
<td></td>
<td>&lt; 2</td>
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<td>glutaronitrile</td>
<td>-29</td>
<td>286</td>
<td>112</td>
<td>0.995</td>
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<td>adiponitrile</td>
<td>4</td>
<td>295</td>
<td>163</td>
<td>550</td>
<td>0.962</td>
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<tr>
<td>pinelonitrile</td>
<td>&gt;176</td>
<td>112</td>
<td>176</td>
<td>0.947</td>
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<tr>
<td>3-methoxypropionitrile</td>
<td>-62</td>
<td>165</td>
<td>66</td>
<td>390</td>
<td>0.939</td>
<td>1.72</td>
</tr>
<tr>
<td>3-(dimethylamino)-propionitrile</td>
<td>-43</td>
<td>171</td>
<td>63</td>
<td>0.87</td>
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<td></td>
</tr>
<tr>
<td>methyl cyanoacetate</td>
<td>-13</td>
<td>87</td>
<td>113</td>
<td>505</td>
<td>1.127</td>
<td>0.2</td>
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<td>ethyl cyanoacetate</td>
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<td>210</td>
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<td>2-methylglutaronitrile</td>
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<td>270</td>
<td>115</td>
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<td>isobutryonitrile</td>
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<td>8</td>
<td>250</td>
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<td>THF</td>
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<td>65</td>
<td>-14</td>
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<td>2-MeTHF</td>
<td>-137</td>
<td>80</td>
<td>-11</td>
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<td>1,3-DL</td>
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<td>4-Me-1,3-DL</td>
<td>-125</td>
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<td>-2</td>
<td>0.983</td>
<td>0.60</td>
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</tr>
<tr>
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<td>-83</td>
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<td>41</td>
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<tr>
<td>2-isobutyl-4-Me-1,3-DL</td>
<td>-152</td>
<td>112</td>
<td>41</td>
<td>0.895</td>
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<td></td>
</tr>
<tr>
<td>2-Pr-4-Me-1,3-DL</td>
<td>137</td>
<td>32</td>
<td>90</td>
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<tr>
<td>monoglyme (DME)</td>
<td>-69</td>
<td>85</td>
<td>0</td>
<td>200</td>
<td>0.868</td>
<td>1.1</td>
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<td>diglyme</td>
<td>-64</td>
<td>162</td>
<td>57</td>
<td>190</td>
<td>0.945</td>
<td>2.0</td>
</tr>
<tr>
<td>triglyme</td>
<td>-45</td>
<td>216</td>
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<td>195</td>
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</tr>
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<td>tetraglyme</td>
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<td>275</td>
<td>141</td>
<td>266</td>
<td>1.01</td>
<td>&lt; 0.01</td>
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<td>diethoxyethane</td>
<td>-74</td>
<td>121</td>
<td>20</td>
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</tr>
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<td>butyl diglyme</td>
<td>-60</td>
<td>256</td>
<td>118</td>
<td>0.88</td>
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<td></td>
</tr>
<tr>
<td>progllyme (dipropylene glycol dimethyl ether)</td>
<td>-80</td>
<td>&gt;280</td>
<td>149</td>
<td>215</td>
<td>1.04</td>
<td>12</td>
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<tr>
<td>diethylene glycol tertbutyl ethyl ether</td>
<td>195-205</td>
<td>0.892</td>
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<tr>
<td>N-methylpyrrolidone</td>
<td>-24</td>
<td>202</td>
<td>91</td>
<td>270</td>
<td>1.028</td>
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<tr>
<td>3-methyl-2-oxazolidinone</td>
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<td>270</td>
<td>110</td>
<td>1.17</td>
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<td>ethylene carbonate</td>
<td>35</td>
<td>244</td>
<td>143</td>
<td>1.321</td>
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<td>propylene carbonate</td>
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<td>132</td>
<td>455</td>
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<td>isobutyl methyl ketone</td>
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<td>57</td>
<td>449</td>
<td>0.801</td>
<td>15</td>
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<tr>
<td>sec-butyl acetate</td>
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</tr>
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<td>n-butyl acetate</td>
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<td>126</td>
<td>74</td>
<td>0.88</td>
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<td></td>
</tr>
<tr>
<td>dimethyl carbonate</td>
<td>5</td>
<td>91</td>
<td>18</td>
<td>1.063</td>
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<td></td>
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<td>126</td>
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<td>0.969</td>
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<td></td>
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<td>ethyl acetate</td>
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<td>77</td>
<td>77</td>
<td>0.902</td>
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<td></td>
</tr>
<tr>
<td>methyl butyrate</td>
<td>-84</td>
<td>102</td>
<td>102</td>
<td>0.898</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethyl butyrate</td>
<td>-93</td>
<td>120</td>
<td>120</td>
<td>0.878</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} At 20-25°C.
1.4 Ionic Liquids

1.4.1 Overview

ILs are salts or mixtures of salts (composed solely of ions) with a low melting temperature – often below room temperature. ILs usually consist of asymmetric organic cations and inorganic anions. The most commonly used cations for ILs are imidazolium or aliphatic quaternary ammonium cations with various anions, such as halides (Cl⁻, Br⁻, I⁻), NO₃⁻, CH₃CO₂⁻, BF₄⁻, CF₃SO₃⁻, PF₆⁻ and TFSI⁻. Table 1-4 shows some examples of typical IL cations.

ILs are considered to be “designer solvents” due to the ability to modify the physical and chemical properties of the salts by the selection of different cations, anions and alkyl side chain substituents (R groups). Many ILs are liquids over a very broad temperature range (-80 °C to 250 °C or higher) with low or negligible vapor pressure; moreover, ILs may have low flammability, high thermal stability and high ionic conductivity. ILs are therefore being extensively explored as replacements for conventional organic solvents in electrochemical, catalytical, synthetic and engineering processes due to their inherent safety, which significantly reduces the emissions of traditional volatile organic compounds (VOCs) resulting in atmosphere pollution.
Table 1-4. Examples of IL cation structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="1,3-dialkylimidazolium" alt="Image" title="IM10R⁺" /></td>
<td>1,3-dialkylimidazolium (IM₁₀R⁺)</td>
</tr>
<tr>
<td><img src="1,2,3-trialkylimidazolium" alt="Image" title="IM11R⁺" /></td>
<td>1,2,3-trialkylimidazolium (IM₁₁R⁺)</td>
</tr>
<tr>
<td><img src="tetraalkylammonium" alt="Image" /></td>
<td>Tetraalkylammonium</td>
</tr>
<tr>
<td><img src="N,N-dialkylpyrrolidium" alt="Image" title="PY₁R⁺" /></td>
<td>N,N-dialkylpyrrolidium (PY₁R⁺)</td>
</tr>
<tr>
<td><img src="N,N-dialkylpiperidinium" alt="Image" title="PI₁R⁺" /></td>
<td>N,N-dialkylpiperidinium (PI₁R⁺)</td>
</tr>
<tr>
<td><img src="N,N-dialkylmorpholinium" alt="Image" title="MO₁R⁺" /></td>
<td>N,N-dialkylmorpholinium (MO₁R⁺)</td>
</tr>
</tbody>
</table>

1.4.2 Applications

There are three major areas for the application for ILs, including electrochemical, analytical and engineering applications.⁵⁰ All of these applications are based on the favorable properties of these salts including solvation power, negligible volatility, non-flammability, wide electrochemical window, etc. For example, BASF uses ILs for an acid scavenging process, the so-called “BASIL™” process.⁵⁸ Air Products uses ILs as a liquid support for the storage of highly toxic gases because they offer good dissolution performance for a variety of molecular species in the liquid phase without imparting solvent impurities.⁵⁹ ILs may potentially also be used as Li-ion battery electrolyte materials which displace conventional molecular solvents.
1.4.3 Future Li Batteries and Ionic Liquids

The unique characteristics of ILs make them potentially excellent candidates for battery electrolyte applications. IL-LiX electrolytes have a relatively high ionic conductivity. The very low to negligible vapor pressure of ILs at ambient pressure permits the use of polymeric pouches for batteries rather than the metal cans now used which saves on both manufacturing cost and battery weight. ILs can be easily dried under vacuum at elevated temperature, while conventional electrolyte solvents must be distilled and/or dried over molecular sieves, and then stored under rigorously controlled conditions to avoid moisture (water is unstable at the high voltages of Li-ion batteries). But the strongest motivation for utilizing ILs in battery electrolytes stems from the combination of their exceptional electrochemical stability and low volatility/flammability.

Research on materials for Li-ion batteries has undergone explosive growth in the last decade. Current challenges for advanced battery development revolve around finding alternative electrode materials such as Sn- or Si-based alloy anodes and new metal oxide cathode materials, especially those suitable for high voltage applications (>4.3 V). The desire to increase the battery voltage (from the current 3.6 V with LiCoO₂) stems from the need to increase the battery energy density for plug-in hybrid electric vehicle (PHEV) applications. Greater energy density will reduce the size and cost of the batteries which is crucial for reducing the overall cost of PHEVs. Unfortunately, the current state-of-the-art dual carbonate solvent with LiPF₆ electrolytes which work well for small commercial Li-ion batteries are unsuitable for these new high-voltage electrode materials. Further, the safety concerns
mentioned above associated with the current state-of-the-art electrolytes largely preclude their use in the very large battery packs required for PHEVs where thermal management is much more problematic. Alternative electrolyte materials must therefore be found for PHEV Li-ion batteries, yet the range of materials suitable for such high-voltage electrolytes is quite limited. Compounding this search is the need to also improve battery safety by reducing or eliminating the use of volatile/flammable organic solvents. Thus, a tremendous amount of attention has been focused in recent years on IL-based electrolytes.

1.5 Dissertation Overview

The research objective has been to explore the thermophysical and transport properties of ILs and their mixtures with lithium salts (LiX). These mixtures may become the electrolyte materials essential for the success of safer, high-voltage next-generation lithium batteries targeted for PHEVs and/or EVs. At present, there is only a limited amount of data available in the literature regarding the thermal stability, phase behavior and transport properties of IL-LiX electrolytes. Such information, however, is crucial for determining the electrolyte safety characteristics and useful operating temperature range, as well as for clarifying the composition-temperature relationship for other properties such as ionic conductivity.

The thermal phase behavior, thermal stability and other properties (viscosity, density and conductivity) are reported in this dissertation for the neat ILs containing 1-alkyl-3-methylimidazolium (IM$_{10R}^+$, R = 1, 2 and 4 for methyl, ethyl and butyl, respectively) or N-alkyl-N-methylpyrrolidinium (PY$_{1R}^+$, R = 3-5) cations with TFSI$^-$ or FSI$^-$ ([N(SO$_2$F)$_2$]$^-$).
anions, as well as their mixtures with LiTFSI or LiFSI salts. Ternary (three component) electrolytes (1-x) PY14TFSI-(x) PY13FSI-0.3 M LiX mixtures (X = TFSI− and PF6−) have also been examined. The coordination of the Li+ cations has been studied (using crystal structures and spectroscopy), as it plays an essential role in the ion conductivity and charge-discharge reactivity in the battery. Aprotic solvent additives with varying structures and concentration have also been added to IL-LiX mixtures and the physical properties fully characterized. The immediate impact of this research will result in improved IL electrolyte performance for electrochemical energy storage devices, but the broader impact will be more significant as this may enable the safe use of high energy battery packs for PHEV and related applications.

**References**


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Chapter 2. Experimental Procedures

2.1 Materials

1-Methylpyrrolidine (C\textsubscript{5}H\textsubscript{11}N, 97%), 1-methylimidazole (C\textsubscript{4}H\textsubscript{6}N\textsubscript{2}, 99%), 1,8-diazabicyclo[5.4.0]undec-7-ene (C\textsubscript{9}H\textsubscript{16}N\textsubscript{2}) and alkyliodides were purchased from Aldrich and used as-received. LiTFSI and lithium bis(fluorosulfonyl)imide (LiFSI) were purchased from 3M Company (St. Paul, MN) and Dai-ichi Kogyo, Seiyaku Co., Ltd (Japan), respectively. The salts were dried at 120°C under vacuum for 12 hrs. before use.

2.2 Sample Preparation

The experimental procedure utilized for the synthesis of all of the ILs was similar to that used for the N-methyl-N-alkylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PY\textsubscript{1R}TFSI) salts: 1-methylpyrrolidine was combined with a stoichiometric amount of alkyliodide (i.e., 1-iodopropane for PY\textsubscript{13}TFSI) in ethyl acetate to synthesize the PY\textsubscript{1R}I salt precursor (Fig. 2-1). This reaction is highly exothermic and can be very fast for shorter alkyl chain lengths.\textsuperscript{1} Thus, ethyl acetate was used as a solvent to absorb the heat produced during the reaction and dilute the solution, thereby slowing the reaction rate. An ice bath was also used as needed during this step to further slow the reaction to prevent or reduce side-reactions and the formation of contaminants. Care was taken to minimize exposure of the reagents to light and oxygen due to the reactivity of the alkyliodides. The resulting white or yellow crystalline PY\textsubscript{1R}I salts were washed with fresh ethyl acetate 5 times (using a separation funnel) to remove unreacted reagents and contaminants until pure white salts were obtained.
The second step of the IL synthesis involved a metathesis reaction in which the I\(^-\) anion was exchanged with the TFSI\(^-\) anion. The iodide salts and LiTFSI are soluble in water, but the ILs are not. Thus, if these salts are mixed in water, the ILs will separate from the solution as a new liquid phase leaving LiI in the aqueous phase (Fig. 2-1). Therefore, the purified PY\(_{1R}\)I salts were dissolved in deionized (DI) water resulting in clear, colorless solutions. Stoichiometric amounts of LiTFSI dissolved in DI water were added and the mixtures were stirred to ensure complete mixing. The resulting aqueous phase with dissolved LiI was then removed and the remaining ILs were washed 8 times with fresh DI water to purity the PY\(_{1R}\)TFSI salts. The salts were then heated while stirring on a hot plate for several hrs. at 120-140 °C to remove most of the residual water. To remove other impurities, activated carbon was added and the mixtures were stirred on a hot plate at 140 °C for 48 hrs. The mixtures were then cooled to room temperature, ethyl acetate was added to form dilute solutions and these were then filtered through an activated alumina column to remove the activated carbon (and impurities). The ethyl acetate was then removed by a rotary evaporator. Finally, the ILs were dried at 120 °C overnight and the temperature was then increased to 140 °C for another 8 hrs. (to remove the residual ethyl acetate and water). After purification and drying, the PY\(_{1R}\)TFSI (R = 3-5) salts were clear, colorless liquids at room temperature. The materials were stored in hermetically sealed bottles in a N\(_2\) glovebox (water concentration < 0.5 ppm).
IL-LiX and IL-LiX-solvent mixtures were prepared in the glove box by combining the appropriate amounts of the IL and LiX salts (and solvent for the ternary mixtures) in hermetically-sealed glass vials, and then heated on a hot plate while stirring to form homogeneous mixtures. The resulting IL-LiX and IL-LiX-solvent mixtures were clear, colorless and odorless with a moisture content below 10 ppm (tested by Karl-Fischer titration). The vials with the mixtures were stored in the glovebox.

