batteries

Review

Beyond Organic Electrolytes: An Analysis of Ionic Liquids for Advanced Lithium Rechargeable Batteries

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Abstract: The fast-growing area of battery technology requires the availability of highly stable, energy-efficient batteries for everyday applications. This, in turn, calls for research into new battery materials, especially with regard to a battery's main component: the electrolytes. Besides the demands associated with solid ionic conduction and appropriate electrochemical behaviour, considerable effort will be necessary to thoroughly reduce safety risks in terms of flammability, leakage, and thermal runaway. Consequently, completely new classes of electrolytes need to be developed that are compatible with energy storage systems. Despite the progress made in solid polymer electrolytes, such materials have suffered from limitations to their real-world application. Now, ionic liquids are considered a class of electrolytes with the most potential for the creation of more advanced and safer lithium–ion batteries. In recent decades, ILs have been widely explored as potential electrolytes in the search for new breakthroughs in the ESS field, such those associated with fuel cells, lithium–ion batteries, and supercapacitors. The present review will discuss ILs that present high ionic conductivity, a lower melting point below 100 °C, and which feature up to 5–6 V wide electrochemical potential windows vs. Li^+/Li. Furthermore, ILs exhibit good thermal stability, non-flammability, and low volatility—all of which are attributes realized by appropriate cation–anion combinations. This paper seeks to review the status of research concerning ILs, along with the advantages and challenges yet to be overcome in their development.

Keywords: ionic liquids; non-aqueous electrolytes; hybrid electrolytes; LIBs; thermal stability; high-temperature batteries

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1. Introduction

1.1. Overview of LIBs

In recent years, lithium batteries have been used as storage devices for "green" sources of energy. The evolution of LIBs is shown in Figure 1a. The range of applications, involving different technologies, including that associated with large electric vehicles like buses, electric cars, and light electric vehicles—electric bicycles, golf carts, small cars, forklifts—demonstrates how vital lithium–ion batteries are in today's scientific world. They also find application in battery-powered electric instruments such as lawn mowers, electric saws, drills, remote control toys, wind energy storage devices, solar apparatus, warning lights, UPS, small medical appliances, laptops and mobile phones. Two factors make lithium–ion batteries the key player in such applications: their high energy density, possibly as high as 250 Wh/kg or 800 Wh/L, and their flexibility in design, allowing them to be made into various shapes and sizes. These form the very basis on which these batteries are considered an apt choice for such a wide array of devices, in turn fostering more improvement and research in the area of battery technology [1]. Their light-weight design, rapid charging capacity and superior performance compared with other types of batteries keep them at the head of the generation in terms of advanced battery technology.

After hydrogen and helium, lithium is the third lightest element, containing just three electrons, and, compared with conventional battery lead and zinc, it has an extremely high energy density. Among all metals, it has the highest specific energy with respect to weight and also the highest electrochemical potential. Furthermore, the molecular mechanisms, such as those concerning the reaction of lithium with carbon into lithium carbonate, are already known [2]. There are three major benefits that lithium provides in battery technology. Firstly, it is very reactive, meaning that, most of the time, it loses its outermost electron, letting the current pass through the battery. Next, it is much lighter than the metals used in any other battery. Thirdly, because lithium has very strong chemical reactivity, it can retain a large amount of energy in its atomic bonds, meaning that a very high energy density is achieved in lithium–ion batteries. Commonly, the main components composing an LIB are the cathode, the anode, the electrolyte, and the separator, as illustrated in Figure 1b. Among these, the electrolyte is an important medium by which to carry Li^+ ions during the charge/discharge process [3]. Some constraints may exist for using lithium–ion in batteries, such as the difficulty in recycling it [4], but it nonetheless maintains its supremacy as a battery material.

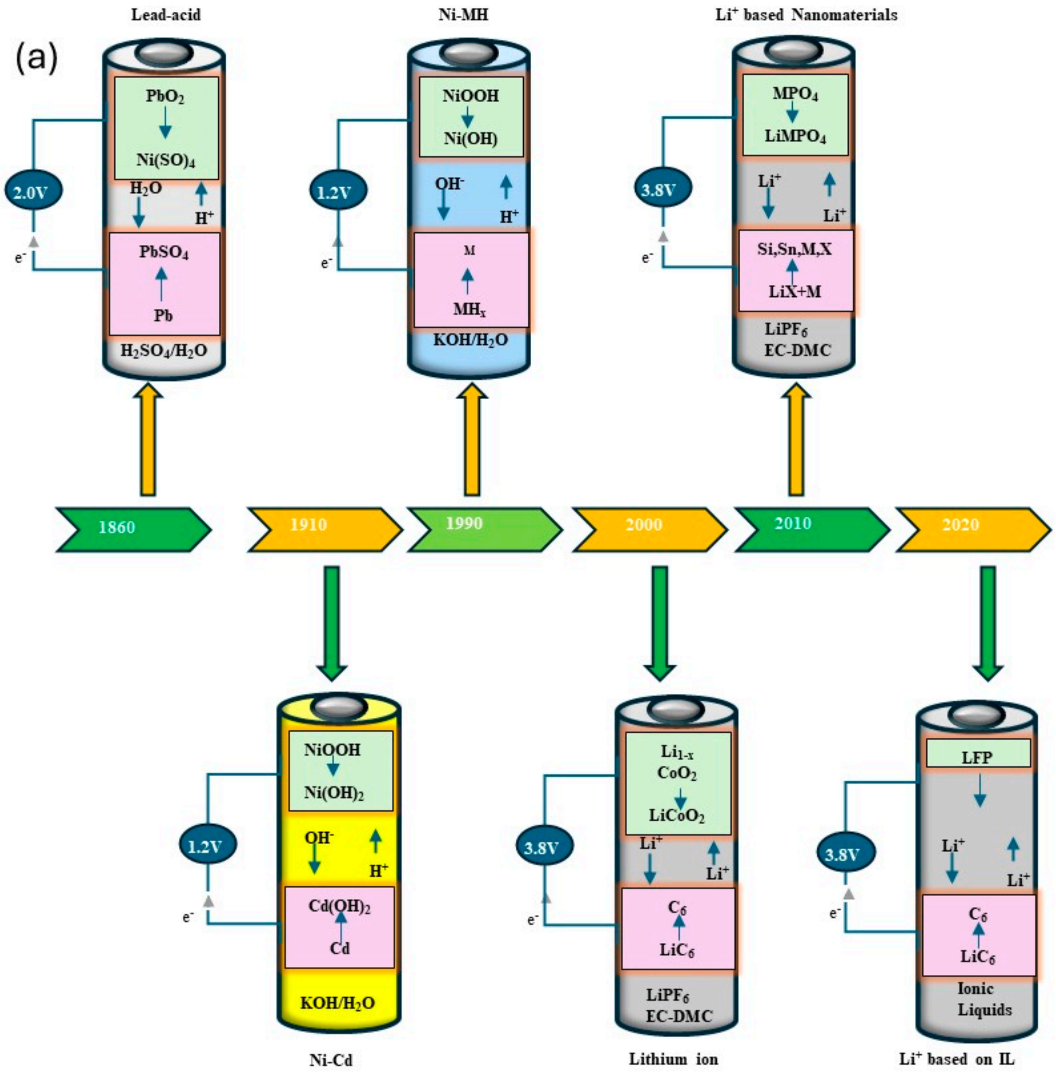


Figure 1. *Cont.*

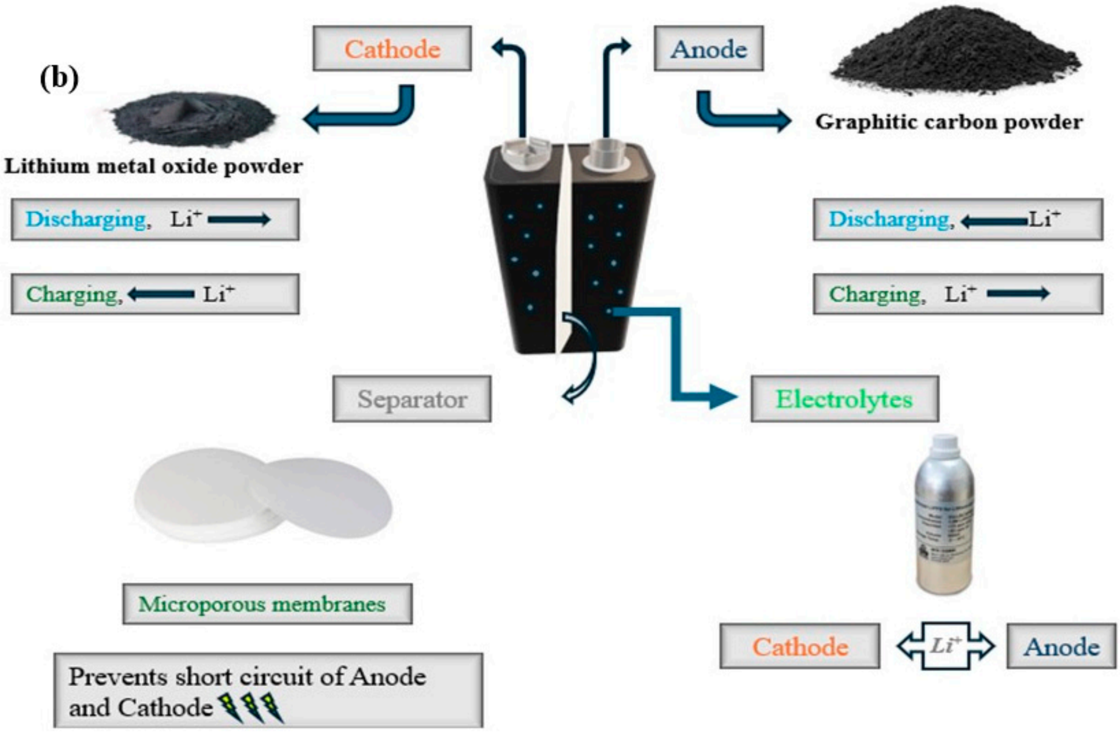


Figure 1. (**a**) Progression in battery technology over years. (**b**) Major elements of a lithium–ion battery with widely used materials.

1.2. Electrolytes for LIBs

As explained above, the electrolyte is a basic element of an LIB. In principle, for an electrolyte to perform satisfactorily in LIBs, there are some properties which they need to have, all of which are vital to the battery's performance. These include the excellent transport properties that provide the ability for the fast flow of lithium ions through the electrodes during charge and discharge processes, the chemical and electrochemical stability needed for the protection of both electrolyte and electrode during the process of charging and discharging for long-term performance and safety, and the wide operating temperature range, which is made possible by the low melting points coupled with high boiling points and which allow the electrolyte to work under variable temperatures and low vapor pressure, in turn reducing the possibility of safety hazards with respect to leakage or flammability of the battery system and increasing the general safety ranking [4–7].

Many electrolyte systems are being made available for LIBs. The improvement of different kinds of electrolytes, such as aqueous, organic, and other non-aqueous systems, has thus become the focus of research. Victor Raul Raul Jauja Ccana et al. [8] have reported an aqueous electrolyte based on lithium acetate and urea that offered a high ionic conductivity with an electrochemical stability window of up to 3.2 V. The electrolyte also showed the specific capacity of 105 mAh/g over 200 cycles. Nanako Ito et al. [9] proposed a deep eutectic solvent based on 1,3-dimethylurea derivative and lithium bis(fluorosulfonyl)amide (LiFSA) [2:1 ratio], which exhibited an electrochemical stability window of 4.49 V and charge retention capacity of 179 mAh/g. Qiao et al. [10] showcased the limitation of the ethylene carbonate (EC)-based electrolyte, 1.5M LiTFSI-Pyr + LiTFSI-G3, which showed an electrochemical stability window of 4.8 V and a charge retention of 100 mA/g even after 3000 cycles. Kaoru Dokko et al. [11] used sulfolane (SL) and dimethyl sulfone (DMS) as an electrolyte for lithium–ion batteries, which resulted in a relatively high Li^+ transference number (>0.6) and good charge–discharge behaviours.

The use of an electrolyte depends on the compatibility of the other components of a battery, shown in Figure 1b, so it is very important to consider these factors before using or synthesizing a new electrolyte. The major role played by graphite in LIBs is that of the anode material. In the graphite layers, there should always be present a passive layer called a solid electrolyte interphase that provides the path for the insertion and extraction of Li^+ ions. This is often developed within the first few charge–discharge cycles, stabilizing the anode by allowing the permeation of lithium ions in order to improve its efficiency [12], otherwise exfoliation takes place as a result of any failures in the proper SEI formation on the surface of the graphite. In this way, a portion of the material of the anode degrades and places the entire functionality and battery life at risk. In the absence of the stability of SEI, graphite becomes less effective at cycling lithium ions and the capacity and efficiency of the lithium–ion battery is generally reduced [4–6,13–15]. Nowadays, more economical dry electrodes are also used in sustainable lithium ion batteries as an environmentally friendly electrode [16]. Lithium salts can be used for enabling the Li^+ ion motion inside the LIBs and, for state-of-the-art LIBs, the main choice is $LiPF_6$. On the contrary, $LiPF_6$ suffers from a high thermal and chemical instability, decomposing upon contact with even relatively small amounts of water to deliver HF acid. Nevertheless, beyond all of these disadvantages, the compatibility of $LiPF_6$ with most organic solvents allows the development of highly conductive electrolytes. In addition, the salt takes part in the passivation layer formed on the aluminium current collector at the cathode side, thus helping to reduce the aluminium dissolution and hence the degradation of the cathode material.

Thousands of alternative lithium salts have been proposed, beyond $LiPF_6$, over the last two decades. In this context, additives are usually added in trace amounts, normally below 5%, for various improvements to the quality of the electrolyte film. Vinylene carbonate is one of the most popular additives for improving the SEI formation process. Thus, there is the urgent development of advanced electrolytes which show excellent ionic conductivity and which can meet the demands of further advanced energy storage systems. Discussion in this review article will focus only on electrolytes, with an emphasis on the use of ionic liquids.

