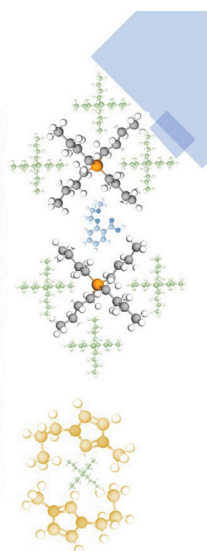
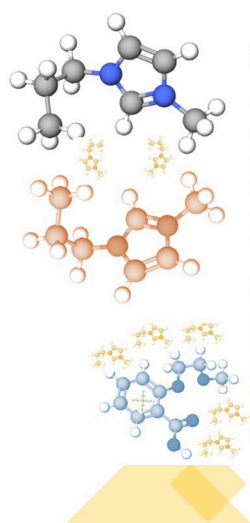


Fluorine-Free Ionic Liquids and Electrolytes

From Synthesis to Energy Storage Applications



Mukhtiar Ahmed

Chemistry of Interfaces

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SUMMARY

Since their introduction by Sony in 1990, lithium-ion batteries (LIBs) have acquired a sizable market share. They have the best energy densities, a high open circuit voltage, a low self-discharge rate, no memory effect, and a slow loss of charge when not in use. These properties make them the most popular rechargeable batteries for portable gadgets, electric vehicles and aerospace applications. They do, however, pose major safety issues since the conventional electrolytes are made of fluorinated salts dissolved in volatile organic solvents, the former being meta-stable at ambient temperature and the latter being flammable with a high vapour pressure. Thus, there is an urge to develop thermally and electrochemically stable non-fluorinated electrolytes to improve the safety and performance of batteries. Electrolytes based on ionic liquids (ILs) offer a range of advantages over traditional electrolytes including low volatility and high thermal and electrochemical stabilities, and can additionally be made fluorine-free and task-specific. In addition, the transport properties of ILs can be controlled by structural design of chemical functionalities to reduce the ionic interactions and enhance the ion mobilities.

This thesis is focussed on the development of new fluorine-free ILs and electrolytes for safer energy storage applications. An overview of synthesis, physicochemical and electrochemical characterizations of six different families of ILs and their structurally analogous electrolytes based on the aromatic heterocyclic rings, oligoether based aromatic and aliphatic carboxylates, oligoether phosphates and aromatic sulfonyl anions coupled with *n*- tetrabutylphosphonium-, imidazolium-, pyrrolidinium -based and alkali metal cations is presented. The structures and purity of the new anions, their intermediate products and the ILs are characterized by using multinuclear NMR, FTIR and mass spectrometry. These studies are further complemented by using NMR diffusometry to investigate the relative anion and anion mobilities and understand the possible interaction mechanisms between the oppositely charged ions within the ILs and the electrolytes, and especially, the influence of Li⁺ addition in the IL-based electrolytes. Among the synthesized ILs, the aromatic oligoether-based ILs showed the best electrochemical stabilities and aromatic sulfonyl-based ILs exhibited highest ionic conductivities and thermal stabilities.

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Mukhtiar Ahmed

List of papers

This thesis is based on the following six papers:

- (I) Aromatic Heterocyclic Anion Based Ionic Liquids and Electrolytes
Mukhtiar Ahmed, Soniya Rao, Andrei Filippov, Patrik Johansson, and Faiz Ullah Shah
Phys. Chem. Chem. Phys., 2023, 25, 3502-3512

- (II) Ionic Liquids and Electrolytes with Flexible Aromatic Anions
Mukhtiar Ahmed, Andrei Filippov, Patrik Johansson, and Faiz Ullah Shah
Chem. Eur. J., 2023, 29, e2023010

- (III) Pyrrolidinium- and Imidazolium-Based Ionic Liquids and Electrolytes with Flexible Anions
Mukhtiar Ahmed, Andrei Filippov, Patrik Johansson, and Faiz Ullah Shah
(*Manuscript*)

- (IV) Ambient Temperature Liquid Salt Electrolytes
Sourav Bhowmick, **Mukhtiar Ahmed**, Andrei Filippov, Laura C Loaiza, Faiz Ullah Shah and Patrik Johansson
Chem. Comm., 2023, 59, 2620

- (V) Sweet Ionic Liquid Electrolytes for Supercapacitors
Mukhtiar Ahmed, Gaurav Tatari, Andrei Filippov, Patrik Johansson, and Faiz Ullah Shah
(*Manuscript*)

- (VI) Flexible Sweet Ionic Liquids and Electrolytes
Mukhtiar Ahmed, Natsuki Morimoto, Andrei Filippov, Patrik Johansson, and Faiz Ullah Shah
(*Manuscript*)

My contribution to the papers:

- (I) I designed the study together with my supervisors, performed all the synthesis and analyses except for computational study and PFG NMR, in which I partly participated during experiments. I authored the first draft and finalized it with comments from the co-authors.
- (II) I planned all the work with the consents of my supervisors, synthesised all the compounds, performed all the analyses and experiments except for PFG NMR, in which I partly participated during experiments. I wrote the first draft and finalized it with comments from the co-authors.
- (III) I designed the study together with my supervisors, carried out all the synthesis, performed all the analyses and experiments except for PFG NMR, in which I partly participated during experiments. I wrote the first draft of the manuscript and finalized it with comments from the co-authors.
- (IV) Took part in the idea development, synthesis especially in the initial stages, experiments, and analysis data. I was also partially involved in writing at revising stage.
- (V) I planned the initial project with my supervisors, carried out all the synthesis and performed all the analyses and experiments, except for PFG NMR and super capacitor studies, in which I partly participated during experiments. I wrote the first draft of the manuscript and finalized it with comments from the co-authors.
- (VI) I designed the study together with my supervisors, carried out all the synthesis, performed all the analyses I wrote the first draft of the manuscript and finalized it with comments from the co-authors.

To my Grand Mother (Dadi)
Sorry, I was not with you at your last
breath.

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1. Introduction

The continual rise in world's population, as well as societal economic and technical progress, has resulted in an increase in global energy demand, posing severe problems and environmental challenges. The vast extraction and consumption of fossil fuels, resulting in CO₂ emissions and pollution into the atmosphere, have hasten global climate change.¹ As a result, the use of renewable energy sources such as solar and wind energy is gaining emphasis to minimize greenhouse gas emissions. To compete with the most utilized fossil fuels, energy provided by fundamentally discontinuous and intermittent renewable sources requires effective storage for grid stability and global distribution.^{2,3}

To this end, the development of rechargeable batteries with high energy and power density, fast cycling rates, long service life, and made of economical materials could enable a gradual shift to ecologically friendly energy supply in the near future.^{4,5} Furthermore, replacing internal combustion engines with zero-emission electrified systems *i.e.* electric vehicles (EVs) on a wide scale might reduce greenhouse gas emissions even further.⁶ Preliminary efforts in this direction have already been made, with environmental regulations in place in numerous countries that encourage the use of EVs through consumer incentives.⁷ However, in order to compete with the traditional vehicles, the real dissemination of EVs is dependent on the development of energy storage systems with high volumetric and gravimetric energy and power densities, safety and cost.⁸

Different types of batteries are being created and used based on different sorts of redox mechanisms and chemistries such as lithium-ion batteries (LIBs), lead acid batteries (Pb-A), nickel cadmium batteries (Ni–Cd), and Ni–MH (nickel metal hydride batteries) are just few examples of the most common batteries.⁹ Among all, LIBs, are the most versatile and appealing energy storage systems and have triggered the global scale diffusion of a vast array of portable electronic devices, the demand of which is exponentially increased during the last 25 years, and will continue to be the most compelling choice not only for EVs but also other energy storage applications.¹⁰ Significant efforts are being made by both academia and industry to produce new generations of batteries that are suitable for the upcoming challenging applications in terms of gravimetric and volumetric power density, energy density, durability, as well as sustainability and environmental compatibility.^{11,12}

However, the safety issues are mainly related to flammability of the conventional electrolytes that are currently being used in LIBs. This drawback is progressively becoming even more serious, as the size of LIBs increases for their use in large energy storage devices such as hybrid electric vehicles (HEVs), and energy storage systems (ESSs) for smart grids.^{13,14} Figure 1 depicts the increase in demand for LIBs from 19 gigawatt hours (GWh) in 2010 to 285 GWh in 2019, and expected to reach 2,000 GWh by 2030, accounting for around 8% of the global energy supply. In terms of installed capacity, passenger and commercial electric cars continue to be the most common applications for LIBs, followed by stationary (energy) storage.¹⁵

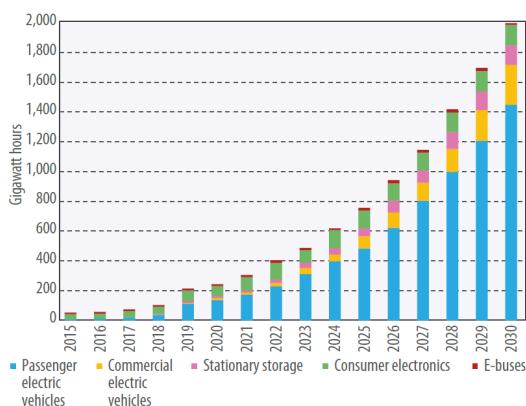


Figure 1. Global LIB materials demand forecast from electric vehicle sales, 2015–2030 (thousands of tonnes, GWh). Adapted from ref. 15.

2. An Electrolyte

An electrolyte acts as a medium between the two electrodes to transport ions and to compensate the charge of redox reactions occurring inside the anode and cathode.¹⁶ Although an electrolyte is not directly engaged in a charge-storing redox process and neither directly influence the voltage or capacity of a battery, it is an important component with a significant impact on the overall performance and safety of any battery.¹⁷ The separation of oxidation and reduction in electrochemical processes is intrinsically dependent on charge compensation *via* ionic currents. Because ion transport is often much slower than electron transport, the power output is directly tied to the electrolyte's ion transport capabilities.¹⁸ Even more crucially, while the electrolyte is not engaged in charge-storing redox processes, it does take part in other redox events, and the harsh electrochemical environment of high-energy-density LIBs eventually leads to an electrolyte (side) reactions, which put extra responsibilities on the electrolyte and to perform,

all of which must be executed flawlessly.¹⁹ Figure 2 shows schematic of a typical LIB comprising a cathode, an anode, a separator and an electrolyte.²⁰

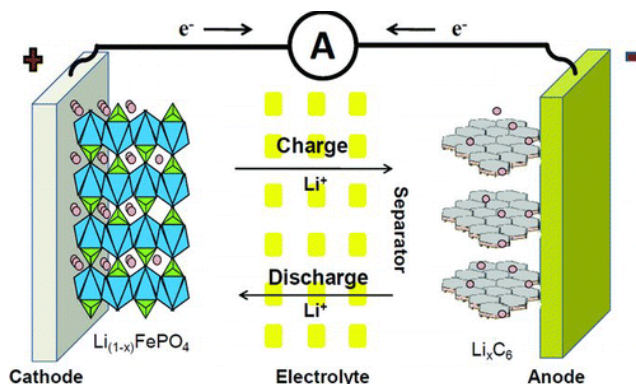


Figure 2. Schematic of a lithium-ion battery. Adapted from ref. 20.

