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Chapter

Application of Ionic Liquids in Rechargeable Li-Ion Batteries: A Comprehensive Guide to Design, Synthesis and Computational Aspects

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Abstract

The breathtaking pace of the development of smart and wearable gadgets, electric vehicles and many other ultraportable devices has ushered into the era of rapid development of rechargeable batteries with enhanced safety, high-performance, high gravimetric and volumetric energy density. New battery chemistries are being constantly explored to identify better electrolytes that are environmental-friendly, non-flammable, reusable and most importantly ultra-customizable for high-performance applications. Ionic liquid, by virtue of its unique set of tunable properties, is a natural choice from both academic and industrial perspectives. A general guiding principle of ionic liquid synthesis proceeds via an appropriate selection of precursors from the ionic liquid toolbox and reaction with the alkyl halide followed by the metathesis or simple acid-base reaction yielding the final ionic liquid. This study is a complete and extensive treatise on the usage of the ionic liquids in the electrolytes of secondary batteries concerning (i) the design philosophy, (ii) synthesis, (iii) characterization, (iv) new chemistry and electrode material development (v) cell performance, (vi) cell safety, and (vii) comprehensive computational protocols encompassing all the aspects of the electrolyte and electrode-electrolyte interactions.

Keywords: ionic liquids, electrolyte/electrolyte additive, secondary battery, density functional theory, molecular dynamics, Monte Carlo simulations

1. Introduction

Batteries are all around us. They are mainly of two types: primary (non-rechargeable) and secondary (rechargeable). Economically and also from a materials sustainability point of view, rechargeable batteries should replace the primary cells wherever possible. Intense research is going on to make our planet cleaner through

sustainable and ecofriendly technologies. Through constant innovation, battery materials are being perfected in terms of cost effectiveness, cycle lives, energy and power densities, cell voltages and cell safety [1, 2]. Rechargeable batteries are the electrochemical devices which can transform chemical energy into electrical energy and vice versa. This is called the “Rocking Chair” mechanism. The battery mainly consists of three parts: Anode, electrolyte and cathode. When a battery is operated, redox reactions take place: reduction and oxidation take place at cathode and anode respectively during discharge. While charging, the reactions are reversed. In order to maintain the charge balance in a battery driven electrical circuit, the resulting current from anode to cathode need to be compensated by ion transport through electrolyte inside the cell. If the electrolyte is liquid, there is a need for a separator between electrodes to prevent short-circuit.

Among the most popular commercially available rechargeable batteries, lithium ion batteries (LIBs) are having higher gravimetric and volumetric energy densities [3] which make them smaller, lighter and energy dense than others. These parameters are of crucial importance for modern automotive and portable electronic industries.

The other advantages of LIBs are low self-discharge and lack of memory effect. Schematics of internal structure of a LIB is shown in **Figure 1**. LIBs were first commercialized by Sony Corporation in 1991 [4]. The following decade can be marked by intense advanced engineering of LIBs. In 2005, Sony again introduced the first tin based anode battery [5] (Nixelion™) with 30% more battery capacity resulting in an expeditious increase in LIB sales for automotive applications [6].

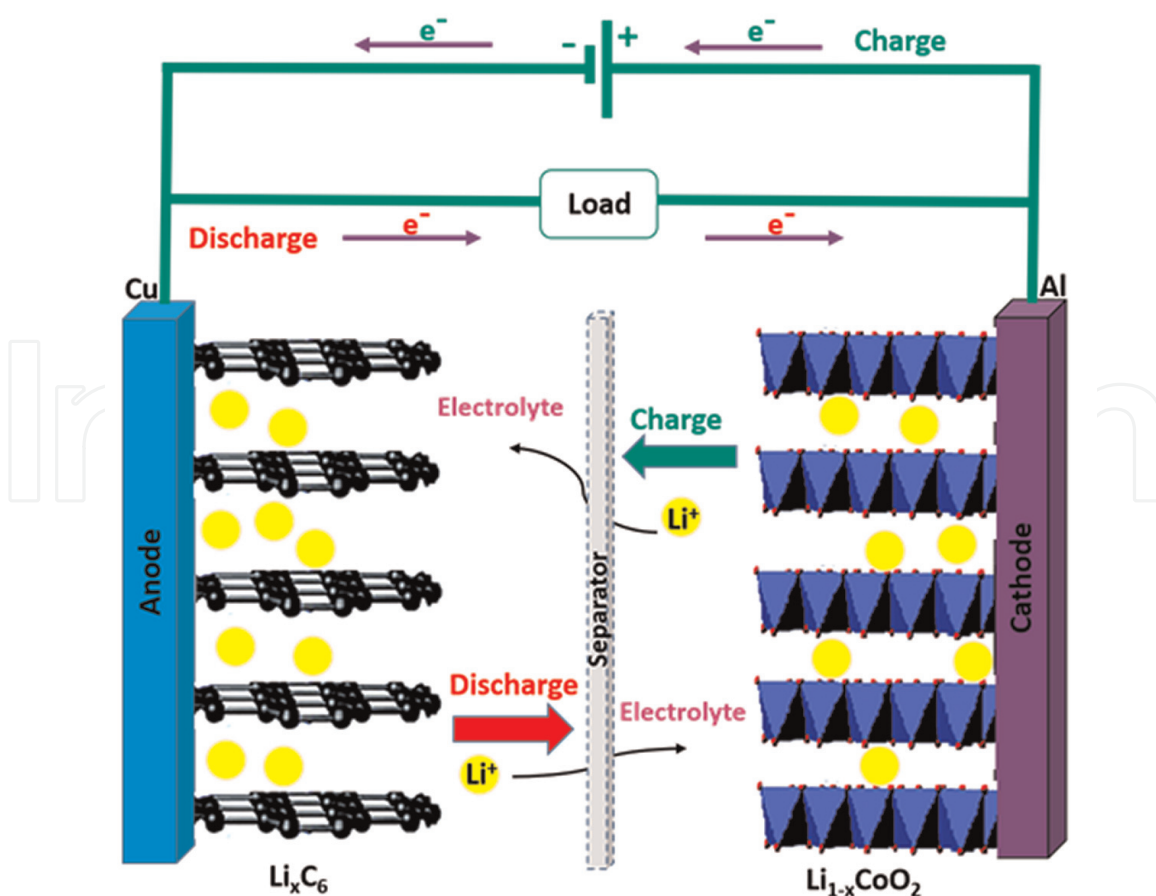


Figure 1. Schematics of internal structure of a lithium ion battery.

Battery electrolyte plays a very crucial role in performances. Electrolyte is a medium of transportation of ions. There are many types of electrolytes available in the market in the form of solid, liquid, gel and polymer. Some important and desirable properties of electrolyte are (i) solid electrolyte interface (SEI) formation which protects the electrodes from degradation and also prevents anion intercalation, (ii) wide electrochemical window which determines the stability range of batteries; and improving: (iii) chemical stability, (iv) ionic conductivity, and (v) salt solubility. Liquid electrolyte is advantageous because of their high ionic conductivity. The most popular commercial LIB electrolytes was developed by Tarascon *et al.* [7], which contains lithium hexafluorophosphate (LiPF_6 ; a lithium salt) dissolved in a mixture of organic carbonates (ethylene carbonate and dimethyl carbonate). This electrolyte has high salt dissociation, low viscosity, moderate ionic conductivity and cost-effective. However, it also has serious shortcomings in the form of being flammable, sensitive towards hydrolysis and toxic. There is an urgent need to identify a possible solution for reducing irreversible lithium losses and flammability. One of the most attractive routes to address these problems is through the introduction of additives or optimization of electrolyte composition [8].