1.3. Ionic Liquids (ILs)

Molten salts made of an organic cation and organic or inorganic anion and with a melting temperatures below 100 °C are termed ionic liquids (ILs) [17]. Systems incorporating ionic liquids gained significant importance after the discovery of the first of their kind: $[N(C_2H_5)H_3][NO_3]$ [18]. Recently, awakened interest in ionic liquids has been provoked by some of the remarkable properties that ionic liquids possess, such as their remarkable ionic conductivity, reaching between 1 and 10 mS/cm at room temperature; their extended electrochemical stability window of about 3–5 V; their excellent thermal stability; non-flammability; low toxicity; low vapor pressure; and their non-volatility. All of these factors are highly valued in applications [19] and make such applications much safer than those utilizing organic solvent-based electrolytes, paving the way for the extensive study of their applications [20,21].

ILs with a melting point below the ambient room temperature are known as room-temperature ionic liquids (RTILs) [22], these ILs are made up of an organic/inorganic anion and an organic cation, both with a relatively larger size and molecular weight [17]. The essence of the physico-chemical properties of ionic liquids is given by the type of interactions between cation–anion pairs: Coulombic interactions, H-bonding, and Van der Waals interactions. This flexibility when tuning those interactions, together with the possibility of the modification of individual ions, provides a real basis for the design of a wide range of functionalized ILs, whose properties are fitted according to need [23]. Ionic liquids are materials with much lower melting points when compared with ionic crystals because of their lower lattice energy and much weaker Coulombic attraction between the large organic cation and anion. Because they are so much larger, the ions interact much more weakly with one another; as such, they have a much lower lattice stability and, therefore, lower melting points [24,25]. In most cases, ILs are diversely synthesized with various substituents on both the cation and the anion, though the ones that are typically used are normally prepared with the usual imide-type anions, borates, and halides. Common cations include phosphonium [26] imidazolium [27], piperidinium [28], and quaternary ammonium or pyrrolidinium [29] compounds. Chain length, the position of the substituents, and cation dimensions are some of the more influential parameters that drastically affect viscosity, electrochemical behaviour, ionic conductivity, and thermal stability. Aspects such as these have contributed to the large-scale acceptance of ILs as electrolytic components of various energy storage systems. Along with some of the unique advantages that they offer, like better interface development, enhanced safety, and excellent electrochemical stability, a significant improvement in the performance and reliability of such devices has been attained [27].

1.4. Ionic Liquids (ILs) for Lithium–Ion Batteries

As the years pass, the demand for ESSs has increased and, according to that demand, new technologies have been adapted to improve ESSs. Figure 2a shows the growth in the rechargeable battery market for ESSs from 2005 to 2030. Before 2005, Pb–acid batteries contributed more than 80% of total energy production in GWh. In 2023, their estimation was maintained at around 50–60% on the moderate scale, while, by the end of 2030, LIBs are expected to have taken over the battery sector with more than a 50% share in the total production of energy [30–32].

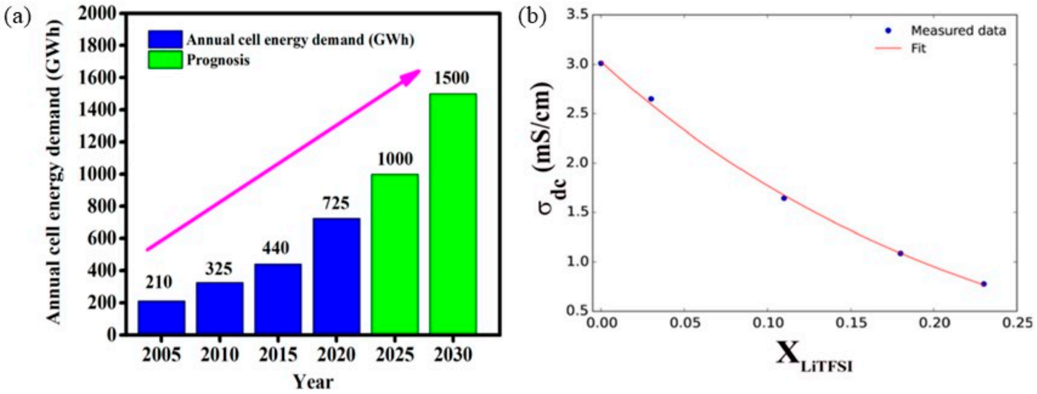


Figure 2. (**a**) Progress and prognosis of energy requirements from 2005 to 2030. (**b**) Graph showing ionic conductivity of LiTFSI in $Pyr_{1,4}$TFSI, plotted against the mole fraction of LiTFSI. Adapted with permission from [33]. Copyright 2015, Wiley.

Typically, the active material at the cathode in LIBs is composed of metal oxides, whereas graphite is the major active material at the anode side. Over the past decades, extensive efforts have been directed toward enhancing energy density by developing high-capacity anodes and high-voltage cathodes. The electrolyte is one of the prime components of an LIB in various aspects. Modern electrolytes are generally composed of a mixture of lithium salts and organic carbonates, such as diethyl carbonate (DEC), ethylene carbonate (EC), ethyl methyl carbonate (EMC) etc. [34,35]. While such electrolytes have many advantages concerning ionic conductivity and capacity, serious problems also arise concerning safety. These originate from thermal instability, flammability, and volatility and are indeed major threats to LIBs. Additionally, these solvents have the ability to intercalate and exfoliate graphite firmly; however, this behaviour is not seen with ionic liquid electrolytes because ILs cannot intercalate at such a high potential [36]. Ionic liquids, for lack of a better term, are considered a promising alternative with which to balance most of the drawbacks of liquid electrolytes. In fact, ILs remove flammability risks and provide excellent electrochemical stability, reduce possibilities of leakage, and improve thermal stability. Thus, ILs are considered a safer alternative by which to improve the safety of batteries.

Rothermal et al. [37] prepared an adequate IL-based Pyr_{14}TFSI–LiTFSI electrolyte mixture for "dual-graphite" electrode LIB cell configurations. Besides the fact that this IL-electrolyte showed very good electrochemical stability, it favoured the formation of a stable SEI onto the graphite anode. Surprisingly, the cell discharge capacity rose from 50 mAh/g to 97 mAh/g. The lithiation and DE lithiation of Li^+ ions in LIBs are greatly influenced by the blending of two or more dissimilar kinds of anions. Very recently, Balabajew et al. [33] discussed the cell performance of $Pyr_{14}TFSI$ with variable-concentration LiTFSI electrolytes. The results were found to show that the ionic conductivity of the electrolyte decreases significantly during the increment of the mole fraction of LiTFSI. In turn, the ionic conductivity loss via the cluster formation of $[Li(TFSI)_n]^{(n-1)-}$ is coupled with the extension of the battery's lifetime by Li^+ ion migration in combination with the originally coordinated $TFSI^-$ shell. Higher-order $[Li(TFSI)_n]^{(n-1)-}$ clusters, in turn, decrease the diffusion coefficients of Li^+ and $TFSI^-$ (Figure 2b).

2. Classification of ILs

By chemical form, ionic liquids generally fall into one of three different categories: protic ionic liquids, aprotic ionic liquids, and zwitterionic liquids. Of these three, between PILs and AILs, as similar as they are physiologically, the major distinction occurs in relation to a free or accessible proton on the cation for PILs, where none exists for AILs and their exit charges in the zwitterionic type.

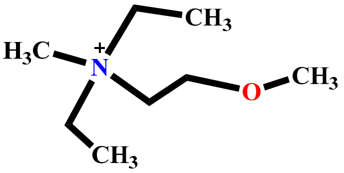
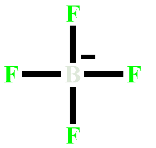
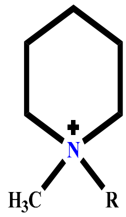
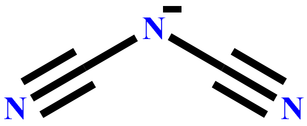
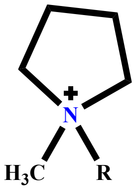
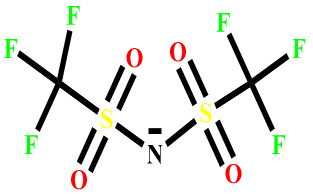
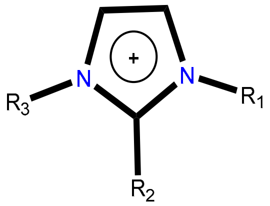
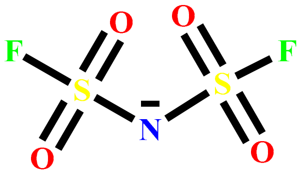
2.1. Protic Ionic Liquids (PILs)

PILs are considered a subclass of ILs. Typically, PILs are prepared by neutralization reactions between a Brønsted acid acting as a proton donor and a Brønsted base acting as a proton acceptant [38,39]. Protic ionic liquids possess all of the characteristics that make ionic liquids so attractive but, in many instances, provide the added advantages of easier, less costly synthesis relative to aprotic ionic liquids, properties that make PILs attractive candidates for application as components of electrolytes in electrochemical devices. Until recently, however, PILs have not been utilized in such a way. This organic cation was found to be unsuitable for electrochemical applications due to its acidic proton and high reactivity with lithium; hence, the focus shifted toward AILs. In 2013, Bockenfeld et al. [40] demonstrated that, in PILs with less than 20 ppm water, the labile proton located on the cation is no longer "free" and does not contribute to the reversible processes of protonation and deprotonation. This finding opened up new avenues by which to exploit PILs in electrochemical devices. This work also demonstrated that the LFP electrode is effectively usable with the electrolytes containing dry polymer ionic liquids and does not undergo structural changes. In general, the efficiency of the LFP-made cathode in PIL-based electrolytes looks very promising, showing favourable capacity and cycling stability.

2.2. Aprotic Ionic Liquids (AILs)

AILs are widely used ILs as electrolytes in lithium–ion batteries (LIBs). The high thermal stability, good ionic conductivity, low volatility, and low flammability are the reasons for this. For more than a decade, much research has been undertaken on AILs with the aim of tuning its properties so as to be more suitable for electrolytes. Several combinations of anions and cations are used to realize AILs, most importantly imidazolium, piperidinium, pyrrolidinium, and pyridinium as cations, while PF_6^-, tetrafluoroborate (BF_4^-), and bis(trifluoromethanesulfonyl)imide $\left(TFSI^-\right)$ are the most used anions, as shown in Table 1. However, such a combination of anions and cations influences significantly different properties of ILs. For instance, imidazolium cations enable the preparation of ILs with higher conductivity when compared with ILs based on pyrrolidinium and piperidinium cations. In turn, using these latter two kinds of cation provides ILs with a broader ESW compared with imidazolium-based ILs [41]. The thermal stability of ILs based on PF_6^- is always much lower compared with that based on $TFSI^-$ [42]. AILs based on FSI^- also exhibit comparably low viscosity to $TFSI^-$ based AILs [42,43].

Table 1. Widely used combination of anions and cations with their structures.

Cations	Anions
 **N,N-diethyl-N-methyl-N(2-methoxyethyl) ammonium, [DEME]$^+$**	 **Tetrafluoroborate, [BF$_4$]$^-$**
 **N-methyl-N-alkyl piperidinium [C$_n$mpip]$^+$**	 **Dicyanamide, [dca]$^-$**
 **N-methyl-N-alkyl pyrrolidinium [C$_n$mpyr]**	 **Bis(trifluoromethanesulfonyl)amide, [NTf$_2$]$^-$**
 **1,2-dialkyl methylimidazolium, [C$_n$C$_n$mim]$^+$**	 **Bis(fluorosulfonyl)imide, [FSI]$^-$**

The extensively used AIL in the past has been N-butyl-N-methyl pyrrolidinium bis (trifluoro methane sulfonyl) imide (PYR$_{14}$TFSI). This is a hydrophobic AIL that is air stable and displays very good thermal stability. The viscosity and ionic conductivity of PYR$_{14}$TFSI at 20 °C are found to be 95 mPas and 1.85 mScm^{-1}, respectively—considerably good values for an electrolyte—and its electrochemical stability window (ESW) is more than 5.5 V [42,44]. Several tests, performed by Lewandowski et al. [41] with PYR$_{14}$TFSI in combination with different cathodic and anodic materials, have demonstrated that ionic liquid-based LIBs with outstanding cycling stability can be envisioned. Other AILs, in particular those based on different imidazolium cations combined with the TFSI$^-$ anion, have shown similar promising behaviour. FSI$^-$ was considered in several recent studies owing to the fact that this anion allows for the preparation of electrolytes that show higher ionic conductivities than TFSI$^-$ and sometimes even PF$_6^-$ based systems. For example, the conductivity of PYR$_{14}$FSI at 20 °C is ca. 4 mS/cm, i.e., twice that of PYR$_{14}$TFSI at the same temperature. In contrast, FSI$^-$-based ionic liquids usually show lower thermal stability than their TFSI$^-$-based homologues [42]. When these AILs exhibit impressive film forming ability and stability, the studies showed that the effective SEI that is possible from FSI$^-$ and TFSI$^-$ lack these properties of FSI$^-$ (Figure 3) [45–47]. LiTFSI has a lower molecular weight (197 g) compared with LiFSI (297 g). Despite this, cells using LiFSI demonstrate higher specific energy, which is a critical factor for applications requiring high energy density, such as electric vehicles [48]. The majority of AILs used in energy storage systems (ESSs) are imidazolium based, pyridinium based, phosphonium based, pyrrolidinium based, or ammonium based, given in Figure 4a.