Certain characteristics must be considered while developing an electrolyte system for an energy storage device in general, and LIBs in particular, which are enlisted below²¹;

- a. To prevent the side reactions such as breakdown of an electrolyte, the electrolyte should be chemically and electrochemically stable. The chemical and electrochemical instability of an electrolyte results in an irreversible charge loss due to the salt depletion and ion conduction obstruction, lowering the overall ionic conductivity.
- b. To decrease cell polarization at high current densities, the electrolyte should provide high ionic conductivity ($> 10^{-3} \text{ S cm}^{-1}$). The amount of charge carriers (salt concentration) and the mobility of ions, which is affected by viscosity of the electrolyte, affects ionic conductivity. With a significant concentration of the ionic salt and a low solvent viscosity, high ionic conductivity may be achieved.
- c. The electrolyte salt should exhibit minimum ionic interactions to prevent ionic interactions and thus provide high ion mobility and ionic conductivity.
- d. The electrolyte should remain liquid over a wide temperature range. The temperature range necessary to keep an electrolyte in a liquid state has a direct impact on the operational temperature range of the rechargeable batteries. Because ions mobility is restricted in the solid form, the ionic conductivity of a liquid electrolyte drops dramatically when solidified at lower temperatures.
- e. The ions of an electrolyte should be small, which not only affect the volumetric and gravimetric energy densities, as well as the total cost of energy storage.

- f. In last but not the least, an electrolyte should be nontoxic. Because the electrolyte may come in contact with the users in the event of a leakage, a non-toxic electrolyte is essential for mobile devices.

2.1 Problems with Conventional Electrolytes

Typically, an electrolyte is made by dissolving a lithium salt such as LiPF_6 in organic solvents such ethylene carbonate (EC) combined with linear aliphatic carbonates, primarily dimethyl and/or diethyl carbonates (DMC and DEC).^{22,23} In this case, the electron-withdrawing effect of the fluoride's aids in the distribution of negative charges, decreasing the lattice energy of the salt, promoting ion dissociation, and facilitating salt dissolution in common organic solvents.²⁴ It is worth mentioning here that, the use of graphite as an anode material was made possible exclusively by the discovery that when EC reductively degraded at the graphite surface creating a stable, electrically insulating, but ionically conducting solid electrolyte interphase (SEI).²⁵ This electrolyte solution has undoubtedly contributed to the tremendous commercial success of LIBs over the last 25 years, and it is undoubtedly an excellent system for small-scale portable electronic devices. However, for large-scale applications such as EVs, raise valid issues about safety in various perspectives, which are detailed below one by one.²³

2.1.1 Flammability

The organic solvent-based liquid electrolytes of LIBs are flammable by nature. The cascading thermal runaway event, which is regarded as the primary source of battery safety issues, is one of the most catastrophic failures of the LIB systems. Thermal runaway occurs when an exothermic process becomes uncontrollable. When the temperature of the battery rises over *ca.* 80°C, the rate of exothermic chemical reaction inside the battery increases, further heating the cell and thus resulting in a positive feedback cycle. The continuously rise in temperature, particularly in the case of large battery packs, may result in fire and explosion. Understanding the underlying causes and processes of thermal runaway can thus help in the design of new functional and safer electrolytes to improve the safety and durability of batteries.²⁶ The thermal runaway process may be separated into three stages, as shown in Figure 3.

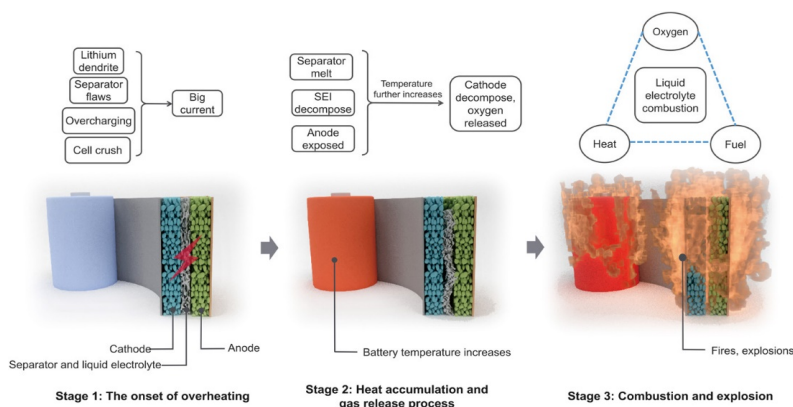


Figure 3. The three stages of the thermal runaway process of a battery cell. Adopted from ref. 26.

Stage 1: The onset of overheating. The battery changes from a normal to an abnormal state, and the internal temperature starts to increase. Stage 2: Heat accumulation and gas release process. The internal temperature quickly rises, and the battery undergoes exothermic reactions. Stage 3: Combustion and explosion. The flammable electrolyte combusts, leading to fire and even explosion.

2.1.2 The Fluorine Content

The conventional electrolyte salt, LiPF_6 , contains about 75% fluorine content by weight, which is proven to decomposition at elevated temperature producing PF_5 and LiF , the former rapidly reacts with traces of water to release HF and PF_3O (Figure 4).¹⁷ These decomposition products are extremely reactive towards both cathode and anode, adversely affecting the performance of a battery cell.²⁷ Fluorinated electrolyte components are also a source of worry during battery recycling, since they can pose major safety and environmental risks during handling and processing, including the release of poisonous HF and PF_5 . Fluorine appears to be unavoidable in traditional battery systems, not only as a part of the electrolyte but also widely used as a component of binder in the form of polyvinylidene difluoride (PVdF).²⁸ With such a large level of fluorine contents in batteries, a slew of concerns arises, not only in terms of the battery cell performance, environmental and occupational safety but also at the recycling stages.¹⁷

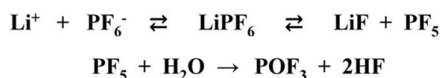


Figure 4. The decomposition pathway of LiPF_6 .

2.1.3 The Possible Solution

Keeping in mind the problems associated with fluorine contents and flammability of the conventional electrolytes, creating non-fluorinated and non-flammable electrolytes is becoming an essential task to improve safety of electrolytes. Such fluorine-free electrolytes must meet a number of requirements including high thermal and electrochemical stabilities and high ionic conductivity. The emphasis has consequently been on developing fluorine-free electrolyte salts with weakly coordinating anions, in which the charge is delocalized over the anion and thus the dissociation energy is reduced.²⁹ Many of these non-fluorinated salts have been revealed higher thermal and electrochemical stabilities and proven to be competitive with "conventional" battery electrolytes in terms of ionic conductivity. Another important feature of the LiPF₆ electrolyte system is its ability to passivate aluminum cathode current collector, owing to its fluorine atoms.¹⁷

The fundamental issue with fluorine-free electrolyte salts is their poor performance at high potentials in passivating the aluminum, although corrosion tests using LiBOB-based electrolytes have demonstrated that the [BOB]⁻ anion may passivate aluminum in the same way as [BF₄]⁻ or [PF₆]⁻ anions.³⁰ This passivation is hypothesized to be due to the formation of borate-containing species on aluminum, particularly AlBO₃, as revealed by Electrochemical Quartz Crystal Microbalance (EQCM). These findings suggest that fluorinated electrolytes are not always necessary for aluminum passivation and there is a clear possibility of developing fluorine-free electrolytes. In addition, developing fluorinated-free electrolytes would be a significant step towards developing more recyclable batteries with lower environmental concerns. Extensive research efforts are being made in recent years to identify and develop new electrolytes that might potentially address the problems associated with fluorinated electrolytes. Electrolytes based on ionic liquids (ILs) in general offer a range of suitable advantages including low volatility, high thermal and electrochemical stabilities, high ionic conductivity and can additionally be made fluorine-free and task-specific. The synthetic diversity allows for the design of appropriate functional groups with specific properties.^{31,32}

3. Ionic Liquids

In this section, I will start with brief history and background of ionic liquids (ILs, followed by a discussion of some of their basic structural features with respect to the role of cation and anions on overall physicochemical properties and, the synthesis and purification procedures of IL. Following that, will explore role of IL as electrolytes and try to explain why fluorine-free IL -base electrolytes are beneficial as compared with over their fluorine counter parts, and will then finally conclude with a discussion onion of ambient liquid metal salts as next-generation electrolytes.

3.1 Brief History and Background

Ionic liquids (IL) are salts that melts below 100 °C or ambient temperature liquids referred as room temperature ionic liquids (RTIL), usually made up of bulky organic cation coupled with charge-delocalized inorganic/organic anions. Ethanolammonium nitrate was the very first IL discovered by S. Gabriel and J. Weiner in 1888.³³ The RTIL with a melting point of 12 °C introduced in 1914 by P. Walden was ethylammonium nitrate (EAN), which was created by neutralizing ethylamine with concentrated HNO₃.³⁴ EAN has physical properties comparable to water in that it is transparent, colorless and odorless but has a relatively higher viscosity. These early ILs were created to be utilized as solvent medium in high-temperature nuclear fuel reprocessing. However, due to their limited temperature range and chemical instability (as they rapidly interacted with air and moisture) and were not practicable.³⁵ Hurley and Wier have described the second generation of ILs made by combining alkylpyridinium chlorides with AlCl₃ in 1951.³⁶ Unfortunately, many of the second-generation ILs were not stable in the presence of moisture, highly corrosive, toxic, and regulating their acidity/basicity was a difficult task.³⁷

Later, in 1992, Wilkes and Zaworotko have introduced moisture- and air-stable ILs from imidazolium cations and tetrafluoroborate anion, the combination revealed much better physical properties than the previously known ILs.³⁸ The extra π -electrons of the imidazolium cation greatly enhanced the positive charge delocalization *via* the creation of a resonance structure, lowering the melting point significantly below ambient temperature. The [BF₄]⁻ anion is also chemically stable and relatively less reactive towards ambient moisture. Soon after this discovery, a research interest into ILs has been continuously growing and ILs have attracted the attention of academic and industrial researchers.

functional groups that engage in the reaction or process, giving rise to the idea of "task-specific ionic liquids"- in summary, ILs, promise a great level of flexibility.^{47,84} The diversity of ILs, on the other hand, is a double-edged sword. The challenge that invariably arises is selecting "*the ideal IL*" from the large chemical space for a specific application.