The role of additives in electrolyte is to facilitate one or more of the following phenomena: Formation of stable solid electrolyte interface (SEI) on electrodes, protect cathode from over-charge, reduce gas generation, improve thermal stability and ionic conductivity and increase coulombic efficiency. They are typically categorized as SEI supporting, flame retardant and over-charge protective additives. The SEI supporting additives are again classified into three groups: reaction type, reduction type and SEI improver. The reaction type additives react with intermediate solvents and participate in SEI formation. The reduction type additives generally decompose prior to the electrolyte solvent's decomposition while charging and help in formation of SEI. The last type i.e. SEI improvers are re-dissolved in the inorganic SEI layer to prevent continuous growth of SEI further, thus enhancing the performance of LIB. **Figure 2** depicts the design strategy of a high energy rechargeable batteries.

Ionic Liquids (ILs) have been proposed as electrolytes in LIBs for recent years. For example, Kim *et al.* [9] developed the battery prototype of $\text{Li}/\text{LiFePO}_4$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$ using pyrrolidinium-based ILs and their performance characterization are

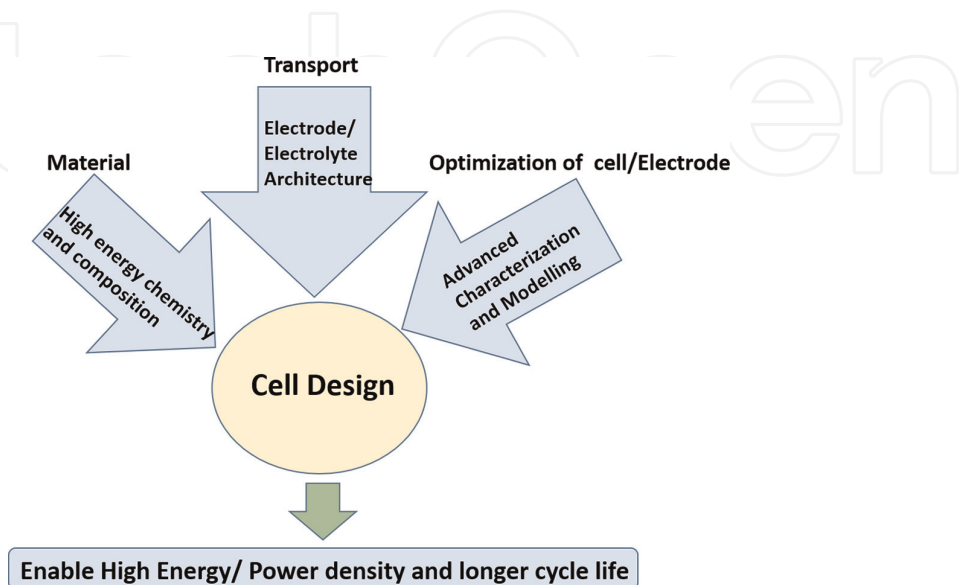


Figure 2.
Design strategy of a high energy rechargeable batteries.

described therein. T. Yim *et al.* [10] discussed the usage of room temperature ILs as an alternative to conventional carbonate-based electrolyte for LIBs. Masayoshi Watanabe *et al.* [11] described the application of ILs in energy storage devices. Sato *et al.* [12] found a novel ammonium IL, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide) as an electrolyte for electrochemical devices. T.D Vo *et al.* [13]. had studied the safety aspect of 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) in carbonate solvents (EC-PC). H. Park *et al.* [14] used over-lithiated lithium nickel oxide (Li_2NiO_2) as a sacrificing positive additive for LIBs. Guerfi *et al.* [15] used mixtures of ILs ((trifluoromethylsulfonyl imide) as anion and 1-ethyl-3-methylimidazolium as cation) along with organic electrolyte to enhance cell safety and electrochemical performances. H. Saruwatari *et al.* [16] found that addition of bis(oxalato)borate anion in 1-ethyl-3-methyl-imdazolium tetrafluoroborate formed SEI which improved the performances in battery. N. Plylahan *et al.* [17] showed that for high temperature LIB, pyrrolidinium-based hybrid ILs might be a good choice. In summary, using ILs as an electrolyte/electrolyte additive in lithium ion batteries may resolve many concerns in LIBs.

2. General features, synthesis and characterization of ILs

Green technology refers to the application of scientific principles for the purpose of emission reduction, conservation of water, waste reduction and increasing energy efficiency compared to their conventional counterparts. From the early age of alchemy, there has been huge interest in the study of species in solution. Solvents can be of any type of liquids but sometimes they are hazardous and create environmental pollution. The examples of common solvents are chloroform, dichloromethane, carbon tetrachloride, acetone, chlorofluorocarbon (CFC), ethylene carbonate (EC), dimethyl carbonate (DMC) etc. Traditionally, these solvents have been used as reaction media for the synthesis of fine chemicals, pharmaceuticals, petrochemicals and energy storage applications however, they have some drawbacks: (i) mostly they are used in large amounts, and (ii) usually they are volatile. In the chemical industry, the major problem is the large volume of hazardous wastes as by-products. When these are dumped into the environment it causes air, water and soil pollution. These volatile organic compounds (VOC) which evolve harmful gasses have low thermal stability, pose danger to human life and disbalance the ecosystem. So, introducing greener and cleaner technology in both industry and academia is a high priority agenda [18]. More specifically, green chemistry is the design of processes which can reduce or eliminate the generation of harmful/hazardous substances. Hazardous materials are categorized as physical (e.g. flammable and explosive), toxicological (carcinogenic and mutagenic), and environmental (affecting ozone depletion, climate change, and global warming) [19, 20]. To minimize the chemical wastes from industries, refinements and redesign are necessary for conventional chemical processes [12]. At present scenario, low volatile, recyclable, reusable and thermally stable solvents, in particular, “neoteric solvents” would be ideal for chemical industries. According to the guidelines of Montreal Protocol [21], four alternate technologies are possible. They are (i) solvent free synthesis, (ii) use of supercritical fluids, (iii) use of water as solvent, and (iv) use of room temperature ionic liquid. Solvent free synthesis is not feasible all the time. For supercritical fluids, they need special conditions (e.g. a feasible or at least favorable T_c , P_c etc.). For the last two decades, water has been used as a useful solvent medium but as it is a protic solvent, it has the tendency to hydrolyze. Another major limitation

of water is the low miscibility with organic reagents. So, ILs as reaction media are a better and generic option for many applications.

ILs are molten salts that are liquid below 100°C and consist entirely of ions [22–25]. Mostly ILs are comprised of bulky, asymmetric organic cations and organic or inorganic anions (**Figure 3**).

The most common IL cations are alkylammonium, alkylphosphonium, *N,N*-dialkylimidazolium as well as *N*-alkylpyridinium and alkylthiozolium cations. The anions may be as simple as halides (chloride, bromide or iodide), nitrate, tetrafluoroborate, haloaluminates, hexafluorophosphate etc. Nowadays, alkyl sulfates and alkyl sulfonates and even more often fluorinated and perfluorinated anions such as triflate, $[\text{CF}_3\text{SO}_3]^-$, bis(fluorosulfonyl)imide $[(\text{FSO}_2)_2\text{N}]^-$ and bis(trifluoromethylsulfonyl)imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ are employed. There are several functionalized cations which are very popular (**Figure 4**).