### 2.3 Instruments and Techniques

$^1$H NMR spectra were used to identify the structure of the ILs and verify their purity. All NMR spectra were measured at room temperature on a Varian Gemini 200 MHz Spectrometer. Deuterated acetonitrile (CD$_3$CN, 99.8 atom% D, contains 1% v/v TMS) was used as the solvent to dissolve the samples (the ILs are insoluble in CDCl$_3$). The $^1$H NMR spectrum of pure CD$_3$CN has a peak at 1.94 ppm due to impurities such as CHD$_2$CN, while a small amount of water is detected at 2.13 ppm. $^2$ Elemental analysis, collected by Atlantic Microlab, Inc., was also used to identify the purity of the ILs. Both $^1$H NMR spectra and
elemental analysis data indicated that the ILs were of electrochemical grade purity. The water concentration of the ILs was determined using a Mettler Toledo Karl Fischer Coulometer DL39. The ILs were stored in the glove box prior to Karl Fischer analysis and then transferred into the instrument quickly. The water concentration of all of the samples was below 20 ppm.

DSC measurements were performed using either a TA Instruments Q1000 or Q2000 differential scanning calorimeter with liquid N₂ cooling. The instruments were calibrated with cyclohexane (solid-solid phase transition at -87.06 °C, melt transition at 6.54 °C) and indium (melt transition at 156.60 °C). Hermetically sealed Al pans were prepared in the glove box. Typically, samples pans were slowly cooled (5 °C min⁻¹) to -150 °C and then heated (5 °C min⁻¹) to 100 °C or higher (determined by the composition of the sample). It was sometimes necessary to cycle the samples in the DSC at various subambient temperatures in order to fully crystallize the samples. Some of the sample pans were also stored in a freezer prior to analysis and then transferred into the instrument quickly (to aid in crystallization for slowly nucleating samples).

TGA measurements were performed using a TA Instruments Q5000 thermogravimetric analyzer. The thermal stability was initially analyzed by heating from room temperature to 600 °C (variable-temperature measurements) under either an air or N₂ atmosphere (>99.99%, water concentration 2-5 ppm). Selected samples were then analyzed isothermally at different temperatures for 900 min. under an N₂ atmosphere to determine the long term stability of the materials at a given temperature.
Viscosity measurements were conducted using an Anton Paar SVM 3000 Stabinger viscometer. The tests were performed from 15-100 °C with a 1 °C min\(^{-1}\) heating rate. Measurements were taken in 5 °C steps. At least 2.6 ml sample sizes were needed for the measurements and great care was taken to not expose the samples to air (and thus water) prior to and during the measurements. Ethyl acetate and N\(_2\) gas (>99.99%, water concentration 2-5 ppm) were used to clean the instrument after the measurements and the water concentration of the samples was tested before and after the measurements.

The ionic conductivity was determined through impedance spectroscopy, using two electrode cells with platinized carbon electrodes. The impedance was measured while heating from -40 °C to 100 °C. Experiments were performed from 1 MHz to 20 Hz with a 10 mV AC perturbation and no DC bias. The impedance data, which were separated out into the real and imaginary components, were collected with standard electrochemical impedance hardware (Solartron 1260A impedance analyzer and 1287A potentiostat/galvanostat). The data were graphed in the form of Nyquist plots (imaginary vs. real impedance) and the IL resistance was taken as the point where the data crossed the real axis at high frequency.\(^3\) Cell constants were determined for each cell using aqueous KCl standard solutions at 25 °C.

Raman spectra were collected from -150 °C to 100 °C with a Jobin-Yvon LabRAM HR800 spectrometer. Spectra were excited with the 632.8 nm line of a HeNe internal laser. The measurement time was 10 seconds with five accumulations. For the measurements, the samples were placed in a cavity on a stainless steel plate in a hermetically sealed Linkam
LTS350 heating/cooling stage in the glovebox. The stage was then transferred to the spectrometer and Raman spectra were measured over the frequency range 100-1800 cm\(^{-1}\).

X-ray structural determination was done by Dr. Paul Boyle in the Department of Chemistry at North Carolina State University. Crystals were mounted on a nylon loop with a small amount of Paratone N oil. X-ray measurements were made on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer. Data collection was carried out using Mo K\(\alpha\) radiation. The unit cell dimensions were determined from a symmetry constrained fit of the reflections. The data collection strategy was a number of \(\omega\) and \(\phi\) scans. The frame integration was performed using SAINT.\(^4\) The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.\(^5\) The structures were solved by direct methods using the XM program.\(^6\) Most non-hydrogen atoms were obtained from the initial solution. The remaining non-hydrogen atomic positions were derived from subsequent difference Fourier maps. 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.\(^7\) Crystallographic figures were drawn using Mercury 2.2 software.
References

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Chapter 3. Ionic Liquids (ILs)

3.1 Thermophysical Properties

The main force between the cations and anions in ILs is the Coulombic attraction $E_c$:

$$E_c = \frac{MZ^+Z^-}{4\pi\epsilon_0r}$$

where $M$ is Coulomb's constant (the value of $M$ depends upon the medium around the charged objects), $Z^+$ and $Z^-$ are the ion charges, $\epsilon_0 \approx 8.85418782 \times 10^{-12}$ F m$^{-1}$ and $r$ is the cation-anion distance. The large, unsymmetrical ions typical in ILs, however, lead to weak interactions between the ions. In addition, the charge can be distributed over ions through resonance (charge delocalization), further reducing the overall charge density. The salt's lattice energy may thus be significantly reduced which can lead to a low melting point.

The liquid range of ILs can be very wide ($\sim 300$ °C) as many ILs decompose at very high temperature. For the TFSI$^-$-based ILs with N-alkyl-N-methylpyrrolidinium cations (i.e., PY$_{1R}$TFSI), only a 2-3 wt% mass loss occurs after heating the ILs at 250 °C for 900 min. (Fig. 3-1); TFSI$^-$-based ILs with 1-alkyl-3-methylimidazolium cations (i.e., IM$_{10R}$TFSI), however, are less thermally stable (Fig. 3-2). The straight lines for the mass loss suggest that there is no nucleation process occurring for thermal degradation. The focus on ILs with the TFSI$^-$ anion is due to the fact that a wide variety of cations form low melting salts with this anion (i.e., the $T_m$ of the PY$_{14}$X salts are PY$_{14}$TFSI: -18 or -7 °C (see below), PY$_{14}$PF$_6$: 70 °C and PY$_{14}$BF$_4$: 150 °C).$^{1-3}$
Fig. 3-1. Isothermal TGA traces of PY$_{18}$TFSI at 250 °C (N$_2$ atmosphere).
Fig. 3-2. Isothermal TGA traces of (a) IM$_{101}$TFSI, (b) IM$_{102}$TFSI and (c) IM$_{104}$TFSI (N$_2$ atmosphere). The temperature for each measurement is indicated in the figure.
In Chapter 1, it was noted that LiTFSI in aprotic solvents has been found to corrode the Al current collector used in Li batteries. There is, however, preliminary evidence which strongly suggests that Al corrosion in IL-LiTFSI mixtures is inhibited. Table 3-1 shows the thermal transitions and crystalline phases of TFSI⁻ based ILs. The thermophysical properties of ILs are diverse: a number of the ILs (with IM₁₁₁⁺, IM₁₁₂⁺, PY₁₁⁺, PY₁₂⁺, PY₁₄⁺, PY₁₅⁺, PY₁₆⁺, PI₁₁⁺, PI₁₂⁺, PI₁₆⁺, MO₁₁⁺, MO₁₂⁺, MO₁₃⁺, MO₁₄⁺) undergo solid-solid phase transitions; other salts (with IM₁₀₃⁺, IM₁₁₄⁺, PI₁₄⁺, PI₁₅⁺) cannot be crystallized; yet other salts (with IM₁₀₂⁺, PY₁₃⁺, PY₁₄⁺) are polymorphic (different crystalline phases form depending upon the salt's thermal history). The $T_g$ temperature also varies between the related classes of salts: PY₁₁⁺ (-80 to -87 °C), PI₁₁⁺ (-73 to -75 °C), and MO₁₁⁺ (-58 °C) suggesting a link between the cation head group and transport properties/mobility of the ions.

Recently, a new set of ILs based upon the bis(fluorosulfonyl)imide (N(SO₂F)₂⁻ or FSI⁻) anion has attracted significant interest. A variety of synthesis techniques have been reported for the FSI⁻ anion and the crystal structure is known for LiFSI, KFSI and CsFSI. The PY₁₃FSI and PY₁₄FSI ILs have a low $T_m$, low viscosity, high conductivity and high electrochemical stability making them desirable materials for many electrochemical technologies. The thermal stability of such ILs was analyzed using both variable-temperature and isothermal TGA measurements. Fig. 3-3 indicates that the initial mass loss for both ILs is independent of the atmosphere (air or N₂). The onset point for mass loss (1 wt%) is about 219-231 °C for PY₁₃FSI and 189-198 °C for PY₁₄FSI. Approximately 15-20 wt% of the original IL remains after decomposition when heated under an N₂ atmosphere. If,
instead, air is present, a second thermal process begins near 400 °C and finishes near 600 °C leading to the complete volatilization of the thermal degradation products (Fig. 3-3). The isothermal TGA measurements indicate that neither IL looses mass on storage at 100 °C for 24 hrs. (Fig. 3-4). Both ILs, however, loose approximately 9-10 wt% of their mass on heating at 150 or 175 °C.

**Table 3-1.** Thermal transitions and crystalline phases of ILs.\(^{26}\)

<table>
<thead>
<tr>
<th>salt cation</th>
<th>phase transitions (°C)</th>
<th>crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_a )</td>
<td>( T_{IV,IV} )</td>
</tr>
<tr>
<td>IM(_{101})</td>
<td>-83</td>
<td>25</td>
</tr>
<tr>
<td>IM(_{102})</td>
<td>-92</td>
<td>-16</td>
</tr>
<tr>
<td>IM(_{103})</td>
<td>-89</td>
<td>NA</td>
</tr>
<tr>
<td>IM(_{104})</td>
<td>-87</td>
<td>-1</td>
</tr>
<tr>
<td>IM(_{111})</td>
<td>-19</td>
<td>103</td>
</tr>
<tr>
<td>IM(_{112})</td>
<td>-17</td>
<td>25</td>
</tr>
<tr>
<td>IM(_{113})</td>
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<td>-77</td>
<td>NA(?)</td>
</tr>
<tr>
<td>PY(_{11})</td>
<td>-37</td>
<td>21</td>
</tr>
<tr>
<td>PY(_{12})</td>
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<tr>
<td>PY(_{13})</td>
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<td>MO(_{14})</td>
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Note that PY\textsubscript{14}FSI did not loose any significant mass on heating at 125 °C, whereas PY\textsubscript{13}FSI did, but only after a long delay. This suggests that a nucleation process occurs for the decomposition. The data further suggest that the same degradation mechanism occurs for both ILs up to 175 °C resulting in a thermally stable degradation product. Heating to higher temperature, however, leads to greater mass loss. Heating both ILs at 250 °C results in an initial rapid mass loss down to about 18 wt% after which limited mass loss occurs in agreement with the variable-temperature data (for an N\textsubscript{2} atmosphere). Note that the thermal degradation behavior of the FSI\textsuperscript{-} salts (Fig. 3-4) differs markedly from that of the TFSI\textsuperscript{-} salts (Figs. 3-1 and 3-2) for which the thermal degradation was linear with time at a given temperature.
Fig. 3-3. Variable-temperature TGA heating traces (5 °C min⁻¹) of PY₁₄FSI in an (a) N₂ and (b) air atmosphere.
Fig. 3-4. Isothermal TGA traces of PY\textsubscript{18}FSI: (a) R = 3 and (b) R = 4 (N\textsubscript{2} atmosphere). The temperature for each measurement is indicated in the figure.

DSC heating and cooling traces for PY\textsubscript{13}FSI and PY\textsubscript{14}FSI are shown in Fig. 3-5. Although both salts significantly supercool (hysteresis between the \(T_m\) and crystallization temperature), crystallization does occur readily on cooling. In fact, it was not possible to quench the salts into an amorphous phase using cooling rates up to 40 °C min\(^{-1}\). In all cases the salts crystallized. PY\textsubscript{13}FSI undergoes several exothermic transitions on cooling (Fig. 3-5). On heating, multiple endothermic transitions were observed including a low energy solid-solid phase transition (phase III-II) with a peak at -83 °C, a solid-solid phase transition at -19
°C (phase II-I) and a \( T_m \) at -9 °C (phase I-L). The identity of the broad endothermic transition with a peak temperature of -50 °C and subsequent exothermic transition near -45 °C is not clear. These latter transitions were reproducible in some scans and completely absent (flat baseline) in others. One possibility is that the peak present at -50 °C corresponds to the crystallization of another (kinetic) phase which is dependent upon the thermal history of the salt. After melting this phase (at -50 °C), the resulting liquid then crystallizes (the exothermic transition) into the thermodynamically-stable phase II structure. Thermal decomposition occurs on heating the PY\(_{13}\)FSI above 150 °C. The melting point of PY\(_{13}\)FSI has been previously reported to be -18 °C.\(^7\) The method used to determine this \( T_m \) was not provided. It is possible that the onset of the solid-solid phase transition was mistakenly identified as the onset of melting. PY\(_{14}\)FSI also undergoes several endothermic transitions on heating (Fig. 3-11). Sharp endothermic transitions at -45 °C, -28 °C and -18 °C correspond to a phase III-II, phase II-I and phase I-L (\( T_m \)) transitions, respectively. The identity of the small peak near -34 °C is not clear. This peak is not found to be reproducible in repeated heating/cooling traces. It may be that this peak is associated with a kinetically (but not thermodynamically) stable phase as suggested above for PY\(_{13}\)FSI.
Fig. 3-5. DSC cooling and heating traces (5 °C min⁻¹) of (a) PY₁₃FSI and (b) PY₁₄FSI.
3.2 Transport Properties

ILs, in contrast with polymers and colloidal suspensions, are Newtonian fluids as their viscosity is constant regardless of the strain rate.\textsuperscript{27} The viscosity of ILs, in general, is much higher (between 10 cP to 500 cP at room temperature) than most common molecular solvent.\textsuperscript{27} For example, IM\textsubscript{10}FSI is reported to have a low $T_m$ of -13 °C, a viscosity of 18-25 cP and a high conductivity of 15.4-16.5 mS cm\textsuperscript{-1} (at 25 °C) (a very low viscosity and high conductivity, respectively, for ILs).\textsuperscript{7,8} The viscosity of ILs is mainly governed by the electrostatic attraction between the cations and anions, the tendency to form hydrogen bonds, the strength of Van der Waals interactions and the degrees of freedom within the ions.\textsuperscript{28-39} The general order of increasing viscosity with respect to the anion is\textsuperscript{27}:

$$\text{TFSI}^- < \text{BF}_4^- < \text{CF}_3\text{CO}_2^- < \text{CF}_3\text{SO}_3^- < \text{F}_2\text{C}_2\text{SO}_3^- < \text{F}_7\text{C}_5\text{SO}_3^- < \text{F}_7\text{C}_3\text{CO}_2^- < \text{H}_3\text{COSO}_3^- < \text{H}_3\text{CCO}_2^- < \text{F}_9\text{C}_4\text{SO}_3^-$$

The viscosity is also strongly affected by small changes in the cation structure. The general order of increasing viscosity with respect to the cation is:

$$\text{IM}_{10R}^+ < \text{PY}_{1R}^+ < \text{PI}_{1R}^+ < \text{MO}_{1R}^+$$

Larger cation size generally leads to higher viscosity. In addition, it has generally been found that the viscosity of ILs increase with increasing alkyl side chain length possibly due to the increase of Van der Waals interactions.\textsuperscript{40} The density of ILs linearly decreases with increasing temperature and increases with decreasing alkyl side chain length, as expected.