The majority of IL used in research and development are consists of fluorinated anions combined with the few very famous cations – pyrrolidinium, imidazolinium, sulfonium and phosphonium. The simplest way to create a new IL is to tailor the side chain on the cation with various alkyl, alkoxy, and branched chains. These modifications on the cation are good for some applications where specific groups are required, but they are ineffective for other applications, such as electrochemical ones, because the side chain has little impact on the cation's charge center, which is primarily involved in the process of redox reaction. These chains can only influence the ionic and other secondary interactions within bulk liquids; certainly, this can affect transport properties, but not electrochemical. For example, altering the side chain of an imidazolium cation while leaving the other group constant results in almost the same electrochemical stability window, but with significant difference in ionic conductivity.^{49,50} As previously stated, only a few families of cations are known on which the entire IL chemistry is based, and many other potential heterocyclic species in organic chemistry, such as oxazole, thiazole, triazole, piperazine, pyrazine, pyrazine, and many others, need to be explored further in IL chemistry. In summary – *IL chemistry needs more positive counter parts*. Anions have a distinct chemistry from cations since the negative charge is delocalized across the entire ion or on some regions of it. The attached group also has a clear impact on the charge delocalization, depending on whether the group is withdrawing or donating electrons. For instance, we found that shifting the heteroatom's position on an aromatic carboxylic acid ring significantly alters transport and electrochemical properties of ILs.⁵¹ We also found that for IL based on aromatic acids functionalized with oligoether side chains change their electrochemical and transport properties depending on how the oligoether chain is positioned in relation to the carboxylate group of anions.⁵² In summary – "*anions are negative but yet have a positive impact on overall properties of ILs.*"

3.3 Synthesis of Ionic Liquids

Synthesis of IL (which is the main topic of this thesis and "ILs" refer to aprotic ionic liquids hereafter) usually requires the reaction of anion and cation precure, and prior to reaction, these precursors are usually synthesised (and purified) separately. These three steps necessitate

separate synthetic procedures, with the last step often requiring direct neutralization or metathesis reaction or a direct alkylation reaction, which differ significantly from classic organic synthesis of molecular solvents and small organic molecules/salts, this step can be further be divided into two steps. The first step (which I refer to as the *cooking step*), with the starting reagents combined in the correct molar ratio, dissolved in solvent of choice, and stirred/heated for a certain amount of time, - very much close to the traditional organic synthesis, but the second step - purification (which I refer to as the *harvesting step*) is completely different. Usually classical purification techniques - crystallisation, column chromatography or distillation are the commonly used for the purifications of organic compounds. Crystallization; for ILs the packing behaviour are quite different from common salts/organic compounds, and these ionic materials are purposely designed in to not pack well into a crystal lattice to lower the melting points, and most of the them are glasses formers rather than crystals at lower temperatures, and also crystals of these materials commonly liquefy upon contact with even small amounts of solvents, thus crystallisation is by default not a promising approach for the purification of ILs – although it can be done sometimes, such as for the some higher melting halides ILs and ionic plastic crystals.⁵³⁻⁵⁶ Column chromatography is a promising approach for purifying organic molecules; it is a life saver for an organic chemist and has been used by all organic chemists at some time. Because of the enormous quantity of eluent and stationary phase necessary for the purification, this approach is not as promising as large-scale preparative chemistry, especially given that ILs are generally utilized as solvents themselves. Finally, because of the high boiling point of ILs, distillation is not ideal for normal purification but can be used in certain circumstances with specialist equipment.

Broadly speaking, ILs can contain two type of impurities, volatile and non-volatile, former can be the solvent (reaction medium) and unreacted starting materials (mostly alkyl halides), and latter can be the side products formed during reaction, these some could be some inorganic salts, or and again some unreacted solids. Evaporation is the most common and successful process for separating ILs from volatiles, in which IL is held in a vacuum at elevated temperatures for a set period or purged with an inert carrier gas. Non-volatile impurities are removed by passing IL solutions in appropriate solvents through activated carbon or an alumina plug. Washing is another promising method for purifying non-volatiles. This involves selecting solvents in which ILs are insoluble, for example, due to their high polarity, ILs are normally not soluble in non-polar solvents such as ethers and hexanes, washing with solvents can remove some unreacted and side products, and if IL is hydrophobic, water is the best solvent to remove

solid materials. However, all these approaches have limitations. For example, activated carbon treatment fails if the IL is adsorbed, and washing might result in loss of products and yield.

In summary – it is almost impossible to completely purify ILs once impurities get into ILs, the optimal strategy is to optimize the ILs' synthetic procedure and avoid formation of impurities. To this end, commercially available starting materials with less purity level must be purified prior to before use in reaction. For example, simple alkyl halides can be purified by washing with concentrated HCl, 10% aqueous NaHSO₃, and then water, dry it over anhydrous K₂CO₃, and fractionally distilled,⁵⁷ and methylimidazole can be purified by first stirred over KOH and distilled, dried with sodium metal, and distilled again.⁵⁸

3.4 Ionic Liquid-Based Electrolytes

There are several advantages of IL-based electrolytes over conventional organic solvent-based electrolytes. First, as mentioned above, the concerns related to thermal instability, vapor pressure and flammability of the organic solvent-based electrolytes including afflict modern battery technology. Because of this thermal sensitivity, batteries must be cooled in many new applications using larger scale units.⁵⁹ Not only does this reduce the specific energy density obtainable (per weight or volume), but it also raises the cost owing to the additional engineering necessary to prevent thermal runaway (and possible fire or explosion). Currently, the prices of modern battery systems are mainly driven by the accompanying hardware rather than the cells (80% system costs vs. 20% for EVs and 60% system costs vs. 40% for stationary batteries). Batteries with IL-based electrolytes might not require sophisticated control systems for heat management due to their negligible vapour pressure and higher thermal stabilities. While ILs and their binary or ternary salt mixes have broad electrochemical windows and adequately high ionic conductivity, the main drawback is their poor low-temperature charge-transport properties.⁶⁰ When compared to the supply of cooling systems, mild heating in conjunction with appropriate insulation is less expensive to construct.⁶¹

The second, and more significant, application of IL-based electrolytes is their use in next-generation batteries, particularly the ones that contain metal anodes. Among them are lithium-sulfur and lithium air (oxygen) batteries, as well as ongoing research on replacing the graphite anode in lithium-ion batteries with metallic lithium.⁶² According to literature, several of the anions that give the finest liquid characteristics in IL-based electrolytes also have a significant impact on the efficiency with which lithium may be reversibly oxidized and reduced.⁶³ For

example, in the case of Li-S batteries, this is the basis for the final negative electrode (in terms of energy density).⁶⁴ ILs and combinations of ILs with other solvents and additives have been examined as appropriate electrolytes since several of the cations and anions that are typical components of ILs share features of salts currently used in Li-S batteries.⁶⁵

3.4.1 Fluorinated Ionic Liquid-Based Electrolytes

The most commonly studied IL-based electrolytes are based on fluorinated anions, *i.e.* bis(trifluoromethanesulfonyl)imide (TFSI)[−] and more recently bis(fluorosulfonyl)imide (FSI)[−] anions.⁶⁰ Typically, these electrolytes are made by dissolving LiTFSI/LiFSI salts in their parent ILs with well-known cations such as phosphonium, pyrrolidinium, imidazolium, morpholinium or piperidinium.⁶⁶⁻⁶⁸ The H(TFSI) was first synthesised by Fotopoulos and DesMarteau as the highly acidic amine acid.⁶⁹ The same group investigated its chemistry further in subsequent publications and the favourable electrochemical properties of its Li-salt, such as wide ESW, reversible Li plating and stripping, and a relatively high conductivity were investigated initially in polymer matrixes⁷⁰ and later in liquid solution.^{71,72} This was motivated in part by the desire to replace the unstable Li[PF₆] salt with a chemically more stable lithium salt having comparable transport properties.⁶⁰ Some of the commonly studied fluorinated anions are shown in Figure 6.

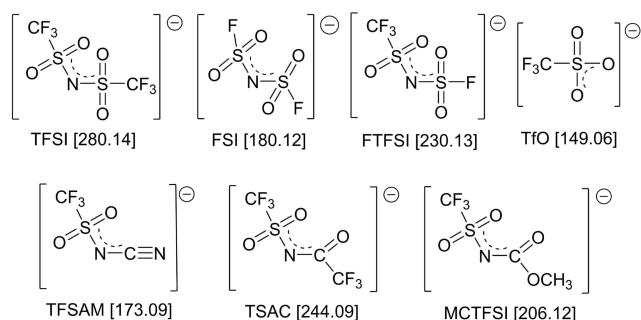


Figure 6. Imide type anions and their molar masses in []. Adapted from ref. 71.

Because of the low basicity, high degree of charge delocalization⁷³, and the presence of perfluorinated conferred by the two trifluoromethylsulfonyl groups in the [TFSI] anion, MacFarlane's group was able to create thermally and electrochemically stable ILs coupled with pyrrolidinium cations in 1999.⁷⁴ These anions have gained tremendous attentions in the ILs community, especially the ones working on energy storage devises. Katayama *et al*⁷⁵ and Matsumoto *et al*.⁷⁶ have reported the first studies on the lithium electrochemistry of TFSI-

based ILs. The creation of a protective (semi-passivating) SEI was hypothesized as the main cause of the reversible plating and stripping of lithium on numerous substrate materials. A number of spectroscopic methods were used to describe the SEI that occurs on lithium electrodes in subsequent studies.^{77,78} As a result, numerous groups have demonstrated how a lithium metal electrode may function well in a device with an electrolyte based on a [TFSI] IL.⁷⁹⁻⁸²

These investigations have emphasized not only advancement in fundamental physicochemical features, but also the critical chemical role of sulfonyl- and fluoro-functionalities in the creation of a stable SEI on the electrode surfaces. Detailed combined XPS, SEM, and electrochemical investigations of SEI layers generated by chemical and electrochemical ion breakdown have revealed important information about their chemical composition, shape, and stability.

Despite the considerable efforts, a relatively small success with [TFSI]-based ILs have been realized. Overall, it appears that:⁶⁰ (i) the conductivity of mixtures of lithium salts and [TFSI]-based ILs is only just sufficient for low rates of charge-discharge duty; (ii) lithium-ion transport is sub-optimal at typical concentrations, limiting their higher rate performance; and (iii) the SEI formed in the presence of [TFSI]⁻ anion does not provide long term stability to the lithium electrode. Another disadvantage of thermally stable [TFSI]-based salts is that they cannot preserve the aluminum current collector in LIBs above 3.7 V vs. Li⁺/Li.^{83,84} This problem is worsened at high temperatures due to the breaking of passivation layer and increased solubility of surface species. It has been demonstrated that during the early stages of aluminium corrosion, Al_x[TFSI]_y complexes were generated as a result of the interactions with the protective Al₂O₃ layer.⁸⁵ Although these complexes are moderately soluble in typical carbonate solvents and hence lack of passivation action, certain ILs may hinder their dissolution.

Furthermore, fluorinated ILs require laborious synthetic routes and hence relatively expensive, and the presence fluoride species pose risks to human health and the surrounding environment. From a safety and environmental standpoint, this has naturally sparked research towards the design of new fluorine-free IL-based electrolytes that can potentially replace fluorinated IL-based electrolytes.

3.4.2 Non-Fluorinated Ionic Liquid-Based Electrolytes

The transition from a traditional fossil-energy dominated world to a clean electrified world require a greener and sustainable energy storage technology. Therefore, there is an urge to replace the fluorinated electrolytes with non-fluorinated and greener electrolytes. One of the first attempt was undertaken in the mid-1990s to synthesize salts based on aromatic anions (following the Hückel rule) as prospective battery electrolytes, the idea was well supported by molecular modeling.⁸⁶⁻⁸⁸ Among the various aromatic anions synthesized by cyclization, LiTDI salt (lithium 4,5-dicyano-2-(trifluoromethyl)imidazolate) was produced on a considerable scale.⁸⁹ LiPDI (lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolate) and LiHDI (lithium 4,5-dicyano-2-(n-heptafluoropropyl)imidazolate) were also created.^{90,91} The newly created unique salts were thermally stable, and unlike LiPF₆, they were also moisture stable. Furthermore, voltammetric tests indicated that the aromatic salts (LiTDI and LiPDI) based electrolytes were extremely stable on the surface of Pt electrode even in a broad potential window of 4.8 V *vs* Li⁺/Li.⁹²

In early 2012, Johansson *et al.*⁹³ presented the notion of pseudo-delocalized anions, which are anions having discrete positive and negative charge regions. Computer-aided calculations were used to evaluate these lithium salts as prospective electrolytes for lithium batteries, and fascinating synthetic targets for future study. Later in 2016, the hypothesis was validated, and the same group synthesized the first generation of pseudo-delocalized anions-based lithium and sodium salts.⁹⁴ The salts have been thoroughly characterized using Raman and FT-IR spectroscopic techniques, thermogravimetry, X-ray crystallography, and ionic conductivity and electrochemical stability window measurements as aqueous electrolytes to reveal both basic properties in terms of thermal stability and solubility, as well as the ion-ion interactions and coordination. Together, they provided a picture of the salts potential as electrolyte components, especially for use in sodium-ion batteries and low voltage fluorine-free aqueous lithium-ion batteries.