With permutation and combination of these cations and anions, a large number of ILs can be designed for specific applications [13, 24]. In fact, for 1,3-functionalized

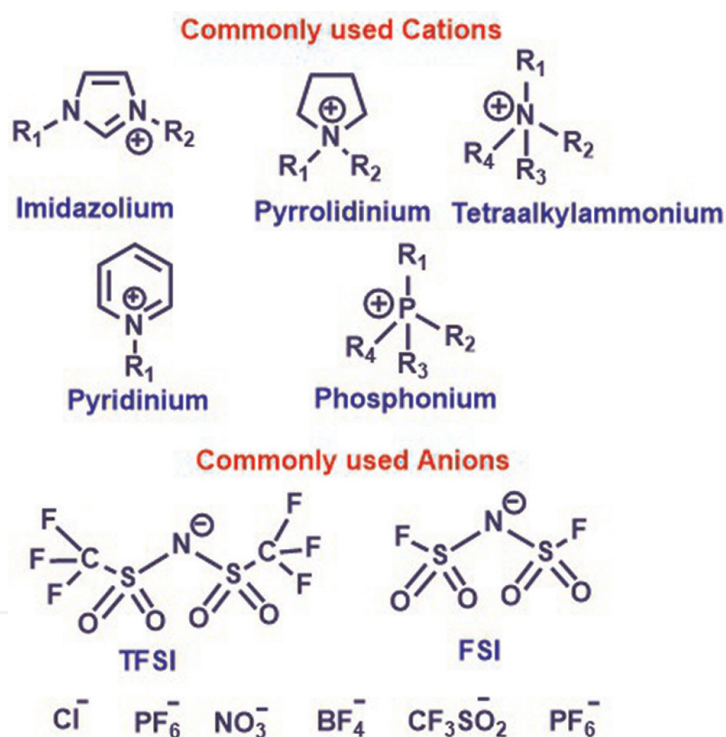


Figure 3.
The ionic liquid tool cabinet: Frequently used cations and anions for ILs.

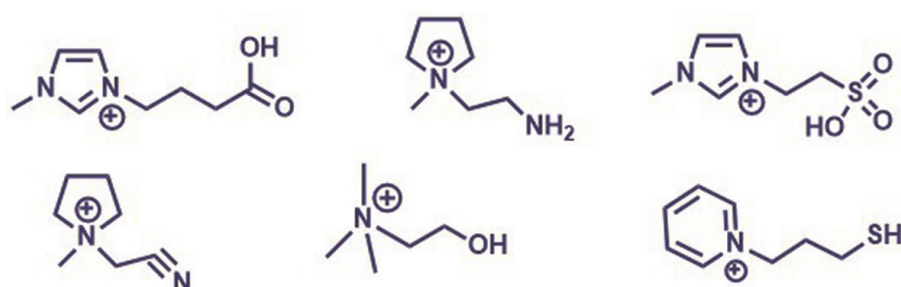


Figure 4.
Functionalized cations of ILs.

imidazolium derivatives, there are 30,000 entries in the CAS database [26]. That is why, RTILs are also known as “designer solvents”.

Although, one can certainly identify an optimal IL for any specific application, there still might be some pros and cons. The choice of cations and anions have a great influence not only on the physical properties but also in thermodynamics and the kinetics of the reactions involved for specific applications. As a rule of thumb, anions control the chemistry and the cations refine the physical properties like viscosity, solubility, flammability, density etc. Thus, for a targeted application, tuning of the properties of ionic liquids is very important. **Figure 5** depicts the number of publications on ILs in rechargeable batteries from 2010 to May 2022.

2.1 Synthesis of room temperature ionic liquids

Depending upon the structures, properties and applications, four different generations of ionic liquids have been reported till date [27, 28]. The first generation ILs are those whose physicochemical properties can be strengthened by simply changing their cations and anions. They have been extensively used as solvent of the reaction media but they are ecotoxic in aquatic environments. When functionalized cations e.g., dialkylimidazolium, alkylpyridinium and phosphonium or anions e.g., tetrafluoroborate and hexafluorophosphate are introduced to play a particular chemical role, it is called second generation ILs. They are stable in aquatic environments and mainly used as lubricants, complex ligands and materials for energy applications. The third generation ILs are synthesized from some low-toxic, biologically active ions e.g., amino acids and choline, which have nearly identical physical properties of classical ILs. These task specific ILs [29] have antifungal and antibacterial properties etc. They are the good choices for drugs/biomolecule delivery, bio sensing and regenerative medicines. Recently, in 2018, the fourth generation ILs [30] have been introduced. Unlike the three previous generations, these ILs go beyond the traditional salt-in-solvent solutions and therefore not readily predictable by simple rule of mixtures. Typically, they are custom-designed aryl-alkyl-substituted ILs. They offer some unique application in bio preservation and offer tremendous future potential owing to their intrinsic biocompatibility.

Since the present study focuses on the ILs for LIB applications, we have confined our discussion only to the synthesis of first and second generation room temperature ILs.

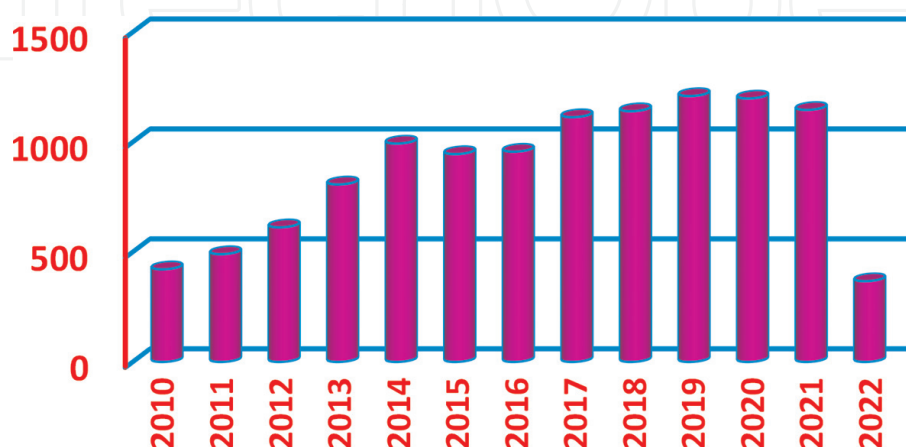


Figure 5. The number of publications on ILs in rechargeable batteries from 2010 to 2022 (all data are taken from “Scifinder” up to 16th of May 2022).

Fewer steps are required for their synthesis. The first synthetic step for both first and second generation ILs [27] are common. First of all, one has to choose the corresponding precursor which after reaction with alkyl halide gives halide intermediate. This intermediate undergoes either metathesis (anion is exchanged with group 1 metal salts) or simple acid-base reaction to give final ionic liquid. The synthetic route of Imidazolium-based ionic liquids were given by Huddleston *et al.* [31] and Stark *et al.* [32]

From **Figure 6**, it can be seen that 1-alkyl-3-methylimidazolium ionic liquid is obtained from corresponding halide precursors either by metathesis or by treatment with acids with stoichiometric ratios. Among halides, chlorides are mostly preferred. Sometimes the alkylation is carried out in an autoclave at elevated temperature and autogenous pressure without addition of any solvent if the chloroalkane (e.g., chloroethane) is gaseous at room temperature. But their higher homologues can be synthesized under reflux at atmospheric pressure. Same method can be followed for the pyridinium, piperidinium or any other ILs. The synthesis of third and fourth generation ILs follow the green path and thus is not very easy to synthesize. Particularly, attaining high purity becomes increasingly challenging for the higher generation ILs and often additional precautions need to be taken [28, 33].

