



# Advanced Applications of Ionic Liquids



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# ADVANCED APPLICATIONS OF IONIC LIQUIDS

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# Role of polymeric ionic liquids in rechargeable batteries

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## 14.1 Introduction

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The depletion of fossil fuels has created an urgent demand for alternative energy supplies. Inexhaustible energy sources for example the sun and wind are considered possible options. As a result of the exhaustion of fossil fuels, there is a pressing need for alternate energy technologies. Renewable energy sources like solar and wind are being considered as possible alternatives, to store these energies batteries are playing an important role as a source of storage device. Research on pure energy sources like solar, wind, and hydro has begun, however, the most important drawback in creating smart use of this energy is the correct current storage thanks to the sporadic nature of those sources of energy. This requires the efficacious energy storage technologies of batteries and supercapacitors [1,2].

Ionic liquids (ILs) are salts dissolved in water in a convincing situation, the term is limited to salts with melting points below certain temperatures, such as 100°C (212°F). Lack of electrical charge molecules is distinguished from ions by their making up the majority of ordinary liquids

like water and gasoline, whereas ions make up the majority of ILs. Liquid electrolytes, ILs, molten salts, liquid salts, ionic fusions, and ionic glasses are some of the terms used to describe these materials [3,4].

IL is used in many aspects of energy storage and conversions, as well as clean and sustainable energy, are in high demand. Lithium batteries and fuel cells, for example, have already made a substantial impact in this area.

Extensive research supports the development of innovative materials for these devices. Carbonate electrolytes are used in lithium-ion batteries (LIBs), making them the most energetic rechargeable battery. A comprehensive and active research program has been undertaken to develop new materials for use in these devices. For example, LIBs used carbonate-based electrodes, which resulted in higher energy densities in the development of secondary batteries.

However, these volatile organic compounds (VOCs) can create safety concerns when using LIBs in high-energy applications for example in electric means of transport or power grid network. In addition, side reactions, the solubility of the electro-active components, and the solvent volatility make conventional electrolytes in the form of carbonates unsuitable for use in non-LIBs for example lithium-sulfur and lithium-oxygen batteries. Rapid water evaporation and the associated reduction in proton conductivity proton-conducting films, mainly Nafion-R, limit the use of fuel cells above 100°C.

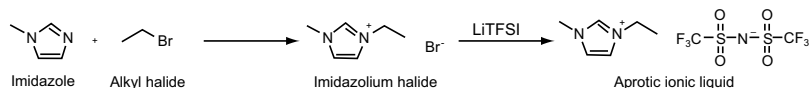
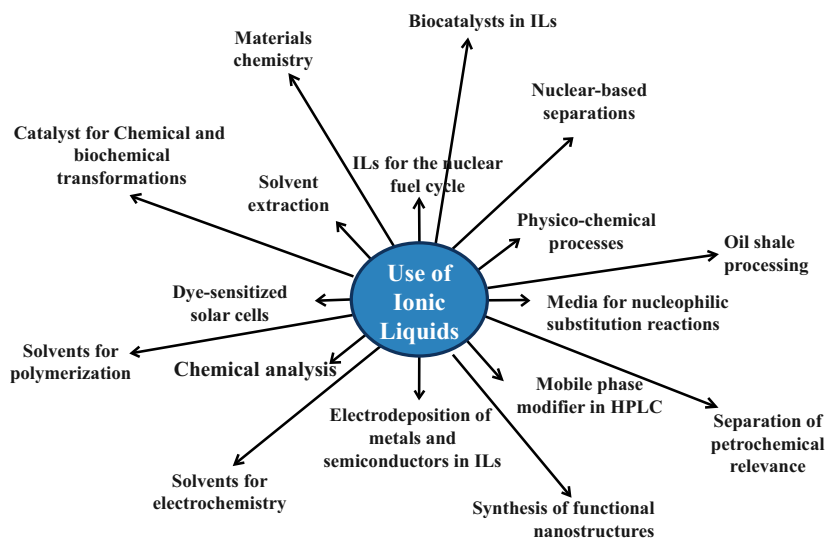
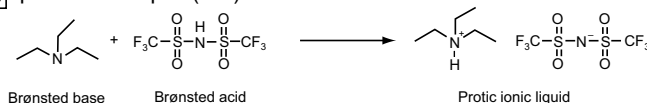
When studying chemistry, ILs opened up a new era of matter. ILs have also had a major impact on the chemical, pharmaceutical, biotechnology, and energy industries as well as gas processing, processing, and recycling.

In the field of materials chemistry, ILs are a relatively recent study topic. Chemical processing, medicines, biotechnology, energy, gas management, and material processing have all benefited from the usage of ILs [5,6]. A battery's LIBs and supercapacitors use ILs as alternate electrolytes because of these advantages [7,8].

## 14.2 Classification of ionic liquids based on their chemical structure

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ILs are divided into different classes based on their chemical structure. One of the most important classes of ILs, ILs contain non-proton and proton ions [9]. The characteristics of aprotic ionic liquids (AILs) and polymeric ionic liquids (PILs) are similar, but the most significant distinction between the two types of ILs is the presence of "accessible" (or free) protons on the PIL cation. PILs (protic and aprotic ILs) are two of the most significant types of ILs with applications (Fig. 14.1).

**(A) aprotic ionic liquid (AIL)****(B) protic ionic liquid (PIL)**

**FIGURE 14.1** Ionic liquid classes and applications (A) Classes of ionic liquids AIL and PIL. (B) Applications of ionic liquids in various fields.

### 14.2.1 Protic ionic liquids as electrolytes for lithium-ion battery

PILs are a kind of IL that is created by transferring protons from Brønsted acid for regeneration. Because of the “free” proton they have, they have several intriguing characteristics (e.g., hydrogen bond). Pure PILs or PIL mixes with acetonitrile or water have been proposed as super-capacitor electrolytes. Due to the “free” proton they have, they have several interesting characteristics (e.g., a hydrogen bond). Pure PILs or mixtures of PILs with acetonitrile or water have been proposed as electrolytes of supercapacitors. A study of proton conductivity of PIL-based polymers was also conducted in the context of its application in fuel cells [10]. Little attention has been made to the use of PIL as an electrolyte solvent in LIBs. As a result, PIL is much cheaper than aprotic

IL, is easier to manufacture, and is environmentally friendly, so it has the potential to be used in LIBs [11]. Gel polymer electrolytes (GPEs) are the blends of organic solvents with inorganic salts, like ethylene carbonate/ propylene carbonate/ sodium iodide etc. [12,13]. To produce a pure bipolar moment, the polymer host must have excessive chemical resistance and strong functional groups without electrons [14].