Brennecke *et al.* proposed the synthesis of fluorine-free ILs based on aprotic heterocyclic anions (AHAs).⁸⁹⁵ This study revealed that the ILs with both planar anions and cations have lower viscosities and higher ionic conductivities than those with more spherical geometries, while still retaining competitive EWs. Savateev *et al.*⁹⁶ presented the synthesis of three novel "completely organic" ILs, composed of heterocyclic cation and anion building blocks with high thermal and electrochemical properties. However, due to the presence of heteroatoms in both counter parts

makes these systems heavy and resulted in a lower ionic conductivity as compared to the conventional fluorinated IL-based electrolytes.

Shah *et al.*⁹⁷ have reported on the ion dynamics in fluorine-free, hydrophobic, and hydrolytically stable phosphonium bis(salicylato)borate, (P_{4,4,4,8})(BScB) IL-based electrolytes. However, these electrolytes have provided lower ionic conductivities than the conventional IL-based electrolytes due to the larger molecular masses of the cation and anion. More recently, Shah *et al.*⁹⁸ have introduced new classes of fluorine-free ILs composed of tetra(*n*-butyl)phosphonium (P₄₄₄₄)⁺ and tetra(*n*-butyl)ammonium (N₄₄₄₄)⁺ cations paired with 2-furoate (FuA)[−], tetrahydro-2-furoate (HFuA)[−], and thiophene-2-carboxylate (TpA)[−] anions. The effect of electron delocalization in anion and the mutual interactions between cations and anions on their physical and electrochemical properties was investigated in detail. Combined experimental and theoretical investigation revealed that the nature of the cation and anion, as well as electron delocalization in the anion, has a substantial influence on the physical and electrochemical characteristics of the ILs. Thermal investigation demonstrated that tetra(*n*-butyl)phosphonium-based ILs have lower glass transition temperatures and are thermally more stable than the tetra(*n*-butyl)ammonium-based ILs with common anions. The aromatic structure of 2-furoate and thiophene-2-carboxylate anions improved electrostatic interactions with cations, resulting in very stable ILs.

It was further demonstrated that the aromatic anions (FuA) and (TpA)-based ILs are more thermally stable and have larger ESWs than the analogous nonaromatic anion-based ILs (HFuA). Bearing in mind the superior physiochemical and electrochemical properties, (P₄₄₄₄)(FuA) IL was doped with Li(FuA) salt in different molar ratios to make LIB electrolytes.⁹⁹ It was revealed that the electrolytes have T_{onset} temperatures below 568 K and provide adequate ionic conductivities across a wide temperature range. The pulsed field gradient nuclear magnetic resonance (PFG-NMR) investigations indicated that the (FuA)[−] anion diffuses quicker than the (P₄₄₄₄)⁺ cation in the pristine (P₄₄₄₄)(FuA) IL; however, doping of the neat IL with a Li salt slows down the anion diffusion. Over the entire temperature range investigated, the Li⁺ ion interacts strongly with the carboxylate functionality in the (FuA)[−] anion and diffuses slower than other ions. ⁷Li NMR and Fourier transform infrared (FTIR) spectroscopy indicated interactions of the Li⁺ ion with the carboxylate group of the anion. With increasing Li⁺ ion concentration, the transference number of the Li⁺ ion has increased.

Passerini *et al.*¹⁰⁰ have synthesized *N*-methyl-*N*-butylpyrrolidinium (Pyr₁₄)-based ILs with two different cyano-based anions, namely dicyanamide (DCA) and tricyanomethanide (TCM), and their mixtures with the respective Li salts (1:9 salt:IL molar ratio), as well as their mixtures (DCA–TCM), as potential electrolytes for lithium metal batteries (LMBs). The electrolytes exhibited high ionic conductivity (5 mS cm⁻¹) at ambient temperature, as well as an ESW up to 4 V, making them appropriate for low-voltage LMBs such as Li–sulfur batteries. The SEI formed by this class of IL-based electrolytes is studied for the first time, in addition to the detailed physicochemical (viscosity, ionic conductivity) and electrochemical (ESW, stripping/plating, and impedance spectroscopy in symmetrical Li cells) characterizations. X-ray photoelectron spectroscopy (XPS) revealed a SEI dominated by a polymer-rich layer including carbon–nitrogen single, double, and triple bonds, resulting in an excellent ionic conductivity and mechanical stability, as well as the cycle stability.

3.5 Ambient Temperature Liquid Alkali Metal Salts

As discussed in the previous sections, IL-based electrolytes have obvious advantages over traditional organic solvent-based electrolytes, but they do have some issues that should be tackled. IL-based electrolytes are typically made by dissolving a lithium salt in a parent IL (in which the ILs act as a solvent for the lithium salts), which adds complexity by introducing another (organic) cation from the IL solvent. An extra organic cation in the system means additional electrostatic interactions, which will adversely affect the transport properties of the electrolyte. In addition, during lithiation, quaternary ammonium-based cations intercalate into graphite together with Li⁺ ions, as was shown when propylene carbonate (PC) was utilized as an electrolyte solvent for graphite anodes.¹⁰¹ The IL cation intercalation and deintercalation into graphite were largely reversible, resulting in irreversible consumption of Li⁺ storage sites by the IL cations, as a result capacity fading occurred during cycling.

This logic led to the invention of several room-temperature (RT) metal-based ionic liquids (MILs) for use as solvent-free liquid electrolytes. Today there exist only few examples of MILs and most of them are based on fundamental synthetic design – longer alkyl chains with ether groups connected to bulky anion. The ether groups operate as metal solvating ligands, dissociating the metal cation (typically Li⁺) from the anion's core atom. To render the very first MILs, Fujinami and Buzoujima, for example, functionalized aluminate anions with ether groups.^{102,103} Watanabe *et al.* created lithium ILs from Li⁺ and borates with additional electron-drawing groups to minimize the anionic basicity.¹⁰⁴ Similarly, carboxylate oligoether metal salts

maintained a liquid state at ambient temperature.^{105,106} Langwald and co-workers explored extensively different synthesis routes to obtain some new MIL families, specifically difluoro alkoxy boranes and trialkyl borates, where oxyethylene substituents are of different lengths and connected to different electron-withdrawing groups.^{107,108} The triethylene glycol-based 1,2,3-triazolate lithium salt revealed a glass transition temperature of -50 °C and remained liquid at ambient temperature.¹⁰⁹ And more recently we have reported on six phosphate-anion-based alkali metal salts, all of them are liquid at room temperature, with glass transition temperatures ranging from -61 to -29 °C, and thermal stability of at least 225 °C.¹¹⁰

In summary – the field of fluorine-free IL-based electrolytes in general and MILs in particular is still in its early phases, and much more R&D is needed to develop new performant electrolytes that can compete with the conventional fluorinated IL-based electrolytes. There is, however, little or no information available on the systematic battery performance of non-fluorinated IL-based and MIL-based electrolytes.

4. Experimental

In this section general experimental procedures and methodologies used in this thesis are detailed.

4.1 Materials

Unless otherwise noted, all commercial reagents were utilized without any additional purification. 2-picolinic acid (2-PyrA), nicotinic acid (3-PyrA), isonicotinic acid (4-PyrA), pyrazinoic acid (2,5-PyrA), 2,6-pyridinedicarboxylic acid (Pyr-2,6-diA), salicylic acid (ACS reagents, >95 % purity), 4-toluenesulfonyl chloride (ACS reagents, >97 % purity), 2-ethoxyethanol (>99 % purity), *iso*-propoxy ethanol (>99 % purity), diethylene glycol monoethyl ether (>99 % purity) 1,2-dimethylimidazole (ACS reagents, >97 % purity), *n*-methylpyrrolidine (ACS reagents, >97 % purity), 1-bromobutane (>99 % purity), silver(I) oxide (>99.9 % purity), 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (>97 % purity), 2-(2-methoxyethoxy)acetic acid (>97 % purity), aqueous solution of tetrabutylphosphonium hydroxide (40 wt % in water), methoxyethyl bromide saccharine (ACS reagents, > 97 % purity)lithium hydroxide monohydrate (ACS reagents, >98 % purity) were received from Sigma-Aldrich. Sodium sulphate, methanol, dichloromethane (DCM) and diethylether were purchased from VWR (BDH) chemicals.

4.2 Synthesis

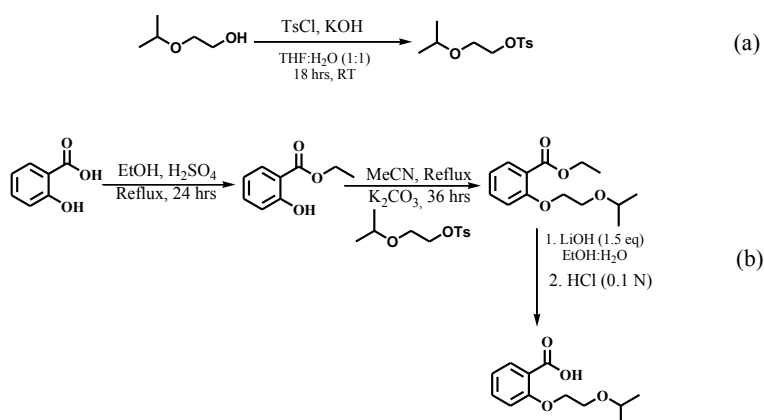
As discussed above, the synthesis of ILs usually involves separate synthesis of cation and anion and finally both cation and anion are reacted together under optimised conditions to the desired IL. The detailed synthesis and characterization of each intermediate, anion, cation and the IL is discussed in the corresponding paper. Here, a summary of few compounds is presented.

4.2.1 Synthesis of Anion Precursors

Solution of potassium hydroxide (0.38 g, 6.9 mmol, 1.2 equiv.) in water (20 mL) was dropped into the *iso*-propoxy ethanol (0.9 g, 8.6 mmol, 1.5 equiv.) over 5 minutes and after complete addition the mixture was further stirred for 10 minutes. Solution of 4-toluenesulfonyl chloride (1.1 g, 5.7 mmol, 1 equiv.) in THF (500 ml) at room temperature was dropped into the mixture under vigorous stirring over 50 minutes and resulted solution was further stirred at ambient temperature for 24 hours. 250 mL of water was added to reaction mixture and extracted with DCM (3 x 100 mL). The organic layer was dried over Na₂SO₄, gravity filtered, and the solvent

was removed by rotary evaporation, a pale-yellow liquid was obtained and used in the next step without any further purification.