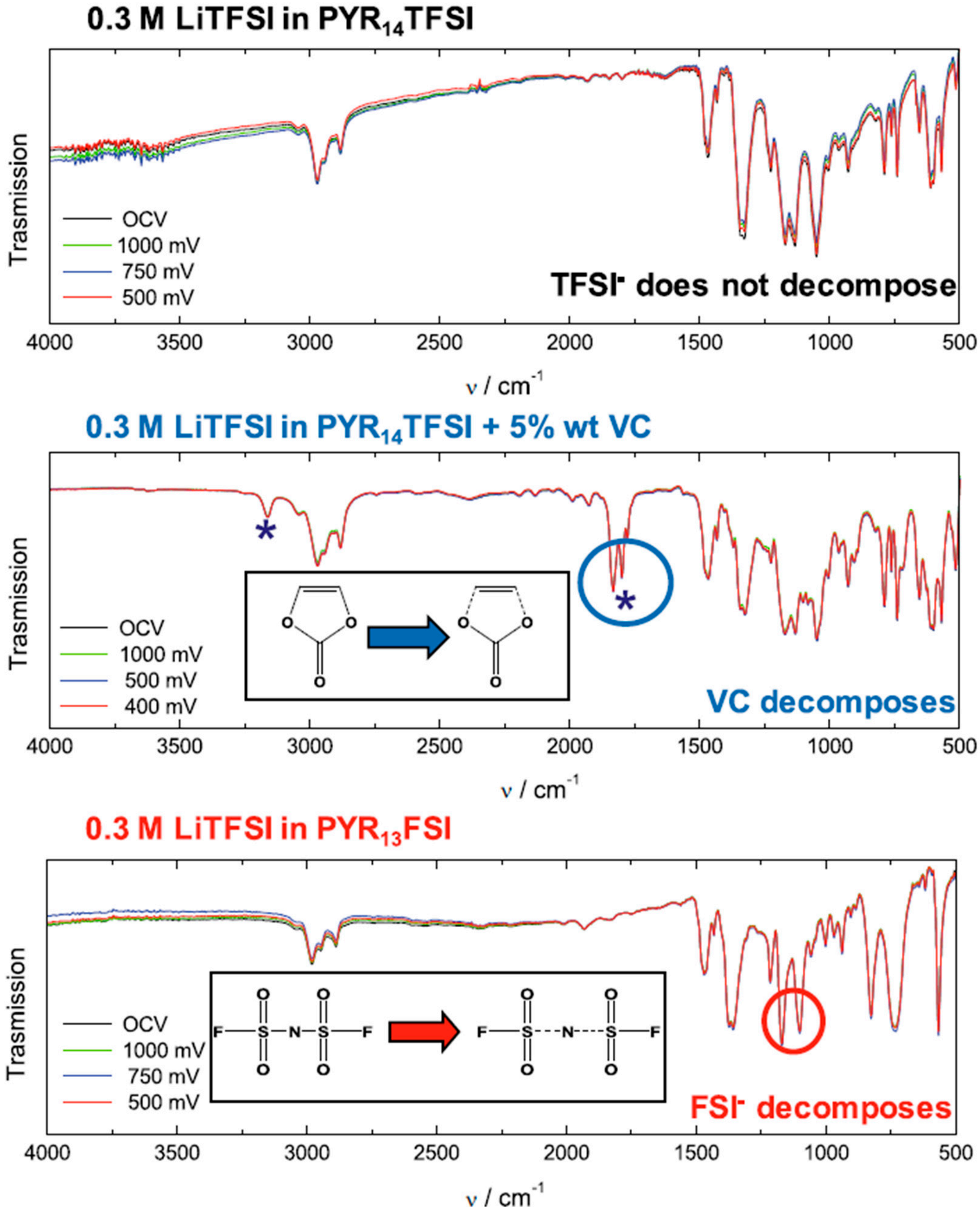


Figure 3. FTIR spectra of pyrrolidinium-based ionic liquids (ILs) frequently employed in lithium–ion batteries obtained in-situ: $PYR_{14}TFSI$ and $PYR_{13}FSI$. At 500 mV vs. Li/Li^+, the $TFSI^-$ anion remains stable, while the FSI^- anion shows signs of decomposition. Consequently, when using $PYR_{14}TFSI$ with a graphite anode, an additive such as vinylene carbonate (VC) is necessary. In contrast, $PYR_{13}FSI$ can be utilized without any additives due to its inherent film-forming properties. Adapted with permission from [1]. Copyright 2017, Springer.

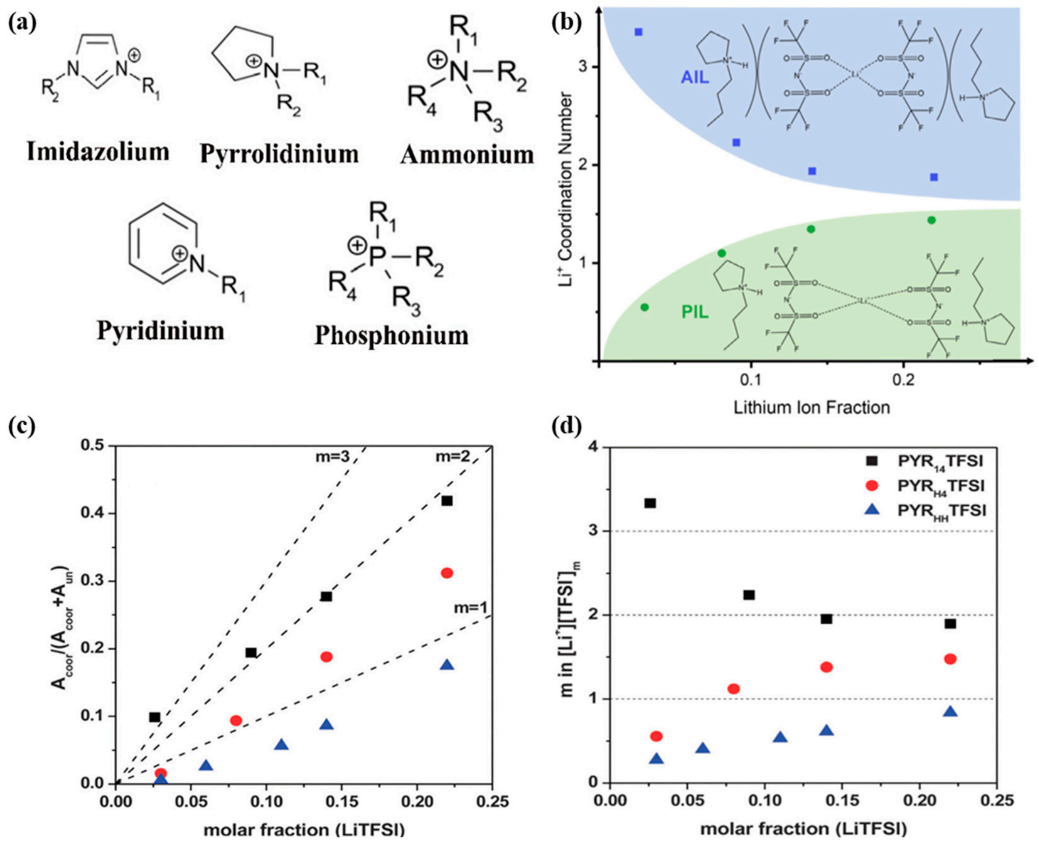


Figure 4. (**a**) Most commonly used AILs. (**b**) Impact of the type of IL on lithium–ion coordination in electrolytes based on [TFSI]$^-$. The number of TFSI anions surrounding Li$^+$ is shown by the Li coordination in the figure. Adapted with permission from [49]. Copyright 2021, Elsevier. (**c**) The ratio of lithium-coordinated TFSI anions as the molar fraction of LiTFSI. (**d**) The lithium coordination numbers (m) in relation to the molar fraction of LiTFSI for PYR$_{14}$TFSI, PYR$_{H4}$TFSI, and PYR$_{HH}$TFSI. The dashed lines serve as visual guides for the lithium coordination numbers (m). Adapted with permission from [50]. Copyright 2014, Royal Society of Chemistry.

AILs and PILs are studied here based on their conductivity. Like anion–cation combinations, the similar is rather comparable [49]. It is germane to note, however, that in these two classes of ionic liquids, the conduction mechanisms may fundamentally be quite different. For aprotic ionic liquids, on the one hand, the principal ionic transport comes through a vehicular mechanism wherein the ions move under the influence of, and with limitations imposed by ion–ion interactions as well as medium viscosity [51]. There is also another type of conduction mechanism possible in PILs due the presence of protons. In such a system, which also contains both proton donors and acceptors, protons can easily cross over the electrolytes by hopping, similar to the Grotthuss effect in aqueous media, thereby enhancing proton transport and thereby the overall ionic conductivity in PILs [52,53]. This hopping phenomenon is exaggerated by the considerable content of water in PILs. Furthermore, this is a temperature-dependent phenomenon; it might, for example, overshadow the general conduction mechanisms taking place in the ionic liquid at the glass transition temperature of a PIL. This shows that, in an ideal case, conduction could be somewhat insensitive to viscosity and allow for superior ionic mobility independent of viscosity changes [54].

Reports indicate that AILs and PILs with analogous anion–cation combinations exhibit similar viscosities, and that the most effective method to reduce viscosity in both cases is to diminish the strength of the interactions between the anion and cation. Regrettably, as of now, it remains impossible to accurately forecast the effects of certain ion combinations on the characteristics of ionic liquids (of any type) [49]. Consequently, a substantial quantity of ionic liquids, encompassing both aprotic and protic varieties, exists. The objective is to comprehend the impacts of many characteristics, including cation ring size, alkyl chain length, anion size, and the extent of fluorination, on their properties. Their synthesis and characterization have been conducted. The research conducted by Susan et al., among others, offers valuable insights into a diverse array of PILs, facilitating the identification of general themes, as noted in [55,56]. (1) Strong bases and acids, such as bis(trifluoromethane)sulfonimide (HTFSI) and HBF_4, generally result in highly ionic PILs [57]; (2) the anion seems to have a stronger impact on the viscosity of PILs compared with the cation (the latter is not the case for AILs) [57–59]; (3) highly fluorinated anions diminish Van der Waals forces, whereas elongated alkyl chains on the anion augment viscosity [39,58]; (4) consequently, the weak hydrogen bonds within the PIL will lead to an overall increase in ion mobility [60]. This has increasingly begun to be recognized as a key parameter in PILs, in that reducing such a parameter—for example, by the use of less favourably stacked cations or by charge delocalization on the anion—significantly reduces ion–ion interactions, often with very large effects on performance and conductivity [61]. The interactions of the $TFSI^-$ anions with protic ionic liquids and aprotic ionic liquids have been studied by Menne et al. Figure 4b illustrates that the addition of LiTFSI increases the coordinating TFSI anions in the electrolyte. Although the coordination number of TFSI anions to lithium in $PYR_{14}TFSI$ is one order of magnitude higher than that of its protic ionic liquids, $PYR_{H4}TFSI$ and $PYR_{HH}TFSI$, it is noteworthy that the opposite trend of $PYR_{14}TFSI$ with respect to $PYR_{H4}TFSI$ and $PYR_{HH}TFSI$ can be seen, especially at low LiTFSI molar fractions such as 0.03, as shown in Figure 4c,d. More precisely, an increase in the molar fraction of LiTFSI in $PYR_{14}TFSI$ has been found to decrease the coordination number of lithium. Similarly, the enhancement of the molar fractions of LiTFSI in $PYR_{H4}TFSI$ and $PYR_{HH}TFSI$ was found to increase the coordination number of lithium correspondingly [50].

2.2.1. Imidazolium-Based ILs

Much interest in ILs for their application as electrolytes in lithium–ion batteries and supercapacitors has been focused on imidazolium-based ILs thanks to their tuneable physico-chemical properties combined with low viscosity and high ionic conductivity. Typical representatives of such ILs, very often of mainly nonamphiphilic nature, are the 1-ethyl-3-methylimidazolium ($EMIM^+$) and 1-butyl-3-methylimidazolium ($BMIM^+$) cations. It has been reported that the electrochemical potential window for $BMIMBF_4$ reaches as high as 3.5 V, which is much better as compared with regular electrolytes such as KOH, with a maximum of 1 V, and $LiPF_6^-$, with a maximum of 2.5 V. Therefore, due to the increased electrochemical potential window, imidazolium-based ionic liquid has become a promising candidate by which to increase energy storage device performance [62]. Boujibar, O et al. [63] found that, in addition to having a wide electrochemical window (up to 3.5 V) and electrochemical stability, ethyl-methyl imidazolium tetrafluoroborate ($EMIMBF_4$) electrolytes have a large specific capacitance (198.15 F/g) and decent energy density (82.93 Wh/kg), and power density (3487 W/kg). Pham, D. T. et al. [64] documented that, for graphene blocks bridged with a carbon nanotube in a supercapacitor, $BMIMBF_4$ electrolytes can yield an electrochemical window as high as 4.0 V. Energy and power densities reached respective values as high as 110.6 Wh/kg and 400,000 W/kg, with a correspondingly high specific capacitance of 49 F/g. Momodu et al. have reported a 3.0 V stable potential window for (EMIM)(TFSI)-based ILs from capsicum seed-porous carbon [65]. Que, M. et al. [66] studied a more suitable electrolyte for LIBs, showing thermal stability of up to 370 with a good potential window of around 4.8 V, the electrolyte was prepared by a mixture of (EMIM)(TFSI) incorporated into 3P(MPBIm-TFSI). Zaghib et al. [67] demonstrated that a gel electrolyte containing lithium bis(fluorosulfonyl)imide (LiFSI) exhibited a high reversible capacity of 360 mAh/g and a high Coulombic efficiency of 91.6%. The $LiFePO_4$ cathode showed a reversible capacity of 160 mAh/g and a Coulombic efficiency of 92%. Poor electrical conductivity and higher viscosity at low-temperature applications are the two major features of imidazolium-based ionic liquids that act as barriers to large-scale industrial applications. In the last decade, many publications have centred on the addition of hydrophobic proton organic solvents to enhance low-temperature electrical conductivity in imidazolium-based ionic liquids.