The conductivity of an electrolyte is a measure of the available charge carriers and their mobility.\textsuperscript{27} The conductivity of ILs is typically lower than that of inorganic salts dissolved in
organic solvents. The large size of the cations of the ILs results in a low mobility, thus limiting the conductivity. The anion size, however, appears to have an indirect relationship with the conductivity. For example, ILs with smaller anions such as $[\text{CH}_3\text{CO}_2]^-$ tend to have a lower conductivity than ILs with larger anions such as $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$. But, in general, the conductivity of ILs at room temperature is above 1 mS cm$^{-1}$.

The conductivity and viscosity relationship for ILs is often described by the Walden rule:

$$\Lambda \eta = \text{constant (temperature dependence)}$$

where $\Lambda$ is the molar conductivity and $\eta$ is the viscosity. Molar conductivity, instead of the absolute conductivity $k$, normalizes the effects of molar concentration and density on the conductivity. Fig. 3-6 is a Walden plot for a range of ILs.
Fig. 3-6. Walden plot for a range of ILs. The straight reference line with the slope of 1 is plotted from the data of a 0.01M KCl solution.\textsuperscript{41}

The ILs near the KCl reference line (area between label (A) and (B) in Fig. 3-6), such as $[\text{C}_2\text{mpyr}][\text{dca}]$ ($\text{C}_2\text{mpyr}$ is $\text{PY}_{12}^+$; DCA is $\text{N(CN)}_2^-$), suggesting that these ILs are composed of individual mobile ions (ionization is almost 100%). Another group (area between label (B) and (C) in Fig. 3-6), such as $[\text{P}_{6,6,6,14}][\text{NTf}_2]$ ($\text{NTf}_2$ is TFSI\textsuperscript{-}), fall well below the KCl reference line due to incomplete ionization (separation of ions). MacFarlane \textit{et al.} did an extensive investigation of this group and concluded that the IL had only 10% of the ionic conductivity that would be exhibited if the IL behaved according to the 0.01 M KCl line.\textsuperscript{41} ILs below label (C), such as $[\text{P}_{6,6,6,14}][\text{Cyc}]$, had an ionicity as low as 4%.\textsuperscript{41} The Walden plot of Fig. 3-6 is not an accurate, but rather a qualitative, tool for assessing the ionicity of ILs.\textsuperscript{41}
Many researchers are looking for more precise ways to plot the conductivity and viscosity data. MacFarlane's group suggested ion size is an important factor and proposed an adjusted Walden plot in which the molar conductivity is plotted vs. \( \log (\eta^{-1}(1/r^+ + 1/r^-)) \), where \( r^+ \) and \( r^- \) are the “effective” cation and anion sizes (Fig. 3-7). 

![Adjusted Walden plot for a range of ILs.](image)

**Fig. 3-7.** Adjusted Walden plot for a range of ILs. 

Ion diffusion coefficients and ion transport numbers are often used to evaluate the transport properties of electrolytes. Ion diffusion coefficients are measured by either electrochemical or NMR methods. The results from both methods are roughly equivalent. The ion diffusion coefficient increases when the conductivity increases. The ion transport number indicates the fraction of the total conductivity carrier by a specific charged species. The Moving Boundary method and the Hittorf method are used to measure cation and anion transport numbers, respectively. The transport numbers of several non-haloaluminate ILs,
however, cannot be measured from the above methods. The NMR method therefore provides the transport numbers for such ILs.

3.3 Anion Conformations (TFSI/FSI)

The TFSI anion is well known to be flexible with two low energy conformations of \( C_1 \) and \( C_2 \) symmetry, in which the –CF\(_3\) groups are either on the same side or opposite side of the S–N–S plane, respectively (Fig. 3-8). Fujii et al. used Raman spectroscopy and DFT calculations to study TFSI and noted that the enthalpy difference of these two conformers is 3.5 KJ mol\(^{-1}\).\(^{50}\) A Raman band at 398 cm\(^{-1}\) is attributed to the \( C_2 \) conformer; while a 407 cm\(^{-1}\) band is attributed to the \( C_1 \) conformer. The \( C_2 \) conformer is more stable than the \( C_1 \) conformer. They also studied IM\(_{102}\)TFSI and concluded that both conformers are present in equilibrium, but the \( C_2 \) conformer is more favorable than the \( C_1 \) conformer.\(^{50}\)

![Fig. 3-8. Anion conformations for the TFSI anion. (a) \( C_1 \) and (b) \( C_2 \) conformers (two views of each shown) (N (blue), C (gray), S (gold), O (red), F (green)).\(^{26}\) 52]
The IM$_{102}$TFSI salt has polymorphic thermal phase behavior with at least two different crystalline phases able to form depending upon the thermal history of the salt. This is demonstrated in Fig. 3-9 using three different DSC experiments to crystallize IM$_{102}$TFSI: initially (Fig. 3-9a), the sample was cooled slowly (5 °C min$^{-1}$) from room temperature to -150 °C, and then heated to 100 °C, with the $T_m$ at -17 °C. The sample was then (Fig. 3-9b) quickly cooled (20 °C min$^{-1}$) to -150 °C, heated and annealed at -30 °C for 5 min., cooled to -150 °C and heated to 100 °C. This procedure resulted in a single peak for the $T_m$ at -10 °C instead. The same sample was then (Fig. 3-9c) rapidly quenched to -150 °C (resulting in partial crystallization) and heated to 100 °C. In this case, the partially amorphous sample began to crystallize near -65 °C. Two melting peaks at -16 and -10 °C were then noted. This can be explained by the formation of two different crystalline phases for IM$_{102}$TFSI - one is a thermodynamically favorable IM$_{102}$TFSI (IA) phase formed during slow cooling with a $T_m$ at -16 °C, while the second is a kinetically favorable IM$_{102}$TFSI (IB) phase with a $T_m$ at -10 °C. The crystal structures for both crystalline phases are known.$^{26,51}$ In each structure, the IM$_{102}^{+}$ cations have the same conformation, but the TFSI$^{-}$ anions have different conformations with either $C_1$ or $C_2$ symmetry (Fig. 3-8).$^{51-56}$
Fig. 3-9. DSC heating traces (5 °C min⁻¹) of IM₁₀₂TFSI. (a) the sample was cooled slowly (5 °C min⁻¹) from room temperature to -150 °C, and then heated to 100 °C, (b) the sample was quickly cooled (20 °C min⁻¹) to -150 °C, heated and annealed at -30 °C for 5 min., cooled to -150 °C and heated to 100 °C, and (c) the same sample was rapidly quenched to -150 °C and heated to 100 °C.

Fig. 3-10. C₂-C₂ anion disordering for the TFSI⁻ anion (four views shown) (N (blue), C (gray), S (gold), O (red), F (green)).²⁶
In addition to the flexible conformations noted above for TFSI⁻, this anion is able to adopt a $C_2$-$C_2$ conformational equilibrium in a variety of crystalline salts such as Et₄NTFSI (Fig. 3-10).\textsuperscript{57}

The FSI⁻ anion also adopts $C_1$ and $C_2$ conformers, where the two F atoms are located either on the same or opposite side of the S-N-S plane, respectively (Fig. 3-11).\textsuperscript{58} Raman bands at 293, 328, and 360 cm\textsuperscript{-1} are attributed to the $C_2$ conformer, while bands at 305, 320, and 353 cm\textsuperscript{-1} are attributed to the $C_1$ conformer. The enthalpy difference between these two conformers is 4.5 KJ mol\textsuperscript{-1}. Both conformers are present in equilibrium at room temperature in the IM₁₀₂FSI IL.\textsuperscript{59}

![Diagram of FSI⁻ anion conformations](image)

Fig. 3-11. Two main conformations of the FSI⁻ anion and their relation with the two FSNS dihedral angles defining the conformational energy landscape of the ion: (a) $C_2$ “trans” conformer and (b) $C_1$ “cis” conformer. The red bars indicate the position of the oxygen atoms that lie close to the S-N-S plane of the ion.\textsuperscript{58}

### 3.4 Ionic Packing and Ionic Disordering

While several differences are noted in the solid-phase phase transitions due to the variations in the cation ring size and shape of PY₁₁TFSI and PI₁₁TFSI, the crystalline phases
of these two ILs at low temperature are essentially isostructural. In addition, they have a very similar $T_m$. Similar ion structure and/or a similar $T_m$, however, does not necessarily mean that the ions have the same ionic packing at low temperature. Functional groups may influence the ionic packing. For example, the ionic packing of PI$_{11}$TFSI and MO$_{11}$TFSI are significant different despite the fact that the MO$_{11}^+$ and PI$_{11}^+$ cations are essentially the same size and shape. This is due to the O atom in the MO$_{11}^+$ cation with its two electron lone-pairs which result in repulsive interactions with neighboring ether oxygens and anions, which are absent for the CH$_2$ group in the PI$_{11}^+$ cation. In addition, variation in cation alkyl chain length has a great influence upon the ionic packing. With increasing alkyl chain length, crystallization (nucleation) is generally more sluggish. For certain salts, crystallization is not possible (or is at least extremely difficult). For example, upon slow cooling (5 °C min$^{-1}$), crystallization occurs readily for DBU$_R$TFSI ($R = 1$ and 2) (DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene), while no crystallization occurs for $R \geq 3$ (Fig. 3-12) (to crystallize the $R = 3$ and 5 salts, they must be cooled below their $T_g$, then warmed and annealed below their $T_m$ — the $R = 4$ salt could not be crystallized).
The TFSI$^{-}$ $C_2$-$C_2$ conformational disorder frequently results in a number of solid-solid phase transitions with the ordered crystalline solid increasingly resembling the disordered liquid state. For example, for DBU$_1$TFSI at -173 °C, only a small amount of disorder is found in the crystal structure (Fig. 3-13). At -30 °C (just before the II-I solid-solid phase transition), however, one of the two cations becomes disordered over two sites (Fig. 3-13). Just after this transition, the X-ray data indicate that the cations are completely disordered in the solid structure, while the anions adopt the $C_2$-$C_2$ conformational disordered state, but remain essentially fixed in position.
3.5 Rotational Isomerism of Tetraethylammonium Cations

Fig. 3-14 is the DSC heating trace of Et$_4$NTFSI. The Et$_4$NTFSI salt was cooled (5 °C min$^{-1}$) to -100 °C, heated (5 °C min$^{-1}$) to -20 °C, held at -20 °C for 5 min. in order to fully crystallize the salt (as phase III), then cooled to -150 °C and finally heated (5 °C min$^{-1}$) to 200 °C. The neat Et$_4$NTFSI salt undergoes a dramatic phase transition at approximately 3 °C. In the low temperature phase (phase III, < 3 °C), all of the Et$_4$N$^+$ cations have an all-trans (tt.tt) or Greek cross conformation (Fig. 3-15) in which the ions are ordered. After
the first solid-solid phase transition, however, only 20-25% of the Et₄N⁺ cations have this conformation with the other cations adopting a *trans-gauche* (tg.tg) or Nordic cross conformation (Fig. 3-15). The TFSI⁻ anions remain uncoordinated (due to steric shielding of the positive charge on the cations), but also undergo structural changes associated with the first solid-solid phase transition. This phase transition is clearly evident in the powder XRD patterns between 0-5 °C (Fig. 3-16). A second, low energy solid-solid phase transition at 54 °C (Fig. 3-14) results in a slight increase in the fraction of Et₄N⁺ cations with (tt.tt) conformations, but no significant variation in the TFSI⁻ anions. The powder XRD patterns indicate that only a few weak reflections disappear between 50-55 °C (Fig. 3-16) in agreement with the low energetics of the transition just noted. No further transitions occur up to the solid-liquid melt transition (*Tₘ*) at 105 °C (Fig. 3-16). Surprisingly, this does not result in any large variations in either the Et₄N⁺ cation or TFSI⁻ anion conformations. The high temperature plastic-crystalline solid phase just prior to melting thus has ionic disorder resembling that of the liquid melt state. Raman characterization indicates that the anions in the ordered phase (phase III) adopt the *transoid* (*C₂*) conformation. In the liquid phase, however, over 70% of anions adopt the *C₁* conformation.
Fig. 3-14. DSC heating trace of Et₄NTFSI. The peak temperatures (°C) are indicated for each peak.

Fig. 3-15. Projections of the Et₄N⁺ conformers along their pseudo $C_4$ axis: (a) $(tt.tt)$ and (b) $(tg.tg)$.

\(^{61}\)
Fig. 3-16. Variable-temperature powder XRD data for Et₄NTFSI. The temperature (°C) is noted on the right.²⁶

The Et₄N⁺ cation (tt.tt) form is found in the 672-673 cm⁻¹ Raman range and the (tg.tg) form in the 661-663 cm⁻¹ range (Fig. 3-17(a)).⁶¹ The full-width-at-half-maximum (FWHM) of the (tt.tt) form remains relatively constant at 7.7±0.4 cm⁻¹, whereas the FWHM of the (tg.tg) component increases steadily from 6 to 10 cm⁻¹ (Fig. 3-17(b)).⁶¹ There is a big change in both position and FWHM from phase III to phase II, but these parameters change continuously from phase II to phase I and phase I to the liquid phase.
Fig. 3-17. Temperature dependence of the (a) position and (b) FWHM for the $v_5$ (NC$_4$) line of the (tt.tt) (∗) and (tg.tg) (+) conformers of the cation in Et$_4$NTFSI.$^{61}$
Fig. 3-18. Populations of \((tt.tt)\) conformers for the \(\text{Et}_4\text{N}^+\) cation (black circles) and \(\text{C}_2\) conformers for the \(\text{TFSI}^-\) anion (open circles) as a function of temperature.\(^{61}\)

Fig. 3-18 shows the populations of \((tt.tt)\) conformers for the \(\text{Et}_4\text{N}^+\) cation and \(\text{C}_2\) conformers for the \(\text{TFSI}^-\) anion as a function of temperature.\(^{61}\) The \((tt.tt)\) and \(\text{C}_2\) conformers are stable in the ordered phase (below the phase III to II transition), then decrease dramatically during the phase transition from III to II. Upon further heating, however, the \((tt.tt)\) conformers start to increase in the solid phase II. The \((tt.tt)\) and \((tg.tg)\) conformers reach an equilibrium in the solid phase I and liquid phase; while the \(\text{C}_1\) conformers dominant the liquid phase.\(^{61}\)

The plot of the ionic conductivity of \(\text{Et}_4\text{NTFSI}\) vs. temperature is shown in Fig. 3-19. The neat \(\text{Et}_4\text{NTFSI}\) salt has a low conductivity \((\sim 10^{-8} \text{ S cm}^{-1})\) at low temperatures \((tt.tt)\) and \(\text{C}_2\)
conformers). The conductivity begins to gradually rise, however, after the first solid-solid phase transition at 3 °C. This phase transition corresponds to a large structural change in the crystal with some of the ions becoming disordered.\textsuperscript{57,61} The conductivity of the neat Et$_4$NTFSI salt reaches $10^{-4}$ S cm$^{-1}$ at 95 °C (10 °C before melting) due to the progressive ion disordering which occurs with increasing temperature, as noted above.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{arrhenius_plot}
\caption{Arrhenius plot of the ionic conductivity of Et$_4$NTFSI.\textsuperscript{26}}
\end{figure}