Because most ILs are liquids at room temperature, they can be utilized as electrolytes without the need for a solvent medium. However, using organic liquid electrolytes has some drawbacks for devices, including leakage, corrosion, and a lack of supply.

To solve these issues, the scientific community then proposed using ILs with polymer electrolytes (PEs) to maintain the mechanical qualities of ILs while still preserving their good electrochemical properties [15]. Because many PEs have low ambient temperature conductivities, this is the case. Therefore, they are ideal as solvents and electrolytes, and their internal ionic conductivity is important for electrochemical applications. ILs have unique properties that make them ideal for a wide variety of energy-related applications [16].

#### 14.2.2 Aprotic ionic liquids as electrolytes for lithium-ion battery

ILs are attractive for producing LIB electrolytes because of, their sturdy thermal stability, and low vapor pressure. For more than a decade, scientists have studied the use of IL in LIBs and used unusual forms of cations and anions to make AILs. The cations that have been researched the most include imidazolium, pyridinium, pyrrolidinium, and piperidinium. They are used in a mixture with lithium salt to generate electrolytes excellent for LIBs.

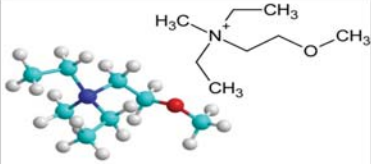
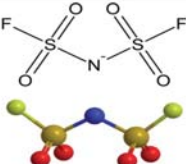
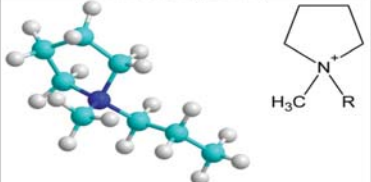
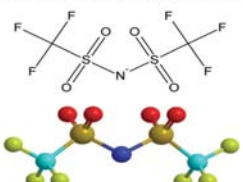
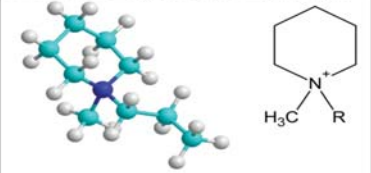
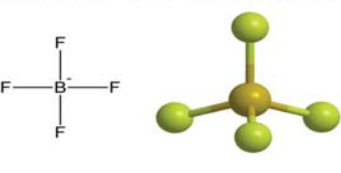

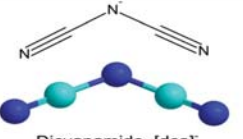
Tetrafluoroborate ( $\text{BF}_4^-$ ),  $\text{PF}_6^-$ , and per-fluoro-alkyl as di-(trifluoro methane sulfonyl imide) (TFSI) and di-(fluoro sulfonyl imide) (FSI) are the common anions shown in Fig. 14.2. These AILs are mixed with lithium salts to create LIB-compatible electrolytes.

Lithium salts often contain anions that are used to reduce the weight of electrolyte solutions. It is often referred to as “solvent-free” because it does not require a solution to form these liquid electrolyte solutions [17].

The cation–anion pair has a significant influence on the properties of ILs. For example, the addition of imidazolium cations enables the production of IL with higher conductivity than the pyrrolidinium and piperidinium cations.

For example, the inclusion of imidazolium cations can produce IL with higher conductivity than pyrrolidinium and piperidinium cations [16,18]. Using these cations instead of imidazoles allows for the synthesis of ILs with a wide electrochemical stability window [17].



Cations	Anions
 <p><i>N,N</i>-diethyl-<i>N</i>-methyl-<i>N</i>-(2-methoxyethyl) ammonium, [DEME]<sup>+</sup></p>	 <p>Bis(fluorosulfonyl)imide, [FSI]<sup>-</sup></p>
 <p><i>N</i>-methyl-<i>N</i>-alkyl pyrrolidinium, [C<sub>n</sub>mpyr]<sup>+</sup></p>	 <p>Bis(trifluoromethanesulfonyl)amide, [NTf<sub>2</sub>]<sup>-</sup></p>
 <p><i>N</i>-methyl-<i>N</i>-alkyl piperidinium, [C<sub>n</sub>mpip]<sup>+</sup></p>	 <p>Tetrafluoroborate, [BF<sub>4</sub>]<sup>-</sup></p>
 <p>1,2-dialkyl methylimidazolium, C<sub>n</sub>C<sub>m</sub>mim<sup>+</sup></p>	 <p>Dicyanamide, [dca]<sup>-</sup></p>

\* R groups – typically ethyl, propyl, butyl.

# this compound (along with many other nitrogen centred anions) is described as an “amide” in the inorganic literature, but incorrectly as an “imide” in the materials and electrochemical literature. FSI should also be described as an amide (i.e. FSA) but that is so uncommon in this field that we have retained FSI in this article.

FIGURE 14.2 Ion families in common ionic liquids used in lithium-ion batteries [16].

The FSI-based AILs have a lower viscosity than the TFSI-based AILs. With the properties of imidazole ions, it is clear that one of the main advantages of using an IL-based electrolyte is that the properties of the electrolyte can be modified by changing the composition of the cations and anions.

## 14.3 Introduction to Li batteries

The power stored using a battery is converted from chemical energy into electrical energy by redox chemistry. An electrical source can be converted into chemical, power for the life of a battery. Rechargeable lithium batteries have become very popular in electrical energy storage



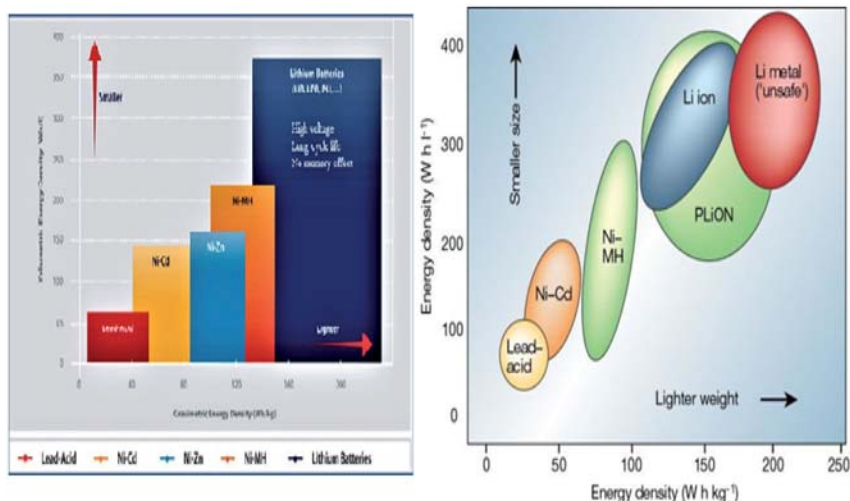


FIGURE 14.3 Compare battery types.

systems because of their high-powered capacity, operating current, prolonged existence life, and less self-discharge (Fig. 14.3) [19,20].