A solution of 2-isopropoxyethyl 4-methylbenzenesulfonate (38.7 g, 0.15 moles, 1.5 equiv. in 100 ml of dry acetonitrile), methyl salicylate (15.2g, 0.1 moles, 1 equiv.) and potassium carbonate (69 g, 0.5 moles, 5 equiv.) in a dry acetonitrile (250 mL) was heated at 70 °C under N₂ and continuous stringing for 48 hours. The yellow suspension was filtered off and the solid was washed with 60 mL of acetonitrile. The extract and washes were concentrated via rotary evaporation. The residue was extracted with DCM (3 x 50 mL). The organic phase was washed with water (6 x 150 mL). The organic layer was dried over Na₂SO₄, gravity filtered, and the solvent was removed by a rotary evaporation to afford the product B2 as a yellow oil. In the next step, B2 was dissolved in THF:MeOH (1:1, 50 mL) and dropped into the aqueous solution of LiOH.H₂O (3 equiv.), stirred at room temperature for 12 hours, neutralized with 0.1 M HCl and extracted with DCM (3 x 25 mL). The organic phase was washed with water (6 x 150 mL), dried over Na₂SO₄, gravity filtered, and the solvent was removed by rotary evaporation to afford the product 2-(2-isopropoxyethoxy)benzoic acid (2-IEBA) as a dark yellow liquid. All the acids were separated in good yields ca. 60%.



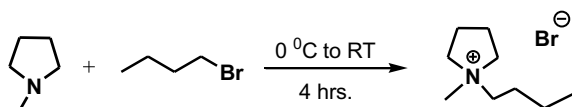
Scheme 1. Synthesis of anion precursor - 2-(2-isopropoxyethoxy)benzoic acid (2-IEBA).

4.2.2 Synthesis of Cation Precursors

The most frequent approach for producing aprotic ILs is the direct quaternization reaction between alkyl bromide and the charge neutral base in S_N² reaction fashion, with halide group serving as the leaving group.¹¹¹⁻¹¹³ Mostly, these reactions are exothermic and complete in a few minutes with a high yield. It is worth mentioning that bromides are preferable over

chlorides since they create significant elimination byproducts with a low yield of the desired salt. Lower temperatures and the absence of oxygen and water during the alkylation process also aid in suppressing unwanted side reactions. Excess alkyl halides are typically employed to accelerate the reaction forward since they can be easily removed by rinsing the product with non-polar solvents.

In a typical procedure (Scheme 2), alkyl bromide was dropped into the amine at a *ca.* 0 °C, during addition the solution became turbid. The temperature was gradually raised to room temperature and the mixture was stirred further for few hours. After that, diethyl ether was added and the solution was further stirred for one hour. The product can be filtered - if the salt is solid and/or extract the solution with water in case of oily products. The excess of solvent was evaporated and dried in an oven at a higher temperature for at least few days before proceeding to the next stage.

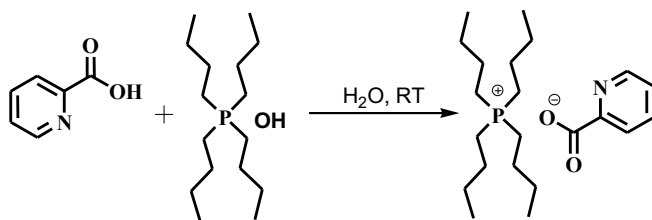


Scheme 2. Synthesis of cation precursor.

4.2.3 Synthesis of Ionic Materials

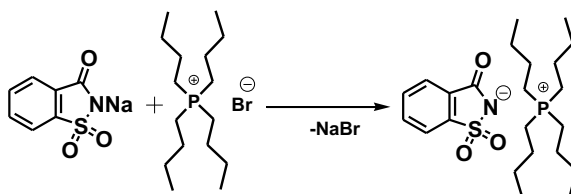
For the synthesis of ILs, two common methods are used: direct neutralization and metathesis reaction. In direct neutralization, acids act as anion precursors and hydroxide salts as cation precursors, and to create IL both are combined in water at ambient conditions. In metathesis, halides salts (cation precursors) are reacted with metal salts normally Na and Li (anion precursors) in appropriate solvent under optimized conditions. When compared to both methods, the neutralization method is more efficient, straightforward and results in quantitative yield of ILs; the only by product in this reaction is water, which is easy to remove. On the other hand, metathesis reaction involves the appropriate solvents and can produce some unwanted side products; the normal side product is metal halides, which are ionic like ILs and complicate purification stages. This method is extremely successful when the ILs are hydrophobic, the metal salts can be extracted with the water. In this work both of methods used to create new ILs. For direct neutralization reaction, an of the *n*-tetrabutylphosphonium hydroxide was added dropwise into the stirred aqueous solution of the corresponding acids (Scheme 3). The reaction mixture was stirred at room temperature for four hours and progress of the reaction was

monitored *via* thin layer chromatography (TLC) and upon completion of the reaction water was removed under reduced pressure using a rotary evaporator. The products were washed three times with 50 ml of diethyl ether before being dissolved in dichloromethane and dried over anhydrous Na₂SO₄. Finally, the solution was filtered, residual solvent was removed under reduced pressure, and the final products were dried in a vacuum oven at 80 °C for more than 4 days. All the products were separated in quantitative yields.



Scheme 3. Example of IL synthesis *via* neutralization reaction.

For metathesis reaction (Scheme 4), an equivalent amount of halide salts was dropped into the aqueous solution of Na salts at ambient temperature and stirred for 24 hours. Extracted with DCM for thrice, organic layer was separated, dried with sodium sulphate, solvent was evaporated under vacuum at elevated temperature, the viscous gel thus obtained was vacuumed at 80 °C for 4 days.



Scheme 4. Example of an IL synthesis *via* metathesis reaction.

4.2.4 Synthesis of Lithium Salts

All the lithium salts were prepared by direct neutralization of acids with Lithium bicarbonate (LiHCO₃). Under continuous stirring, aqueous solutions of the acids were treated with solid LiHCO₃ in small portions, until the generation of gas bubbles stopped. All the salts were obtained in quantitative yields after lyophilization and subsequent drying in vacuo. One specific example for synthesis of lithium salt is presented below.

Synthesis of LiSac: Saccharine was placed in a water-methanol (1:1) mixture, and an equimolar amount of LiOH was steadily added until the combined solution became clear. After complete

addition, the reaction mixture was agitated for another 6 hours before water was evaporated under vacuum at raised temperature, producing a white solid that was dried at 80 °C for 4 days.

4.3 Physiochemical Characterizations

4.3.1 Nuclear Magnetic Resonance Spectroscopy

The structures and purity of all the synthesized ILs were confirmed by using a Bruker Ascend Aeon WB 400 (Bruker BioSpin AG, Fallanden, Switzerland) NMR spectrometer. CDCl₃ was used as a solvent. The working frequencies were 400.21 MHz for ¹H, 100.64 MHz for ¹³C, and 162.01 MHz for ³¹P. Data were processed using Bruker Topspin 3.5 software.

4.3.2 FTIR Spectroscopy

The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of samples were recorded using a Bruker IFS 80v spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and diamond ATR accessory, employing the double-side forward-backward acquisition mode. The total number of scans was 256, co-added and signal-averaged at an optical resolution of 4 cm⁻¹.

4.3.3 Thermal Analysis

Thermogravimetric analysis (TGA) was performed using a PerkinElmer TGA 8000 under N₂ gas at a heating rate of 10 °C per min using ca. 2-4 mg samples. The onset of decomposition temperature, *T*_{onset}, was calculated from the intersection of the baseline weight and the tangent of the weight versus temperature curve using Pyris software. Differential scanning calorimetry (DSC) was performed using a PerkinElmer DSC 6000 on 2-5 mg of sample placed in an aluminum pan. DSC data were collected at a scanning rate of 5 °C min⁻¹ for both cooling and heating traces ranging from -75 to 200 °C. To maintain an inert environment inside the sample chamber, dry N₂ gas was delivered at a constant flow rate of 20 mL min⁻¹. The *T*_g was determined by using the inflection mid-point of the initial S-shaped transition slope and determined from the onset with the aid of Pyris software.

4.3.4 Pulsed Field Gradient Diffusometry

NMR self-diffusion measurements were performed using a Bruker Ascend/Aeon WB 400 (Bruker BioSpin AG) NMR spectrometer with a resonance frequency of 400.27 MHz for ¹H and 155.56 MHz for ⁷Li. Pulsed-Field Gradient (PFG) NMR self-diffusion measurements were performed on ¹H with a PFG NMR probe Diff50 (Bruker) with a maximum amplitude of the

magnetic field gradient pulse of 29.73 T m^{-1} . The samples were placed in a standard 5 mm NMR glass tube and closed with a plastic stopper to avoid contact with air. Prior to measurements, each sample was equilibrated at a specific temperature for 30 min. The details of the PFG NMR technique for measuring molecular diffusion coefficients are available elsewhere.¹¹⁴ The diffusivity of a molecule is the diffusion decay (DD) of amplitude A of NMR spectral line, obtained by Fourier transformation of a descending half of stimulated-echo (StE), as a function of the amplitude of applied pulsed field gradient. For the stimulated echo pulse sequence used, diffusion decay of A in the case of simple non-associating molecular liquid can be described by the Eq.(1):¹¹⁵

$$A(g, \delta, t_d) = A(0) \exp(-\gamma^2 g^2 \delta^2 D t_d) \quad (1)$$

where $A(0)$ is the factor proportional to the proton content in the system, and to spin-lattice and spin-spin relaxation times, γ is the gyromagnetic ratio for a used nucleus; g and δ are the amplitude and duration of the gradient pulse; t_d is the diffusion time; and D is the self-diffusion coefficient. t_d was in the range 4-100 ms for ^1H diffusion and 5-15 ms for ^7Li diffusion.

4.4 Electrochemical Characterization

All the electrochemical characterizations were performed by using a Metrohm Autolab PGSTAT302N electrochemical workstation with a FRA32M module for impedance measurements, all of which were controlled by Nova 2.02 software. Prior to each measurement, the electrodes were polished with a 0.25 m of Kemet diamond paste.

4.4.1 Linear Sweep Voltammetry

A sealed Microcell HC from RHD instruments was used to hold about 70 μL of sample. Linear sweep voltammetry (LSV) was performed with a three-electrode setup: a Pt wire with a diameter of 0.25 mm and/or GC with a diameter of 2 mm as working electrodes (WE), a Pt crucible as counter electrode (CE), as well as sample container, and an Ag wire coated with AgCl as a pseudo-reference electrode (RE). Both cathodic and anodic scans were recorded at a rate of 1 mV s^{-1} . The electrochemical potentials were calibrated using ferrocene (Fc) as internal reference and shifted using $E_{\text{Li/Li}^+} \approx E_{\text{Fc/Fc}^+} + 3.2 \text{ V}$.¹¹⁶ The ESWs limits were defined by a 0.1 mA cm^{-2} cut-off current density.