2.2 Characterization of ILs

The synthesized ILs should be free from any impurities such as organic solvents, chloride ions, water etc. because final purity of ILs has a very strong influence on the

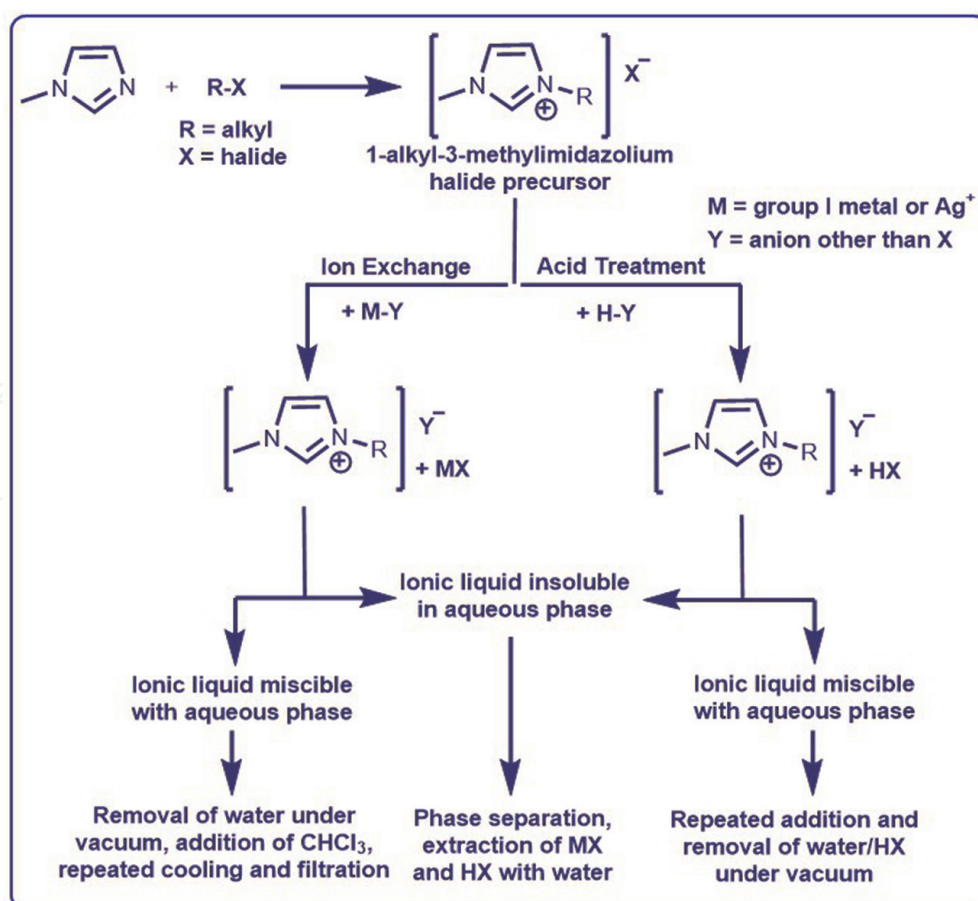


Figure 6. Common synthetic route for the preparation of IL; reproduced from ref. [28].

physicochemical properties. Therefore, during synthesis proper care should be taken. The identity of synthesized ILs are established by Nuclear Magnetic Resonance (NMR) spectroscopy, Fourier Transform Infrared (FT-IR) spectroscopy, Electrospray ionization mass spectrometry (ESI-MS) and Elemental (CHN) analysis. Additionally, Karl Fischer titration is an important technique to quantify the trace amount of water present in the synthesized IL.

2.3 Physicochemical characteristics of ILs

ILs have many interesting properties depending upon the choices, which make them very attractive candidates for diverse applications. Some of them are as follows: (i) very negligible vapor pressure, (ii) high thermal stability, (iii) wide electrochemical window, (iv) tunable properties, (v) nonflammable, and (vi) the most importantly, environment friendly. Thermodynamic properties such as activity coefficients, densities and transport properties like viscosity, conductivity and diffusion coefficients have a great influence in reactivity of ILs towards chemical processes. In a review, Heintz [34] has described the thermodynamics and thermophysics of ILs in non-aqueous solvents.

As ILs are ionic in nature, they are highly conducting materials [35]. This property makes ILs the ideal candidate for applications in electrochemical devices. Just like other properties, conductivity of ILs also can be adjusted by deliberate choice of cations and anions as both moieties can contribute to it. It can also be enhanced by increasing the temperature. Sometimes, the aggregation or ion pairing in neat solution leads to reduction in ion mobility thus reducing the conductivity. As a side note, studies have shown that in the solar cell applications, the conduction is enhanced via Grotthuss hopping alternatively than the typical transfer mechanisms [36, 37].

Viscosity plays a major role in determining the physical properties. Generally, the viscosities of IL are higher than that of common solvents [31]. If alkyl chain length of IL is increased, the viscosity is increased because of more Van der Waals interaction between cations [38]. It can be minimized by functionalization of side chains. The anions also play an important role. The tendency to form hydrogen bonds and symmetry of anions have a great influence on viscosity of ILs. It decreases with increase in temperature due to the reduction in Van der Waals interaction between cations and anions. The impurities such as water, organic solvents and chloride ions have great influence on viscosities [39]. For example, 0.01 molal bmimCl has viscosity of 154 cP whereas 0.5 molal bmimCl has viscosity of 201 cP. Generally, Imidazolium based ILs have lesser viscosities than ammonium based ILs [40]. The viscosities can be tuned by structural modification of ions.

The electrochemical stability window (ESW) of an ionic liquid is the range in electric potential wherein that particular ionic liquid is stable (not decomposed) either by the reduction of constituting cation or by the oxidation of anion [35]. Generally, the window for ILs lie in between 3.0 V and 6.4 V [41–44]. The precise range of electrochemical windows depends on the nature of cations and anions. Fluorine containing anions generally show a wide range. All Imidazolium-based ILs show cathodic stability about -2 V Vs saturated calomel electrodes [41–44].

The ILs generally possess high thermal (and radiation, useful for nuclear application) stability because of their negligible vapor pressure. Detail studies have been reviewed by Maton *et al.* [45] and Bier *et al.* [46]. Xue *et al.* [47] described the long-term stability of protic, polymerized and mixtures of ILs in their perspective article. Literature reveals that, their decomposition temperature are generally in the range of

280–490°C. Thermal stability is generally determined by thermogravimetric analysis (TGA). The decomposition temperature is very much dependent on the structure of the consisting cations and anions [48]. Generally, the anions are more responsible than cations for the decomposition of ILs. For same cation, the decomposition temperature is increased with more hydrophobic anions [31] e.g. for $[\text{C}_4\text{mim}]^+$ the decomposition temperature varies in the following way: Cl^- (254°C) < I^- (265°C) < PF_6^- (349°C) < BF_4^- (403°C) < NTf_2^- (439°C).

ILs are still expensive than conventional solvents. Because of their low vapor pressure, the classical ILs may not be harmful in atmospheric condition but they may cause severe contamination in aquatic environment due to their potential toxicity and nonbiodegradability. To make them economical and environment friendly, there is a need to recycle those ILs for future use. Recyclability of ILs is one of the main reasons for their increasing popularity among the scientists and engineers. There are several processes available for IL recovery. Wu *et al.* [49] have summarized the different IL recovery processes which might be a guide to future researchers. Toxicity is also a major issue for the biomedical application of ILs. Using structure-activity relationship, the toxicity and biocompatibility can be tailored for ILs [50]. Zhao *et al.* [51] and Ranke *et al.* [52] have highlighted some toxicological advances of new generation ILs.

3. Different types of ILs used in rechargeable batteries

Table 1 summarizes the salient features of different IL precursors and their derivatives for specific electrochemical systems to enhance different performance/stability/safety metrics. These can be a good guiding principle for customizing IL for a specific battery application.