In effect, phosphorous oxide has a completely high potential for Li batteries, making it a very not unusual manner of improving their electricity density [21]. In recent years, Li batteries have exhibited a power density of 100–200 Wh/kg, making them improper for cars. Steel lithium has been used as an anode for a long term; however, when coupled with natural liquid electrolytes, lithium dendrite development is the most important trouble with Li batteries [22,23].

Furthermore, the usage of those flammable and volatile liquids is exposed for its safety at hazard. In addition, because of their electrochemical instability at better voltages, these natural liquid electrolytes cannot be used in batteries [24].

Therefore, an alternative electrolyte is required for the safe use of lithium metal in batteries. Owing to their mechanical, thermal, and electrochemical stability permanence in addition to their safety and flexibility, PEs have become established in Li batteries [25].

Ions can move about in the ion transport host matrix, which is a polymer matrix with free space. Organic salts are usually dissolved in a polymer concentration to form solid polymer electrolytes (SPEs). If a polar group is present in the polymer matrix, it affects whether it can easily interact with the cations and if the bond rotation is limited [26]. Due to their flexibility in large chains and their ability to remove many biological/unnatural chemicals, polymer poly(ethylene) oxide (PEO) electrolytes in various polymer matrices have been extensively studied [27,28].

## 14.4 Basics of ionic liquids

Organic salts, ILs, molten salts, or organic salts are all examples of ILs. Bulky, distinct, weak organic cations and organic and inorganic anions are the most common IL mechanisms [29].

Water and organic solvents may have nonvolatility, high thermal stability, and high ionic conductivity are features of solvents (and electrolytes). In other words, when it comes to the features of ILs, it is important to remember that the abovementioned characteristics are not always present in all ILs, which opens up the possibility of creating new task-specific ILs. Fig. 14.4 demonstrates the general cations and anions of ILs that are used in batteries [30].

Because of low lattice energy and weak ionic bonds between cations and ionic salt anions, ILs are separated (NaCl, KCl, etc.). The result is high conductance, low vapor pressure, glass transition temperature and high melting temperature, excellent heat and electrochemical stability, low deposition, and easy recovery. Table 14.1 presents some of the properties of IL.

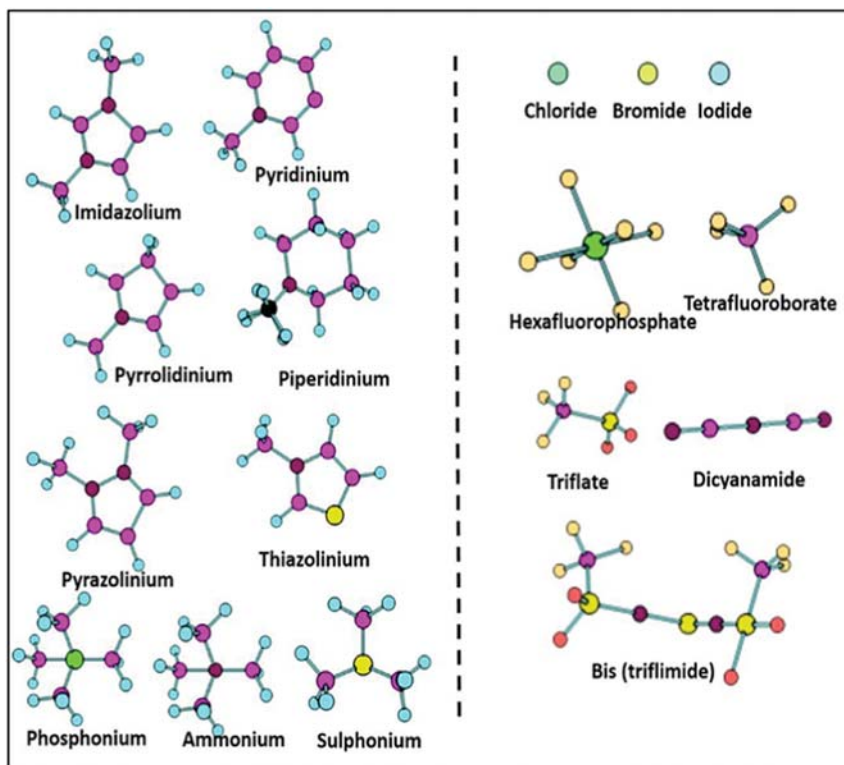


FIGURE 14.4 General cations and anions for ionic liquids in batteries.

TABLE 14.1 Ionic liquids properties

Ionic liquids	$T_g$ (C)	$T_m$ (C)	$T_d$ (C)	$\sigma$ (mS/cm)	$\eta$ (cP)
PYP <sub>1,4</sub> -TFSI	−87	−6	—	2.69	60
[EMIM][BF <sub>4</sub> ]	−93	−11	450	14 at 25°C	43 at 20°C
[EMIM][PF <sub>6</sub> ]	—	60	—	5.2 at 26°C	—
[EMIM][TFSI]	−98	4	440	8.8 at 20°C	28 at 25°C
[BMIM][Cl]	—	41	254	—	1534 at 50°C
[EMIM][FSI]	—	12.9	—	16.5 at 25°C	24.5 at 25°C
[HMIM][PF <sub>6</sub> ]	−78	−61	417		585 at 25°C
[BMIM][PF <sub>6</sub> ]	−76	10	390	1.8 at 25°C	312 at 25°C
[BMIM][TFSI]	−104	−4	439	3.9 at 20°C	52 at 25°C
[OMIM][PF <sub>6</sub> ]	−82	−40	376	—	682 at 25°C
[HMIM][BF <sub>4</sub> ]	−82.4	−18	409	1.22 at 25°C	439

### 14.5 Organic and inorganic ionic liquids in electrical storage systems

At normal temperatures, ILs are referred to as molten salts, a form of substance that contains both organic cations and inorganic/inorganic anions [31,32]. It is significant that the separation of polymer ions into ILs reduces the electrostatic force of the ions and separates them, lowering the melting temperature. In organic synthesis, chemical detection, life sciences, green chemistry, and storage systems that can generate electrical energy ILs are used as solvents [33,34]. ILs are utilized as electrolytes and solvents in different ways, since the advantages of ILs, like variable polar nature and ionic conductance, low volatile nature, exceptional thermal stability, and low flammability, have contributed to several advantages and uses in electrical energy storage [35,36].