2.2.2. Pyrrolidinium-Based ILs

In recent years, pyrrolidinium-based ionic liquids have gained a leading position for application as LIB electrolytes due to their excellent electrochemical stability, large electrochemical windows, and very low volatility. Thus, these ILs have particularly interest for high-voltage and high-temperature applications, offering a much safer and more efficient alternative to conventional organic solvent-based electrolytes. Various methods have been attempted for the introduction of pyrrolidinium-based ILs in LIBs: with fluorinated linkers, as dual network gel electrolytes, and as mixed plastic crystal electrolytes [68]. Modification of the pyrrolidinium cation increases the ionic conductivity of IL-based electrolyte solutions. Among such compounds, N-butyl-N-methyl pyrrolidinium (trifluoro methyl sulfonyl) imide ($Pyr_{14}TFSI$) has recently gained much interest in ESS application because of its very good thermal and electrochemical stability, with high supporting voltages up to 5.5 V and good thermal stability up to 300 °C [69,70]. Katcharava and co-workers [71] proposed a pyrrolidinium based IL exhibiting electrochemical stability up to 7 V and a thermal stability up to 370 °C, the study also showed that the ionic conductivity of the electrolyte is about 10^{-4} S Cm^{-1}. Yang et al. [72] reported a pyrrolidinium-based IL, N-propyl-N-methylpyrrolidiniumbis (trifluoromethanesulfonyl) imide ($Pyr_{13}TFSI$) mixed with organic additives and LiTFSI which exhibited an electrochemical potential of 4.8 V, high thermal stability, non-flammability, and low viscosity, showing its suitability for use as an electrolyte in LIBs. Reinoso et al. [73] studied ionic liquid solution of Pyr14TFSI with lithium salt LiTFSI into a sintered lithium, aluminium, titanium (LATP) ion-conducting porous ceramic to form quasi-solid-state hybrid electrolytes. The latter exhibits high ionic conductivity of about 10^{-3} $S{\cdot}cm^{-1}$ at 303 K, enhanced ion transfer number tLi+, and a wide electrochemical window of 4.7–4.9 V when compared with Li^+/Li. Quezada et al. [74] reported a safer LIB which uses 1 M-LiNTF2 mixed with 1-methyl/butyl-1-propyl pyrrolidinium bis(trifluoromethanesulfonyl) imide ((MPPyr/BMPyr)(TFSI)) and zinc stannate as an anode material. This provided a discharge capacity of 306.3 mAh/g for BMPyrTFSI and 296.2 mAh/g for MPPyrTFSI. The present paper underlines how diverse structures of cations in IL electrolytes could influence lithium–ion battery performance and takes up these two examples in order to point out differences in the observed electrochemical behaviour. Deb et al. presented an active polymer membrane based on (P(VDF-HFP)), fabricated by a pyrrolidinium ionic liquid-based nanofluid, which can widen the electrochemical potential window to as high as approximately 5.3 V vs. Li/Li^+ in lithium–ion batteries [75]. During supercapacitor electrode development, Kalinova et al. [76], developed a new class of pyrrolidinium-based protic ionic liquids showing better conductivity. Among them, one ionic liquid showed an exceptional cycle life of up to 7000 cycles, with capacitance retention as high as 87%.

2.2.3. Quaternary Ammonium-Based ILs

Quaternary ammonium-based ILs are considered the most suitable eligible and promising electrolytes for ESSs, with slight modifications due to their excellent electrochemical stability and wide potential window, usually above 5 V when compared with Li^+/Li. The same ILs are highly attractive in terms of the improved safety and performance of LIBs in high-energy and high-temperature applications. Quaternary ammonium cation-based ILs can offer several advantages concerning electrochemical stability and reduced viscosity, advantages which are necessary for effective lithium–ion transport and for the operation of the batteries. The important features related to the adoption of quaternary ammonium-based ILs in LIBs are discussed based on interesting insights drawn from recent work. In contrast with imidazolium- and pyrrolidinium-based ILs, quaternary ammonium ILs present such advantages because the shorter alkyl chains reduce the viscosity and enhance the ion mobility of the former, making them much more suitable for ESS high-voltage applications. Shiro Seki et al. [77] investigated the electrochemical properties of the quaternary ammonium cation [N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis (trifluoromethylsulfonyl) amide (DEMETFSA)], the study found that the lithium transport number was 0.13, indicating adequate charge/discharge reversibility over 100 cycles within a voltage range of 4.2 to 3.0 V. Honghe Zheng et al. [78] investigated the combination of trimethylhexylammonium (TMHA) with bis(trifluoromethane) sulfonylimide (TFSI), which demonstrated commendable performance, achieving a capacity of 108.2 mAh/g and a Coulombic efficiency of 91.4% during the first cycle with decreasing temperature; however, the capacity also decreases due to increased internal resistance and higher activation energy for lithium ion transfer across the electrode/electrolyte interface in a reversible cell. Cycled lithium metal symmetric cells were shown to be stable out to 100 cycles when operated at 2 mA/cm^2 and 50 °C. Full-cell cycling on an NMC811 cathode also demonstrated satisfactory performance out to 4.3 V under the same conditions, realizing 100 cycles with significant utilization of the active material in the cathode, about 12 mg/cm^2 [79]. A new class of dialkoxy functionalized quaternary ammonium ionic liquids (ILs) has been introduced by Zhengjian and co-workers [80] characterized by low viscosity and high ionic conductivity at room temperature. These ILs demonstrated an impressive electrochemical window of up to 5.57 V. Yongjin Mai et al. [81] studied synthesized organosilicon-functionalized quaternary ammonium ionic liquids (ILs) with oligo(ethylene oxide) substituents, which displayed excellent thermal stability, decomposition temperatures between 310 and 350 °C, and electrochemical stability, with electrochemical windows ranging from 3.9 to 4.7 V. These ILs were also miscible with commercial carbonate electrolytes, enabling the creation of hybrid electrolytes that preserved good lithium storage performance and cycling stability in lithium–ion batteries.

2.2.4. Pyridinium-Based ILs

Pyridinium-based ionic liquids are of great interest as a new generation of electrolytes for LIBs, considering their specific properties such as high electrochemical stability, large-scale electrochemical windows, and low volatility. Such properties make pyridinium-based ILs very promising for high-voltage, high-temperature applications, overcoming some of the disadvantages of traditional electrolytes. The following response discusses the prospects of pyridinium-based ILs as electrolytes for LIBs, considering their electrochemical properties, compatibility with lithium salts, and challenges in their application. Pyridinium-based ILs have shown excellent electrochemical stability, with a large electrochemical window that is suitable for application in high-voltage LIBs. A wider electrochemical window allows the pyridinium-based ILs to work at a voltage such that conventional carbonate-based electrolytes are already oxidatively decomposed [82]. The functional groups, such as ether linkers in ILs, enhance their electrochemical stability based on pyridinium. These modifications further improve ionic conductivity and thermal stability, enabling their use in high-temperature applications outside the capabilities of conventional electrolytes. These combined features make pyridinium-based ILs a promising choice for use in energy storage systems under extreme conditions [83]. Maegerita Moreno et al. [84] have reported pyridinium-based ILs via the formulation of 0.1LiTFSI-0.3PYR$_{13}$TFSI-0.6PYR$_{13}$FSI, which exhibited a high ionic conductivity of 10^{-3} S cm^{-1} at −20 °C and an electrochemical stability window of 5 V, indicating its potential use in lithium batteries. This ternary electrolyte formulation is compatible with high-voltage NMC cathodes that have capacities of 135 mAh g^{-1}, which are significant when compared with conventional alkyl carbonate-based solutions.

2.2.5. Phosphonium Based ILs

The phosphonium-based ILs show promise due to their unique physico-chemical properties. They possess several positive attributes, such as outstanding thermal stability, tuneable viscosity, and increased ionic conductivity—attributes that are considered paramount when seeking to gain improvements in the aspects of performance and safety in LIBs. In this chapter, different discussions, based on related studies, have been offered in terms of electrochemical behaviour and thermal stability and their possible application in LIBs using phosphonium-based ILs. Katsuhiko Tsunashima et al. [85] have reported a study which investigated phosphonium-based electrolyte triethyl(2-methoxyethyl) phosphonium bis(trifluoro methyl sulfonyl)imide [$P_{222(201)}$-TFSI] with a high discharge capacity of 155 mAh g^{-1} and which can retain a capacity of more than 85% over 50 cycles. Xinrong Lin et al. [86] have discussed the development of (mono-$(C_6)_3PC_{10}$TFSI) with 1.6 M LiTFSI, showing a conductivity of 1 mS cm^{-1} at 100 °C to 0.01 $mScm^{-1}$ at room temperature. This increase in conductivity, coupled with the electrolyte's thermal stability, supports the potential application of these batteries in high-temperature environments, such as oil exploration. Daniel Rogstad et al. [87] have reported the use of a phosphonium-based IL, P_{111i4}FSI, with 0.79 m and 3.0 m concentrations of LiFSI, revealing that 0.79 m LiFSI in P_{111i4}FSI results in better Coulombic efficiencies. The study also revealed an increase in lithium–ion mobility at elevated temperature, particularly for the P_{111i4}FSI-based electrolyte, giving 1 Ah/g at a 2 C rate at 60 °C.

2.3. Zwitterionic Liquids

Zwitterionic liquids, though less explored, are important class of ILs as they have high ionic conductivity, thermal stability and safety. Zwitterionic liquids are composed of tethered cations and anions, which contribute to their high melting points and thermal stability. The synthesis of various zwitterions has shown that their melting points are generally higher than those of simple ionic liquids, often exceeding 100 °C [88]. Zwitterionic liquids show many advantages in applications under low temperatures. The zwitterionic liquid-based gel electrolyte shows the highest conductivity and lithium–ion transference number below sub-zero temperatures ever reported among the many conventional gel electrolytes [89]. Hence, such materials are also suitable for applications at places where the temperature usually varies. Dai et al. [89] introduced a novel zwitterionic liquid (ZIL) encapsulated in a SiO_2 matrix, demonstrating a high conductivity of 3.36×10^{-4} Scm^{-1} at -40 °C. Addressing the low-temperature challenges of ILs, the study also revealed that the electrolyte exhibited excellent cycling stability and a capacity of 91.6 mAh g^{-1} at the 600th cycle at 0.5 °C and 0 °C and maintains a capacity of 67.1 mAh g^{-1} at -20 °C, outperforming most conventional electrolytes. Kang et al. [90] explored zwitterionic liquid COfs as electrolytes for LIBs, their study presents a zwitterionic covalent organic framework (Zwitt-COF) as a solid electrolyte that enhances the dissociation and transport of lithium ions, achieving a high room-temperature ionic conductivity of 1.65×10^{-4} Scm^{-1} and demonstrating a wide electrochemical stability window. Masahiro Yoshizawa et al. [88] synthesized a zwitterionic liquid which, when coupled with LiTFSI, should significantly increase the ionic conductivity of about 8.9×10^{-4} Scm^{-1} at 100 °C and show a decrease in the glass transition temperature to -37 °C.

Kun wang and coworkers [91] studied a zwitterion polymer electrolyte (zPU-SPE) which demonstrated an ionic conductivity of 7.4×10^{-4} S/cm at 25 °C. This electrolyte includes a high tensile break strength of 1700%, an adhesion energy of 487.5 J/m^2 and a low cell resistance of 280 W/cm^2. Significantly, it was found that its capacity decreased by only 3% after 500 cycles indicating its best suitability for lithium–ion batteries. Daniel Nuevo et al. [92] synthesized a novel zwitterionic liquid, one based on methyl sulfoxide imidazolium combined with bis (trifluoromethylsulfonyl) amide ($LiNTf_2$) and which exhibits ionic conductivity up to 3.4×10^{-5} S/cm at 30 °C and 2.9×10^{-5} S/cm at 120 °C. The study reports the synthesis of novel, non-flammable zwitterionic electrolytes consisting of 93 wt% zwitterionic ionic liquid and 7 wt% ethylene carbonates (EC), the electrolyte showcased an electrochemical window of 1.65–5.1 V and an ionic conductivity of 1×10^{-3} S/cm at 20 °C [93].

3. Physico-Chemical Properties of ILs

3.1. Thermal Stability

Thermal stability was set in terms of the working temperature of the organic electrolytes in a battery, such as dimethyl and ethylene carbonate and $LiPF_6$, and the hazard of explosion at high temperature owing to their flammability and combustion at around 50–60 °C [94]. Thus, at high temperatures the explosion hazard increases. Their non-flammability is a source of ILs highly thermally stable nature. In other words, they are not easily combustible and/or explosive when acting as a secondary lithium battery in extremely high heat, and would have a high threshold of heat runaway [13]. Xu et al. [13] have indicated that specific ionic liquids (ILs) featuring 1-alkyl-3-methylimidazolium or 1,3-dialkylimidazolium cations can attain thermal stability up to 400 °C. Examples are 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8mim]PF_6$) and 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim]PF_6$), which decompose at 416 °C and 438 °C, respectively, in turn allowing for their application at high temperatures in lithium–ion batteries. In this case, the ILs may withstand extreme temperature conditions without combustion or explosion. Several attempts have been made to establish the thermal stability of ILs by potentiometric titration. Among other results, the thermogravimetric decomposition temperatures of 278 °C for 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), 291 °C for 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), and 392 °C for 1-butyl-3-methylimidazolium methane sulfonate ($[BMIM][CH_3SO_3]$) have been determined (Figure 5a). The mechanistic pathway of [BMIM]Cl is shown in Figure 5b.