IL precursor classes	ILs + additives	Electro-chemical System	Salient features	Reference
Imidazolium-based ILs	HMITFSI, MEMITFSI	Li/ LiMn _{1.5} Ni _{0.5} O ₄	Wide (~ 5.5 V) ESW and possible parasitic anodic reactions while charging at the high potentials	[53]
	LiTFSI in AMImTFSI	Li-Sulfur	Lithium polysulfide dissolution is suppressed and exhibit good cycling capacity	[54]
	EMIM ⁺ -encapsuled ionogel	Li/LiFePO ₄	Reversible Li ⁺ intercalation/deintercalation behavior and stable even after 120 cycles at 0.5C	[55]
	IMI _{1,201} TFSI, IMI _{1,10201} TFSI	Li/LiFePO ₄	Increased conductivity with less viscosity, capacity retention is up to 92% at lower current rate	[56]
Pyrolidinium-based ILs	BMPTFSI	Li/ LiMn _{1.5} Ni _{0.5} O ₄	Wide (~ 5.5 V) ESW and possible parasitic anodic reactions while charging at the high potentials	[53]
	Py ₂₄ TFSI-LiTFSI + PVdF-HFP + EC + PC	Li/Li	Wide ESW, high degradation temperature and high lithium ion transport	[57]

IL precursor classes	ILs + additives	Electro-chemical System	Salient features	Reference
	PYR ₁₍₂₀₁₎ TFSI, PYR ₁₄ TFSI	Li/LiFePO ₄	Suppresses crystallinity and increase cation solvation	[55]
	PYR ₁₃ TFSI, PYR ₁₃ FSI	Li/NMC	Ion transport properties is enhanced (about 10 ⁻³ S cm ⁻¹ at -20°C) and wide ESW of 5 V	[58]
	Pyr1,3FSI-LiTFSI	Li-LiCoO ₂	Lithium dendrite growth is effectively suppressed and exhibit good cycling performances at 4.4 V	[59]
	BMPyrTFSI, MPPyrTFSI	Zn stannates / Li	Safer electrolytes and potential candidate to replace graphite as the anode material in more complex devices.	[60]
Pyridinium-based IL	B ₃ MePyTFSI, B ₄ MePyTFSI	Li/LiFePO ₄	High ionic conductivity and exhibit better cycling capacity by enhancing cation solvation	[55]
Tetraalkylammonium-based ILs	N111(1O2) FSI	Li-Air	Possesses low viscosity (~111.4 cP) and initial capacity is 3.75 times higher than reference material	[61]
	DEMETFSA - LiTFSI	Li-LiCoO ₂	Charge/discharge reversibility is increased	[62]
Phosphonium-based IL	mono-(C6) 3PC10- TFSI	Li-LiCoO ₂	High decomposition temperature (355°C), good conductivity (1.7 mS cm ⁻¹) at 100°C and enhanced specific energy and capacity retention	[63]

Table 1.
Representative ILs as electrolytes used in rechargeable battery with corresponding electrochemical systems.

4. Tailoring the properties of rechargeable batteries using IL electrolyte additives

4.1 Ionic conduction

Polymer electrolytes, in spite of its mechanical strength and stability, have a low ionic conductivity at a temperature below its glass transition temperature [64]. ILs have been recently studied as plasticizers in polymer electrolyte. Polymer doping with ILs and polymerization with ILs as solvent are the widely used methods to incorporate ILs in polymer electrolytes [65]. The ions in the ILs react with donor species of the polymer molecule thus reducing the intermolecular interaction. This increases disorder and causes an increase in Li-ion conductivity [66]. Even when polymer is added in small concentration in ionic liquids (gel or polymer-in-salt ionic liquids), the ionic conductivity of the gel polymer is greater than the pure electrolyte, due to the reduction in the overall viscosity of the gel, explained by polymer breathing model [67].

4.2 Solid electrolyte interphase (SEI)

As the ILs [68–70] have high oxidation potential (~ 5.3 V vs. Li^+/Li^0), they may serve as alternative electrolytes for LIBs. The major drawback with ILs is their high viscosity due to which the Li^+ ion conductivity is reduced. Imidazolium-based ILs are the most appropriate candidates for LIBs due to their relatively lower viscosity and a high Li-salt solubility at room temperature. In order to form a stable SEI layer on the graphite anode, some electrolyte additives (EC or VC) must be added because these ILs have poor stability below 1.1 V vs. Li^+/Li^0 [43].

In a stable battery cell, the relative electron energies in the cathode, anode and electrolyte have been schematically depicted in **Figure 7**. Here cathode is the oxidant and anode is the reductant and ΔE_p is the electrochemical stability window (roughly the energy difference between the HOMO and LUMO of the electrolyte). μ_A and μ_C are the chemical potential and ϕ_A and ϕ_C are the work function of anode and cathode respectively. In absence of any passivation layer (SEI), if the chemical potential of anode is more than the LUMO of the electrolyte, then it will reduce the electrolyte by transferring the electron to the LUMO of the electrolyte and if the chemical potential of the cathode is less than the HOMO of the electrolyte, then it will oxidize the electrolyte by transferring the electron to the cathode from the HOMO of the electrolyte. For thermodynamic stability of the battery cell, the following relationship must hold: $e \cdot V_{oc} = \mu_A - \mu_C \leq \Delta E_p$; where e is the electronic charge and V_{oc} is the open circuit voltage of the battery cell. Hence the SEI layer provides the kinetic stability to increase the V_{oc} provided the solvent window of the electrolyte is not too large and the SEI layer formation is ensured by either $\mu_A > \text{LUMO}$ and/or $\mu_C < \text{HOMO}$.

An optimized concentration of ionic liquid as additive to an organic liquid carbonates may tackle the problem of flammability without much compromise in the Li-ion transport and it also helps in SEI formation that in turn provides protection from the degradation of electrode surface [72, 73]. In our previous work, an imidazolium-based

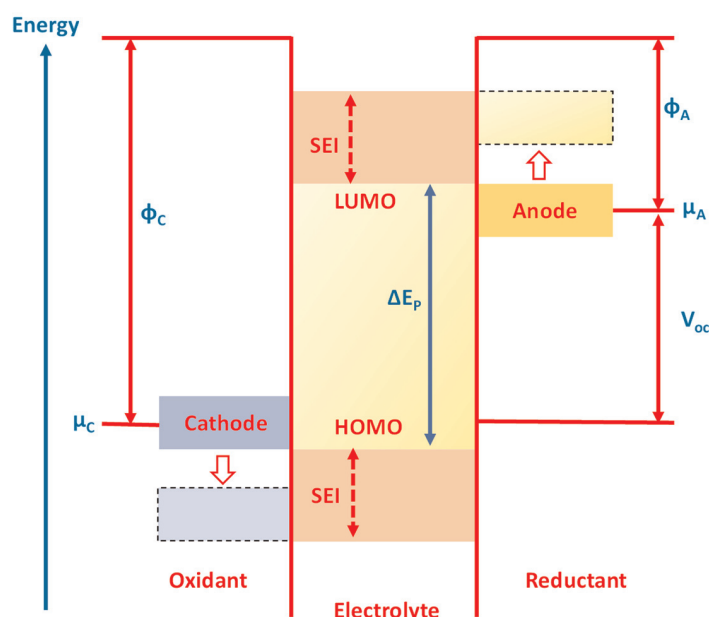


Figure 7. Schematic open-circuit-diagram of an electrolyte in a thermodynamically stable battery cell. Copyright; reprinted with permission from ref. [71].