### 14.6 Ionic liquid-based polymers electrolytes historical background

Because of its interesting characteristics, synthetic polymer materials developed quickly in the industrialized world. Various research groups created physicochemical and theoretical techniques needed to explore polymeric materials at the same time.

Owing to their intriguing features, synthetic polymer materials have developed quickly in industrialised nations. Numerous researchers independently developed the physicochemical and computational techniques needed to study the polymeric materials. Wright et al. reported that poly (ethylene) oxide (PEO) compounds with sodium thiocyanate, potassium thiocyanate, and sodium iodide show ionic conductivity [37].

Instead of looking for high-performance electrolytes, the focus is shifting to more recent industries such as high-performance composites and fibers (such as Kevlar). The importance of Wright's paper was explored by Armand et al. in 1978, who advocated using a salt-polymer combination as a solid electrolyte [38,39].

In 20 years in a new field of PE, inventions and widespread distribution of portable microelectronics and electronics have emerged, and there is a strong demand for extremely lightweight rechargeable batteries, high performance, and affordable.

In the beginning, electrolytes become increasingly necessary as a result. Several methods for limiting the crystallinity of polymer materials were discovered. In the beginning, several methods for limiting the crystallinity of polymer materials were discovered [40].

The third decade, around the 1990s, saw the widespread acceptance of LIBs in addition to a fast increase in the production of low-cost portable devices. PEs made from amorphous PEO were referred to as "classics." The new electrolyte is a high salt or angel salt PE, and a gel electrolyte containing solvent molecules is used in the polymer matrix [41].

Environmental contamination is a serious problem in today's globe, owing to a variety of human activities, including electricity generation. As a result, a lot of attention is being paid to sharpening equipment with harmless materials that provide outstanding performance. PEs is also experiencing significant changes, such as the use of natural polymers and feasible solvent and plasticizer replacements [42].

The preparation and analysis of inorganic and inorganic polyethylene represented advancement in polyethylene research in the fourth decade. Owing to their mechanical, thermal, electrochemical, and chemical stability and their excellent conductance at room temperature, these materials promise excellent use in lithium rechargeable batteries [43]. Also, the addition of minerals to the chemical makeup and the creation of new classes of synthetic gels and IL-based PEs have created a whole new family of materials [44,45].

## 14.7 Polymeric ionic liquids for rechargeable lithium-ion batteries

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As IL molecules are added to a polymer chain, PILs or ionic polymerization liquids (polymer ILs) are produced. This is a new type of

functional polymer that blends the characteristics of room temperature ILs with the polymer structure. Produces a new type of functional polymer. As a result of Ohno's and his co-workers' insight [46,47]. PILs play an important role in various energy storage systems, as in batteries and supercapacitors, as well as conversions (fuel cells) and electro-mechanical applications (actuators and sensors) [48,49].

PIL, with a unique combination of polymer and anti-ion, has tuneable properties such as glass transition temperature and solubility that enable a multitude of new applications. The mechanical stability, increased process capability, robustness, spatial control capability, and other benefits of using PIL over IL are just a few of the benefits.

Used as a SPE, PIL has a variety of architectures, as shown in Fig. 14.5. PILs with variety of architectures (Fig. 14.5) were extensively used as SPEs. Researchers made attempts to investigate the relationship between the structure-ionic conductivity of the PIL-based SPEs with respect to the type of cation and anion present in PILs [48,49].

#### 14.7.1 Emerging of ionic liquid-based polymer electrolyte

There is serious research for energy solutions in vehicles with the rising need for clean, dependable, and internationally inexpensive electricity and energy. Many efforts to find novel materials and appropriate design methods have resulted as a result of this. PEs have made significant progress toward high safety and noticeable efficiency. ILs are suitable materials for integration with PE because of their high conductivity; chemical resilience, low toxicity, and favorable electrochemical characteristics [50]. These are molten salts with bulky asymmetric organic and mineral anions that can be used at a comfortable temperature. IL has been used as possible solvents that are inherently unsafe to PE. ILs have been dubbed "green solvents" since they are non-volatile, soluble, and evaporation resistant [51]. ILs have also been used to increase the ambient temperature conductivity of PEs. The IL, *N*-alkyl-*N*-methylpyrrolidinium per fluoro-sulfonylimide, was used by Passerini et al. to aid conductivity enhancement in a PE [52].

The development of a compelling amorphous phase was described using the zinc ionic conductivity of PE 1-ethyl-3-methyl-imidazolium, bis (trifluoro-methane-sulfonyl) imide (EMIMTFSI). PE EMIMTFSI ion conductor zinc ion di(trifluoromethanesulfonyl) imide (EMIMTFSI) ion conductor is effective, and the development of an amorphous phase is compelling proof of existence [53]. Because the properties of a liquid are determined by the careful selection of IL-imidazolium, pyridinium, alkylammonium, alkyl-phosphonium, pyrrolidinium, guanidinium, etc., IL is aprotic and aprotic depending on the type of cation. They can

