Ionic Liquids and their Applications in Lithium Batteries

Christopher Daly Literature Seminar November 21, 2013

Water is the most abundant molecule in the world and completely integral to living systems; it is known as the 'universal solvent.' However, other solvents have often been used for scientific processes, as a result of needs for differing polarities, boiling points etc. These solvents are other small molecules that are in the liquid phase at room temperature. Over the past 15 years, there has been a surge of interest in ionic liquids (Fig. 1), an alternative solvent with many interesting qualities. First discovered in 1914[2] and patented in 1934,[3] ionic liquids are very different than conventional liquids and have exhibited unique properties that provide possible solutions to current problems in several fields or research.

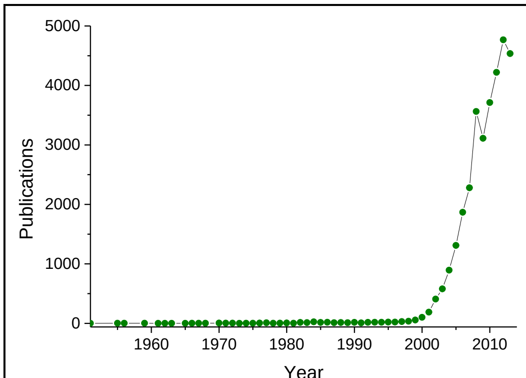

Figure 1. Graphical display of the literature publications per year with the term "ionic liquid" in the title, abstract, or key words. *Note: 2013 is not yet over.*[1]

Ionic liquids are, quite simply, liquids that are composed of ionic species, and most examples consist of only one cation and anion pair. They used to be called molten salts, but that term has since been abandoned due to the false implication of a high temperature, corrosive, viscous fluid. The term ionic liquid, or low melting ionic liquid, is now used to describe an ionic system that is liquid below 100°C. Many ionic liquids are liquids at room temperature and have even been shown to have melting temperatures as low as -96°C.[4]

To further elucidate these liquids, it is helpful to describe a prototypical ionic liquid system. One of the first developed ionic liquid systems is a combination of 1-ethyl-3-methylimidazolium chloride ([EMI]Cl) and aluminum chloride ($AlCl_3$) (Fig. 2).[5] The $AlCl_3$ will complex with the chloride from the [EMI]Cl to yield $[EMI]^+$ and $AlCl_4^-$.[5] The $[EMI]^+$ cation is still one of the more commonly used, and other cation derivatives are very similar. There has been expansion of the diversity of the anions in recent years, however. Now, a typical anion in an ionic liquid system is the *N*,*N*-bis(trifluoromethane)sulphonamide (TFSI) anion (Fig. 2).[6] It has been shown that ionic liquids behave somewhat similarly to water or other dilute electrolyte solutions, having freely dissociated 'ions' which are just cation anion pairs that have dissociated from each other.[7] There are two basic chemical properties that allow these ionic systems to be liquid below 100°C unlike most ionic systems. Generally, the cation must be large and asymmetrical, and the anion must have delocalized charge.[6] These two properties prevent ordered crystal structures in the liquid.

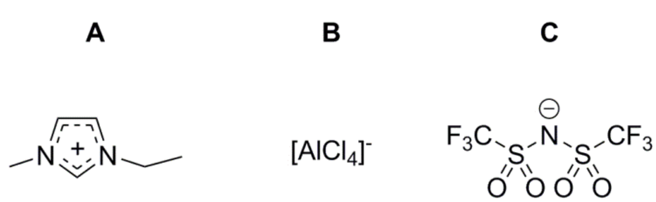

Figure 2. Schematic of some commonly used ions in ionic liquids. A) $[EMI]^+$ cation. B) $AlCl_4^-$ anion. C) TFSI anion.[5,6]

Surprisingly, many reactions can be performed normally in ionic liquids, and some reactions have even displayed higher yields than in conventional solvents.[8] However, it does not require an advanced chemistry background to realize that chemical interactions in an ionic liquid medium, rather than a molecular solvent, will bring drastic changes. These differences lead to some very useful properties in some cases. The advantages, when compared to molecular solvents exhibit:[2,4,5,9]

1) little to no vapor pressure below 100°C,
2) many possible combinations of ions (known as the 'designer solvent'),
3) wide potential windows,
4) non-flammable behavior,
5) ability to exclude water,
6) high conductivity, and
7) high solubility of metal salts.

These advantages have led to acknowledgement of the potential for ionic liquids to provide a valuable alternative solvent option.