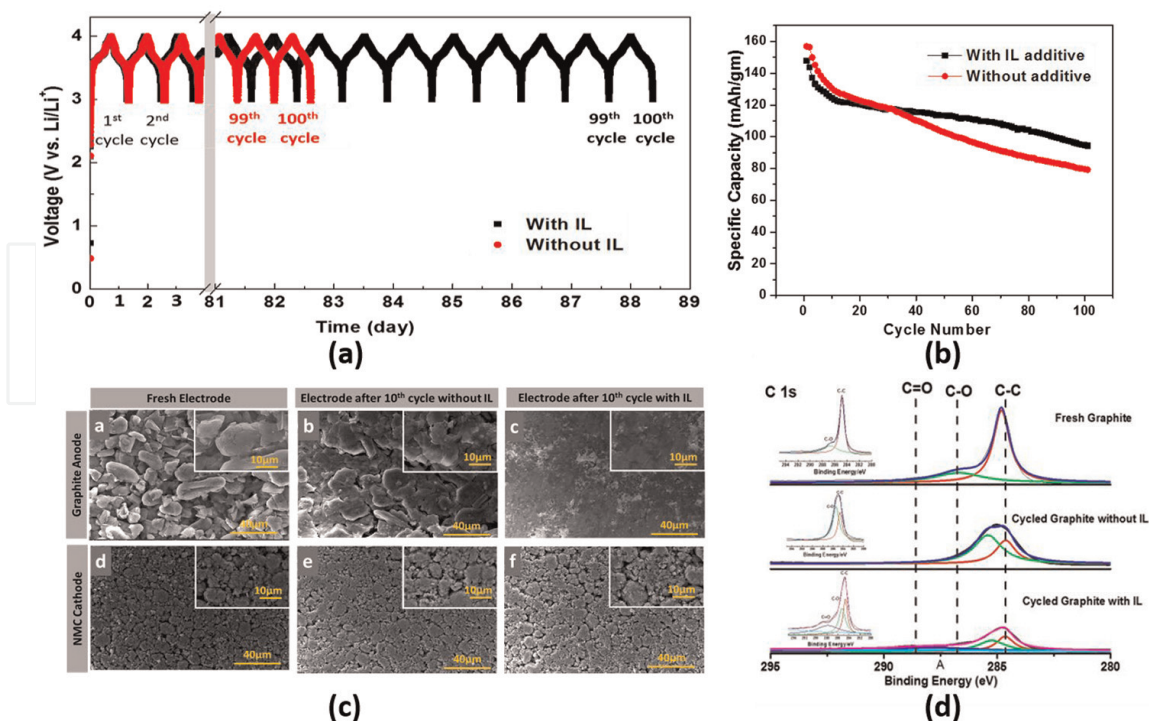


Figure 8.

(a) Galvanostatic charging and discharging (100 cycles) of the cells with and without IL with cell voltage between 3.0 V to 4.0 V and a break plot from 3 to 81 days. The cell with IL (black) provides at least 6 days more service than without IL. (b) Cyclic discharge curve of the cell in electrolyte without and with IL, (c) SEM micrographs of both the electrodes before and after cycling, and (d) C 1s XPS spectra of graphite electrodes with IL and without IL; copyright; reprinted with permission from ref. [72]. Copyright 2020 Springer Nature.

non-flammable dicationic ionic liquid was synthesized and was used (20 mM) as an additive to the conventional organic electrolytes for LIBs (**Figure 8**).

It has been found that the addition of IL enhances the discharge capacity of the LIBs by 22% and capacity retention is ~73%. The SEM micrographs and XPS study with IL revealed that a stable SEI has been formed during cycling.

Further, this strategy may further increase the oxidation voltage (lower HOMO energy) of the hybrid electrolyte from that of the carbonate. Unfortunately, till date the use of IL as a sole electrolyte for secondary batteries is still a challenge.

5. Theoretical considerations

5.1 Overarching theoretical and computational paradigm

Computational methods have been widely used for the fundamental understanding of many novel materials. Similarly, simulation of the ionic liquids enables researchers to understand its behavior and tailor its properties. When ILs are used as solvents in battery electrolytes the charge present in the solute polarizes the solvent around it, thus a reaction potential acts on the solute which alters its charge distribution with respect to normal charge distribution in the vacuum. Thus, for the simulations of ILs, the solvent effect is of paramount importance in predicting their properties. Two different methods have been developed for studying the effect of solvent on the molecule. One includes consideration of explicit solvent molecules

around the solute and studying it as a single system. The second method involves the usage of average properties of solvent with the assumption that the solvent is a macroscopic continuum medium instead of individual molecules. In the first approach the number of solvent molecules considered explicitly is limited and with a large number of molecules it becomes computationally expensive, especially in first principle calculations. Thus, the second approach is widely used to find the properties of a solute in the presence of a dielectric solvent using first principle calculations. Many continuum solvent models have been proposed such as the Apparent Surface Charge (ASC) method, Born approximation method and so on. One of the widely used methods is the ASC method. In this method the reactive potential due to the continuum solvent is calculated by considering surface charge density on the boundary of the solute. The boundaries enclose the cavities which in turn are formed by the superposition of nucleus centered spheres [74] with Van der Waal radius. The reaction potential is given by Eq. (1)

$$V_{RP}(\vec{r}) = \int_S \frac{\sigma(\vec{s})}{|\vec{r} - \vec{s}|} d^2s \quad (1)$$

where $\sigma(\vec{s})$ is the surface charge density and $V_{RP}(\vec{r})$ is the reaction potential due to the polarized dielectric medium. The ASC method can be further classified mainly into Polarizable Continuum Model (PCM), Integral Equation Function (IEF)-PCM and Solvent Model based on Density (SMD). In a PCM based ASC model, the surface charges are calculated by the Eq. (2)

$$\sigma(\vec{s}) = \frac{\epsilon - 1}{4\pi\epsilon} \frac{\partial(V_M - V_{RP})_{in}}{\partial\vec{n}} \quad (2)$$

where, ϵ is the dielectric constant of the solvent, V_M is the potential due to the charge within the cavity [75] and \vec{n} is the normal vector to the surface. Another method in the ASC is IEF PCM in which the potentials are redefined using green function from which the surface charges are calculated using a unique solution to the Eq. (3)

$$A\sigma = -g \quad (3)$$

where, A and g are the integral operators [76]. The computation used in all the above ASC methods uses boundary element method in which the surface is discretized and each discrete surface element is provided with discrete charges thus modifying the reaction potential given in Eq. (1)–(4)

$$V_{RP}(\vec{r}) = \sum_y \frac{q_y}{|\vec{r} - \vec{s}_y|} \quad (4)$$

where, q_y is the discrete charges present at the center of the surface elements and y is the number of discrete surface elements on the boundary of the solute [77].

In the PCM and IEF-PCM models, the bulk electrostatic interaction between the charge in the cavity and the dielectric continuum medium is considered in calculating the free energy change of solvation. Considerable improvement can be achieved in SMD, which considers additional interaction parameters accounting for the free energy change associated with the solvent cavitation (creating void space in the

continuum media to accommodate the solute), changes in dispersion energy, and local solvent structure changes. The equation governing this interaction is given by Eq. (5)

$$\Delta G_{CDS} = \sum_o \tau_o A_o(R) + \tau_m \sum_o A_o(R) \quad (5)$$

The SMD uses an IEF-PCM model for electrostatic interaction along with the free energy change described in Eq. (5). For ΔG_{CDS} (free energy corresponding to cavitation, dispersion and solvent structure) the boundary of the solute is taken at the Solvent Accessible Surface (SAS) which differs from the actual Van der Waal radii used in finding the reaction potential as shown in **Figure 9**.