4.4.2 Ionic Conductivity

The ionic conductivity was obtained from the impedance measurements performed in a frequency range from 1 Hz to 1 MHz with an AC voltage amplitude of 10 mV_{rms}. All the impedance spectra were measured during heating and cooling over a temperature range from -20 to 100 ± 0.1 °C. A two-electrode configuration was employed for ionic conductivity measurements, with a wire Pt as WE and a 70 µL Pt crucible as a sample container, as well as CE. The cell constant was calculated using a Metrohm 100 S cm⁻¹ KCl standard solution ($K_{\text{cell}} = 18.5396 \text{ cm}^{-1}$). The cell was thermally equilibrated for 10 minutes before recording the impedance spectra.

5. Summary of the Results

A summary of each paper is presented here, while the details are given in each paper appended to this thesis.

5.1 Paper I

Aromatic heterocyclic anion based ionic liquids and electrolytes.

In this work, we investigate the effect of structural variations in novel ionic materials derived from nicotinic acid more commonly known as niacin, a form of vitamin B₃. Nicotinic acid is chosen due to its sustainable nature, and the small and compact structure of the anion. In addition, structural analogues of nicotinic acid are selected for a systematic comparison, all the anions are based on six-membered aromatic nitrogen heterocycles and coupled with a common tetra(*n*-butylphosphonium) cation (P_{4444}^+), result in two room temperature ionic liquids (RTILs), one semi-solid, and two organic ionic plastic crystals (OIPCs) with melting points > 20 °C. The OIPCs showed plastic crystalline phase, multiple solid-solid transitions, and plastic crystalline and melt phases (Figure 8a).

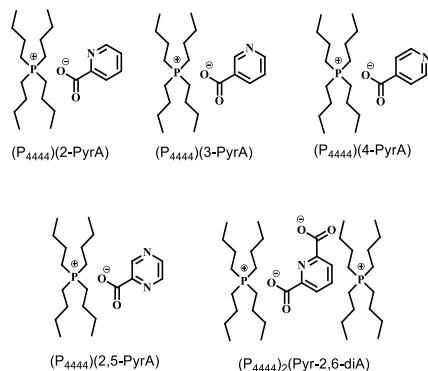


Figure 7. Chemical structures and abbreviations of the five ionic materials on aromatic heterocyclic anions.

The thermal stability of ionic materials mainly depending on the nature of the anion (Figure 8b). The order of thermal stability decrease as: $(P_{4444})(3\text{-PyrA}) > (P_{4444})(4\text{-PyrA}) > (P_{4444})(2,5\text{-PyrA}) > (P_{4444})(2\text{-PyrA}) > (P_{4444})_2(\text{Pyr-2,6-diA})$ and increases as the delocalization of the negative charge on the anion increases. The $(P_{4444})(3\text{-PyrA})$ IL thermal stability vs. the $(P_{4444})(4\text{-PyrA})$ and $(P_{4444})(2\text{-PyrA})$ ILs might be explained by the negative inductive and positive resonance effects (electron-donating effect) of the pyridine nitrogen, which can cause an extended delocalization of electrons lead to a more polarizable structure resulting in

thermally stable anion. In the case of $(P_{4444})(2,5\text{-PyrA})$, the presence of an extra nitrogen atom at 5-position neutralizes the electron withdrawing effect generated by the nitrogen at 2-position and stabilizes the anion to a greater extent as compared to the anion in $(P_{4444})(2\text{-PyrA})$.

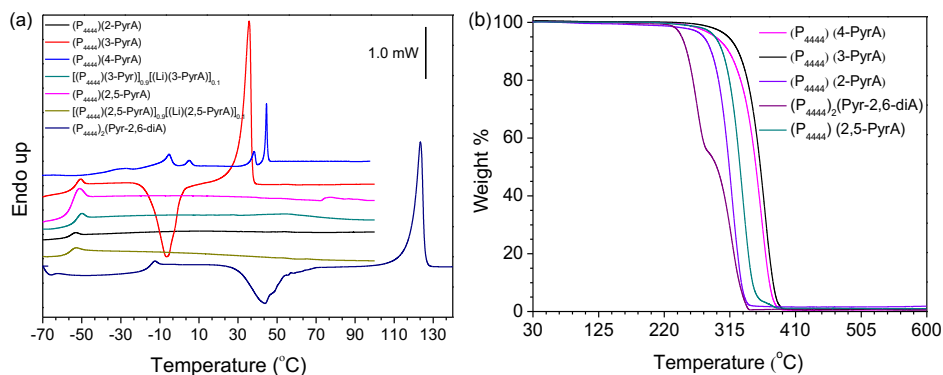


Figure 8. DSC traces for the ILs and the electrolytes on aromatic heterocyclic anions. The traces are shifted along Y-axis for clarity, and TGA thermograms of the neat ILs and the electrolytes on aromatic heterocyclic anions (b).

Doping of the ILs with the analogous lithium salts renders Li^+ conducting electrolytes. The addition of 10 mol % of $Li(3\text{-PyrA})$ salt to $(P_{4444})(3\text{-PyrA})$ slightly shifts the glass transition temperature, reduces transport properties and improves thermal which associated with the smaller radius of Li^+ , causing increases in the ionic strength and/or ion-ion interactions, which are due Li^+ ions interacts with the carboxylate groups of the anions, and proved by FTIR studies, where new asymmetric stretching bands at 1380 and 1400 cm^{-1} appear, alongside a significant broadening of the asymmetric band at 1615 cm^{-1} with distinct shoulders at both sides (Figure 9). This clearly suggests the interaction of the Li^+ ions with the carboxylate groups of the anions. and electrochemical properties, and last can be possibly due to the formation of a passivating layer on the surface of the WE, a similar change for the $(P_{4444})(2,5\text{-PyrA})$ based electrolyte.

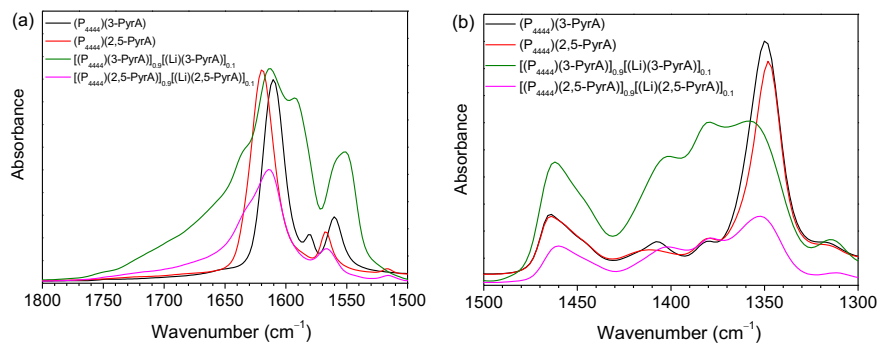


Figure 9. FTIR spectra of the neat ILs and electrolytes based on aromatic heterocyclic anions.

5.2 Paper II

Ionic Liquids and Electrolytes with Flexible Aromatic Anions

Here we present a new class of fluorine-free ILs and their corresponding electrolytes based on anions with aromatic centre and different oligoether chains (Figure 10). The use of a carboxylate group alongside an ether oxygen atom containing chain, make these anions mimic the organic solvents commonly used in LIBs, such as glymes, and carbonates, but with the idea of the advantageous IL properties added in the design – and therefore systematic correlations between anions/ILs and key physicochemical properties are developed, with an emphasis on the ion transport and usefulness as battery electrolyte components.

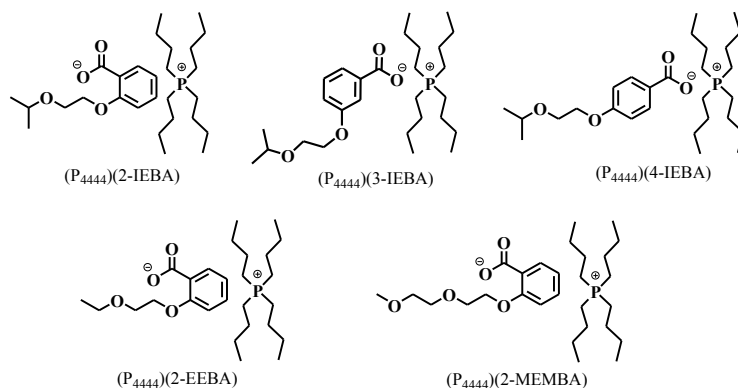


Figure 10. Chemical structures and abbreviations of the ILs.

The nature and position of the oligoether chain affect thermal stability (up to 330 °C), phase behaviour ($T_g < -55$ °C) and ion transport, for example, (P₄₄₄₄)(3-IEBA) and (P₄₄₄₄)(4-IEBA) ILs show relatively higher thermal stabilities and one-stage decompositions. In contrast, the (P₄₄₄₄)(2-IEBA), (P₄₄₄₄)(2-EEBA) and (P₄₄₄₄)(2-MEMBA) ILs exhibit two-stage decompositions, with a major weight loss of *ca.* 70% at the first stage, which, perhaps a bit surprisingly, most probably is due to the decomposition of the (P₄₄₄₄)⁺ cation. The (P₄₄₄₄)(2-IEBA) IL with its ortho substitution on the anion shows the highest conductivity, which is attributed to reduced ion-ion interactions by the repulsion between the terminal isopropyl group of the (2-IEBA)⁻ anion and alkyl chains of the (P₄₄₄₄)⁺ cation. Similarly, the para-substituted (P₄₄₄₄)(4-IEBA) IL has the lowest ionic conductivity because the ether group is far from the carboxylate group and there is no hindrance for the (P₄₄₄₄)⁺ cation to approach the (4-IEBA)⁻ anion. The (P₄₄₄₄)(2-EEBA) IL with a shorter ether chain provide comparable ionic conductivity to the (P₄₄₄₄)(2-MEMBA) IL with a slightly longer ether chain (Figure 11).

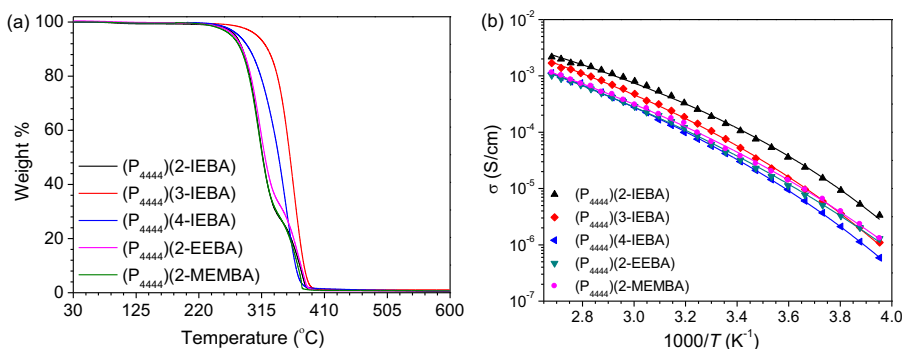


Figure 11. TGA traces of neat ILs with **flexible aromatic anions**. (a), the solid lines indicate the best fit of data using the VFT equation, and LSV curves of the electrolytes (b).

With the aim of application in lithium batteries, electrolytes were created for two of the ILs by 10 mol% doping using the corresponding Li-salts. This affects the ion diffusion negatively, from being higher and equal for cations and anions to lower for all ions and unequal (Figure 12a). This is due to the stronger ionic interactions and formation of aggregates, primarily between the Li^+ ions and the carboxylate group of the anions. Electrochemically, the electrolytes have electrochemical stability windows up to 3.5 V (Figure 12b).