References


Chapter 4. Ionic Liquid-Lithium Salt Electrolytes

4.1 Phase Behavior, Ionic Conductivity and Crystalline Phases of TFSI-Based Ionic Liquids with LiTFSI Mixtures

4.1.1 (1-x) IM_{10R}TFSI–(x) LiTFSI Mixtures

This study focuses on mixtures of LiTFSI with ILs consisting of 1-alkyl-3-methylimidazolium cations and the TFSI⁻ anion (IM_{10R}TFSI with R = 1, 2 or 4 for methyl, ethyl and butyl, respectively):

These ILs were not selected with the intent of optimizing practical battery electrolytes as the dialkylimidazolium cations are well-known to have an unsuitably low electrochemical stability (both cathodic and anodic).¹,² These ILs and the analogous N-alkyl-N-methylpyrrolidinium (PY_{1R}TFSI) ILs, however, are the most widely studied ILs for which the greatest amount of information regarding their properties is available.³⁻¹⁶ It is, therefore, quite informative to compare the phase behavior of IM_{10R}TFSI-LiTFSI mixtures with that of PY_{1R}TFSI-LiTFSI mixtures.³ Note that while aprotic solvent-LiTFSI electrolytes are known to corrode Al current collectors,¹⁷⁻²¹ there is evidence to suggest that such corrosion by the TFSI⁻ anion in ILs is greatly reduced or inhibited.²²⁻²⁴
DSC heating traces for (1-\(x\)) IM\(_{101}\)TFSI-(\(x\)) LiTFSI mixtures are shown in Fig. 4-1a. Adding LiTFSI initially slightly lowers the \(T_m\) of the samples from that of the neat IM\(_{101}\)TFSI salt (\(T_m = 24\) °C). The data indicate that new mixed-salt crystalline phases exist for \(x = 0.50\) and what appears to be a 0.75 composition (corresponding to 1/1 and 1/3 IM\(_{101}\)TFSI/LiTFSI phases, respectively). 1/1 crystalline phases have been previously reported for IM\(_{102}\)CF\(_3\)SO\(_3\)/LiCF\(_3\)SO\(_3\), Et\(_3\)NHCF\(_3\)SO\(_3\)/LiCF\(_3\)SO\(_3\) and IM\(_{102}\)AlCl\(_4\)/NaAlCl\(_4\) mixtures.\(^{25-27}\) In all of these structures, each anion is coordinated to two Li\(^+\) cations. Each Li\(^+\) cation, in turn, is coordinated by four different anions (4-fold coordination) resulting in polymeric [Li\(^+\)...(anion)\(_2\)]\(_n\) chains. For electrostatic neutrality, the organic cations (either IM\(_{102}\)+ or Et\(_3\)NH\(^+\) cations) surround these ionic chains and have a single hydrogen bond to the anions.

The crystal structure of the 1/1 (\(x = 0.50\)) IM\(_{101}\)TFSI/LiTFSI phase (Table 4-1 and Fig. 4-2) bears some resemblance to these structures. Polymeric [Li\(^+\)...(TFSI)\(_2\)]\(_n\) chains are present with each anion coordinated to two Li\(^+\) cations. The difference is that the Li\(^+\) cations now have 6-fold coordination (Fig. 4-3). The IM\(_{101}\)+ cations are located in rows between these ionic polymer chains. The hydrogen bound to the carbon at position C2 of the cation is coordinated through a hydrogen bond to one anion oxygen, while the cation C4 and C5 hydrogens are both hydrogen bonded to a single anion oxygen. One of these hydrogens may also have an additional hydrogen bond to an oxygen from a third anion (Fig. 4-4). Note that oxygen atoms from addition anions are also closely positioned over the positively charged ring nitrogen atoms (not shown in Fig. 4-4) adding further stability to this manner of ion packing. It is notable that all of the anions have the \(C_1\) conformation,\(^{28-32}\) which is also found.
for the anion conformations in crystalline IM$_{101}$TFSI.\textsuperscript{31} In the 1/1 phase with LiTFSI, this conformation is favored as it enables the 6-fold coordination of the anions to the Li$^+$ cations (and IM$_{101}$\textsuperscript{+} hydrogen bonding), whereas in the neat IM$_{101}$TFSI structure, this conformation enables a favorable lattice of hydrogen bonds to form between the cations and anions.
Fig. 4-1. DSC heating traces (5 °C min⁻¹) of (1-x) IM₁₀R TFSI-(x) LiTFSI mixtures: (a) R = 1, (b) R = 2 and (c) R = 4 ($T_m$ and $T_g$ temperatures noted).
### Table 4-1. Crystal and Refinement Data

<table>
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<th>Structure</th>
<th>[IM\textsubscript{101}TFSI\textsubscript{1}][LiTFSI\textsubscript{1}]</th>
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</tr>
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<td>(\Delta\rho)\textsubscript{min,max} (e Å\textsuperscript{-3})</td>
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</tr>
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\[ a \quad R_1 = \frac{\sum ||F_o|| - ||F_c||}{\sum ||F_o||} 
\quad wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \frac{1}{1/2} 
\quad GOF = \frac{\sum w(F_o^2 - F_c^2)^2}{(n-p)1/2} \]
**Fig. 4-2.** Ion packing in the 1/1 ($x = 0.50$) IM$_{101}$TFSI/LiTFSI crystalline phase viewed along the (a) $b$- and (b) $a$-axis (Li (purple), O (red), S (gold), C (gray), F (green)).

**Fig. 4-3.** Ion coordination in the polymeric [Li$^+$(TFSI)$^2$]$_n$ chains in the 1/1 ($x = 0.50$) IM$_{101}$TFSI/LiTFSI crystalline phase (Li (purple), O (red), S (gold), C (gray), F (green)).
The $T_m$ of IM102TFSI is either -17 or -10 °C – the IL is polymorphic with two different crystalline phases able to form depending upon the salt's thermal history (Fig. 3-9). Neither of these phases undergoes a solid-solid phase transition prior to melting. DSC heating traces for \((1-x)\) IM102TFSI-(x) LiTFSI mixtures (Fig. 4-1b) indicate that as the LiTFSI mole fraction \((x)\) increases, the crystallization process becomes more difficult, and no crystalline phase was observed for \(0.25 \leq x \leq 0.50\) mixtures. The $T_g$ of the amorphous samples tends to increase with increasing fraction of LiTFSI, as expected. For samples with a high concentration \((x > 0.50)\), however, a new crystalline peak for a 1/2 \((x = 0.67)\) IM102TFSI/LiTFSI phase is observed. The crystal structure of this phase has been previously reported. The ions of this 1/2 phase form two dimensional planar sheets stacked together. The Li$^+$ cations have 5-fold coordination by anion oxygens (from either three or four different TFSI$^-$ anions). Different anions are coordinated differently, but each anion has either three or all four of the oxygens atoms coordinated to Li$^+$ cations, thereby creating the
planar sheets. The sheets (composed of Li\(^+\) cations and TFSI\(^-\) anions) result in the formation of cavities in which reside two uncoordinated IM\(_{102}^+\) cations.

For the (1-\(x\)) IM\(_{104}\)TFSI-(\(x\)) LiTFSI mixtures, it was not possible to crystallize the samples when \(x \geq 0.15\) using either slower cooling/heating rates (1 °C min\(^{-1}\)) or by annealing the mixtures for extended periods of time at low temperature, despite extensive efforts to do so. Only a fraction of the neat IM\(_{104}\)TFSI phase could be crystallized for dilute samples with \(x < 0.15\) (Fig. 4-1c). Thus, no crystalline phase forms which contains the LiTFSI salt. The \(T_g\) of the \(x = 0.67\) mixture is remarkably low for a sample composed of two-thirds lithium salt.

A comparison of the phase behavior of the IM\(_{10R}\)TFSI and PY\(_{1R}\)TFSI salt mixtures with LiTFSI shows both similarities and differences in behavior. For example, there is no evidence that the IM\(_{10R}\)TFSI salts form a 2/1 (\(x = 0.33\)) IL/LiTFSI phase which is a predominant feature of the PY\(_{1R}\)TFSI mixtures\(^3\). The reason for this is unknown at present. There are no structural models (crystal structures) known for such a composition to aid in clarifying this. The IM\(_{102}\)TFSI salt does, however, form the 1/2 phase (\(x = 0.67\)) which is also a common feature of the PY\(_{1R}\)TFSI mixtures\(^3\). The known structure for this phase shows that cavities form in the Li\(^+\)...TFSI\(^-\) anion planar lattice that hold two organic cations which remain essentially uncoordinated. It is easy to envision that the cations can be readily replaced with other cations of similar size to create the same phase with a different IL. Note that although the 1/2 phases for IM\(_{102}\)TFSI and PY\(_{15}\)TFSI resemble each other, there are also notable differences in the Li\(^+\)...anion coordination (see below). Interestingly, the IM\(_{104}\)TFSI salt does not form this phase. One possible explanation is that the IM\(_{104}^+\) cations are too large.
to fit within the cavities, but this does not explain why the IM$_{101}$TFSI salt also does not form this phase unless it is because the IM$_{101}^+$ cations are too small and leave too much void space in the structure. An alternative, and more likely, explanation, however, is that the coordination in the high LiTFSI composition phase (assumed to be $x = 0.75$) is more energetically favorable than that of the 1/2 phase. The crystal structures are low energy structures formed by optimizing all of the interactions (packing of ions, electrostatics, hydrogen bonding, etc.), not just the Li$^+$...TFSI$^-$ coordination.

In addition, the 1/1 phase forms readily for the IM$_{101}$TFSI salt, but the IM$_{102}$TFSI and IM$_{104}$TFSI salts remain amorphous instead of forming this phase. There is some evidence that the PY$_{10}$TFSI-LiTFSI mixtures also form a 1/1 phase, although this appears to be a metastable phase for some of the ILs. Once again, this variance in behavior may be an ion size/shape effect which prevents the ions from packing together in the optimal manner to form the 'preferred' structures dictated by optimized Li$^+$...TFSI$^-$ coordination and other energetic considerations. The amorphous phase may then be viewed as a 'frustrated' phase in which many of the ions in the frozen glass or supercooled liquid have the same or similar coordination as found in the crystalline phases of similar composition, but the entire ensemble of the crystal structures cannot come together due to the poor fit of the organic cations within such a structure.

It has been suggested that the addition of LiTFSI to either IM$_{102}$TFSI or IM$_{104}$TFSI results in Li$^+$ cations with an anion solvation number of approximately two. A spectroscopic analysis with DFT calculations of possible [Li(TFSI)$_2$] complexes was
conducted in which the conformation of the anion was varied. These complexes were also compared with a \([\text{Li(TFSI)}_4]^3\)- complex. The conclusion was the \(\text{Li}^+\) cations exist in these ILs as \([\text{Li(TFSI)}_2]^+\) complexes in which the anions predominantly have an equal mix of \(C_1\) and \(C_2\) conformations. This type of complex, however, requires that the TFSI\(^-\) anions have two of their oxygen atoms coordinated to the same \(\text{Li}^+\) cation. If one closely scrutinizes the coordination in the 1/2 IM\(_{102}\)TFSI/LiTFSI phase, such coordination is found for anions with both \(C_1\) and \(C_2\) symmetry, although the anions are also coordinated to other \(\text{Li}^+\) cations (as required for such a concentrated composition). The 1/1 \((x = 0.50)\) IM\(_{101}\)TFSI/LiTFSI phase also has anions with two oxygen atoms coordinating the same \(\text{Li}^+\) cation. A molecular dynamics (MD) simulation of \((1-x)\) PY\(_{18}\)TFSI-(\(x\)) LiTFSI \((x = 0.25, R = 1\) and 3) at 227 °C, however, reported that the probability that a single TFSI\(^-\) anion contributes a second oxygen atom to the coordination shell of the same \(\text{Li}^+\) cation was < 5%. The MD simulation work also emphasized the formation of \(\text{Li}^+...O=S=O...\text{Li}^+\) coordination which is present for all of the anions in the known crystalline 1/1 and 1/2 phases (Fig. 4-3). This form of coordination facilitates the creation of polymeric aggregates. Such a liquid structure might reasonably occur with short aggregated ionic chains with anions having both \(C_1\) and \(C_2\) conformations in which all of the anions have two oxygens coordinated to two \(\text{Li}^+\) cations.

Given that the liquid phase is being considered, a variety of forms of coordination may actually coexist. At this time, it is not possible to fully confirm the liquid phase \(\text{Li}^+\) cation coordination, but the interactions between the cations and anions is what dictates the ionic conductivity (mechanisms for \(\text{Li}^+\) cation transport) and other physical properties for these
electrolytes and therefore is of considerable interest. It must be emphasized that the electrolyte components of an ideal battery electrolyte should be unable to crystallize within the battery operating temperature range as the capture of the Li\(^+\) cations in a solid IL-LiX phase generally drastically reduces the conductivity of the electroactive Li\(^+\) cations and thus the ability of the battery to operate.\(^{34}\) With this in mind, the phase information in Figs. 4-1b and 4-1c is intriguing as concentrated electrolyte mixtures may be prepared in which crystallization is completely inhibited. If an explanation for why this occurs is forthcoming, then such information may aid in the optimization of future choices of ILs for battery electrolytes.

4.1.2 (1-\(x\)) PY\(_{15}\)TFSI–(\(x\)) LiTFSI Mixtures

ILs with PY\(_{1R}\)\(^+\) cations and TFSI\(^-\) anions, in particular, have been demonstrated as promising electrolytes for Li batteries.\(^{34-38}\) Despite numerous studies,\(^{3,39-44}\) the phase behavior and electrochemical properties of (1-\(x\)) PY\(_{1R}\)TFSI-(\(x\)) LiTFSI mixtures are not yet fully understood. Binary mixtures of LiTFSI with PY\(_{15}\)TFSI:

have therefore been examined here to add additional insight into the molecular interactions which govern the properties of such mixed-salt electrolytes.
DSC heating traces for the (1-x) PY$_{15}$TFSI-(x) LiTFSI mixtures are shown in Fig. 4-5. The neat PY$_{15}$TFSI salt has relatively simple phase behavior with a single melting endotherm noted at 10 °C. That is the reason why this salt was selected for study, as the neat PY$_{13}$TFSI and PY$_{14}$TFSI salts have more complicated phase behavior due to the formation of polymorphic crystalline phases. Upon the addition of small amounts of LiTFSI, the samples melt at a slightly lower temperature than for the neat IL due to the formation of a eutectic phase. The data indicate that both x = 0.33 (T$_m$ = 28 °C, 2/1 IL/LiX) and 0.67 (T$_m$ = 76 °C, 1/2 IL/LiX) phases form (in common with similar mixtures with PY$_{1R}$TFSI (R = 2-4) ILs). The mixtures also show interesting phase behavior near x = 0.50 as a 1/1 IL/LiX metastable, polymorphic phase (T$_m$ = 22 °C) may also form. An alternative explanation for the observed peak (T$_m$ = 22 °C) may be due to the formation of a eutectic between the x = 0.33 and 0.67 phases. This peak is not found to be consistently reproducible, however, in repeated heating/cooling traces as its formation appears to be strongly dependent upon the sample thermal history (crystallization method) with a peak at 25-26 °C also found (not shown in Fig. 4-5).
The ionic conductivity of the mixtures is shown in Fig. 4-6. The rapid rise in conductivity of the neat IL ($x = 0$) is due to the solid crystalline phase melting into a liquid phase (the neat IL $T_m$ is 10 °C – see Fig. 4-5). Upon addition of relatively low mole fractions of LiTFSI, the onset of melting and the rapid increase in the conductivity occurs at a slightly lower temperature than for the neat IL, in agreement with the lower $T_m$ noted in Fig. 4-5 due to the formation of a eutectic phase. For $x = 0.25$, however, there is a two step increase in the
conductivity. From Fig. 4-5, this is attributed to the melting first of the eutectic phase and then the 2/1 IL/LiX (x = 0.33) phase. A dramatic difference exists in the onset of the conductivity increase between the x = 0.25 and 0.33 compositions. This is because the x = 0.33 composition corresponds to the pure 2/1 IL/LiX phase. Samples with a higher LiTFSI concentration also show a conductivity increase at the same temperature due to the melting of this phase. The x = 0.50 sample shows a two step increase due also to the melting of the 1/2 IL/LiX (x = 0.67) phase.