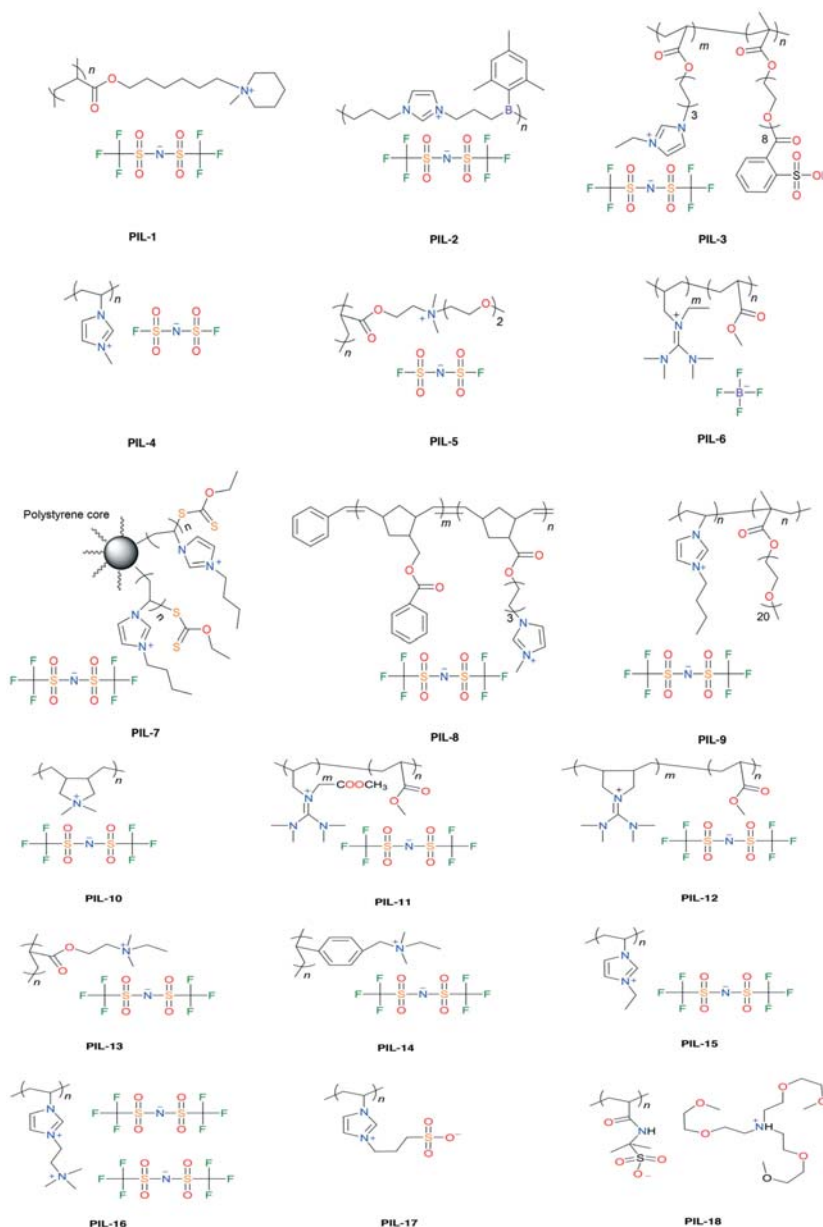
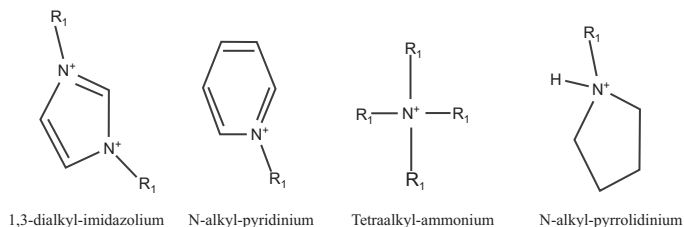


FIGURE 14.5 Chemical structure of PIL used in SPE.

contain ILs that contain metal and anions like halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), polyatomic metals ( $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ) and polyoxometalates, as well as organic anions like nitrate ( $\text{NO}_3^-$ ) and trifluoromethylsulfonylimide

## Cations



## Anions

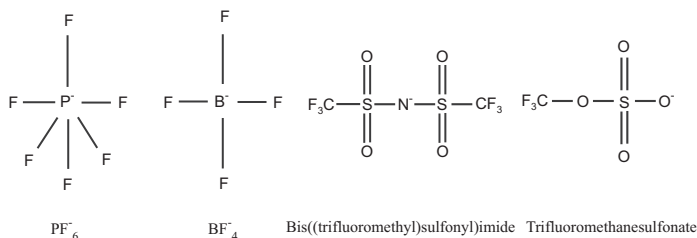


FIGURE 14.6 Examples of cations and anions used to make IL.

(TFSI<sup>−</sup>) and trifluoromethanesulfonate (Tf<sup>−</sup>). Fig. 14.6 depicts a few common ions involved in the production of ILs. They include halides (Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>), inorganic polyatoms (PF<sub>6</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>), inorganic anions such as polyoxometallate, NO<sub>3</sub><sup>−</sup>, TFSI<sup>−</sup>, and Tf<sup>−</sup>. Some common ions are involved in IL production. These cationic chemicals and replacements have a significant impact on IL conductivity, hydrophobicity, melting temperature, viscosity, solubility, and other chemical and physical properties [34]. Conductivity is important in electrolytes because the balance between the interactions of ion pairs has a substantial influence in real-world applications. LIBs make up the vast majority of commercially available batteries. Because they generally employ electrolytes that are volatile and flammable, their use is severely limited. Conductivity is important in electrolytes because the balance between the interactions of ion pairs has a substantial influence in real-world applications.

LIBs make up the vast majority of commercially available batteries. Because they generally employ electrolytes that are volatile and flammable, their use is severely limited. In the early 1980s, lithium-ion polymer cells were presented as a possible answer to safety concerns [54]. Even though these efforts were partially effective, the primary issue of the system remained because liquid organic solvents are flammable. The non-toxic, eco-friendly nature of ILs provides value to the rechargeable battery business in general. Many reports in recent years have demonstrated that integrating ILs will result in a positive outcome shortly [55].



Due to their solubility in solvents or electrolytes, IL electrolytes are often used as suitable alternative battery energy storage systems (BESS) like LIBs. This chapter attempts to summarize the present state of knowledge on the electrochemical, cycle, and physical characteristics of IL-based electrolytes that are relevant to LIB. Solvents like IL can help enhance the performance of environmental and energy storage devices, particularly LIBs, by replacing more flammable organic carbon [56].

One of the most important studies is the active usage of IL. LIBs, for example, employ carbonate electrolytes to achieve the maximum energy density of secondary batteries. However, these VOCs are a safety concern when using LIBs in extensive applications such as electric motors and power grids. For example, LIBs use carbonate-based electrolytes, achieving the highest energy density of any secondary battery developed so far. However, when an LIB is used in more applications in electric motors and power grids, these VOCs pose safety concerns. These concerns have prompted the development of novel IL-based electrolyte compounds. Meanwhile, the nonvolatility and great thermal stability of ILs have allowed some of them to be used as carbon material precursors. For energy applications, this new approach reveals highly functional, task-specific carbon compounds. This article describes the energy consumption of IL.