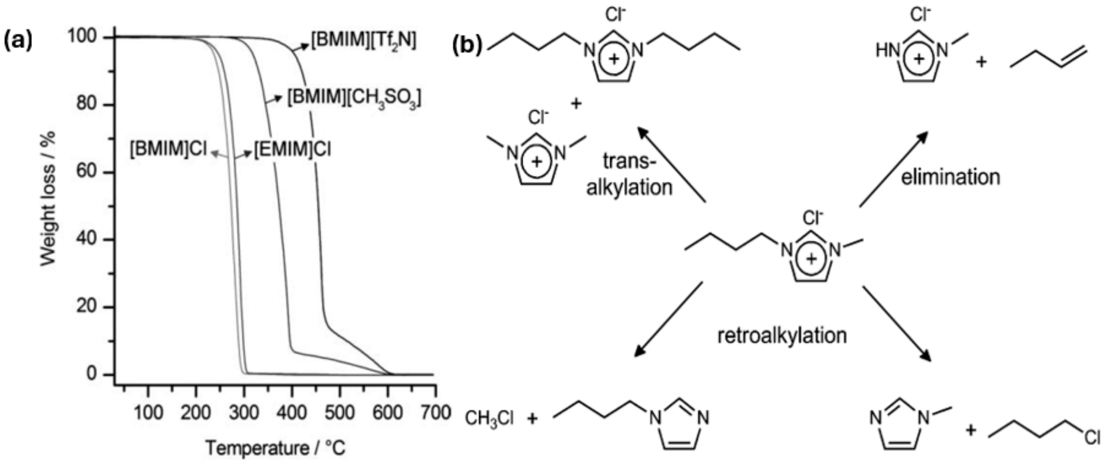


Figure 5. (**a**) TG curves of [BMIM]Cl, [EMIM]Cl, $[BMIM][CH_3SO_3]$ and $[BMIM][Tf_2N]$. ILs were heated at 5 °C min^{-1} under air. (**b**) Proposed pathways for the thermal degradation of [BMIM]Cl. Adapted with permission from [95]. Copyright 2010, Royal Society of Chemistry.

Fox et al. [96] measured the thermal stability of butyl methyl pyrrolidinium bis (trifluoromethanesulfonyl)amide ($[C_4mpy][Tf_2N]$) by TGA and did not detect decomposition up to 400 °C. In contrast, MacFarlane et al. [97] measured the same compound $[C_4mpy][Tf_2N]$ by the $T_{0.1/10}$ method, reflecting 1% degradation after 10 h, and for that method they report a value as low as 271 °C. This might be because TGA bases its working on the action of weight loss and, as such, cannot be used solely in the determination of overall thermal stability.

In conclusion, ILs with the correct modifications have emerged as promising candidates for organic electrolyte replacement in the application of high temperature lithium–ion batteries (HT-LIBs) due to their safer and more thermally stable nature.

3.2. Viscosity and Density

The viscosity of ILs exceed that of organic electrolytes by an order of one to three times, allowing one to examine certain organic electrolytes, such as ethylene carbonate (EC,

η = 1.9 cP) and diethyl carbonate (DEC, η = 0.644 cP) at a 1:1 wt% ratio [98]. The main restriction when using ILs as a electrolyte in LIBs is their viscosity, which is of the order of 20–600 cP [99]. The application of ILs as liquid electrolytes has shown good promise, while their wide industrial use is still very restricted due to some challenges like the need for highly pure materials, their inherently high viscosity, and their high cost of production, among others [100,101]. An improvement in ILs is seen when the temperature increases around 40–50 °C [102,103]. Due to the limited conformational flexibility and bulky size of organic cations, several IL-based electrolytes exhibit high viscosity [97]. Increased viscosity can result in poor wetting between the electrode and electrolyte, combined with lower ionic mobility, as predicted by the Stokes–Einstein equation [104].

$$\mathrm{D} = \frac{\mathrm{K_B T}}{6\Pi\eta\mathrm{r}} \tag{1}$$

where D denotes the diffusion coefficient, T represents the temperature, η denotes the viscosity, $\mathrm{K_B}$ refers to the Boltzmann constant, and r refers to the radius of the sphere.

The viscosity can be controlled by modification of the side chain in IL or by employing the hybrid electrolyte system where an additive is added to the ILs, maintaining its thermal stability but varying its viscosity and conductivity by changing the concentration of the additives, usually organic electrolytes or lithium salts; however, compromise is needed between performance enhancement and HT-LIB safety.

Nareerat Plylahan et al. [105] have reported the improvement of an electrolyte containing ILs (*n*-propyl-*n*-methyl pyrrolidinium bis(trifluoromethanesulfonyl)imide) ($\mathrm{Pyr_{13}TFSI}$) and lithium salt (lithium bis(trifluoromethanesulfonyl)imide) (LITFSI), having a higher viscosity of 180 cP and a lower ionic conductivity of 1.5×10^{-3} $\mathrm{Scm^{-1}}$ compared with the synthesized hybrid. This is achieved by adding 6.5 wt% of propylene carbonate (PC), fluoroethylene carbonate (FEC), and vinylene carbonate (VC). The viscosity of the hybrid electrolyte was found to be 110 cP, and the ionic conductivity was elevated to 3×10^{-3} $\mathrm{Scm^{-1}}$ at a temperature of about 30 °C.

Paduszynski et al. [106] devised a forecasting technique based on the Vogel–Tammann–Fulcher (VTF) equation based on cation + anion + side chain; the general form is shown as Equation (2).

$$\ln\left(\frac{\eta}{(Pa.s)}\right) = A_\eta + \frac{B_\eta}{T - T_{0\eta}} \tag{2}$$

A_η, B_η are the derived coefficients from the linear combination of the respective group contributions, while $\mathrm{T}_{0\eta}$ is a fixed constant irrespective of the type of ionic liquid.

An important factor one should not neglect while considering viscosity is the IR drop or Ohmic drop. Though of relatively low viscosity, RTILs also possess viscosities of around 20–200 mPa·s at 25 °C; however, while their electrochemical conductivity need not be compensated, the compensation of Ohmic drop must be considered while calculating the ionic conductivity. Table 2 clearly illustrates the relationship between viscosity, ionic conductivity, and the Ohmic drop [107].

Table 2. IR drop measurements at 1.0 $\mathrm{mA/cm^2}$ through a disk working electrode.

Viscosity (mPas)	**Conductivity ($\mathrm{mScm^{-1}}$)**	**Resistance (kΩ)**	**IR Drop (V)**		
			d = 1.6 mm	**d = 1.0 mm**	**d = 32 mm**
500–1000	0.1	10	0.2	7.85	80
100–500	1	1	20	785	8
40–100	5.0	0.2	4	157	1.6
20–40	10.0	0.1	2	78.5	0.8

3.3. Electrochemical Window

Although most of the attention in regards to ILs has gone toward their electrochemical properties, their application as electrolytes in supercapacitors, electrochemical synthesis, and batteries has also been widely reported [108,109]. Generally, stability is the main factor in any application involving electrochemistry, which usually limits both the performance and applicability of the electrochemical device at hand. The typically adopted method used to assess such stability involves what is termed the electrochemical potential window. This is a technique of voltage measurement between the cathodic and anodic limits. The cathodic limit corresponds to the reduction potential, while the anodic to the oxidation potential of IL. Thus, the electrochemical potential window fixes the voltage range at which the IL is inert without the start of any redox reaction. Thus, in IL-based electrolytes, the electrochemical stability will be dominated by the reduction and oxidation potentials related to ILs. Hence, there are empirical and theoretical studies in the development of electrolytes showing wider electrochemical windows. More importantly, ionic liquid electrolytes are dependent upon the Li^+ salt in use. Because Li^+ is a Lewis acid, it pulls one lone pair from the anion and hence forms a bond between them. This results in the decrease of the HOMO energy level of the anion and hence affects the whole electrochemical stability of the molecule. What makes these ionic liquids especially interesting is the large electrochemical potential window of >6 V compared with those of ordinary organic solvents with supporting electrolytes: the acetonitrile has a window of 5.0 V, and dichloromethane has 3.5 V, while DMSO has a potential window of 4.4 V [110]. The primary concern regarding ionic liquids (ILs) is their cathodic stability at lower potentials, predominantly due to the cations. Ionic liquids containing nitrogen in a heterocyclic configuration, such as those from the imidazolium family, are inappropriate for application with carbon anodes. The imidazolium cations experience a reduction or breakdown at the carbon electrode when the voltage is lowered to 0.7 V vs. Li^+/Li [111].

Cheng Lian et al. proposed an equation, based on the previous research work of [112] for the cathodic and anodic potential limit V_{CL} and V_{AL}, expressed respectively as follows:

$$V_{CL} = -\frac{\varepsilon_{LUMO}}{e} \tag{3}$$

$$V_{AL} = -\frac{\varepsilon_{HOMO}}{e} \tag{4}$$

Here, ε_{LUMO} and ε_{HOMO} are levels corresponding to LUMO and HOMO energies, respectively. The experiment was performed by Cheng using an RTIL mixture of the EMI, TFSI and BF_4 ions. Where the cathodic limit and anodic limit are determined using the maximum cathodic limit and minimum anodic limit of each ion. The calculations made in the work by computation are visualized below in the following figures, wherein Figure 6a represents the cathodic and anodic limits of all three ions, Figure 6b represents the potential limit of each electrode having symmetry, Figure 6c shows the effect of RTIL composition mixture on the potential window and the electrochemical double layer capacitance (EDLC), and Figure 6d represents the energy density of EDLC calculated by $E = CV^2/2$ for different mixtures, which clarifies maximum energy density at $x = 0.25$.

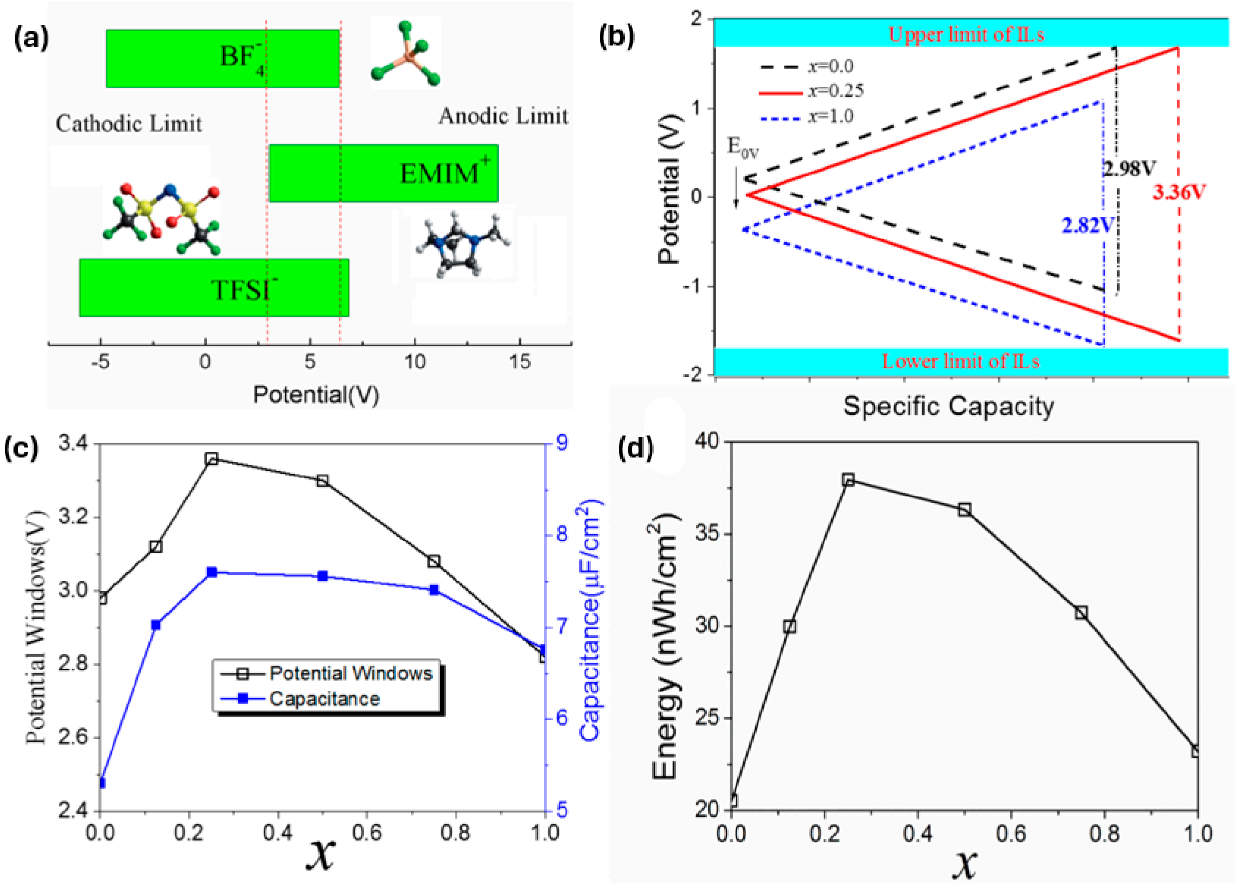


Figure 6. (**a**) Scheme showing the relation of the ESW with respective cathodic or anodic limits for the individual ions; green bars represent the EW ranges for the anions and cations. (**b**) A way of calculating the OPW of different mixtures (χ). (**c**) OPW and capacitance as a function of RTIL composition mixture (χ). (**d**) Energy density as a function of the mole fractions of EMI-BF$_4$ in RTIL mixture (χ). Adapted with permission from [112]. Copyright 2018, American Chemical Society.

3.4. Ionic Conductivity

Ionic conductivity of ILs is comparatively lower than those of organic electrolytes because of their high viscosity, which reduces the mobility of ions. Typical ionic conductivities of ILs will range from 10^{-3} to 10^{-2} at ambient room temperature [113]. One of the crucial parameters to gauge the performance of the electrolytes is ionic conductivity, as it allows the migration of ions between the electrodes during the charging and discharging of batteries. There are several factors which influence the ionic conductivity of ILs, such as size of the ions, structure of ions, viscosity, temperature, etc.