At higher temperature (in the melt for all of the samples), the conductivity tends to decrease sharply with increasing LiTFSI concentration for the mixtures with x > 0.10 (Fig. 4-6). Steric hindrance shields the positive charge of the PY$_{15}^+$ cations from direct interaction with the neighboring TFSI$^-$ anions, but this is not the case with the Li$^+$ cations. Each Li$^+$ cation is coordinated by multiple TFSI$^-$ anions since no solvent is present. Thus, aggregates and perhaps polymeric ionic chains form which increase the viscosity and lower the conductivity as these interactions increase with increasing Li$^+$ cation concentration.
Fig. 4-6. Variable-temperature ionic conductivity of \((1-x)\) PY\(_{15}\)TFSI-(x) LiTFSI mixtures.

The crystal structure of the 1/2 \((x = 0.67)\) phase was determined from single crystal XRD. The crystallographic data is reported in Table 4-2 and a schematic illustration of the structure is shown in Fig. 4-7. As noted previously, the TFSI\(^{-}\) anion is known to be flexible with two low energy conformation with \(C_1\) (cis) and \(C_2\) (trans) symmetry with extensive charge delocalization over the \(-\text{SO}_2\text{N}--\text{SO}_2\)- backbone (Fig. 3-8).\(^{30,32,45}\) Both of these conformations are found in the reported crystal structure, as well as intermediate conformations with a dihedral angle of about 70°. The Li\(^+\) cations are coordinated by either 4 or 5 neighboring anions. For the 5-coordinate Li, two oxygen atoms belong to the same \(C_2\)-TFSI\(^{-}\) anion (two oxygen atoms bound to different sulfur atoms on the same TFSI\(^{-}\) anion), two other oxygens belong to a \(C_1\)-TFSI\(^{-}\) anion and the last oxygen atom is from a third \(C_1\)-TFSI\(^{-}\) anion (Fig. 4-8). Thus, the five oxygen atoms are provided by three TFSI\(^{-}\) anions, one
with the $C_2$ conformation and two with the $C_1$ conformation. For the 4-coordinate Li$^+$ cations, each oxygen atom belongs to one TFSI$^-$ anion. Thus, the four oxygen atoms are provided by four TFSI$^-$ anions, two with the $C_2$ conformation and two with the $C_1$ conformation (Fig. 4-8).

**Fig. 4-7.** Ion packing in the crystal structure of the (left) $(1-x)$ PY$_{15}$TFSI-$(x)$ LiTFSI ($x = 0.67$) and (right) $(1-x)$ IM$_{102}$TFSI-$(x)$ LiTFSI ($x = 0.67$) crystalline phases (two views–rotated 90°) (Li - purple, O - red, S - yellow, N - blue, F - green).
Table 4-2. Crystal and Refinement Data

<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
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<td>$b$ (Å)</td>
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<td>$c$ (Å)</td>
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<tr>
<td>$γ$ ($°$)</td>
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</tr>
<tr>
<td>$V$ (Å$^3$)</td>
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<tr>
<td>$\Delta e_{\text{min,max}}$ (e Å$^{-3}$)</td>
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\[ R_1 = \sum |F_o| - |F_c| / \sum |F_o|.
\[ wR_2 = [\sum (w(F_o^2 - F_c^2)^2)/\sum (wF_o^4)]^{1/2}.
\[ \text{GOF} = \sum [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}.

\[ a R_1 = \sum |F_o| - |F_c| / \sum |F_o|.
\[ b wR_2 = [\sum (w(F_o^2 - F_c^2)^2)/\sum (wF_o^4)]^{1/2}.
\[ c \text{GOF} = [\sum [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}.

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As noted above, the crystal structure of a 1/2 ($x = 0.67$) IM$_{102}$TFSI/LiTFSI phase has also been reported. The structure is somewhat different from that with PY$_{15}$TFSI. In the 1/2 phase with IM$_{102}$TFSI, each Li$^+$ cation is 5-fold coordinated by anion oxygens from either 3 or 4 different TFSI$^-$ anions. As for the 1/2 phase with PY$_{15}$TFSI, the ions form two dimensional sheets stacked together and cavities are created which accommodate two of the PY$_{15}^+$ cations (Fig. 4-7). Two of the PY$_{15}^+$ cations have similar conformations, while the remaining two have notably different conformations (Fig. 4-8). The ionic sheets are stacked together to form the crystal structure. This structure contains discrete anions which are each coordinated to either 2 or 3 Li$^+$ cations (Fig. 4-9).
High resolution, variable-temperature Raman spectroscopy provides additional insight into the TFSI$^-$ anion coordination of the mixtures (Fig. 4-10). This anion has a vibrational band in the 730-770 cm$^{-1}$ region which is due to the expansion and contraction of the entire anion.\textsuperscript{46} For solvent-separated ion pair (SSIP) solvates with uncoordinated TFSI$^-$ anions, this band is positioned at approximately 740-744 cm$^{-1}$.\textsuperscript{5-7,47-49} If the anion is coordinated through its oxygen atoms to one or more Li$^+$ cations, however, the band shifts to a higher wavenumber. Assignment of the bands for specific solvate structures is complicated by both the flexibility of the anion and the diversity of ways in which the anion can coordinate one or more Li$^+$ cations using its four oxygen atoms (Fig. 4-9). In the literature, contact ion pair
(CIP) solvates in which the anion is coordinated to a single Li\textsuperscript{+} cation are assigned to a band at approximately 747-750 cm\textsuperscript{-1}.\textsuperscript{5-7,46-48} Examples of the ion coordination found in crystalline solvates with LiTFSI are shown in Fig. 4-11.\textsuperscript{31,50-53} A Raman analysis of LiTFSI solvates of known crystal structure indicates that the band positions and widths are temperature dependent with the bands broadening at higher temperature and shifting to lower wavenumber. The band assignments at -100 °C are as follows: SSIPs (741-743 cm\textsuperscript{-1}), \(C_1\)-CIP-II (746-747 cm\textsuperscript{-1}), \(C_2\)-AGG-Ib (749-750 cm\textsuperscript{-1}), \(C_1\)-AGG-Iib (751-753 cm\textsuperscript{-1}) and \(C_2\)-AGG-III (748 cm\textsuperscript{-1}) (Fig. 4-11). Unfortunately, a comparison of Figs. 4-9 and 4-11 shows that none of these forms of ionic association corresponds to the coordination noted for the anions in the 1/2 PY\textsubscript{15}TFSI/LiTFSI phase. For the latter, the ionic association can be classified as \(C_1\)-AGG-Ia (\(C_1\) anion coordinated to two Li\textsuperscript{+} cations through two oxygens), \(C_1\)-AGG-Ib (\(C_1\) anion coordinated to two Li\textsuperscript{+} cations through three oxygens) and \(C_2\)-AGG-IIb (\(C_2\) anion coordinated to three Li\textsuperscript{+} cations through four oxygens). This, combined with the close proximity of some of the vibrational bands with differing forms of coordination, makes it difficult to assign the bands unequivocally in Fig. 4-10. Thus, further structural and Raman characterization of known solvates with LiTFSI is necessary to aid in the deconvolution and assignments of the vibrational bands. Fig. 4-10 indicates, however, that the pure IL (\(x = 0\)) consists only of uncoordinated anions, as expected, due to the steric shielding of the positive charge on the nitrogen of the PY\textsubscript{15}\textsuperscript{+} cations. As noted above, the band positions are a function of temperature. The peak position and FWHM of the band for the uncoordinated anions (\(x = 0\)) shifts and broadens with increasing temperature due to increased variability in the anion
geometry with increased thermal energy. The $x = 0.20$ mixture when crystalline (-150 °C, -20 °C) and in the liquid phase (80 °C) contains both uncoordinated anions and CIP species. The majority of the anions in the $x = 0.33$ phase appear to be CIPs (anions coordinated to a single Li$^+$ cation, perhaps with two oxygens). As noted above, it has been suggested from a vibrational spectroscopic analysis that, for low LiTFSI concentrations, [Li(TFSI)$_2$]$^-$ species form with bidentate coordination of the Li$^+$ cations by two oxygen atoms from one anion with a $C_2$ conformation and two oxygen atoms of another anion with a $C_1$ conformation (i.e., a CIP solvate in terms of the TFSI$^-$ coordination).
Fig. 4-10. Raman spectra of \((1-x)\) PY$_{15}$TFSI-\((x)\) LiTFSI mixtures at different temperatures.
Fig. 4-11. TFSI anion coordination to Li$^+$ cations found in crystalline (solvent)$_n$:LiTFSI solvate structures: (a) $C_{1}$-SSIP$^{31}$ (b) $C_{2}$-SSIP$^{50}$ (c) $C_{1}$-CIP-II$^{51}$ (d) $C_{2}$-AGG-Ib$^{52}$ (e) $C_{1}$-AGG-IIb$^{50}$ and (f) $C_{2}$-AGG-III$^{53}$ (coordination bonds are dashed and Li$^+$ cations are black—the conformation of the anion is indicated).

The $x = 0.50$ sample appears to be a mixture of the coordination for the $x = 0.33$ and 0.67 samples. The DSC data indicate that there may be a eutectic between these two latter phases which would explain this. The manner, in which this sample is crystallized, however, affects the coordination observed. It is possible to crystallize this sample to give a prominent peak at 751 cm$^{-1}$ with a corresponding decrease in the peaks at 747 and 757 cm$^{-1}$ (Fig. 4-12). This indicates that, under certain conditions, a different crystalline phase (perhaps a 1/1 PY$_{15}$TFSI/LiTFSI phase) may form rather than a mixture of the 2/1 and 1/2 phases.
Fig. 4-12. Variable-temperature Raman spectra of the (1-x) PY_{15}TFSI-(x) LiTFSI (x = 0.50) sample: (a) cooled (5 °C min\(^{-1}\)) to -150 °C, heated (5 °C min\(^{-1}\)) to 100 °C and (b) cooled (5 °C min\(^{-1}\)) to -60 °C, heated (5 °C min\(^{-1}\)) to 3 °C, held for 15 min. cooled (5 °C min\(^{-1}\)) to -150 °C, heated (5 °C min\(^{-1}\)) to 100 °C.

At -150 °C, the x = 0.67 sample is a crystalline solid with the ion coordination noted above. The Raman data indicate that peaks are present at about 747, 750 and 757 cm\(^{-1}\). Three different forms of anion coordination are found in the structure (Fig. 4-9), but none of these
correspond to CIP coordination. Thus, it may be that either the $C_1$-AGG-Ia or $C_1$-AGG-Ib forms of coordination result in a band at 747 cm$^{-1}$ (as is found for the $C_1$-CIP-II form of coordination). The band at 757 cm$^{-1}$ appears to be a new band not previously reported. This band is only present in the crystalline 1/2 PY$_{15}$TFSI/LiTFSI phase. Interestingly, once this phase melts, the band disappears. It is tempting to therefore assign this to the $C_2$-AGG-IIb coordination as this form of ion linkage would be the most difficult to maintain in the disordered liquid state. These data suggests that the initial minimal decrease in conductivity in the liquid phase upon the addition of low amounts of LiTFSI to the ILs may be due to the formation of individual [Li(TFSI)$_2$]$^+$ species which do not significantly disrupt the dynamics of the ionic mobility. For such compositions, most of the conductivity is, in fact, due to the uncoordinated ions of the IL. In contrast, a further increase in the LiTFSI concentration results in the formation of larger ionic aggregates (chains and then networks) in which the Li$^+$ cations serve as links or crosslinks between the aggregated anions. This increasing aggregation of the ions is the explanation for the rapid decrease in the conductivity (and rapid increase in viscosity) of the mixtures in the liquid state with increasing LiTFSI concentration.

4.1.3 (1-$x$) Et$_4$NTFSI–(x) LiTFSI Mixtures

(1-$x$) Et$_4$NTFSI-(x) LiTFSI mixtures were then selected for characterization. Et$_4$NTFSI was chosen since the neat salt forms several plastic crystalline phases$^{24}$ and IR and Raman vibrational spectroscopy may be utilized to examine the molecular conformations of the
Et$_4$N$^+$ cation and TFSI$^-$ anion, as well as the Li$^+$...TFSI$^-$ interactions (Figs. 3-17 and 3-18).5

DSC heating traces for the (1-\(x\)) Et$_4$N(TFSI)-(\(x\)) LiTFSI mixtures are shown in Fig. 4-13 and the corresponding phase diagram is reported in Fig. 4-14 (\(x = 0\) is neat Et$_4$NTFSI and \(x = 1\) is neat LiTFSI). Two mixed salt crystalline phases form (1/1 and 1/2 Et$_4$NTFSI/LiTFSI) for \(x = 0.50\) and 0.67, respectively. A eutectic point is found with a composition of approximately \(x = 0.25-0.33\) and a \(T_m\) of 31–33 °C (Figs. 4-13 and 4-14). No solid solutions are present in the phase diagram. Neither the 1/1 nor 1/2 phases display any solid-solid phase transitions. These phases have a \(T_m\) at 52–54 °C and 84–86 °C, respectively.
Fig. 4-13. DSC heating traces (10 °C min⁻¹) for (1-x) Et₄NTFSI-(x) LiTFSI mixtures.
It is interesting to note that the 1/1 and 1/2 Et$_4$NTFSI/LiTFSI mixed salt crystalline phases have $T_m$ values which are comparable to those for the PY$_{1R}$TFSI/LiTFSI mixtures.\cite{3} Preliminary results suggest that is not the case for Me$_4$NTFSI/LiTFSI mixed salt crystalline phases. In this latter system, 2/1 and 1/2 (Me$_4$N$^+$/Li$^+$) mixed salt phases appear to form and a eutectic may exist near an $x = 0.15$ composition (Fig. 4-15). These phases, however, all appear to melt near or above 100 °C. In this case, the 2/1 phase has a higher $T_m$ than the more concentrated (with LiTFSI) 1/2 phase. It may be that the small Me$_4$N$^+$ cation is less disruptive to the Li$^+...$TFSI$^-$ coordination than larger organic cations such as Et$_4$N$^+$ and PY$_{1R}^+$; this, in turn, results in a higher $T_m$. Alternatively, an entirely new form of packing/ionic
coordination may occur in these mixed salt phases relative to the salts with Et₄N⁺ and PY₁R⁺ cations.