The first two advantages are the most discussed in a general sense (not specific to an application). Many molecular solvents have high vapor pressures, leading to release of volatile organic compounds (VOCs) which are harmful to the environment. VOC emissions currently hinder large scale syntheses in industry,[10] so ionic liquids are seen as 'green' solvents due to their low vapor pressures. Even though there are ionic liquids that are fairly non-toxic, the 'green' solvents moniker can be misleading, as many ionic liquids are extremely toxic.[11] Ionic liquids are highly tunable; both changing the ratio of cation to anion and using a different cation or anion can drastically change solvent properties. For molecular solvents, there is not much that can be done to change or tune the properties of the solvent. Not readily apparent before comparison to ionic liquids or other alternative solvents, the lack of tunability for these conventional solvents means that the science is dictated by an underwhelming selection of solvents, rather than enabled through careful solvent selection. There are over a million potential two-component systems of ionic liquids as compared to about six hundred molecular solvents used today.[4]

The rest of the advantages (3-7) listed above have all lent themselves to various applications, both in academic literature and industry. The wide potential window, non-flammability, high conductivity, and dissolution of metal salts make these liquids an intriguing option for electrolytes in lithium batteries, which is discussed in more detail below.[12,13] The ability to dissolve metal salts while excluding water has led to the attempt to use ionic liquids to deposit metals that don't often deposit well in water, such as aluminum.[9] Surprisingly, one of the more promising fields for application of ionic liquids is in biofuel cells using cellulose.[6] There have already been moderate successes designing an ionic liquid that solubilizes cellulose at room temperature[14] and stabilizes the enzymes necessary for the cellulose breakdown,[15,16] an interesting advance for a solvent that is not water. The chemical company, BASF, has been using ionic liquids in an acid scavenging process called BASIL (biphasic acid scavenging using ionic liquids) for a decade now, showing that ionic liquids have potential, at the least, to be used in a commercial sense.[17]

One of the more interesting and exciting applications for ionic liquids is as an electrolyte medium in Lithium batteries. Due to constantly increasing energy demands, supply limits, and adverse environmental effects of consumption of the more prevalent energy sources today, alternative energy sources and energy storage are imperative fields of advancement for science today.[18] An important problem with the common lithium battery electrolyte media, ethylene carbonate-dimethyl carbonate (EMC-DMC), is that it does not conduct ions very well.[9] One of the other important limits in current electrolyte media of lithium batteries is that there is a narrow potential window. It has been shown that an accidental overcharge in the EMC-DMC lithium batteries can force rampant oxidation that leads to device failure. Figure 3 shows that ionic liquids can have a wide potential window, at least compared to water.[2]

However, it has been shown that there may actually be recurring side reactions in the lithium battery cell,[13] though advances have been made in aprotic quaternary ammonium salts to solve this problem.[19] The main advantage for use of ionic liquids in lithium ion batteries is in safety. The aforementioned unwanted side reactions with the EMC-DMC organic electrolyte can cause fire or even explosion in the event of a short circuit or overcharge. While not an issue for small-scale batteries, large-scale energy storage requires a solution to the safety issue for use of lithium batteries.[6] Ionic liquids are more stable, non-volatile, and non-flammable. There are important advances being made in the inclusion of ionic liquids in both lithium-ion batteries and lithium-air batteries.[20] The conductivity and potential windows of ionic liquids seem to be generally comparable to the EMC-DMC organic electrolyte, and the stability of ionic liquids is better, but it remains to be seen if the cost and performance can be optimized to allow for commercial use.

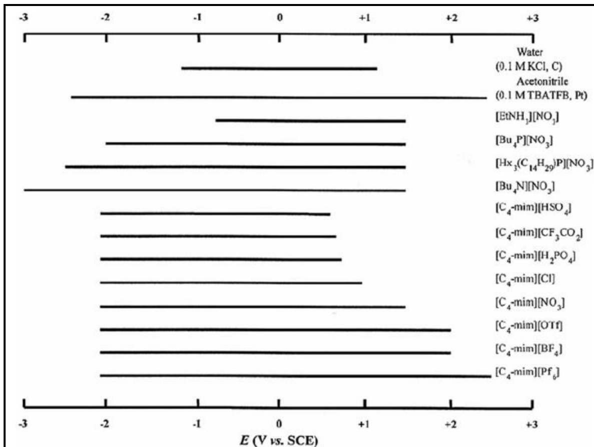

Figure 3. Graphic showing potential windows of common ionic liquids against aqueous water.[2]

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