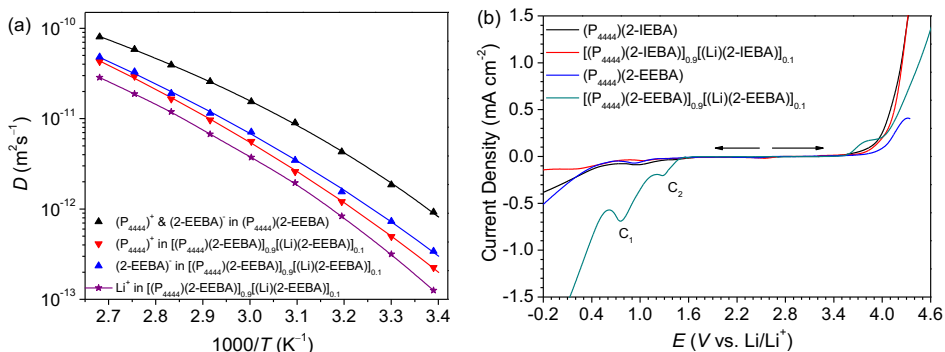


Figure 12. Ionic conductivity as a function of temperature for the electrolytes (a), the solid lines indicate the best fit of data using the VFT equation, and LSV curves of the electrolytes (b).

5.3 Paper III

Pyrrolidinium- and Imidazolium-Based Ionic Liquids and Electrolytes with Flexible Anions

This study comprises of the synthesis and physicochemical characterizations of the new class of fluorine-free ionic liquids (ILs) and electrolytes based on aliphatic flexible oligoether anions, 2-(2-methoxyethoxy)acetate, (MEA) and 2-[2-(2-methoxyethoxy)ethoxy]acetate, (MEEA) coupled with pyrrolidinium and imidazolium cations (Figure 13).

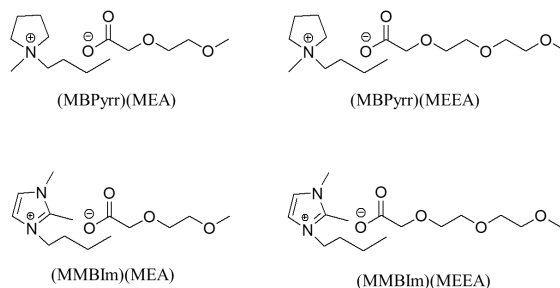


Figure 13. Chemical structures and abbreviations of ionic components of the ILs presented in this study.

Keeping the anion constant, the thermal decompositions of the imidazolium ILs proceed over a wider temperature region than the pyrrolidinium analogues, suggesting contribution of the imidazolium ring towards thermal stability. Having same cation, the IL with a bulkier oligoether anion is somewhat thermally more stable than the IL with a smaller anion, which is contradictory to the ILs with oligoether cations. This can be attributed to the oxygen electronegativity in the ether chain, which in cations weakens the covalent bond between the positively charged “*hetro*” atom and the alpha carbon, favouring thermal breakdown, while in the case of anion it rather stabilizes the negative charge and somehow prevents the thermally induced decomposition.

For the ILs with (MEEA) anions, Li^+ conducting electrolytes are created by doping the ILs with 30 mol% of LiMEEA. The structural flexibility of the oligoether functionality in the anion results in glass transition temperatures (T_g) as low as -60°C for the neat ILs and the electrolytes (Figure 14a). The imidazolium-based electrolyte reveals better thermal stabilities but higher T_g and lower electrochemical stabilities than the corresponding pyrrolidinium-based analogues. As compared to neat ILs, the electrolytes displayed lower ionic conductivity due to the decrease in free volume as a result of increased Coulombic interaction between the Li^+ ion and the anion,

leading to aggregates formation. Electrolytes with imidazole have higher ionic conductivity at lower temperature but the difference diminishes at higher temperatures, mainly result from increased amounts of charge carriers. In the case of the electrolytes, the pyrrolidinium-based electrolyte revealed wider ESW than the imidazolium one Figure 14b. These ESWs (*ca.* 2.8–3.6 V vs Li/Li⁺) are narrower than the previously reported ILs and their electrolytes containing non-fluorinated anions, but comparable with the conventional LIB electrolyte, 1 M LiPF₆ in EC:DMC (ESW 3.7 V vs Li/Li⁺).

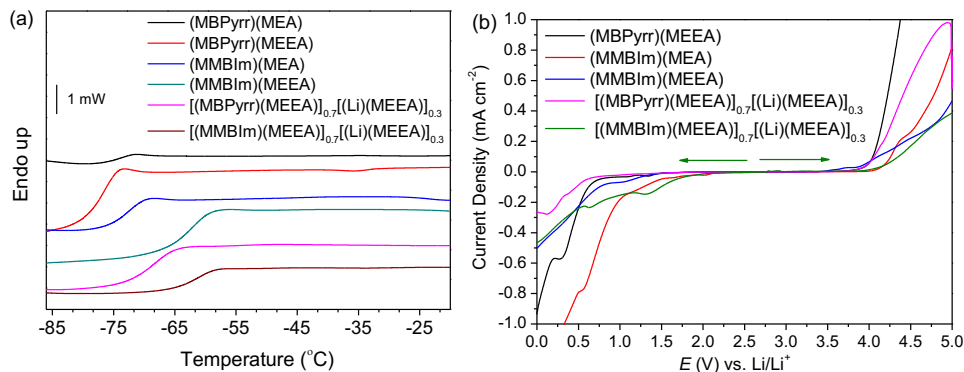
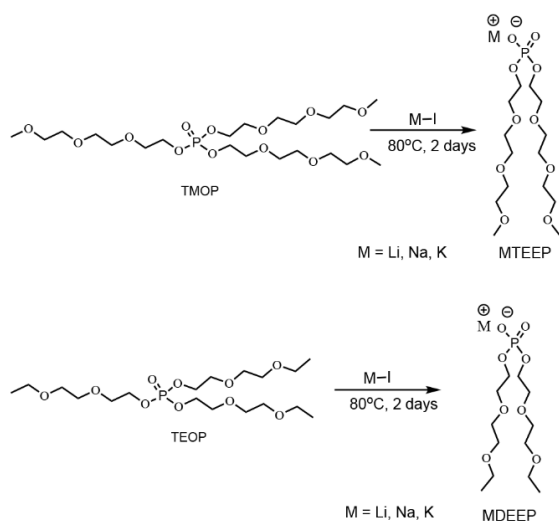


Figure14. DSC traces for the neat ILs and the electrolytes (a) are shifted along Y-axis for clarity, and the LSV curves of the neat the ILs and the electrolytes (b)

5.4 Paper IV

Ambient Temperature Liquid Salt Electrolytes

With the goal to create ambient temperature liquid alkali metal salts, inspired by basic IL anion design criteria in general and the TOTO anion in particular, we created two different oligoether phosphate anions, bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl) phosphate [TEEP]⁻ and bis(2-(2-(2-ethoxyethoxy)ethyl) phosphate [DEEP]⁻, from their corresponding neutral tris(2-(2-(2-methoxyethoxy)ethoxy)ethyl) phosphate (TMOP) and tris(2-(2-(2-ethoxyethoxy)ethyl) phosphate (TEOP), respectively (Scheme 5). The design idea is that the phosphorus content also will bring flame-retardant properties and that the long ethylene oxide-based side chains will provide both asymmetry and structural flexibility.



Scheme 5. Synthesis of phosphate-based alkali metal salts.

The dynamic TGA data revealed the decomposition temperatures (T_d) to be in the range 230 to 292 °C (Figure 15a). The influence of the alkali metal cation is clear as the Li/K-salts are more stable. The reason being that the Na-salts have a two-step decomposition path, <250 °C and >300 °C, and the Li/K-salts have all their weight loss in a single step. Ultimately this must be due to differences in the ion-ion interactions.

The DSC traces all show presence of glass transition temperatures (T_{gs}), confirming all salts to be glass forming liquids (Figure 15b), that are significantly affected by the nature of the alkali cation, likely originating in different ion-ion interactions. The lower T_{gs} of the Li-salts indicate

lower crystallization rate and stable supercooled state. Overall, these salts present significantly lower T_{gs} than the popular M-TFSI salts with $T_{gs} > 60$ °C.

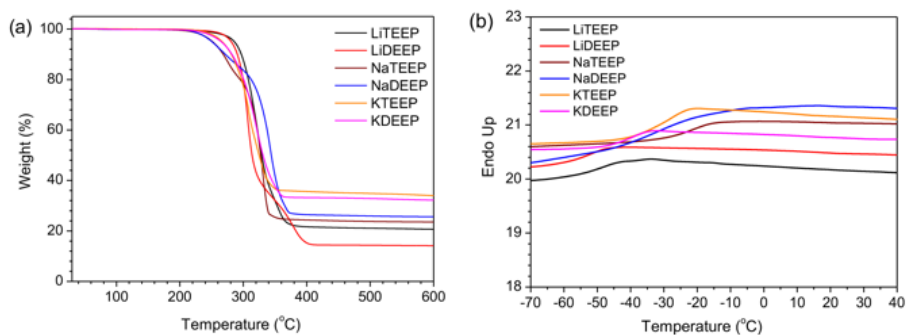


Figure 15. (a) Dynamic TGA thermograms and (b) DSC traces of our six salts.

5.5 Paper V

Sweet Ionic Liquid Electrolytes for Supercapacitor

Four new ionic liquids (ILs) based on saccharin (Sac) anion coupled to the most commonly studied pyrrolidinium, imidazolium, and phosphonium cations are synthesized (Figure 16). All the four ILs are created by a simple metathesis, which entails combining “*onium*” bromide salt with sodium saccharine using water as a solvent. All the ILs are synthesised with single-step reaction from readily available and relatively low-cost starting materials and, therefore, the ILs can be produced on large-scale, which is a key benefit to their widespread utility. The resulting ILs are miscible with polar organic solvents such as acetone, DCM, acetonitrile, and ethanol but insoluble in less polar solvents such as ether, *n*-hexane, and toluene. In terms of water solubility, (MBPyrr)(Sac) is soluble and hydrophilic, whereas imidazolium-based salts are sparingly soluble, while (P₄₄₄)(Sac) is insoluble - hydrophobic, consistent with phosphonium IL with TFSI anions. Turning to aggregate state, the (MBPyrr)(Sac) is solid at ambient temperature, while other three ILs are liquid.

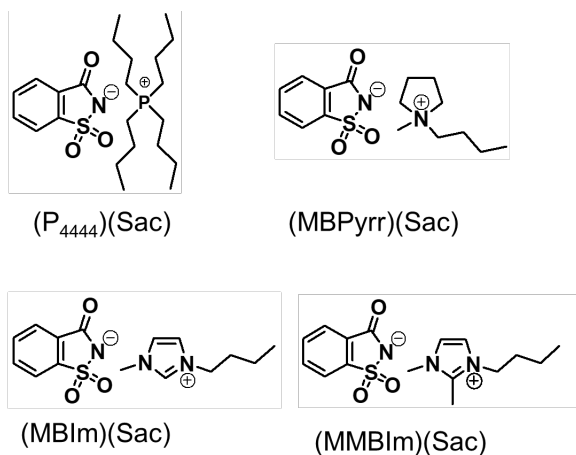


Figure 16. Chemical structures and abbreviations of synthesized ILs.