**Fig. 4-15.** DSC heating traces (10 °C min⁻¹) for (1-x) Me₄NTFSI-(x) LiTFSI mixtures.³³

The ionic conductivity variation with temperature of the (1-x) Et₄NTFSI-(x) LiTFSI mixtures is shown in Fig. 4-16. Upon the addition of just 1 mol% LiTFSI to the Et₄NTFSI salt, the conductivity behavior changes drastically. On heating, the conductivity of ~10⁻⁸ S cm⁻¹ begins to steadily and rapidly increase near 0 °C. This appears to be due to the solid-solid phase transition of the neat Et₄NTFSI salt even though the Li⁺ cations of the eutectic mixture reside in the 1/1 phase. Such a conductivity increase is observed for all of the samples containing the eutectic composition (i.e., those with 0 < x < 0.50) (Fig. 4-16). The samples with x = 0.05-0.40 also show a rapid increase in the conductivity near 30 °C due to the melting of the eutectic composition. This increase does not occur for the x = 0.01 sample.
This may be due to the very small fraction of the eutectic composition present in this sample which lies below a percolation threshold. The formation of a small amount of liquid phase which is not interconnected within the solid would not significantly influence the ionic conductivity. The \( x = 0.50 \) and 0.67 samples have a low conductivity until about 52 and 84 °C, respectively, whereupon the 1/1 and 1/2 crystalline phases melt and the conductivity increases several orders of magnitude.

**Fig. 4-16.** Ionic conductivity of \((1-x)\) Et₄NTFSI-(x) LiTFSI mixtures.\(^{33}\)
4.2 Improved Thermal Stability of Ionic Liquids Through Lithium Salt Addition

Although many ILs are widely reported to have high thermal stability, only limited data is available regarding this crucial property. Here the thermal stability of mixtures of LiTFSI has been examined with the widely used ILs IM$_{10R}$TFSI with R = 1, 2 and 4 for methyl, ethyl and butyl, respectively:

![Chemical structure of IM$_{10R}$TFSI](image)

The lithium salt is found to confer improved long-term, high temperature thermal stability to the ILs. This observation suggests a potential new route to tuning the thermal stability of diverse ILs.

Where thermal stability information is available, it generally consists of variable-temperature TGA measurements,$^{57-59}$ such as those shown in Fig. 4-17. These data suggest that the neat IM$_{10R}$TFSI (R = 1, 2 and 4) salts have very similar thermal stability given that the onset point for mass loss (1 wt% at 308-320 °C) and degradation profiles are nearly the same. Approximately 1-3 wt% of the samples remains after decomposition when these salts were heated to 600 °C under an N$_2$ atmosphere. Interestingly, the onset point for mass loss for the anhydrous LiTFSI salt is similar to the IM$_{10R}$TFSI salts, but mass loss then occurs more rapidly at a lower temperature than for the ILs.
Fig. 4-17. TGA heating traces (N₂ atmosphere) of variable-temperature (5 °C min⁻¹) measurements of LiTFSI and IM₁₀₈TFSI ILs.

Isothermal measurements, however, provide a more accurate depiction of the resistance of the ILs to thermal degradation, but such information is not widely available.⁶⁰-⁶⁵ Fig. 4-18a shows isothermal TGA measurements (900 min., 250 °C) for the same ILs. These ILs have linear degradation profiles at this temperature and clearly there are significant differences in the thermal stability of the salts with varying cation alkyl chain length with the longer alkyl chains reducing the thermal stability to a greater extent. These data suggest that variable-temperature analysis does not provide an accurate depiction of the thermal stability of the ILs. Fig. 4-18b indicates that, as expected, less weight is lost on heating at a lower temperature (200 or 225 °C).
Fig. 4-18. TGA traces (N₂ atmosphere) of IM₁₀R TFSI ILs: (a) isothermal (900 min., 250 °C) measurements and (b) mass remaining after the isothermal TGA runs (N₂ atmosphere, 900 min.) at different temperatures.

The isothermal TGA measurements of the (1-x) IM₁₀R TFSI-(x) LiTFSI mixtures are shown in Fig. 4-19. The pure IM₁₀₂ TFSI and IM₁₀₄ TFSI ILs loose approximately 8-9 wt% of their mass on heating at 225°C. Adding 20 mol% LiTFSI increases their thermal stability noticeably with more than 97 wt% of the original mass of the mixtures remained after 900 min. Heating the ILs at 250 °C results in a mass loss of about 18 wt% and 25 wt%, respectively, for the pure IM₁₀R TFSI (R = 2 or 4) ILs. The addition of LiTFSI, however, again reduces this weight lost with a notable improvement in stability even for the addition of
only 5 mol% LiTFSI. Note that the error bars are relatively small (from repeated measurements) suggesting some minor variability is to be expected in such measurements, but consistent results are obtained. Note also that the improved thermal stability does not vary linearly with the LiTFSI fraction of the sample.

Fig. 4-19. Mass remaining after isothermal TGA runs (N₂ atmosphere, 900 min) for (1-x) IM₁₀₄TFSI-(x) LiTFSI mixtures, open patterns for 225 °C and filled patterns for 250 °C; squares for R = 2 and triangles for R = 4.

Quantum chemical calculations have suggested that IM₁₀₄TFSI decomposes by the thermal degradation of the anion releasing SO₂:

\[
\begin{align*}
\text{IM}^{+}_{104} + \text{SO}_{2} \rightarrow \text{N} \text{N} \text{S} \text{F}_3 \text{C} \text{S} \text{N} \text{S} \text{O} \text{C} \text{F}_3 \text{O} \text{C} \text{F}_3 \text{O} \text{S} \text{N} \text{C} \text{F}_3 \text{O} \text{C} \text{F}_3 \text{O} \text{S} \text{N} \text{C} \text{F}_3 \text{O} \text{C} \text{F}_3 \text{O} + \text{SO}_2
\end{align*}
\]

The IM₁₀₄⁺ cation is not degraded by this proposed process. This may indeed be the initial mechanism for IL degradation, but full degradation of the cations and anions must follow for
the almost total mass loss observed. It therefore seems evident that the Li⁺...TFSI⁻ (oxygen atom) ionic interactions which form hinder the overall degradation process. Although the neat anhydrous LiTFSI salt does lose mass more rapidly on rapid heating than the ILs (Fig. 4-17), it has a superior thermal stability up to at least 250 °C (Fig. 4-19) which may originate from similar extensive Li⁺...TFSI⁻ coordination.

The addition of LiTFSI to the ILs affects not only the thermal stability, but also other properties such as viscosity. Such changes in properties may impact the utility of the ILs for applications in which a high IL thermal stability is desired (e.g., high-temperature lubricants). The change in IL properties is to be expected given the extensive Li⁺...TFSI⁻ ionic interactions which occur. Viscosity data (Fig. 4-20) indicate that adding LiTFSI does induce an increase in the viscosity, especially for the 40 mol% LiTFSI samples. There is a wide variability in the viscosity for both sets of mixtures below about 80 °C. Heating to higher temperature, however, results in only a modest further reduction in the viscosity. Although differences are found in the viscosity of the two ILs with a given amount of LiTFSI at lower temperatures (Fig. 4-20), these differences are less significant above about 40 °C.

An improved understanding of how ILs thermally degrade and what factors hinder or prevent this is needed for many of the commercial uses of these intriguing liquid salts. The addition of lithium salts to the ILs to reduce the thermal degradation not only changes the physical properties of the mixtures, but also is likely to change the tendency of the ILs to absorb water from the atmosphere (further changing the properties of the mixtures). The data reported, however, do suggest that it is possible to tune the thermal properties of ILs by
controlling the molecular-level interactions that occur between the ions – whether by lithium salts or other additives.

![Graph showing variable-temperature viscosity of (1-x) IM_{10R}TFSI-(x) LiTFSI mixtures.]

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**Fig. 4-20.** Variable-temperature viscosity of (1-x) IM_{10R}TFSI-(x) LiTFSI mixtures (squares for R = 2 and triangles for R = 4).

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### 4.3 Conclusions

The phase behavior of IL-LiX mixtures is complicated. Many IL-LiX mixed salt crystalline phases (2/1, 1/1 and 1/2 IL/LiX) are able to form in which the Li\(^+\) cations are coordinated by anion oxygen atoms and the organic cations remain either uncoordinated or have weak hydrogen bonding to anions. Some crystalline phases are metastable; while other
mixtures are unable to be crystallized (a crystallinity gap exists for specific compositions). With increasing concentration of LiX, the thermal stability of the IL-LiX mixtures improves, the viscosity increases and the conductivity decreases due to the Li$^+$···anion coordination.

References


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Chapter 5. Physical and Electrochemical Properties of Binary Ionic Liquids Mixtures

5.1 Overview

ILs tend to have a high viscosity, especially at low temperature, and the ionic conductivity typically drops off rapidly with the corresponding rapid increase in viscosity. For sub- to near-ambient temperature applications, however, electrochemical devices require fast ion transport. Unfortunately, no single IL reported thus far combines suitable electrochemical characteristics with a reasonable conductivity and viscosity at low temperature.

Previous work has demonstrated that ILs can be combined to give mixtures with enhanced ionic transport properties and electrochemical stability,\(^1\)\(^-\)\(^3\) while also providing excellent compatibility with carbonaceous electrodes.\(^4\)\(^-\)\(^6\) Generally, those ILs based upon bis(perfluoroalkanesulfonyl)imide anions with smaller anions (lower molecular weight, MW) are found to have a higher ionic conductivity than those with larger anions, as well as a lower viscosity.\(^7\) In addition, ILs with asymmetric anions often exhibit a lower \(T_m\) than those with symmetric anions resulting from unfavorable ion packing within the crystal lattice.\(^8\)

In this work, two different ILs sharing the PY\(_{14}^+\) cation, but with two different structurally similar anions, TFSI\(^-\) and (trifluoromethanesulfonyl)(nonafluorobutanesulfonyl)imide (IM\(_{14}^-\)) have been combined (Scheme 5-1). PY\(_{14}^+\)TFSI was selected because of its high conductivity in the molten state (1.8\times10^{-3} \text{ S cm}^{-1} at 20 °C) in conjunction with its wide electrochemical stability window,\(^7\) whereas PY\(_{14}^+\)IM\(_{14}^-\) displays the interesting property
of not being readily crystallizable.\textsuperscript{7} The physical and electrochemical properties of (1-\(x\)) PY\textsubscript{14}TFSI-(\(x\)) PY\textsubscript{14}IM\textsubscript{14} mixtures (Table 5-1) over a wide temperature range are presented and discussed here. It should be noted that although no lithium salt has been incorporated into the IL mixtures studied, it has been shown that the conductivity and electrochemical stability of IL-LiX mixtures can be directly correlated with the properties of the pure ILs.\textsuperscript{9}

![Chemical structure of ions in PY\textsubscript{14}TFSI and PY\textsubscript{14}IM\textsubscript{14}](image)

**Scheme 5-1.** Chemical structure of ions in PY\textsubscript{14}TFSI and PY\textsubscript{14}IM\textsubscript{14}.

### 5.2 Results and Discussion

The DSC heating traces for the (1-\(x\)) PY\textsubscript{14}TFSI-(\(x\)) PY\textsubscript{14}IM\textsubscript{14} mixtures are shown in Fig. 5-1. The pure PY\textsubscript{14}TFSI (\(x = 0\)) melts near -7 °C with no other transitions detected.\textsuperscript{7,10} In contrast, the pure PY\textsubscript{14}IM\textsubscript{14} (\(x = 1\)) could not be crystallized in the DSC pans, remaining liquid even at very low temperatures. This is likely ascribed to the unfavorable packing of the highly asymmetric IM\textsubscript{14}\textsuperscript{-} anion that remarkably lowers the lattice energy of the IL.\textsuperscript{7} The progressive addition of PY\textsubscript{14}IM\textsubscript{14} to PY\textsubscript{14}TFSI hinders (in low concentration) or inhibits (in higher concentration) the crystallization of the mixtures. Such behavior is highlighted by a melting peak shift from -7 °C (\(x = 0\)) to -10 °C (\(x = 0.10\)) (Fig. 5-1). The phase transition
peak broadens with less material crystallizing upon PY$_{14}$IM$_{14}$ addition. For PY$_{14}$IM$_{14}$ mole fraction equal to or higher than 0.20, the binary mixtures could not be crystallized in the DSC pans despite repeated cycling at low temperature, i.e., the melting peak disappears, and no feature with the exception of the $T_g$ was observed. The absence of a crystalline phase for $x \geq 0.20$ indicates that the IL mixtures remain amorphous, even at very low temperature. This suggests that the highly asymmetric anion IM$_{14}^-$ prevents the crystallization of the mixtures, instead resulting in solidify as a glassy state at very low temperatures. The $T_g$ does increase somewhat with increasing PY$_{14}$IM$_{14}$ mole fraction (Fig. 5-1), e.g., from -83 °C ($x = 0.20$) to -75 °C ($x = 1$), thus progressively approaching the behavior of the pure PY$_{14}$IM$_{14}$ material.

Table 5-1. Physical properties of (1-$x$) PY$_{14}$TFSI-(x) PY$_{14}$IM$_{14}$ mixtures. The density ($d$) and the viscosity ($\eta$) values were measured at 20 °C, while the conductivity ($\sigma$) is also given for -20 °C.$^8$

<table>
<thead>
<tr>
<th>$x$</th>
<th>$d$/g cm$^{-3}$</th>
<th>$\eta$/mPa s</th>
<th>$\sigma$/mS cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 °C</td>
</tr>
<tr>
<td>0</td>
<td>1.399±0.002</td>
<td>100 ± 10</td>
<td>(4.0±0.4)×10$^{-5}$</td>
</tr>
<tr>
<td>0.10</td>
<td>1.413±0.002</td>
<td>130 ± 20</td>
<td>(2.1±0.2)×10$^{-3}$</td>
</tr>
<tr>
<td>0.20</td>
<td>1.427±0.002</td>
<td>150 ± 20</td>
<td>(7.5±0.8)×10$^{-2}$</td>
</tr>
<tr>
<td>0.30</td>
<td>1.440±0.002</td>
<td>160 ± 20</td>
<td>(5.4±0.5)×10$^{-2}$</td>
</tr>
<tr>
<td>0.40</td>
<td>1.449±0.002</td>
<td>n. a.</td>
<td>(4.1±0.4)×10$^{-2}$</td>
</tr>
<tr>
<td>0.50</td>
<td>1.462±0.002</td>
<td>260 ± 30</td>
<td>(3.6±0.4)×10$^{-2}$</td>
</tr>
<tr>
<td>0.60</td>
<td>1.473±0.002</td>
<td>n. a.</td>
<td>(2.1±0.2)×10$^{-2}$</td>
</tr>
<tr>
<td>0.70</td>
<td>1.483±0.002</td>
<td>350 ± 40</td>
<td>(1.6±0.2)×10$^{-2}$</td>
</tr>
<tr>
<td>0.80</td>
<td>1.494±0.002</td>
<td>n. a.</td>
<td>(1.1±0.1)×10$^{-2}$</td>
</tr>
<tr>
<td>1</td>
<td>1.512±0.002</td>
<td>550 ± 50</td>
<td>(7.6±0.5)×10$^{-3}$</td>
</tr>
</tbody>
</table>
Fig. 5-1. DSC heating traces (5 °C min⁻¹) of (1-x) PY₁₄TFSI-(x) PY₁₄IM₁₄ mixtures.