The carbon compounds produced from IL are shown. This shows that IL can be used as a new functional material for energy applications, especially as a new building block for catalysts and electrodes. Table 14.2 presents common cation and anion abbreviations found in IL.

TABLE 14.2 General abbreviations for cations and anions in IL.

Cation		
[C <sub>n</sub> mim]	[C <sub>n</sub> mpyr]	[C <sub>n</sub> mpip]
[DEME]	[Nabed]	[Pabed]
[C <sub>n</sub> dmim]	[dema]	[DBU]
Anion		
[TFSA]	[FSA]	[FTA]
[BETA]	[TSAC]	[FAP]
[TfO]	[MS]	[DFOB]
[DCA]		

## 14.8 Li/Na-ion battery electrolyte

LIBs are used as a light source because they have a high power density and high energy density. The generally common components in Li batteries are negative electrodes, highly volatile electrodes containing Li ( $\text{Li-MO}_2$ , M: conversion metals), and organic electrolytes [57,58].

Li is inserted into a negative carbon electrode while charging an LIB and Li is evicted as of a positive  $\text{LiMO}_2$  electrode during the extraction process. Li salts are extensively employed as electrolytes in LIBs, ethylene carbonate (EC) and diethyl carbonate are aprotic molecular solvents used [59,60]. Organic molecular solvents are characterized by their flammability and volatility. The safety of LIBs must be enhanced, particularly in large-scale energy storage systems used as electric cars and power grids.

Alternative energy sources were also investigated, including sodium-ion batteries at room temperature with operating electrolytes [61]. Thermally stable electrolytes are widely used to increase the thermal durability of these batteries [59,62].

Due to the thermal stability, low volatility, and flame retardancy of IL, many researchers plan to use IL as an electrolyte for batteries [63–65]. Chloroaluminate-based IL ( $\text{AlCl}_4$ ) was investigated in IL's groundbreaking research on the battery used [66,67]. However, chloroaluminate anions are sensitive to water and corrosive, therefore, they have not been widely used in chloroaluminate-based ILs in recent years in lithium and sodium battery research. Therefore they have not been widely used in chloro-aluminate-based ILs in recent years in lithium and Na battery research.

The electrolyte also has sufficient electrical stability. When the battery permanently damages the negative electrode and generates an oxidation voltage on the positive electrode, it affects the charging and discharging performance. When the battery is full, the negative and positive electrodes are lowered and discharged separately. Therefore, the electrolyte Li/Na ion batteries have great potential.

## 14.9 Polymer-electrolytes classification

Electric polymer is used to develop electrochemical devices. PE is divided into the following groups based on materials (Fig. 14.7).

### 14.9.1 Electrolytes based on dry solid polymer

Electrolytes based on the dry solid polymer are ion-conducting electrolyte that is made by integrating inorganic salt into a polar

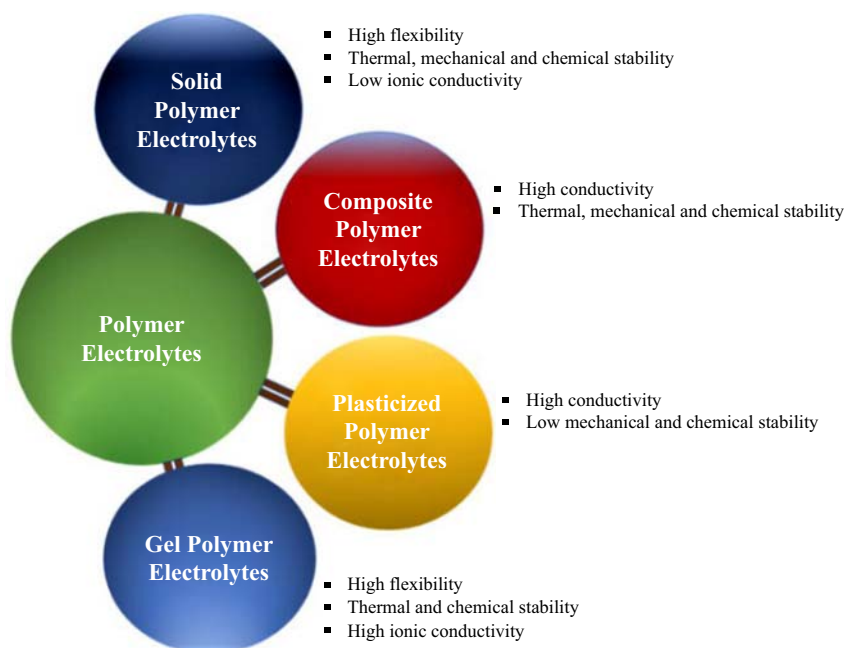


FIGURE 14.7 Polymer electrolytes classification.

polymer [68]. Coordination bonds are formed when the metal ions in the salt electrostatically interact with the polar polymer. The distance between the polymer's functional groups, the molecular weight, the kind of branching, the metal's charge, and other variables that might influence the metal-polymer relationship [69]. Ions begin to migrate from one coordination site to the next when the PE is exposed to an electric field. It happens because the metal ion and functional g have a weaker connection. Because the metal ion and the polymer chain's functional group have a weaker bond.

### 14.9.2 Electrolytes based on plasticized polymer

Plastic PEs are formed by the dissolution of low molecular weight substances such as EC, propylene carbonate, and polyethylene glycol [70]. This reduces  $T_g$  and crystallization while reducing intermolecular and intramolecular interactions between polymer chains and increasing the salt dissociation capacity [71]. This method improves the conductivity of poly-electrolytes but has limitations in terms of mechanical durability, solubility, and lithium electrode reactivity.

### 14.9.3 Electrolytes based on gel polymer

GPEs have advantages over liquid electrolytes, have high conductivity and good electrode contact with the electrolytes, with the advantages of solid electrolytes, safety, mechanical and thermal properties for the production of PEs. It is becoming more and more popular among them. GPEs are safer than liquid electrolytes since they use a polymer to preserve liquid components while simultaneously providing mechanical support. GPE is a polymer that contains a lot of organic solvents and is shipped with the bulk polymer [72]. Due to the desirable properties of IL, IL-based GPE has recently been the focus of research, including excellent conductivity, thermal stability, and low vapor pressure. As a result, GPE can be used as an alternative to liquid electrolytes.