5.2 First principle calculations: Density functional theory (DFT)

DFT is based on the foundational assumption that uses electron density as the main variable instead of the many-body wave function of the electrons thereby significantly reducing the computational complexity of the problem. The basis set is a set of one-particle functions generally used to build molecular orbitals in DFT to convert the complex partial differential equations into a simple form of a linear algebraic equation. Determining the properties of ILs as electrolyte in battery applications can be done based on experimental as well as computational method, but obtaining valuable molecular level insights of these properties through first principle methods allow us to make suitable decisions on the cations and anions to be used and tailor their molecular structures. These methods are widely used to study the effect of cation and anion, and their impact on its ESW, Lithium oxidation/reduction rate at the anode/cathode, Lithium ion conductivity, viscosity, solvation shell constituents etc.

The ESW of an ionic liquid can be calculated by finding the values of HOMO and LUMO energies or by using the thermodynamic cycle method. This is of great significance, e.g. for high voltage batteries the main limitation is the narrow ESW of the conventional electrolytes. In a study performed by Kazebiamnavi *et al.*, both the thermodynamic cycle and HUMO/LUMO method was used for finding ESW of methylimidazolium-based cations with different anions, particularly the effect of alkyl chain length of cation and different anions [78]. Thermodynamic cycle method

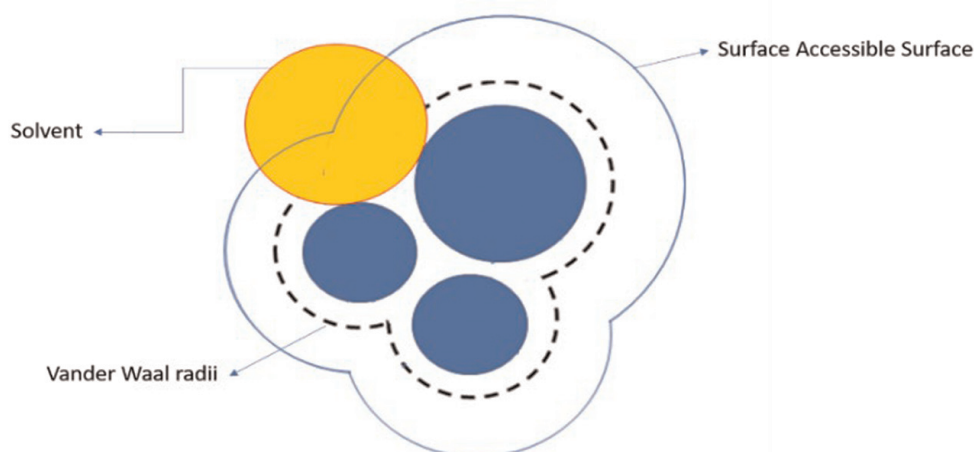


Figure 9. Different cavity boundary surfaces used in SMD method.

splits the charge transfer reaction of the solvated species into three reactions that involve conversion from solvated species to gaseous form, charge transfer reaction of the gaseous form and solvation of the ionized gas [78–80]. The total free energy for oxidation/reduction of a species in a solvent medium is calculated using **Figure 10**.

From the free energy values, the oxidation and reduction potential can be obtained by Eqs. (6) and (7)

$$E_{ox} = -\left(-\Delta G_{sol}^{ox} + \Delta G_{ref}^{ox}\right)/nF \quad (6)$$

$$E_{red} = -\left(-\Delta G_{sol}^{red} + \Delta G_{ref}^{red}\right)/nF \quad (7)$$

where, ΔG_{ref} is the Li/Li + oxidation and reduction Gibbs Free energy and n is the valency for redox couple (for Li/Li+; $n = 1$).

In order to include the effect of the polarizable solvent, a PCM model is used and an iterative self-consistent reaction field (SCRf) is used to calculate the actual charge distribution in the solute cavity. As a first step, the SCRf involves calculation of charge density in a solute molecule with vacuum as its surroundings. The same is then used to calculate the surface charge density that induces the formation of the reaction potential. This reaction potential is then added to the Hamiltonian and the cycle is repeated until the difference in total free energy becomes lesser than the tolerance value [81].

The anions, $[PF_6]^-$ and $[BF_4]^-$ have a lower HOMO and higher LUMO energy when compared to the $[OTf]^-$ and $[TFSI]^-$ ions. This is mainly due to the fact that in $[PF_6]^-$ and $[BF_4]^-$ HOMO and LUMO orbitals are contributed mainly by electronegative Fluorine atoms, while for the latter two it is distributed all over the molecule. The ESW was also calculated using the energy gap between HOMO and LUMO energy levels. It was found that error for thermodynamic cycles peaked up to a value of 15% but for HOMO/LUMO method it peaked around 50% [78].

Another important factor that affects the properties of the IL is the type of solvation shell formed around the Lithium cation. This solvation shell formed around the Lithium determines properties such as viscosity and ionic conductivity. A study done by Angenendt *et al.* [82] uses binding energy of the Lithium salt $[LiAn1]$ and Ionic Liquid anions $[An2]^-$ as means to determine the stable triplets $([Li (An1) (An2)]^-)$

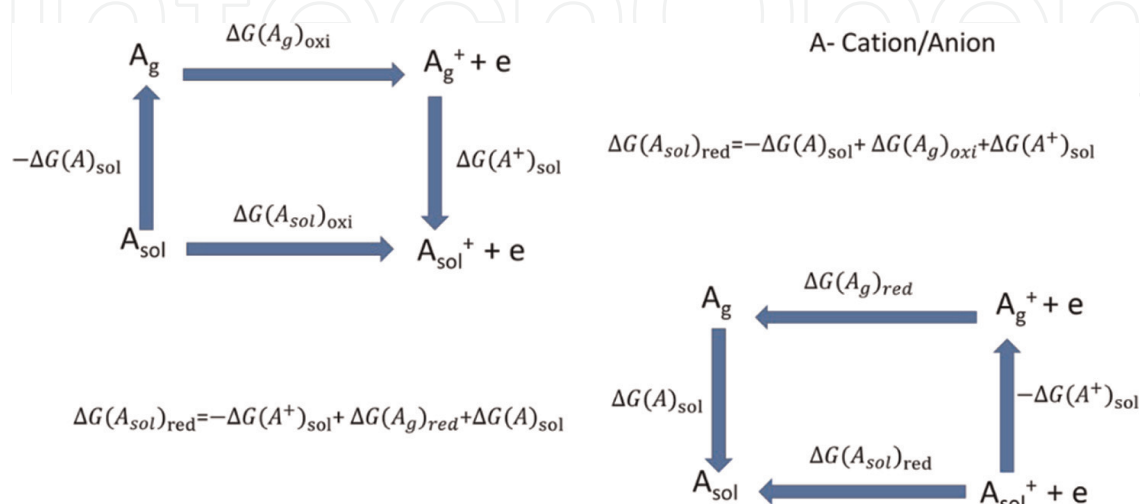
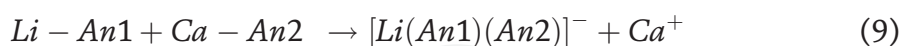
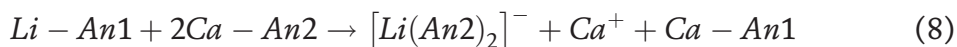


Figure 10. Thermodynamic cycle method for calculating free energy of oxidation and reduction.