The ionic conductivity vs. temperature behavior of the IL mixtures is illustrated in Fig. 5-2. Error bars from repeated measurements fall within the data markers. The pure PY₁₄TFSI (x = 0) material displays a onset for increasing conductivity near -7 °C followed by a steep rise of more than four orders of magnitude. This increase is due to the melting of the IL, in good agreement with the DSC data (Fig. 5-1). From -40 °C to the $T_m$, the PY₁₄TFSI sample exhibits a stable, but low conductivity (e.g., around $4 \times 10^{-8}$ S cm⁻¹), typical of a solid crystalline material. The incorporation of PY₁₄IM₁₄ up to a mole fraction $x = 0.10$ results in a progressive increase in the conductivity at a temperature well below the DSC $T_m$. 
value. This behavior is better highlighted in panel B which magnifies the Arrhenius plot of selected \((1-x)\) PY\textsubscript{14}TFSI-\((x)\) PY\textsubscript{14}IM\textsubscript{14} mixtures \((0 \leq x \leq 0.20)\). No \(T_g\) is evident in the data in Fig. 5-1 for the \(x = 0.10\) sample due to the large fraction of the sample which is crystalline. But it is probable that the PY\textsubscript{14}IM\textsubscript{14} IL remains liquid and may even interacts with some of the PY\textsubscript{14}TFSI preventing it also from crystallizing. Thus, the progressive increase in conductivity is due to this liquid phase dispersed in the crystalline solid. The conductivity data for the \(x = 0.20\) sample (Fig. 5-2) indicate that some of the sample crystallized, in contrast with the DSC data (Fig. 5-1). This is likely due to the difference in the amount of material used for the two measurements (< 15 mg for DSC vs. < 2 g for conductivity). Crystallization relies on nucleation of the PY\textsubscript{14}TFSI (followed by growth). Given the slow crystallization kinetics, the probability of nuclei of critical size forming is much higher in the larger sample. In addition, the conductivity samples were held at -40 °C for 18 hrs. prior to the measurements, whereas the DSC samples were only cycled for several hrs. under a variety of low temperature cycling conditions. The conductivity of the samples with \(x > 0.20\) follows the expected trend for liquid/amorphous electrolytes which is often modeled by VTF behavior.\textsuperscript{11-13} In the molten state, the ionic conductivity of the \((1-x)\) PY\textsubscript{14}TFSI-\((x)\) PY\textsubscript{14}IM\textsubscript{14} mixtures is seen to progressively decrease with the increase of the average \(M_W\) of the mixtures.
Fig. 5-2. (a) Ionic conductivity vs. temperature behavior of \((1-x) \text{PY}_{14}\text{TFSI}-(x) \text{PY}_{14}\text{IM}_{14}\) mixtures and (b) magnified view of the Arrhenius plot of selected \((1-x) \text{PY}_{14}\text{TFSI}-(x) \text{PY}_{14}\text{IM}_{14}\) mixture samples.\(^8\)

The effect on the low temperature ion mobility is more evident in Fig. 5-3 which reports the ionic conductivity vs. \(\text{PY}_{14}\text{IM}_{14}\) mole fraction dependence in the temperature range from -40 °C to 0 °C. When the samples are fully molten, the conductivity of the binary mixtures
decreases linearly with increasing PY14IM14 mole fraction (Fig. 5-4). In particular, for PY14IM14 mole fractions ranging from 0.10 to 0.30, the conductivity values are at least one order of magnitude higher than that of PY14IM14 and more than two order of magnitude higher than that of PY14TFSI (as the latter sample crystallizes). This interesting effect, is due to the ionic confusion present in the binary mixtures that shifts the crystallization and, therefore, the Tm to a much lower temperature. For instance, a conductivity approaching $10^{-4}$ S cm$^{-1}$ is achieved at -20 °C ($x = 0.20$), whereas appreciable conduction values ($> 10^{-5}$ S cm$^{-1}$) are detected even at very low temperatures (-30 °C) for $x$ ranging from 0.30 to 0.40. Table 5-1 reports the conductivity values, obtained at 20 °C and -20 °C, of the IL mixtures investigated.

Fig. 5-3. Ionic conductivity vs. PY14IM14 mole fraction of (1-$x$) PY14TFSI-$x$ PY14IM14 mixtures at different temperatures. The error bars fall within the data markers.8
Viscosity measurements were performed to better understand the conduction phenomena. Fig. 5-4 shows the dependence of the viscosity and resistivity of the mixtures with respect to the PY$_{14}$IM$_{14}$ mole fraction. The measurements were carried out in an interval ranging from a temperature slightly above the $T_m$ to 80 °C. The viscosity, as well as the resistivity, linearly increases with the PY$_{14}$IM$_{14}$ mole fraction (Fig. 5-4 and Table 5-1) through the whole temperature range investigated. This suggests that the resistivity, and thus the conductivity, is directly correlated with the viscosity, e.g., the ion mobility is mostly affected by viscous drag. The progressive decrease in conductivity with increasing fraction of IM$_{14}$ is likely attributed to an analogous, linear increase in viscosity, affected by ion steric hindrance, resulting in a higher ionic resistance of the IL blends.$^{14,15}$
Fig. 5-4. (a) Viscosity and (b) resistivity of \((1-x)\) PY\(_{14}\)TFSI-\((x)\) PY\(_{14}\)IM\(_{14}\) mixtures as a function of the PY\(_{14}\)IM\(_{14}\) mole fraction at different temperatures. Error bars are shown.\(^8\)

The physicochemical properties of the mixtures in the molten state were also investigated in terms of density at different temperatures and PY\(_{14}\)IM\(_{14}\) mole fractions (Fig. 5-4).
The density of pure PY$_{14}$IM$_{14}$ is found to be 7% higher than that of PY$_{14}$TFSI. Fig. 5-5 shows that a slight, but progressive decrease in density of about 5% is observed from 20 °C to 90 °C. The increase of the PY$_{14}$IM$_{14}$ mole fraction results in an almost linear increase in the density. Two linear density vs. composition trends are seen for the (1-x) PY$_{14}$TFSI-(x) PY$_{14}$IM$_{14}$ mixtures with a knee at x = 0.30. This is better seen in Table 5-2 which reports the slope values, calculated for the two different PY$_{14}$IM$_{14}$ mole fraction ranges (e.g., $0 \leq x \leq 0.30$ and $0.30 \leq x \leq 1$, respectively) at various temperatures as shown in Fig. 5-5. Such behavior suggests the rearrangement of the structural organization (leading to less favorable packing) of the ions within the mixtures at a PY$_{14}$IM$_{14}$ mole fraction equal to 0.30 which corresponds to a IM$_{14}$/TFSI mole ratio of about 1/2.
Fig. 5-5. Density vs. PY$_{14}$IM$_{14}$ mole fraction dependence of (1-x) PY$_{14}$TFSI-(x) PY$_{14}$IM$_{14}$ mixtures at different temperatures. The error bars fall within the data markers.\textsuperscript{8}
Table 5-2. Slope values of the density vs. composition plots reported in Fig. 5-5.8

<table>
<thead>
<tr>
<th>$T/ ^\circ \text{C}$</th>
<th>PY$<em>{14}$IM$</em>{14}$ mole fraction range (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 ~ 0.30</td>
</tr>
<tr>
<td>20</td>
<td>0.135 ± 0.003</td>
</tr>
<tr>
<td>30</td>
<td>0.134 ± 0.003</td>
</tr>
<tr>
<td>40</td>
<td>0.132 ± 0.003</td>
</tr>
<tr>
<td>50</td>
<td>0.129 ± 0.003</td>
</tr>
<tr>
<td>60</td>
<td>0.129 ± 0.003</td>
</tr>
<tr>
<td>70</td>
<td>0.131 ± 0.001</td>
</tr>
<tr>
<td>80</td>
<td>0.127 ± 0.004</td>
</tr>
<tr>
<td>90</td>
<td>0.124 ± 0.003</td>
</tr>
</tbody>
</table>

5.3 Conclusions

The physical and electrochemical properties of (1-x) PY$_{14}$TFSI-(x) PY$_{14}$IM$_{14}$ IL mixtures have been investigated. The results show that mixing different ILs generates new materials with improved characteristics with respect to the starting components. The addition of an IL (PY$_{14}$IM$_{14}$) which cannot be crystallized (but which has a relatively low ionic conductivity) to a highly conductive IL (PY$_{14}$TFSI) (which is easily crystallized) was found to significantly enhance the low temperature ionic conductivity ($10^{-4}$ S cm$^{-1}$ at -20°C). Even moderate mole fractions (x = 0.30) of PY$_{14}$IM$_{14}$ are able to prevent the crystallization of the IL mixtures, thus retaining them in the molten state below -40 °C. Mixing of different ILs therefore represents a practical approach to obtaining new electrolytic materials with enhanced properties, as required in electrochemical devices for particular applications, which are not matched by a single IL material.
References


Chapter 6. Phase Behavior and Thermal Properties of Ternary Ionic Liquid-Lithium Salt (IL-IL-LiX) Electrolytes

6.1 Overview

As noted in Chapter 1, state-of-the-art liquid electrolytes consist of mixtures of aprotic carbonate solvents with LiPF<sub>6</sub>. The aim is to mix the solvents together to combine their properties with a synergic, beneficial effect. The mixing of ILs for battery electrolytes may also be of interest. For example, the PY<sub>1</sub>R-TFSI-LiTFSI electrolytes are known to have excellent thermal stability, but also have a relatively low ionic conductivity (and high viscosity) and tend to solidify into crystalline phases at low temperature. In contrast, the PY<sub>1</sub>R-FSI-LiFSI mixtures have a higher conductivity (lower viscosity), form an excellent SEI layer on graphite and remained amorphous, but also suffer from a lower thermal stability than TFSI-based electrolytes. As shown in Chapter 4, the addition of LiTFSI to the IM<sub>10</sub>R-TFSI salts improved the thermal stability of the mixtures. In this chapter, therefore, the properties of PY<sub>1</sub>FSI-PY<sub>1</sub>TFSI-Li<sub>X</sub> (X = TFSI<sup>-</sup> or PF<sub>6</sub><sup>-</sup>) mixtures are explored as electrolytes for Li batteries (Table 6-1 indicates the mole composition of the mixtures).

PY<sub>1</sub>FSI exhibits a low viscosity and a low T<sub>m</sub> (-9 °C) with a high conductivity (6.4 mS cm<sup>-1</sup>) at room temperature. The electrolyte formed by dissolving LiTFSI in PY<sub>1</sub>FSI was reported to allow reversible Li<sup>+</sup> insertion/deinsertion in graphite electrodes (in sharp contrast with related IL-based mixtures with PY<sub>1</sub>TFSI) due to the degradation of the FSI<sup>-</sup> anion to form a favorable SEI layer on the graphite surface. Thus, PY<sub>1</sub>FSI has a lower thermal and electrochemical stability than PY<sub>1</sub>TFSI. PY<sub>1</sub>TFSI and its mixtures with lithium salts are
reported to have a reasonable room temperature ionic conductivity (> 1 mS cm\(^{-1}\)) and an overall stability windows in excess of 5.5 V with the cathodic stability limit exceeding the lithium plating/stripping potential.\(^3\) LiPF\(_6\) was selected because of its wide use and favorable properties as noted in Chapter 1. LiTFSI was also selected for comparison purposes to investigate the effect of the PF\(_6^-\) anions (the TFSI\(^-\) anion is already present in the system). The lithium salt (i.e., LiTFSI or LiPF\(_6\)) concentration was fixed at 0.3M based upon preliminary battery cycling test results obtained on carbonaceous anodes.\(^2\)

**Table 6-1.** Mole composition of \((1-x)\) PY\(_{14}\)TFSI-\((x)\) PY\(_{13}\)FSI-0.3M LiX mixtures (X = TFSI\(^-\) or PF\(_6^-\)). The parameters \(x\) and \((1-x)\) are the mole fractions of PY\(_{13}\)FSI and PY\(_{14}\)TFSI, respectively.

<table>
<thead>
<tr>
<th>PY(_{13})FSI</th>
<th>Mole fraction</th>
<th>Weight fraction</th>
<th>PY(_{14})TFSI</th>
<th>Mole fraction</th>
<th>Weight fraction</th>
</tr>
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<td>0</td>
<td>0</td>
<td>1</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.067</td>
<td>0.067</td>
<td>0.05</td>
<td>0.933</td>
<td>0.95</td>
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</tr>
<tr>
<td>0.132</td>
<td>0.132</td>
<td>0.10</td>
<td>0.868</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>0.255</td>
<td>0.255</td>
<td>0.20</td>
<td>0.745</td>
<td>0.80</td>
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</tr>
<tr>
<td>0.370</td>
<td>0.370</td>
<td>0.30</td>
<td>0.630</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>0.477</td>
<td>0.477</td>
<td>0.40</td>
<td>0.523</td>
<td>0.60</td>
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</tr>
<tr>
<td>0.578</td>
<td>0.578</td>
<td>0.50</td>
<td>0.422</td>
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<tr>
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<td>1.00</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

**6.2 Results and Discussion**

Interestingly, there was significant variation in the DSC heating traces for the same PY\(_{13}\)FSI-0.3M LiPF\(_6\) sample (Fig. 6-1) when various thermal cycling procedures (not shown) were used to crystallize the same sample. The pure PY\(_{13}\)FSI salt crystallizes with a \(T_m\) of -9\(^\circ\)C and also undergoes solid-solid phase transitions at -83 and -19\(^\circ\)C (Chapter 3).\(^1\) Another
peak was found for the pure PY_{13}FSI salt at -50 °C, but this peak was not reproducible.\textsuperscript{1} One explanation for the inconsistency of the data in Fig. 6-1 is that some of the sample may sometimes crystallize into the metastable crystalline phase (not related to the other phase with its two solid-solid phase transitions) with a $T_m$ near -55 °C and immediately after melting, the resulting liquid recrystallizes (since there is still the other solid crystalline phase present) to the more thermodynamically stable phase. This behavior explains much in Fig. 6-1. It does not, however, account for the new peak found near -12 °C. This peak may be due to a new crystalline phase containing both PY_{13}FSI and LiPF$_6$. It is difficult to crystallize this phase, however, and only in the last heating trace shown is a significant amount of this phase present.

**Fig. 6-1.** DSC heat traces (5 °C min$^{-1}$) of (1-x) PY$_{14}$TFSI-(x) PY$_{13}$FSI-0.3M LiPF$_6$ (x = 1).
Fig. 6-2a shows the DSC heat traces for \((1-x)\) PY\(_{14}\)TFSI-(x) PY\(_{13}\)FSI-0.3M LiTFSI mixtures. Pure PY\(_{14}\)TFSI has a \(T_m\) of -6 °C.\(^4\) Adding 0.3M LiTFSI (the \(x = 0\) sample) lowers this \(T_m\) to -10 °C. As the PY\(_{13}\)FSI mole fraction increases (\(x\) increases), the amount of PY\(_{14}\)TFSI that may be crystallized decreases. The data for the \(x = 0.067\) sample is not in complete agreement with expectations. Only a small amount of the sample could be crystallized despite the presence of only a small amount of PY\(_{13}\)FSI and the ready crystallization of the PY\(_{14}\)TFSI-LiTFSI mixture in the absence of PY\(_{13}\)FSI. No portion of the \(x = 0.370, 0.477\) and 0.578 samples could be crystallized despite repeated cycling at low temperature. The \(T_g\) tends to decrease with increasing fraction of PY\(_{13}\)FSI. For the sample containing only PY\(_{13}\)FSI (\(x = 1\)), some of the pure IL is able to crystallize and the \(T_m\) is lower than that of the pure PY\(_{13}\)FSI due to the presence of the 0.3M LiTFSI salt. It is likely that the \(T_m\) and first solid-solid phase transition for the PY\(_{13}\)FSI salt overlap resulting in the noted peak at -18 °C. Again, there is no evidence of a new crystalline phase containing the LiTFSI salt. Rather, this salt remains in an amorphous phase with some of the IL (indicated by a small \(T_g\) for the sample).