### 14.9.4 Electrolytes based on composite polymer

Polymer-based composite electrolytes offer the advantages of nonmetals and polymers and can be used directly in solid metal batteries in the future, proton membrane membranes, and methanol fuel cells, among other applications. It is expected to have high safety, good flexibility, excellent thermal stability, and superior electrolyte performance. However, the lithium-ion guide (lithium-ion, proton, etc.) and weak electrolyte adaptation during the process of transport/discharge, especially when matching high voltage codes and metal lithium codes, are still waiting for better solutions. In addition, the multipurpose Kuwaiti functions are unique, such as healing, flexibility, and antiphizers, which are also desirable for natural disasters in different situations. This should be considered by ion, electrochemical/chemical movements, and polymer-based disasters in dealing with the above issues [70]. It can usually be divided into polymer/polymer mixture and polymer electricity. The components of production devices are affected by their performance. Each component and content/content/content is particularly important in high-performance disasters [71]. The purpose of this research is to progress in polymer-dependent rap, including the effect of materials and their components, on mechanisms for improving the relevant performance.

## 14.10 Ionic liquid-based gel polymer electrolytes application in lithium batteries

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IL-based electrolytes offer some favorable characteristics, and they are widely employed in supercapacitors, batteries, and fuel cells. Lithium batteries are essential because of their high energy density,

versatility, and safety. In recent years, polymer batteries have been used to power all electronic gadgets, including computers, cell phones, power banks, and portable players. One of the primary advantages of GPE, according to Gupta et al., is the creation of a strong interface between the electrodes and electrolytes, which improves the lithium battery cycle's stability. The performance of PEO-based GPE battery has been studied in the literature [73].

The electrochemical performance of GPE-Li batteries based on PEO is shown in Table 14.3. The following researches demonstrate that utilizing GPE instead of liquid solvents in lithium batteries increases battery expandability and electrochemical stability substantially. IL-based GPE not only exhibits high ion conductivity, flexibility, and mechanical stability but also contributes to the capacity, recycling ability, and safety of lithium batteries.

### 14.11 Low melting point alkaline salts in lithium batteries

The MP of conventional lithium salts is over 200°C such as  $\text{LiClO}_4$  is 236°C,  $\text{LiBF}_4$  is 296.5°C, and  $\text{LiPF}_6$  is 200°C. The high electrostatic interaction between lithium and anions is the underlying reason for this. The charge density of lithium ions is high due to the short ion radius, and there is a significant electrostatic attraction between lithium ions and anions. Thus fusion usually requires high temperatures. Some Li inorganic salts have low melting points and should be mentioned here. The M.P. temperature of  $\text{LiClO}_3$  is 128°C, but in the fourth system  $-\text{NaNO}_3$ ,  $-\text{LiNO}_3$ ,  $-\text{LiClO}_3$ ,  $-\text{NaClO}_3$  M.P. at 128°C [86].

$\text{LiAlCl}_3\text{SCN}$  melts at 110°C and may be kept at ambient temperature as a superheated liquid, whereas  $\text{LiAlCl}_4$  melts at 143°C. The  $\text{LiAlCl}_3\text{SCN}$  anion is an asymmetric  $\text{AlCl}_3\text{SCN}$  ligand compound with a symmetric structure, whereas the  $\text{AlCl}_3$  anion has a symmetric structure. Several factors affect solubility, including electrostatic interactions between Li and anions, anion size, anion symmetry, and anion morphology. All of these affect the melting temperature of Li salts [87].

The weak interaction between the fundamental Lewis anion and Li, according to the hard and soft acid and base (HSAB) theory, is feeble. On the other hand, even the Li salt of a large element anion with a low Lewis base has an M.P. significantly higher than room temperature.

According to the HSAB theory, the weak interaction within the major Lewis and Lithium anions is weak. On the other hand, even salts of large element anions with low Lewis bases are M.P. substantially higher than ambient temperature [88,89]. Fujinami et al. studies have shown that the formation of liquid salts of Li was activated by the penetration of ether groups into the aluminate structure [90,91].

TABLE 14.3 The electrochemical performance of GPE-Li batteries based on PEO.

Polymer electrolytes	Li-battery	C-rate	Capacity (mAh/g)	References
PEO <sub>20</sub> LiTFSI[Pyr13TFSI] <sub>1.27</sub>	Li/LiFePO <sub>4</sub> at RT	C/10	115 at 20 cycles	[74]
PEO <sub>20</sub> LiTFSI2[Pyr14TFSI] <sub>4</sub>	Li/NMC at 40°C	C/10	160 at 100th cycle	[75]
PEO <sub>20</sub> LiTFSI[Im12TFSI]	Li/LiFePO <sub>4</sub> at 50°C	C/5	110 at 20th cycle	[76]
PEO <sub>20</sub> LiTFSI[Pip <sub>1.101</sub> TFSI]	Li/LiFePO <sub>4</sub> at RT	C/20	120 at 35th cycle	[77]
PEO <sub>20</sub> LiTFSI[Pip <sub>1.101</sub> TFSI]	Li/Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> at RT	C/20	150 at 40th cycle	[77]
PEO <sub>20</sub> LiTFSI <sub>2</sub> [Pyr14TFSI] <sub>4</sub>	Li/LiFePO <sub>4</sub> at 40°C	C/10	140 at 450th cycle	[78]
PEO + 20 wt.% LiTFSI + 20 wt.%ThdpTFSI	Li/NMC622 at RT	C/10	148 at 150th cycle	[79]
PEO <sub>20</sub> LiTFSI <sub>2</sub> [Pyr14TFSI] <sub>2</sub>	Li/LiFePO <sub>4</sub> at 40°C	C/5	160 at 180th cycle	[80]
PEO-LiTFSI-10wt%EMIMFSI	Li/NCA at RT	C/10	175 at 200th cycle	[81]
PEO + LiFSI + 7.5 wt.% EMIMFSI	Li/LiFePO <sub>4</sub> at RT	C/20	143 at 100th cycle	[82]
PEO + LiTFSI + 12.5% EMIMTFSI	Li/LiMn <sub>2</sub> O <sub>4</sub> at RT	C/10	120 at 10th cycle	[83]
PEO + 20%LiTFSI + 30% (1-butyl 3-methyl yridinium TFSI)	Li/LiFePO <sub>4</sub> at 40°C	C/10	160 at 25th cycle	[73]
PEO + 20%LiFSI + 10% PYR13FSI	Li/GO- LiFePO <sub>4</sub> at rt	C/10	163 at 100th cycle	[84]
PEO + 20 wt.% LiTFSI + 20 wt.% BMIMTFSI	Li/LiMn <sub>2</sub> O <sub>4</sub> at RT		140 $\mu$ Ah/cm <sup>2</sup> at 25 cycle	[85]