The viscosity of ILs is higher than organic solvents, as discussed in the Section 2.2, limiting their conductivity. The viscosity of ILs is due to the strong Coulombic interactions between ions and the steric hindrance resulting from the large ionic species [114].

The reduced ionic conductivity is due to the way in which mobility is decreased by the increased size of the ion. It has been determined that greater thermal energy will decrease the viscosity and that the mobility of the ions will thus increase, resulting in a rise in conductivity in line with the rise in temperature. Most researchers currently focus on low-temperature ionic liquids for the maintenance of battery efficiency during winters and in the cold region.

Several routes are possible and can be followed to enhance the conductivity of ILs, among which are the addition of various low-viscosity diluents such as ethers, carbonates, and hydrofluoroethers. Inclusion of the above classes of compounds has shown remarkable enhancement in the ionic conductivity of IL-based electrolytes [115]; however, it is key to maintain a similar vapour pressure. Matteo Palluzzi et al. [114] have reported the use of fluorinated anions and an optimized alkyl chain length for the cation, resulting in the improvement of ionic conductivity. Gregorio Guzmán-González et al. [116] were able to show that lithium borate ionic liquids (LiILs) could act as single-component electrolytes for LIBs, with high ionic conductivity values of more than 10^{-4} S cm^{-1} at room temperature (25 °C) and high lithium transference numbers, $tLi^+ = 0.4–0.5$, demonstrating their effectiveness in promoting lithium–ion transport. The selected LiILs exhibit a high electrochemical stability of over 4 V and compatibility with lithium–metal electrodes, as evidenced by the stable polarization profiles in plating/stripping tests. In addition, they show promising discharge capacity values of 124 mAh g^{-1} and 75 mAh g^{-1} in lithium–iron phosphate and lithium titanate cells, respectively, at a C-rate of 0.2 C and 65 °C with minimal capacity loss.

Anna Jaosik et al. [117] demonstrated the temperature dependence of the conductivity of ionic liquids by taking the mixture of two ILs, MPImBr (1-methyl-3-propylimidazolium bromide) and $EMImBF_4$ (1-ethyl-3-methylimidazolium tetrafluoroborate) with relative weight percentages as given in the table below. From Table 3 it is evident that, as the Wt% of $EMImBF_4$ decreases, the specific conductivity decreases; however, such a trend is not observed in activation energy $E^\#$ [117].

Table 3. Temperature dependence of ionic conductivity in the mixture containing MPImBr and $EMImBF_4$ [117].

$EMImBF_4$ + MPImBr			
Wt.% of $EMImBF_4$	**χ_{IL} of $EMImBF_4$**	**σ (298 K) [mS/cm]**	**$E^\#$ [kJ/mol]**
100	1.00	13.9	20.3
0.76	0.77	7.3	29.4
0.54	0.55	4.1	28.7
0.39	0.40	2.6	37.1
0.26	0.27	1.7	39.5
0.00	0.00	0.3	57.1

4. Synthesis of ILs

Synthesis of ILs is not a difficult process, but the careful selection and combination of anions and cations are important to obtain a distinctive property required as electrolytes. Some of the important syntheses of widely used ILs are documented in the present review. Barbora Galajdová et al. [3] reported a yield of 84% of methyl tributyl phosphonium bis(trifluoromethyl sulfonyl)imide P_{1444}-TFSI. Methyl iodide (0.3 mol) was added to solution of triphenylphosphine (0.3 mol) in methanol and stirred at room temperature for 3 h followed by distillation of methanol to obtain white solid methyl tributylphosphonium iodide $[P_{1444}]^+[I]$. Later, a 10% aqueous solution of LiTFSI was mixed with 5% solution of $[P_{1444}]^+[I]^-$ in water, which was then heated at 80–90 °C for an hour before being extracted in a separating funnel with ethyl acetate. The resultant organic layer was rinsed with distilled water and dried at 80 °C to eliminate leftover water and ethyl acetate. The schematic is given below in Figure 7.

The same study reported the synthesis of trimethyl sulfonium bis(trifluoromethyl sulfonyl) imide [S_{111}-TFSI], with an overall yield of 85%. trimethylsulfonium iodide (0.5 mol) solution with 500 mL distilled water was then mixed with 500 mL of LiTFSI (0.6 mol). The reaction mixture was stirred at 40 °C for 1 h, after cooling and phase separation, the bottom oily layer consisting of [S_{111}-TFSI] was collected, rinsed with distilled water, and dried overnight at 80 °C [3]. Tzi-Yi Wu and co-workers [22] demonstrated the synthesis of cyclic amine-based Bronsted acidic ILs, including the addition of acids (formic acid, trifluoroacetic acid) dropwise to the flask containing amine compounds over 24 h at room temperature, and with a slight excess amine compound used to ensure a proper and complete reaction. The mixture was heated to 85 °C to remove excess amine and water in vacuum using a rotary evaporator and the compounds were heated at 80 °C for 2 days with phosphorous pentoxide P_2O_5 to remove excess water. The schematic for the reaction is given in Figure 8.

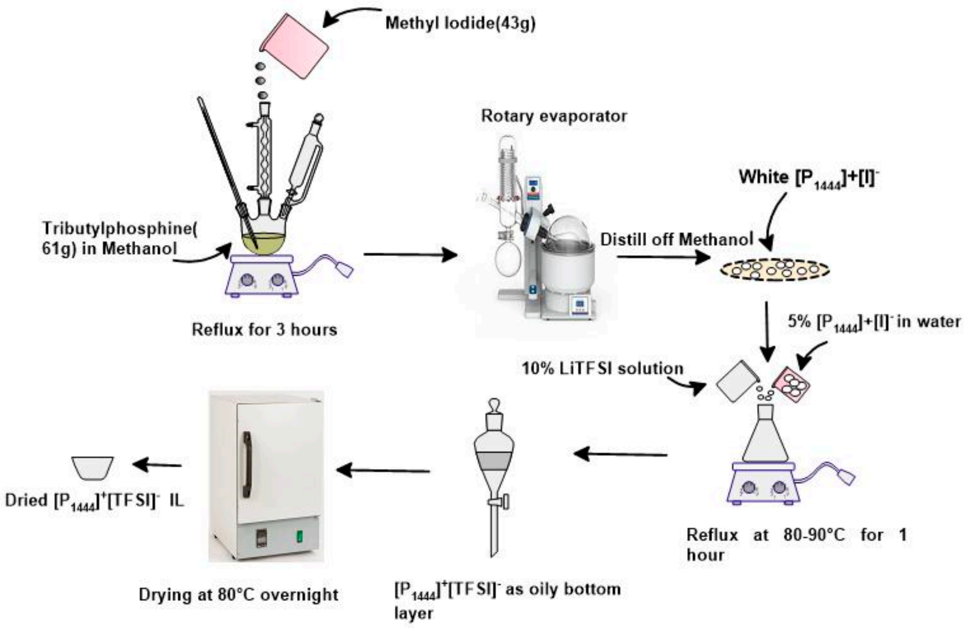


Figure 7. Schematic for the synthesis of methyltributylphosphonium bis(trifluoromethyl sulfonyl)imide [P_{1444}-TFSI].

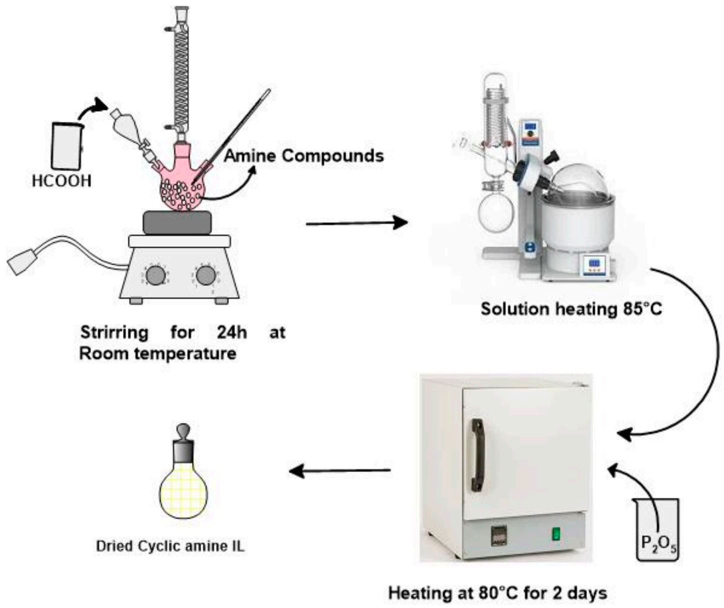


Figure 8. Schematic for the synthesis of cyclic amine-based Brønsted acidic ionic liquids.

Wenlin Zhang et al. [82] described the synthesis of N-butyronitrile-N-methylpiperidinium bis(fluorosulfonyl)imide (PP$_{1,CN}$FSI). The method involves two steps as follows: first, the synthesis of PP$_{1,CN}$Cl and, second, the synthesis of PP$_{1,CN}$FSI by the anion exchange method. 4-chlorobutyronitrile (0.1 mol) was mixed with N-methylpiperidine (0.1 mol) in acetonitrile (100 mL) and stirred using a magnetic stirrer for 5 h at 70 °C to yield PP$_{1,CN}$Cl. Then, PP$_{1,CN}$Cl (0.05 mol) and LiTFSI (0.055 mol) were mixed with 100 mL acetonitrile and refluxed at 40 for 30 h to yield PP$_{1,CN}$FSI, the resulted solution was dried in vacuum at 120 °C for 48 h to obtain colourless IL. A schematic of the synthesis of PP$_{1,CN}$FSI is given in Figure 9 and the mechanism for the above reaction is shown in Figure 10.

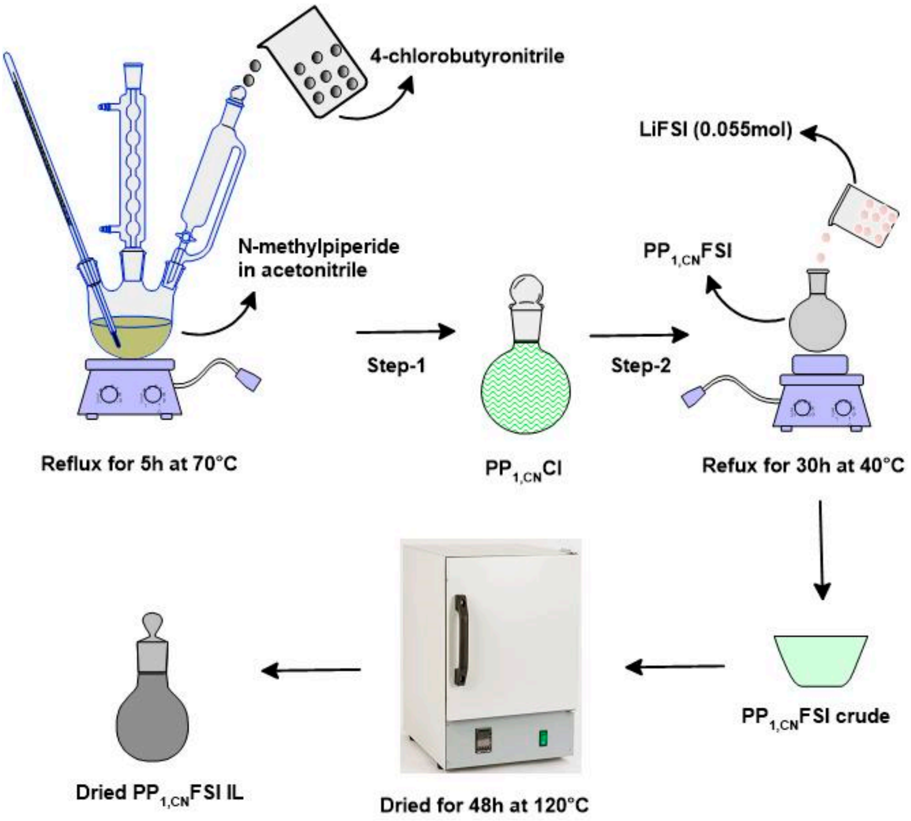


Figure 9. Schematic for the synthesis of N-butyronitrile-N-methylpiperidinium bis(fluorosulfonyl) imide ($PP_{1,CN}FSI$).

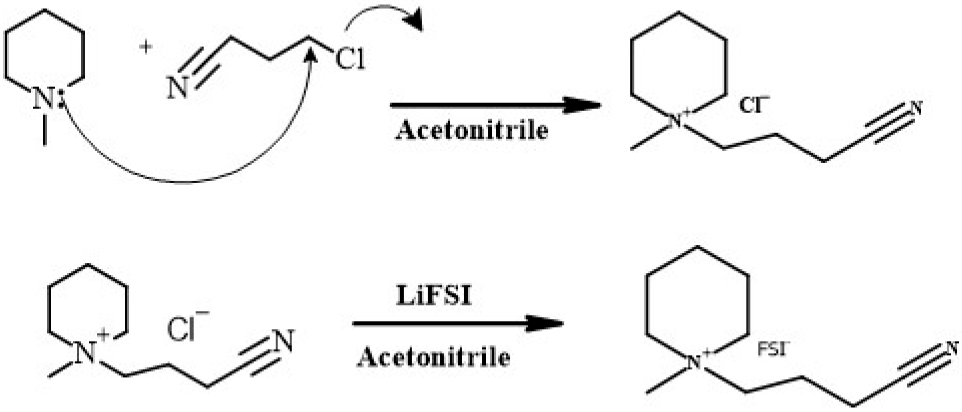


Figure 10. Mechanism for the synthesis of $PP_{1,CN}FSI$.