Fig. 6-2b shows the DSC heat traces for \((1-x)\) PY\(_{14}\)TFSI-(x) PY\(_{13}\)FSI-0.3M LiPF\(_6\) mixtures. For the PY\(_{14}\)TFSI rich samples (\(x = 0, 0.067, 0.132\)), there are clear differences in the melting peaks from what is found for neat PY\(_{14}\)TFSI. These differences may (at least in part) be attributed to the formation of a metastable crystalline phase that may be formed by the pure PY\(_{14}\)TFSI salt,\(^4\) as well as the presence of the 0.3M LiPF\(_6\). Once again, there is no evidence that a new crystalline phase forms containing the LiPF\(_6\) salt for these samples.
Fig. 6-2. DSC heat traces (5 °C min⁻¹) of (1-\(x\)) PY₁₄TFSI-(\(x\)) PY₁₃FSI-0.3M LiX mixtures: (a) 
\[ X = \text{TFSI}^- \] and (b) \( X = \text{PF}_6^- \).
Fig. 6-3 indicates that as the PY$_{13}$FSI mole fraction increases ($x$ increases), the thermal stability of the mixtures decreases (the onset point for mass loss (1 wt%) is about 219-231 °C for PY$_{13}$FSI and 350 °C for PY$_{14}$TFSI). Note that approximately 8-12 wt% of the sample mass remains after decomposition for the $x = 1$ samples and no mass remains after decomposition for the $x = 0$ samples, which is in agreement with what was reported in Chapter 3. For the $x = 0.255, 0.370, 0.477$ and 0.578 samples, a second thermal process beginning near 300 °C and finishing near 500 °C.

Fig. 6-3. Variable-temperature TGA traces (5 °C min$^{-1}$) of (1-$x$) PY$_{14}$TFSI-($x$) PY$_{13}$FSI-0.3M LiX mixtures: (a) X = TFSI$^-$ and (b) X = PF$_6^-$ (N$_2$ atmosphere).
6.3 Conclusions

The addition of small amounts of PY$_{13}$FSI to the PY$_{14}$TFSI-LiTFSI (or LiPF$_6$) electrolytes greatly hinders the ability of the samples to crystallize. The thermal stability of the mixtures is reduced somewhat by the addition of the PY$_{13}$FSI, but remains quite acceptable for Li battery applications. Thus, the use of mixed ILs for such electrolytes appears to be a promising approach to optimizing the properties of electrolytes for advanced Li batteries.

References


Chapter 7. Future Advanced Electrolytes for Li-Ion Batteries

7.1 Overview

The battery electrolyte for PHEVs and EVs must function over a wide temperature range. A reasonable, practical low temperature limit for transportation applications is -30 °C. In addition; the ideal Li-ion battery electrolyte should have high chemical, thermal and electrochemical stability, and be inexpensive and nontoxic. Current electrolytes are composed of organic carbonate solvent mixtures and LiPF$_6$ as the lithium salt. They have very good properties/performance, such as high anodic stability, excellent passivation between the electrolyte and graphite anode, reasonably good cycle life, high ionic conductivity, etc. However, such state-of-the-art electrolytes display poor performance below -10 °C. The electrolyte tends to have stronger solvation interactions at low temperatures, which requires more energy for desolvation (thus decreasing the conductivity and increasing the interfacial impedance). Such electrolytes also vaporize at high temperature, which limits their use for high temperature applications. In addition, LiPF$_6$ decomposes thermally to LiF and PF$_5$, and the latter reacts readily with trace water to form HF and POF$_3$. Another problem with LiPF$_6$ is its thermal reactions with solvents, which are very exothermic and form highly toxic organofluoro compounds. Key among battery research objectives is the need to identify novel electrolyte solutions/materials for advanced Li-ion batteries that can function over a wide temperature range and improve the safety of the battery.

One of the tremendous advantages of IL-LiX mixed salt electrolytes is the absence of volatile, flammable organic solvents. Such mixtures have been demonstrated to have
negligible volatility/flammability. These favorable safety characteristics sharply contrast with
the properties of the state-of-the-art mixed-carbonate solvents used with LiPF6 for which
exploding Li-ion batteries are well known. The conductivity of the binary IL-LiX mixtures,
however, is low relative to the state-of-the-art electrolytes utilized now in commercial Li-ion
batteries. This limits the power (rate at which energy can be recovered) of the battery—a
significant problem with the need for current electronics and electric motors for high power.
To overcome this problem (as well as to form a solid-electrolyte-interface (SEI) layer with
carbon electrodes, if necessary), aprotic solvents may be used as an additive to the IL-LiX
electrolyte (Fig. 7-1) (added in small amounts to tune the properties).

Two different (1-x) PY15TFSI-(x) LiTFSI compositions with x = 0.10 or 0.50 were
therefore selected for study with the solvents ethylene carbonate (EC) or diethyl carbonate
(DEC) added. The x = 0.50 composition has 5 times the number of Li⁺ cations as the x = 0.10
composition with half of the cations in the mixture being Li⁺ cations. Such high LiTFSI
compositions are not generally used, however, due to the high Tm for such mixtures. The
incorporation of small amounts of solvent, however, overcomes this problem. How the
addition of organic solvents affects the electrolyte properties/characteristics has been
examined.
Fig. 7-1. Summary of research approach to modify the IL-based electrolytes.

### 7.2 Results and Discussion

Raman spectroscopy was used to explore the anion and solvent (EC) coordination in the mixtures (Fig. 7-2). The EC ring breathing band near 895 cm\(^{-1}\) (for uncoordinated solvent) is strongly affected with a new peak present at 905 cm\(^{-1}\) for the EC molecules coordinated to Li\(^+\) cations (there is also an anion band present near 902 cm\(^{-1}\)). The anion bands indicate that the addition of solvent significantly reduces the number of AGG solvates (747 cm\(^{-1}\)) present resulting in a large increase in CIP or SSIP (uncoordinated anions) solvates (742 cm\(^{-1}\)). The Li\(^+\) is preferentially coordinated by the carbonyl oxygens of the EC (904 cm\(^{-1}\)) rather than the TFSI\(^-\) anions (747 cm\(^{-1}\)). For the solvent-rich mixtures (high y values), these solvent data
indicate that dilute mixtures with the \( x = 0.10 \) composition contain a significant amount of uncoordinated (or 'free') solvent. In contrast, much less free solvent is present for the \( x = 0.50 \) samples, even in the dilute mixtures, due to the high concentration of LiTFSI. For the salt-rich mixtures (low \( y \) values), however, only a small amount of the solvent (if any) is uncoordinated, particularly for the \( x = 0.50 \) mixtures.
Fig. 7-2. Raman spectra of (1-\(y\)) \([((1-x)\ PY_{15}TFSI-(x)\ LiTFSI]-y)\) solvent mixtures at 20 °C.

The thermal phase behavior of the mixtures with EC is shown in Fig. 7-4. For the \(x = 0.10\) samples, all of the mixtures could be readily crystallized. The \(T_m\) of the IL-LiX mixtures decreases upon the addition of low mole fractions of EC. Similarly, the \(T_m\) of pure EC is
decreased upon the addition of the IL-LiX mixture. A new peak is observed at about -16 °C, which is due to the IL-EC eutectic composition. The peak is not evident for low $y$ values ($y \leq 0.30$) because most or all of the EC molecules available are coordinated to the Li$^+$ cations. No more than four EC molecules, however, can coordinate a Li$^+$ cation so for higher $x$ values where there is excess EC and IL present, the eutectic phase forms.

The DSC heating traces of the $x = 0.50$ mixtures with EC, however, do not show a peak due to this eutectic composition (Fig. 7-3). The formation of this phase is inhibited by the much larger fraction of LiTFSI present (this is no bulk IL present in the mixtures). In fact, many of the samples could not be crystallized despite cycling/annealing the samples extensively at subambient temperature upon the addition of even a small amount of EC. Instead, most of the samples formed an amorphous glassy phase at low temperature. The $T_g$ values for these mixtures are quite low given the large amount of LiTFSI salt that is present. The glass transition ($T_g$) tends to decrease with increasing fraction of EC.
Fig. 7-3. DSC heating traces (5 °C min⁻¹) of (1-y) [(1-x) PY₁₅TFSI-(x) LiTFSI]-(y) EC mixtures - (left) x = 0.10 and (right) x = 0.50 (y is mole fraction of the solvent). $T_m$ and $T_g$ temperatures are noted.

Fig. 7-4 shows the ionic conductivity of the mixtures with EC. Although most of the $x = 0.50$ samples with EC could not be crystallized for the DSC measurements (sample size: 10-20 mg), these samples did crystallize prior to the conductivity measurements when the mixtures (sample size: ~1 g) were stored overnight at -40 °C. As noted previously, the inhibition of crystallization is a highly desirable feature for practical electrolytes as this
prevents the Li\textsuperscript{+} cations from getting trapped in a solid crystalline phase with negligible conductivity.

The conductivity does not change much with increasing EC content at higher temperature. At low temperature, however, the conductivity increases rapidly for modest amounts of added EC. For example, at -40 °C, the conductivity of the $x = 0.10$ mixtures reaches a maximum when $y = 0.60$ and that for the $x = 0.50$ mixtures reaches a maximum when $y = 0.70$. Although the conductivity of the $x = 0.50$ samples is notably lower than that of the $x = 0.10$ samples, the values become quite reasonable ($> 10^{-3}$ S cm\textsuperscript{-1}) for modest amounts of added EC ($y \sim 0.70$ at 20 °C) (about 3-5 EC per Li\textsuperscript{+} cation). The negligible amount of excess (uncoordinated) solvent present for these latter electrolytes results in the electrolyte having low volatility and flammability (Fig. 7-5), but much improved transport properties.
Fig. 7-4. Ionic conductivity of \((1-y) \[(1-x) \text{PY}_{15}\text{TFSI}-(x) \text{LiTFSI}]-y\) solvent mixtures. The temperature (°C) and Li/EC ratio are indicated.

TGA measurements were used to examine the volatility of the solvent and thermal decomposition of the mixtures (Fig. 7-5). DEC and EC were added to the PY\(_{15}\text{TFSI}\)-LiTFSI
mixtures for comparison. The PY$_{15}$TFSI-LiTFSI portion of the samples decomposed rapidly at approximately 400 °C. The mass loss of the mixtures at lower temperature is due to solvent vaporization. DEC has a lower boiling point ($T_b = 126$ °C) than EC ($T_b = 260$ °C).

The solvents are volatilized from the mixtures at a much lower temperature than the $T_b$ of the respective solvents. With increasing LiTFSI content in the mixtures, the solvent is retained until a much higher temperature. This is due to the coordination of the solvent molecules to the Li$^+$ cations (although many anions are present, they are weakly coordinating and thus easily replaced by the solvent molecules in the Li$^+$ cation coordination sphere). (1-$x$) EC-$x$ LiTFSI mixtures (without ILs) form a variety of crystalline phases. In particular, highly concentrated LiTFSI mixtures form an AGG 1/1 EC/LiTFSI phase ($x = 0.50$) for which the solvate crystal structure has been determined. In this structure, each Li$^+$ cation is coordinated to three anions (by four oxygen atoms) and a single EC molecule through the solvent's carbonyl oxygen. These crystal structures provide models for the interactions that can be expected in the IL-LiX-solvent mixtures. Thus, the solvent does not behave like bulk solvent when enough LiTFSI is available to be coordinated by all or most of the solvent. This results in the volatility of the solvent being dramatically reduced relative to the conventional solvents used in Li-ion batteries.
Fig. 7-5. TGA heating traces (5 °C min⁻¹) of (1-y) [(1-x) PY₁₅TFSI-(x) LiTFSI]-y solvent mixtures.

7.3 Conclusions

The sluggish crystallization of the concentrated LiTFSI mixtures is a very positive feature for practical battery electrolytes. It is likely that crystallization can be completely prevented if mixtures of ILs, LiX salts and/or solvent are used for concentrated electrolytes. Such mixtures contain a greater amount of Li⁺ cations than conventional electrolytes, retain the
solvent much better at elevated temperature and are essentially nonflammable. Therefore, electrolytes consisting of concentrated LiX salts mixed with one or more ILs and modest amounts of aprotic solvents may be promising electrolytes for the large-format batteries intended for PHEVs and EVs. Further, many applications will benefit from the ability to tailor the electrolyte or IL viscosity with aprotic solvent additives including chemical synthesis and processing, lubricants, electromechanical actuators, sensors, light-emitting electrochemical cells, etc. This study significantly advances the knowledge of how IL ion structure and the influence of additives determine critical electrolyte physical properties.

References


Chapter 8. Conclusions and Future Work

This dissertation is unique in exploring how molecular-level interactions from varying ion structure impact the physical and chemical properties of ILs and their mixtures with lithium salts, thus enabling the optimal selection of ILs for battery electrolytes and electrochemical capacitors. This project has involved extensive experimental work and characterization (chemical synthesis/purification, glove box utilization, materials analysis (TGA, DSC, NMR, XRD, Raman and UV-VIS spectroscopy), and electrochemical impedance spectroscopy measurements), hypothesis formulation, data analysis, and collaborative work. The relationship between cation and anion structure and the corresponding thermal phase behavior and transport properties of IL-based battery electrolytes has been comprehensively investigated. The thermal phase behavior, thermal stability and other properties (viscosity, density and conductivity) are reported in this dissertation for the neat ILs containing IM_{10R}^+ (R = 1, 2 and 4 for methyl, ethyl and butyl, respectively) cations or PY_{1R}^+ (R = 3-5) cations with TFSI^- or FSI^- anions, as well as their mixtures with LiTFSI or LiFSI salts. Ternary (three component) electrolytes (1-x) PY_{14}TFSI-(x) PY_{13}FSI-0.3 M LiX (X = TFSI^- and PF_6^-) mixtures and (1-y) [(1-x) PY_{15}TFSI-(x) LiTFSI (with x = 0.10 and 0.50)]-(y) solvent (EC or DEC) mixtures have also been examined.

From a fundamental point of view, the Li^+ cation solvation process is crucial to understand because it governs the conductivity mechanisms and lithium transport number, i.e., properties of the electrolyte that are known to strongly affect the performance of Li batteries. The coordination of the Li^+ cations thus has been studied (using crystal structures
and spectroscopy) in detail. The phase behavior of IL-LiX mixtures is complicated. Many IL-LiX mixed salt crystalline phases (e.g., 2/1, 1/1 and 1/2 IL/LiX) are able to form in which the Li$^+$ cations are coordinated by anion oxygen atoms and the organic cations remain either uncoordinated or have weak hydrogen bonding to anions. Some crystalline phases are metastable, while other mixtures are unable to be crystallized (a crystallinity gap exists for specific compositions). With increasing concentration of LiX, the thermal stability of the IL-LiX mixtures improves, the viscosity increases, and the conductivity decreases due to the Li$^+$...anion coordination. The use of limited amounts of molecular solvent as additives to IL-based electrolytes to improve the transport properties, while retaining the low flammability/nonvolatility features, is a promising means of moving the work from a fundamental insight investigation to practical electrolyte materials.

The electrolyte makes up only a portion of the complex Li-ion battery system that must be considered when designing a cell/battery. Many features such as the electrodes, SEI (solid-electrolyte interface) layer formation, separator, current collector, corrosion resistance, etc. need to be taken into account, as all are influenced by the choice of electrolyte materials and are critical for the successful application of new materials in a battery. Li-ion battery technology will almost certainly dominate future transportation applications, but many limitations must be overcome for this to become a reality. The work reported here explores and demonstrates the advantages/limitations of ILs for the demanding application of advanced lithium battery electrolytes.