Dynamic TGA revealed that all the ILs are stable up to *ca.* > 260 °C and showed single-step decomposition (Figure 17a), with a caveat, these stabilities are slightly overstated, and isothermal TGA can only estimate the real long-term thermal stability of IL. Having the same anion, (P₄₄₄)(Sac) showed the highest thermal stability while (MBPyrr)(Sac) displayed the lowest. ILs with C-2 methylated imidazolium cations showed relatively higher thermal stability than the unmethylated cations, the latter is proven to carbene formation. The thermal stability of the (MBIm)(Sac), (MMBIm)(Sac) and (MBPyrr)(Sac) are lower than that of corresponding

ILs with TFSI anion but opposite for (P₄₄₄₄)(Sac) salt. Nonetheless, TGA results show that all four ILs are thermally stable up to 250 °C, which is important for most electrochemical applications.

The differential scanning calorimetry (DSC) traces for all pure IL are reported in Figure 17b. Under the aforementioned experimental protocol, (MBPyr)(Sac) show a single melting temperature (T_m), (P₄₄₄₄)(Sac), (MBIm)(Sac) and (MMBIm)(Sac) exhibit only the glass-transition temperatures (T_g) and behaves like glass forming liquids. Having the same anion T_g increase with moving from (P₄₄₄₄)(Sac), (MBIm)(Sac) to (MMBIm)(Sac), which suggests IL with *N* shows high ionic strength/ ion-ion interaction and thus, higher thermal energy would be required to reach the same ionic mobility as for (P₄₄₄₄)(Sac). For imidazolium-based IL, introducing methyl group at C-2 position results in increasing T_g , in this case, is not just a matter of steric hindrance but is also influenced by the electronic effects of the methyl group, leading to stronger π - π and dispersion interactions. When compared to their fluorinated analogues (MBPyr)(Sac) show *ca.* 40 K higher melting point, which is may be due to the higher molecular symmetry of Sac anion which results in higher molecular forces, for same reason (MMBPyr)(Sac) and (MBPyr)(Sac) show higher T_g values when compared to their TFSI analogues.

Owing to its superior physicochemical properties, (P₄₄₄₄)(Sac) was studied in detail as the electrolyte for the supercapacitor and exhibited an energy density of 45.7 Wh kg⁻¹ at a power density of 2.99 kW kg⁻¹ at 80 °C.

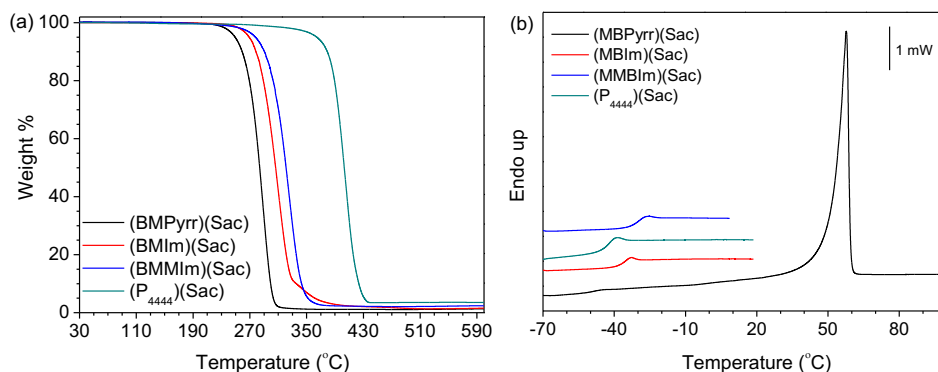


Figure 17. TGA thermograms for the ILs (a) DSC traces for the saccharine derived ILs. The traces are shifted along Y-axis for clarity (b).

5.6 Paper VI

Flexible Ionic Liquids and Electrolytes with Saccharin Anion

The inclusion of ether groups into the cation structure of ionic liquids (ILs) is well recognized to contribute to low viscosity and strong ionic conductivity. The very flexible ether chains are orientated to pack less efficiently in ILs, give more accessible free volume, and improve transport properties. For IL based electrolytes, electrolytes are typically made by dissolving the matching lithium salt in parent IL. Li^+ mobility remains a key difficulty in IL electrolytes because Li^+ ions diffuse slower than cations and free anions in the electrolyte matrix due to strong electrostatic interactions - cluster formation, and Li^+ transport is largely dependent on Li^+ solvate structures. The ether-oxygen is known to play an important role in weakening interactions between Li^+ and the anion and breaking aggregates by providing a new speciation site for the Li^+ to interact with, resulting in a lower solvation number of anions per Li^+ and improved rate performance in batteries.

To this end, we created novel IL by coupling ether functionalized pyrrolidinium, and imidazolium cations with readily accessible and environmentally friendly saccharine (Sac) anion (Figure 18). Saccharine has structural similarities with well-known fluorinated anion compounds such as bis[(trifluoromethyl)sulfonyl]imide (TFSI) and 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide (TSAC), and when customized into ILs, its compact aromatic structure can give enhanced thermal and transport properties. While focusing on LIB electrolyte, doping of the ILs with the analogous lithium salts renders Li^+ conducting electrolytes. Both the neat ILs and the electrolytes are studied with respect to basic physicochemical properties such as ionic interactions and mobilities as well as electrochemical properties.

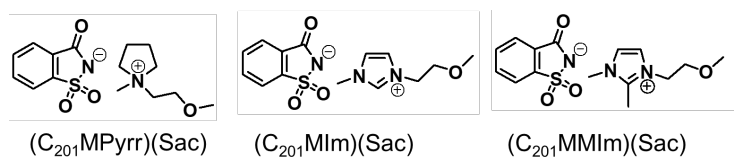


Figure 18. Structure and abbreviations of ILs.

DSC traces of all IL showing only T_g , -behaves like glass formers with no other thermal events are observed in the battery working range of temperature (Figure 19). As expected, imidazolium based IL shows higher T_g than their pyrrolidinium analogues, which can be attributed to the stronger π - π and dispersion interactions -high ionic strength/ ion-ion interaction

and thus, higher thermal energy would be required to reach the same ionic mobility as for pyrrolidinium. When compared to alkyl analogues with ether functionalized, all ILs have lower T_g temperatures, which may be due to high flexibility and oxygen lone pairs of the ether groups and as well as the reduced symmetry of cation, the former due to repulsive interactions between the oxygen electron lone pair of neighboring -OR units and the anions interrupts ion crystal packing rearrangements and hinder crystallization/melting processes, and the latter lowers the lattice energy. Doping Li salts in neat IL increase the T_g which is due to increase ionic interactions.

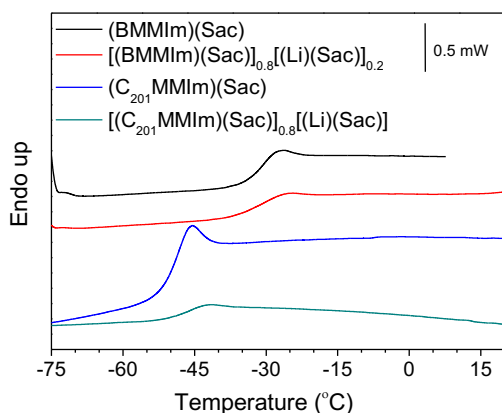


Figure 19. DSC traces of the neat ILs and the electrolytes.

6. Conclusions and Outlook

In this thesis, new classes of fluorine-free anions are introduced and coupled with a range of cations such as phosphonium, pyrrolidinium, imidazolium and alkali metal ions ($\text{Na}^+/\text{K}^+/\text{Li}^+$), to render fluorine-free ILs/Ionic materials. The set of ions are designed with slight structural modifications and detailed structure-reactivity relationship established by keeping one counterpart (cation or anion) constant. The established structure-reactivity relationship significantly contributes to the understanding of how minor structural tuning of one counterpart can have a significant impact on the overall physicochemical and electrochemical properties of the ionic materials. Aiming at energy storage applications, electrolytes are made by mixing lithium salts with the parent ILs, and are detailed with respect to basic physicochemical and electrochemical properties. Some of the key conclusions and outlook are presented below.

The ILs comprising aromatic carboxylate anions coupled to phosphonium cation demonstrated some promising physicochemical and transport properties - which primarily rely on anion chemistry and revealed that electron donating groups present at meta position with respect to carboxylate group can improve the electron delocalization, which aids in the improvement of thermal and transport properties. By substituting aromatic carboxylate anions with saccharin, the electrochemical, transport, and thermal properties improved; the latter two were enhanced further by replacing the alkyl side-chain with ethers on the cation.

Introducing oligoether long ethylene oxide-based side-chains to the anions provided both asymmetry and structural flexibility - resulted in ILs with low T_{gs} . The carboxylate oligoether anions, $(\text{MEA})^-$ and $(\text{MEEA})^-$, coupled with imidazolium and pyrrolidinium cations showed comparable ion transport properties but quite different thermal properties – pyrrolidinium-based ILs exhibited lower thermal stability and T_g . Ambient temperature liquid alkali metal salts with two different oligoether phosphate anions, $(\text{TEEP})^-$ and $(\text{DEEP})^-$, showed some appreciable thermal and electrochemical stabilities, low glass transition temperatures, and moderate ionic conductivities.

For electrolytes, doped with up to 30% Li salts, aggregation formation is evident, which has improved the thermal and electrochemical properties but limiting the transport properties - which do enhance with temperature. Transport studies of the electrolytes showed that the self-diffusion coefficient of the lithium ion is slower than that of the organic cation and anion of the ILs. This is attributed to a mechanism involving solvation by the anion with lithium-ion

exchange between anionic complexes, termed “structural diffusion” as opposed to a “vehicular” mechanism where Li^+ moves with the whole coordination sphere. The neat $(\text{P}_{4444})(\text{Sac})$ IL showed some promising performance as an electrolyte in symmetric graphite-based supercapacitors, and the ambient temperature liquid alkali metal salts revealed some battery performance.

For IL-based electrolytes, determining their solubility, ionic conductivity or even the electrochemical stability window using inert electrodes does not provide a real scenario of their application in working devices, and it should be continued researching and testing of different ILs-based electrolytes in relevant devices to determine their genuine potential for applications in batteries.

Transport properties are the most important aspect of IL-based electrolytes but the structural and dynamical changes in the solvation shell surrounding Mn^+ in a multi-anion environment are yet poorly understood. However, combined NMR diffusometry, molecular dynamics simulations, vibrational and NMR spectroscopic techniques explain that the true nature of the coordination sphere of the metal ion in solution may differ from that found in the solid state, and the identification of the metal ion species in IL-based electrolytes solutions is debatable. The presence of numerous ions with various degrees of coordination can modify the solvation and transport properties of charge carriers in ILs, providing a method to influence the performance in electrochemical processes. In the end, affordable and sustainable ILs and electrolytes are crucial, especially for Na-ion batteries, which are frequently promoted as more affordable and sustainable alternatives to their lithium counterparts.

Finally, through this thesis, I hope to have added piece to the puzzle for developing fluorine-free ILs and electrolytes that are more suitable for LIBs and other energy storage systems without being creating problems for society and the surrounding environment. These formulations, along with new solvent and additive combinations, may lead to a new generation of electrolyte formulations with enhanced functionality in actual battery systems. There is indeed a great potential for R&D within this area!

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