Ninu Madria et al. [118] synthesized 1-Ethoxymethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (MEOMIM-TFSI), with an 85% yield, from 1-ethoxymethyl-3-methylimidazolium chloride (MEOMIM-Cl). To a solution of chloromethoxyethane (118 mmol) at 0 °C was added 91 mmol of 1-methylimidazole dropwise in inert atmosphere which was then stirred at 0 °C for 30 min and at 50 °C for 1 h. The reaction mixture was rinsed with diethyl ether (28 mL) after it was cooled to room temperature, a light yellowish coloured solid (MEOMIM-Cl) is then obtained after drying in high vacuum. The schematic for the synthesis of MEOMIM-TFSI is shown in Figure 11.

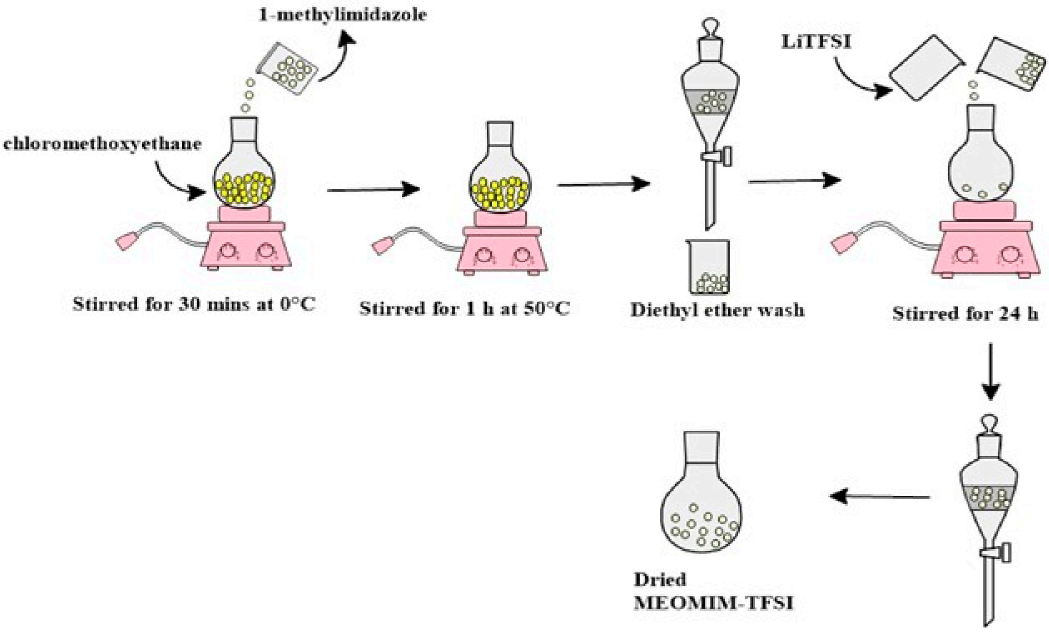


Figure 11. Schematic for the synthesis of MEOMIM-TFSI.

The synthesis of MEOMIM-TFSI was performed by mixing lithium bis (trifluoromethanesulfonyl) imide (81 mmol) to the prepared MEOMIM-Cl (85 mmol) and then stirring for 24 h. The organic layer product, as extracted using the solvent dichloromethane, contains the MEOMIM-TFSI IL [118]. The reaction scheme for the above reaction is given in Figure 12.

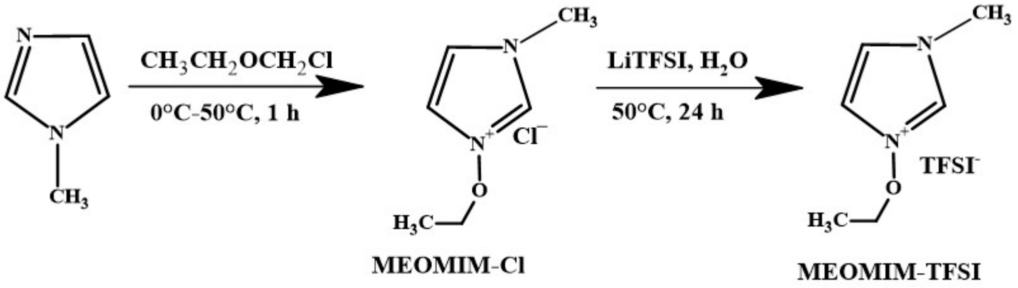


Figure 12. Reaction scheme for the synthesis of MEOMIM-TFSI.

My-Loan-Phung Le et al. [119] studied the synthesis of pyrrolidinium- and piperidinium-based ILs, N-methyl-N-4,4,4 trifluorobutylpyrrolidinium iodide ($Py_{14f}I$) was synthesized by reaction of methylpyrrolidone (5 mol) with 4,4,4-trifluoro-1-iodobutane (1 mol) in 25 mL acetonitrile and stirred overnight, acetonitrile was removed using rotary evaporator and washed with ethanol to finally obtain a yield of 90%.

$Py_{14f}ITFSI$ was synthesized by dissolving $Py_{14f}I$ (1 mol) in LiTFSI (1.5 mol) and 20 mL deionized water, the resulting mixture was dried under vacuum at 120 °C for 48 h. $Pp_{14f}I$ was synthesized by mixing methylpiperidine (5 mol) with 4,4,4-trifluoro-1-iodobutane (1 mol) in 25 mL acetonitrile and the same procedure was followed for the synthesis of $Pp_{14f}TFSI$ as given above [119]. Konrad Grygiel and coworkers [120] synthesized a thiazolium-based PIL by reacting 4-methyl-5-vinyl thiazole (MVTh) with methyl iodide to form 3,4-dimethyl-5-vinylthiazolium iodide, which was then reacted with LiTFSI (or BF_4) and refluxed at 120 °C (170 °C) for 6 h (8 h). The synthetic route for the reaction is given in Figure 13.

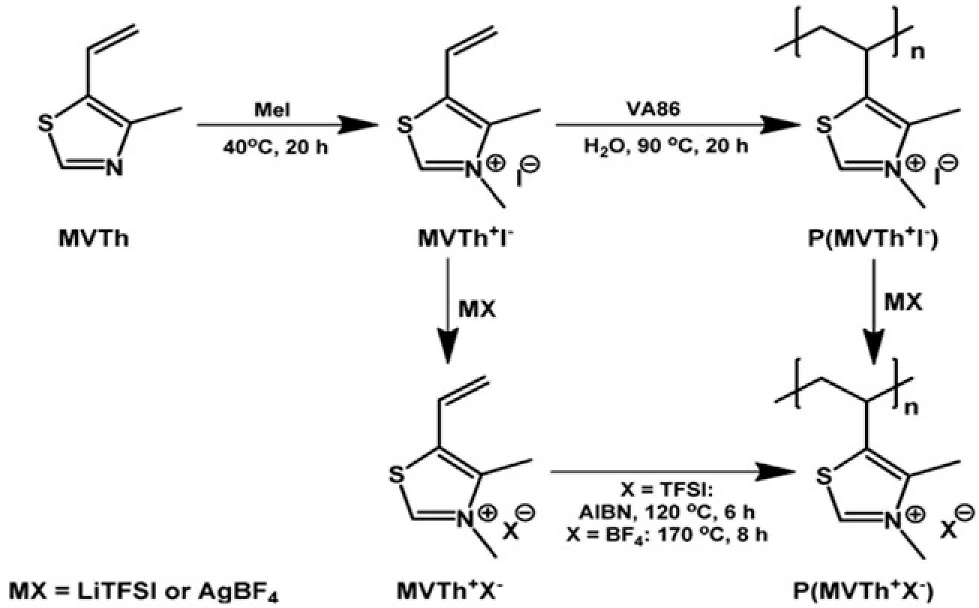


Figure 13. Reaction scheme for the synthesis of P(MVTh$^+$X$^-$).

5. Advancement in Ionic Liquid Electrolyte

There are certain improvements on cane make to the physico-chemical properties of ILs by certain additives and modifications and the most prominent of these are listed below.

5.1. Ionic Liquid with Lithium Salt Binary Electrolyte System

Upon the replacement of LiPF6 with LiFSI salt in the electrolyte, the graphite anode realizes an impressively high initial Coulombic efficiency of 93%. That means LiFSI contributes to efficient charge–discharge cycling from the very first cycle onward, which is highly important for battery performance. LiFSI helps form a stable solid electrolyte interphase layer on the graphite anode. This stability is reflected in a high Coulombic efficiency following the first cycle, although the latter initially drops in some cases to 80% of its value. Because the SEI layer stabilizes, it minimizes the side reactions, which supports high the Coulombic efficiency in subsequent cycles [103].

The addition of lithium salts to ionic liquids forms binary electrolytes with good thermal properties that remove the concept of low conductivity associated with ILs. Zachary et al. [121] have studied the solubility behaviour of different lithium salts, LiTFSI, $LiClO_4$, and $LiPF_6$, in the RTILs bmimACET, bmimSCN, $bmimPF_6$, and EMITFSI. Solubility was measured using FTIR-ATR, and the approach has been verified via repetition of all of the experimental procedures. Figure 14 presents the infrared spectra related to the dissolution of lithium perchlorate ($LiClO_4$) for different concentrations. Here, with an increasing concentration of lithium salt in solution, a peak at about 1350 cm^{-1} was found to be rising along with the corresponding decrease at 1450 cm^{-1} belonging to the peak of the ionic liquid solvent, as shown in Table 4. Notably, the ionic liquid bmimSCN (1-butyl-3-methylimidazolium thiocyanate) had the best solubility for all three lithium salts examined and was able to support remarkably high concentrations greater than 4 M of $LiClO_4$. The lowest solubility of lithium salts was found for $bmimPF_6$ (1-butyl-3-methylimidazolium hexafluorophosphate). Such a phenomenon can be explained by the highly polarizing nature of the thiocyanate ion ($^-$SCN), acting as a good solvent for lithium salts when compared with the relatively weakly polarizing PF_6^- anion.

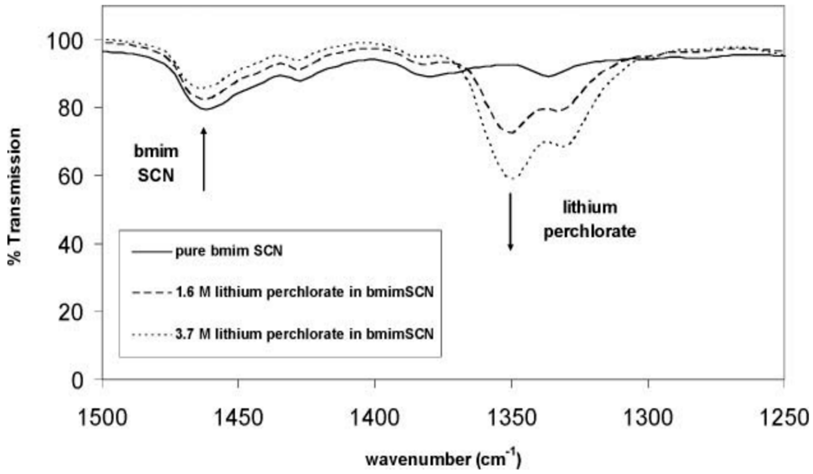


Figure 14. Representative FTIR-ATR spectra of a lithium salt ($LiClO_4$) in an ionic liquid (bmim SCN) solution. Adapted with permission from [121]. Copyright 2014, Royal Society of Chemistry.

Table 4. Solubility of LiTFSI, $LiClO_4$, and $LiPF_6$ in different ILs.

	bmimACET (M)	bmimSCN (M)	bmimPF$_6$ (M)	EMITFSI (M)
LiTFSI	0.18	1.3	0.06	0.4
$LiClO_4$	0.10	4.1	0.09	0.3
$LiPF_6$	0.34	0.60	0.08	0.1

This was further corroborated by their ionic conductivity measured in the temperature range 25 to 75 °C. More importantly, the results show that, in some instances, the ionic conductivity of the ionic liquid–salt solution does not decrease in an inversely proportional manner to the increase in its viscosity [121]. However, ionic conductivity was found to decrease considerably with a decrease in temperature.

There is growing evidence that RTILs resemble molecular organic solvents more closely than high-temperature molten salts. The Jones–Doles equation (Eq.) describes the variation of the viscosity of electrolyte solutions with salt concentration in non-electrolyte solvents [122] given as follows:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC + DC^2 \tag{5}$$

Here, η denotes the viscosity of the salt solution, η_0 represents pure solvent viscosity, C is the salt concentration. The coefficient A, B and D are the coefficients. The $AC^{1/2}$ term is usually not significant at concentrations above 0.05 M [123]. The BC term becomes significant at salt concentrations above 0.5 M, as it accounts for volume effects and ion–solvent interactions. These factors play an important role in influencing the viscosity of the solution at higher concentrations [124].

5.2. Ionic Liquid with Organic Solvent Binary Electrolyte System

Usually, to obtain the desired ILs, multiple ILs or organic solvents are mixed to enhance their physico-chemical properties, such as ionic conductivity, lowering their viscosity to modulate them as suitable electrolytes. Organic solvents, such as dimethyl sulfoxide, acetonitrile, several types of alcohol, cyclic carbonates, and other carbonates added to ILs, increase the ion conductivity many times more than in pure IL electrolytes. The mixed electrolytes prepared from IL and organic liquid components therefore exhibit better electrochemical performance that is explained by lower viscosity and higher ion conductivity [117,125–127].