The ether group acts as a coordination ligand for the Li cation, separating them from the anion's nuclear atom. Researchers developed lithium ILs, which separate the lithium cations from the anions' core atoms by combining them with borates that have electron-withdrawing moieties to minimize the anionic basicity. We created a lithium IL containing Li-containing borate with an electron-withdrawing group and the coordination of the ether ligand of Li. The ether group acts as a binding compound for Li, separating the Li cation from the central atom of the anion.

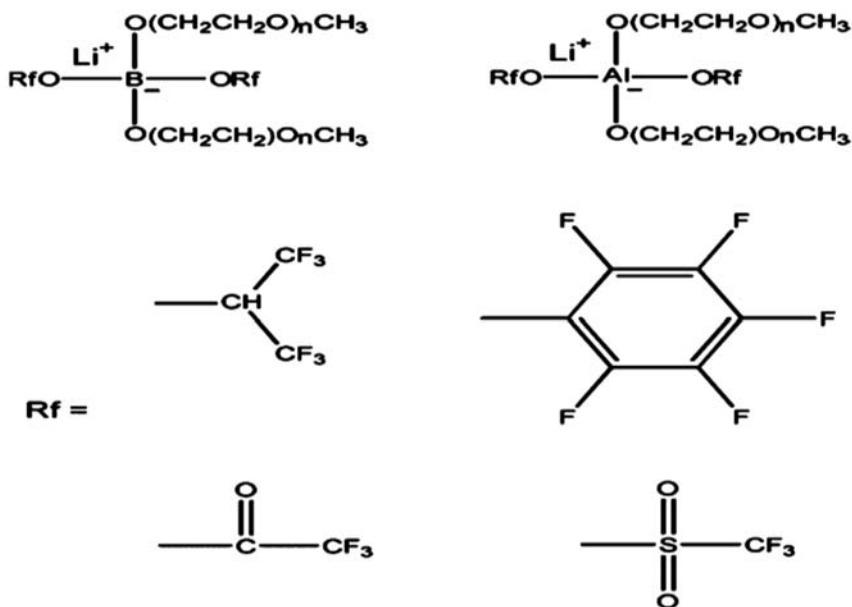


FIGURE 14.8 Structures of Li ILs.

Watanabe et al. have developed a lithium IL containing Li and a borate with a single electron-removing group to reduce the presence of anions. Li also controls the ether and separates lithium via anionic atoms [92,93].

Other alkali metals—IL (Li, Na, and K) can be formed in the same way by using the same ether and larger anions. For example, at room temperature, alkali carboxylate is still a liquid [94], as shown in Fig. 14.8.

## 14.12 Conclusion

The use of IL in combination with organic electrolytes is an interesting method in light of the development of better electrolytes. Some studies have already investigated the effects of various electrolytes on the performance and safety of LIBs, especially in terms of flammability. The IL–solvent interactions were investigated in a few instances. Nonetheless, gaining a better knowledge of these interactions might help with the logical design of these electrolytes.

This latest study seems to be important in this regard. In recent years, there has been increasing research showing that IL may help prevent unwanted reactions such as anodic decomposition of Al or improve the properties of additives such as redox shuttles. As a consequence, the use of



IL as an addition to traditional LIB electrolytes appears to be highly promising, and more studies in this area should be conducted as soon as possible.

Finally, various methods have been proposed to improve the conductivity of PEO-based PEs below the melting temperature. GPEs based on ILs are considered to be the most promising. PEs with these GPEs have improved ionic conductivity, thermal stability, and electrochemical stability. Advantages of lithium batteries include improved electrode–electrolyte interactions, mechanical stability, and safety. They can help to avoid the formation of undesirable dendrites and contribute to the safety of lithium batteries owing to their mechanical stability. It also has excellent electrochemical stability, making it suitable for use in high-voltage, high-energy batteries. These batteries offer excellent electrochemical and periodic stability, as well as flexibility and safety. As a result, these IL-based GPEs can be considered viable alternatives to liquid electrolytes from lithium batteries.

## Abbreviations

<b>AILs</b>	Aprotic ionic liquids
<b>BESS</b>	Battery energy storage systems
<b>BF<sub>4</sub><sup>−</sup></b>	Tetrafluoroborate
<b>EC</b>	Ethylene carbonate
<b>EMIMTFSI</b>	1-Ethyl-3-methyl-imidazolium,bis (trifluoro-methane-sulfonyl) imide
<b>FSI</b>	Di-(fluoro sulfonyl imide)
<b>GPEs</b>	Gel polymer electrolytes
<b>HSAB</b>	Hard and soft acid and base
<b>KSCN</b>	Potassium thiocyanate
<b>ILs</b>	Ionic liquids
<b>LIBs</b>	Lithium-ion batteries
<b>LiBF<sub>4</sub></b>	Lithium tetrafluoroborate
<b>LiClO<sub>3</sub></b>	Lithium chlorate
<b>LiClO<sub>4</sub></b>	Lithium perchlorate
<b>LiPF<sub>6</sub></b>	Lithium hexafluorophosphate
<b>NaClO<sub>3</sub></b>	Sodium chlorate
<b>NaSCN</b>	Sodium thiocyanate
<b>PEs</b>	Polymer electrolytes
<b>PEO</b>	Poly(ethylene) oxide
<b>PF<sub>6</sub><sup>−</sup></b>	Hexafluorophosphate
<b>PILs</b>	Protic ionic liquids
<b>SPEs</b>	Solid polymer electrolytes
<b>Tf<sup>−</sup></b>	trifluoro-methane-sulfonate
<b>TFSI</b>	Di-(trifluoro methane sulfonyl imide)
<b>VOCs</b>	Volatile organic compounds

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# Advanced Applications of Ionic Liquids

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