In other words, ILs, when combined with carbonates and lithium salts, have lower viscosity and better conductivity, which are achieved via the two basic mechanisms of the solvation of Li^+ ions and the dissociation of the lithium salt, improving the mobility of the ions and then of the general performance of the electrolyte [128]. Organic compounds, such as EC and DMC, are already known to exhibit the preferential solvation of lithium ions. This would weaken the interactions by Li^+ ions with anions, such as the Li^+–$TFSI^-$ interaction, in these hybrid electrolytes, thereby improving their conductivity and adding to their effectiveness as electrolytes [129]. More importantly, the lithium clusters could be positively charged after the absorption of neutral organic molecules within the cluster, therefore leading to the subsequent reduction of the hydrodynamic radius of Li^+ ions. This reduced radius will finally result in a higher Li^+ transference number than that obtained in pure IL-based electrolytes. Locally enhanced Li^+ mobility, as caused by this effect, may indicate improved ionic conductivity and overall efficiency of the electrolyte [130]. The improved Li+ mobility increases the limiting current density and the overall rate performance of the lithium–ion cell [131]. Akiko Tsurumaki et al. [132] reported a hybrid electrolyte for LIB application with the addition of 30 wt% and 50 wt% of 1-butyl-1-methylpyrrolidinium hexafluorophosphate ($[Py_{14}]PF_6$) into LP30, which exhibited a very high specific capacity of ~110 mAh/g for up to 200 charge–discharge cycles, with cyclic stability clearly improved.

In that respect, composite electrolytes comprising ionic liquids and organic solvents are very promising for the development of high-voltage lithium–ion batteries, while at the same time improving their high-temperature performance and retaining all of their necessary levels of safety. Proper modulation of the ionic liquid-to-organic solvent ratio in the electrolyte formulation allows proper balancing between improved thermal stability and further improved performance [125].

5.3. Ionic Liquids with Inorganic Materials/MOFs

To overcome the challenges of dendrite formation when liquid electrolytes are used, solid state and quasi-solid electrolytes can be incorporated into ILs, with the aim of improving the high voltage, safety, and increased energy efficiency of LIBs [133–135]. Quasi-solid composite electrolytes, prepared by incorporating ILs into an inorganic matrix, such as SiO_2, ZrO_2, Al_2O_3, or MOFs, have been demonstrated to have thermal stability, excellent ionic conductivity, dendrite inhibition, enhanced Li metal anode/electrolyte interface, and superior rate performance. All of these composite materials have been considered promising electrolytes in terms of Li metal anodes [136–139]. Other applications of SiO_2 and hBN have also been represented by Nan Chen et al. [140,141] in the synthesis of solid ionic liquid-based electrolytes that were found to improve electrochemical stability and energy storage performance. However, the use of inorganic-matrix-based solid-state electrolytes has many drawbacks; their low interfacial contact, inflexibility, and inherent brittleness seriously impede their large scale fabrication for practical application in LIBs [142]. This line has thus triggered research toward the development of organic polymer- and organic gelator-based fixation methods for IL-based electrolytes, which can be said to be the perfect pathway of synthesizing solid-state and IL-based electrolytes, thus improving interfacial contact, flexibility, and overall performance [143]. Barbara E. M. Silva et al. have described the preparation of the Zn-MOFs using the imidazolium-derived zwitterionic liquid 1-(4-ethoxy-1-butylsulfonic acid)-3-methylimidazolium bromide (IL A1). Thus, the resulting Zn-MOFs, especially ZIF-8 and ZIF-7, possess outstanding stability when combined with the imidazolium ionic liquid [144].

Manuel Salado et al. [145] focused on controlling lithium transport using metal–organic frameworks (MOFs). Their study demonstrated that incorporating lithium bis(fluorosulfonyl)imide (LiFSI)-doped 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([EMIm][TFSI]) ionic liquid into a titanium-based metal–organic framework, NH_2-MIL-125(Ti), resulted in an ionic conductivity of 2.13×10^{-3} S/cm at room temperature, with a transference number of 0.58. These findings indicate the improved ionic transport properties of the material and also suggest potential suppression of dendrite formation.

6. Beyond Lithium–Ion Batteries

Besides lithium batteries, ionic liquids are considered as electrolytes in batteries of hydride and protonic systems. Their thermal stability and nontoxic character mean that ionic liquids represent a safer alternative to the classical electrolytes, improving the safety of battery-powered devices at different temperatures.

Xu Liu et.al [146] have proposed a locally concentrated ionic liquid electrolyte with low flammability, using monofluorobenzene (mFBn) as diluent, which enhances the solvation of Li+ ions and further forms a stable solid–electrolyte interphase (SEI) rich in inorganic compounds, giving a Coulombic efficiency of 99.72% for LMAs. This also generates a protective cathode/electrolyte interphase (CEI) on sulfurized polyacrylonitrile (SPAN) cathodes, preventing the dissolution of polysulfides, in turn enabling the cycling of Li/SPAN cells for 250 cycles with a 71% capacity retention, even with only 80% lithium metal excess. Muhamad Imran Ahmad et al. [147] explored the ILs and opened the possibility for their performance as an aqueous electrolyte for zinc–ion batteries beyond the conventional aqueous electrolytes, such as 1 M $ZnSO_4$. Their study identified ILs based on the tetramethyl ammonium cation that afford higher discharge capacity and reduced charge transfer resistance. Hence, ILs may serve as a more benign and cost-effective alternative energy storage in many lithium-based systems. In this context, some ILs have been tested as an aqueous electrolyte with $ZnSO_4$ salt. Indeed, the ILs based on the tetramethyl ammonium cation were effective and provided an initial discharge capacity of 330 mAh/g for IL-assisted electrolytes in comparison with 230 mAh/g for traditionally used 1 M $ZnSO_4$ aqueous electrolytes for a calcium vanadate electrode. Zhiming Zhao et al. [148] have proposed a 'water in ionic liquid' electrolyte for Zn–metal batteries, achieving superior longevity compared with those using typical aqueous electrolytes under lean-electrolyte conditions. Here, the electrolyte showed high stability and an ionic conductivity of 1.18×10^{-2} S cm^{-1} and the confinement of water led to the formation of a stable solid electrolyte interphase (SEI) on the Zn metal anode, enhancing the reversibility of the Zn electrochemistry. Rika Hagiwara et al. [149] developed a sodium–ion battery using ionic liquids as electrolytes and employing sodium chromite and hard carbon as positive and negative electrode materials, respectively, achieving a gravimetric energy of 75 Wh/kg, a volumetric energy density of 125 Wh/L and a capacity retention of 87% after 500 cycles.

7. Challenges in Ionic Liquids

Development of such ILs for LIB electrolytes has opened a very promising pathway toward safety and performance enhancements of the battery. Among these, most critical challenges that still remain to be harnessed are the optimization of ionic conductivity, the ensuring of interfacial stability between ILs and electrode materials, and the improvement of IL compatibility with existing battery components. All of these are discussed in detail in the following with the contribution of some relevant research studies.

7.1. Ionic Conductivity and Stability

Among the major challenges in the handling of ionic liquid electrolytes is the realization of high ionic conductivity at room temperature. Their solid-state counterparts, while much safer, usually exhibit poorer ionic conductivity in comparison with their liquid counterparts. In this work, solid electrolytes of LATP were optimized to an ionic conductivity of 8×10^{-4} S/cm, still lower compared with the conductivity realized in most liquid electrolytes. As such, overcoming this challenge is inevitable for the broad diffusion of solid and ionic liquid electrolytes into practical high-performance lithium–ion batteries [150]. Thus, thermal stability and non-flammability by ionic liquids would justify replacement in conventional liquid electrolytes in many applications. The big challenge remains how high ionic conductivity can be obtained without sacrificing such stability. Safety will surely be improved with ionic liquid crystal electrolytes, yet the further improvement in their ion transport capability is indispensable [151].

7.2. Interfacial Challenges

The interface formed between the electrolyte and the lithium–metal anode has recently been regarded as the leading factor that determines a battery's performance. Of the general issues in most solid-state electrolytes, including ionic liquid-based ones, the interfacial reactions and lithium dendrite growth might lower efficiency and safety [152]. Poor contact of the solid electrolytes with electrodes may further lead to high interfacial resistance and thus the low efficiency of the batteries. This has been addressed in continuous efforts through the addition of protective layers, among other means, using hybrid electrolytes that improve contact [150,153].

7.3. Compatibility with Battery Components

The other big challenge is the compatibility of the graphite anode with the ionic liquid electrolyte. Most conventional liquid electrolytes tend to exfoliate graphite layers due to degradation processes, while ionic liquids try to avoid these by using novel electrolyte structures capable of preventing those destructive events [154]. This property is mainly regarded as the key limitation toward the use of IL electrolytes for LIB applications. While deep eutectic solvents have provided a large potential window, relevant drawbacks have still been highlighted; above all, their high protonic nature likely worsens the overall performance and stability [9].

7.4. Cost and Scalability

The synthesis of ionic liquids (ILs) typically involves intricate chemical processes that are expensive and require specialized equipment, especially for ILs featuring custom anions or cations tailored to improve battery performance [155]. Additionally, the high cost of raw materials and the energy-intensive nature of IL production further drive-up overall costs [156]. These former advantages do not provide ILs with undoubted economic feasibility if the application scale is great. If those ILs are applied to commercial LIBs, they should be at least cost-competitive with the traditionally used electrolyte. Cost reduction was shown to be the most significant barrier to the wide application of ILs [157] and their high cost is a significant barrier to their adoption in cost-sensitive markets, such as those of electric vehicles and grid storage [158].

Due to the precision of the chemical reactions and very high purity levels, the scaling up of ILs has remained difficult. Further complicating the scaling-up of products is that most of the processes that work on a small scale in the laboratory do not usually adapt directly to large-scale industrial production [153]. ILs must be compatible with current battery manufacturing processes to be scalable. This includes ensuring that ILs can be integrated into existing battery designs without requiring significant modifications to production lines [159]. The transition from liquid to solid-state or hybrid electrolytes, which often incorporate ILs, also poses challenges in terms of manufacturing and process adaptation [153].

8. Summary

The overview of recent advances concerning IL electrolytes for energy storage applications has been undertaken, mostly on lithium–ion batteries and supercapacitors. A large electrochemical potential window, very low volatility, and excellent thermal and electrochemical stability are provided by ILs, offering a great opportunity to develop new material for energy storage applications. Furthermore, the interest in its application could allow the development of a new generation of electrolytes for this application. These processes have shown that the strategic inclusion of ILs into mixed electrolytes enhances electrochemical stability, widens the operational window, and enhances energy efficiency. However, traditionally, most conventional solvent-based electrolytes, while exhibiting a good dissociation of lithium salts and ionic mobility, have a number of serious drawbacks, such as high volatility, flammability, and thermal instability. Consequently, the proper selection of cation–anion combination is highly crucial to the attainment of an optimum electrochemical profile in ILs. Thus far, imidazolium-based ILs have indicated relatively low viscosity and high conductivity with regard to the other type, properties highly desirable in both applications. Nevertheless, a large proportion of these experience poor reduction stability, which has been partly solved by some ingenious strategies. Their interaction with organic solvents has a synergistic impact, specifically involving reduced viscosity, enhanced ion mobility, and improved overall performance in electrochemical fields.

ILs thus show promising applications in hybrid electrolytes for high-voltage LIBs, mostly under very harsh conditions. Nowadays, efforts have mostly been focused on enhancing safety and performance through the preparation of liquid, solid-state, and quasi-solid electrolytes. Immobilizations of ILs have been achieved through the use of SiO_2, ZrO_2, Al_2O_3, and MOFs inorganic matrices. Using such combinations, promising results have been achieved in the active suppression of dendrite formation and, thus, a homogeneous deposition at the electrodes. These ILs represent a new class of electrolytes developed during the last decade. Opening new perspectives to improve LIB performance in severe ambient conditions, they exhibit a large electrochemical stability window that may enable an energy density that is unreachable with conventional aqueous solvents. There are problems with high viscosity and cycling performance that need attention, especially with the incorporation of ILs into the structural forms within the state-of-the-art electrode materials such as mesoporous hierarchical architectures. Comparatively, pyrrolidinium-based ILs have shown higher electrochemical tunability, while imidazolium-based ILs are suitable for improved charge cycles as they show higher conductivity.

For example, a carbon-based electrode material—carbon black, graphene, CNTs, and activated carbon—when combined with ILs, could bring a real increase in energy density. Later, zwitterionic liquids were also taken into consideration as one of the possible electrolytes able to work at temperatures higher than 400 °C. A combination of these zwitterionic liquids with MOFs results in an ideal electrolyte for lithium–ion batteries, one that is characterized by high ionic conductivity and good thermal stability.

Though such merits of ILs toward the performance of LIBs still leave much room for their further improvement, mainly by enhancing conductivity without sacrificing thermal stability, inherent low viscosity, or well-controlled vapor pressure. As improvements in ionic conduction are crucial for the enhancement of charge/discharge rate, they are key factors for power output improvement and the overall efficiency of LIBs. These can be realized either by a more adequate choice of cation and anion or by the addition of specific additives which enhance ion mobility without deteriorating the other fundamental properties. Simultaneously, the ILs intrinsic thermal stability must be preserved, especially for demanding applications like electric vehicles and aerospace, as the batteries reach very high temperatures and suffer severe conditions. Any attempt to reduce viscosity will face yet another Achilles' heel of ILs—the compromise between becoming more liquid and retaining the favourable ionic properties, a compromise that is due to the way in which a decrease in viscosity is directly related to improved ion transportation and battery performance. Modifications in IL molecular structure or to the development of hybrid electrolytes combine the best properties from ILs with those of traditional solvents. Furthermore, the low vapor pressure of ILs, which seriously restricts the processes of evaporation, gas generation, and pressure increase of the electrolytes, also plays a very important role in the long-term stability and safety of the vapor pressure control of ILs in sealed battery systems. Further research should be performed to ensure that the ILs will work at extreme temperatures, at high cycling rates or in reactive environments by developing IL compositions with the appropriate properties. Such research would cover the search for synergies with solid-state materials or for a functionalization of ILs that may enhance the tolerance of such ILs against problems such as dendrite formation or degradation. The resolution of such associated challenges will finally allow ILs to realize their full potential and enable the design of more powerful, harmless, high-performance electrolytes for the most demanding Lithium–ion battery applications.

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