formed in the solvation shell (An is used as an acronym for anion). The above method which ignores IL cation interaction is compared with an alternative method which includes interaction of IL cation, which is implemented by Eqs. (8) and (9)



where, An, Ca represents IL anion and cation, respectively. The reaction with lower free energy determines the stable triplet in a ternary system. Even though BF_4^- ions containing triplets were found to be prominent while considering binding energies with the Lithium salt, the cation interaction makes the BF_4^- ion containing triplets less favorable. Kiratidis *et al.* [83] have studied the effect of confined ionic liquids between two surfaces using DFT and found that the surface forces depend on the bulk density of the ionic liquids as well as on the adsorption potential. They have also observed a qualitative similarity in the trend of surface forces for neutral and similarly charged surfaces. Venkataraman *et al.* [84] have studied the interaction between Estrone and Imidazolium-Hydrophobic Ionic liquids using B3LYP/6-31G(d) level of theory. The affinity of Estrone towards the IL with PF_6^- anion is the highest among all other ILs and the interaction is found to have a non-covalent nature. Chen *et al.* [85] have developed an ab initio method to predict the melting point of ionic liquids. SMD-generic-IL solvation model along with the Born-Fajans-Haber cycle is used and found to be in good agreement in comparison to the experimental results with a mean absolute error of 30.5 K and a mean relative error of 8.5%.

5.3 Molecular dynamics studies

Unlike the first-principle methods, MD simulations consider atoms of IL as charged hard spheres. The partial charges are obtained from the Restrained Electrostatic Potential (RESP) algorithm which involves fitting DFT derived Electrostatic Potential (ESP) values calculated at different distances from the molecule's Van der Waal surface. The fitting is an optimization protocol generally based on the least square method which minimizes the sum of mean square error between the actual and fitted potential and a weighted harmonic or hyperbolic function which captures the difference between target and the fitted charge on each atom in a molecule [86]. These partial charges obtained from first principle calculations can only cover the coulombic force acting between charged atoms and ignores the change in the charge distribution within the atoms. Thus, potentials that incorporate the phenomenon of polarization have been developed for MD simulations of ILs. These potentials can be classified broadly into non-polarizable and polarizable potentials. In non-polarizable potential, the partial charge on each atom of the molecule is kept constant throughout the MD simulation. To incorporate the effect of polarization the partial charge obtained from the first principle calculations are scaled by a factor less than unity as a mean field approximation. This model predicted slower dynamics for IL in comparison with experimental results [87]. As the scaling factor is determined for a specific ionic liquid, it lacks transferability between different ILs and it fails to produce good results in case of IL mixtures [88, 89]. To overcome the above limitations, polarizable force fields have been developed for MD simulations of ILs. The polarizable force fields commonly used are Fluctuating Charge method, Drude oscillator method and Induced point dipole method.

5.3.1 Induced point dipole method (IPD)

In the IPD method, a point dipole is considered at the center of each atom in a molecule. For the i^{th} atom in a molecule the induced dipole moment is given by Eq. (10)

$$\mu_i = \alpha_i E_T \quad (10)$$

where, E_T is the total electric field. The total electric field acting on the atom in an induced dipole method is given by Eq. (11)

$$E_T = E_i - \sum_{j=1, i \neq j}^N T_{ij} \mu_j \quad (11)$$

where, E_i corresponds to the electric field acting on atom i due to permanent partial charges and the second term corresponds to the dipole interaction with T_{ij} corresponds to the dipole-dipole tensor and μ_j corresponds to the dipole moment of atom j . The main assumption in this model is that the dipole moment is considered isotropic and the model fails when the distance between two atoms approach $4(\alpha_i \alpha_j)^{1/6}$ in case of a two-atom system. Thus, a Thole damping factor is combined with the standard induced point dipole model to overcome the problem and this combined model is widely used in MD simulations for explicitly using polarizable force fields [90]. Bedrov *et al.* have used APPLE&P [91] force field to study the effect of the induced point dipole method on the thermodynamic properties of several ILs. When the induced point dipole interaction is turned off, the density and the average molecular dipole values are underestimated while the enthalpy of vaporization increases by 20–30%. This was explained by the larger difference in energy for the gas phase between polarized and non-polarized force fields in comparison to the liquid phase. The dynamic properties such as the diffusion coefficient was calculated by the mean square displacement and fitting it with a linear relation. The diffusion coefficient calculated using a non-polarizable field was found to have a lower value when compared to the polarizable fields [92]. The effect of polarizability on the simulation is also observed by considering the site-site partial radial density function. Due to the screening effect provided by the polarizable field no oscillations or small peaks were seen at larger distances in the partial radial density function when compared to the non-polarizable field. In another study by Zhao *et al.* [93], a MD simulation with AMBER potential force field (induced point dipole method) was used to find the effect of pressure on the ionic liquid [C₄mim][PF₆] and a phase change was observed when pressure increased from 5000 bar to 6000 bar. A sudden increase in density was observed, which was in agreement with the Raman spectroscopy results. Further analysis on the possible conformational change of both cation and anion have been performed to correlate with the phase change. The anion had the least effect but the dihedrals of the alkyl chain in the cation changed in such a way that it bends towards the cationic ring causing an increase in density. The radial distribution function showed that the atom near to the ring had no change in dihedral angles but the carbon atom in the farthest of the alkyl chain was displaced a lot towards the ring, thus making ILs with large cationic alkyl chain easily compressible.

5.3.2 Drude oscillator model (DOM)

In DOM, the polarizability of a given atom with partial charge q is modeled by considering two particles, a mobile drude particle at a distance $\vec{d}_{j,\gamma}$ carrying a charge

q_d connected by a harmonic spring of spring constant k and a fixed charge of $-q_d$ placed at the center of the atom. The Total electric field $E_{i,\beta T}$ acting on the atom β of molecule v is given by Eq. (12)

$$E_{v,\beta T} = E_{v,\beta} + q_d \sum_w \sum_\gamma \frac{|\vec{r}_{v,\beta} - \vec{r}_{w,\gamma}|}{|\vec{r}_{v,\beta} - \vec{r}_{w,\gamma}|^3} - \frac{|\vec{r}_{v,\beta} - (\vec{r}_{w,\gamma} + \vec{d}_{w,\gamma})|}{|\vec{r}_{v,\beta} - (\vec{r}_{w,\gamma} + \vec{d}_{w,\gamma})|^3} \quad (12)$$

where, $E_{v,\beta}$ is the electric field acting on the atom β due to the partial charges of the atoms γ in different molecules w and the second term corresponds to the electric field acting on the atom β due to the drude pairs. The force acting on the drude particle can be represented by Eq. (13) [94].

$$q_d E_{v,\beta T} = k \vec{d}_{v,\beta} \quad (13)$$

When this electric field acts on the drude particle, it oscillates about a point at a distance $\vec{d}_{v,\beta}$ from the center of the atom from which the average induced dipole moment can be obtained. The average isotropic dipole moment on atom β is given by Eq. (14)

$$\mu_{v,\beta} = \frac{q_d^2 E_{v,\beta T}}{k} \quad (14)$$

Taylor's expansion with an assumption of negligible distance between the atom and drude particle, reduces Eqs. (12) to (11). As the deflection of the spring can be resolved into its three cartesian coordinates, it incorporates anisotropy in the polarization of the atom which offers an advantage over the previous method [95]. Schroder *et al.* [96] have studied the effect of DOM polarization and compared it with non-polarizable and charge-scaled model on 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. The study revealed that charge-scale method could be used to determine collective dynamics of ILs such as diffusion coefficient of ions in IL. But the local dynamics such as the atomic and molecular dipole values and anion positioning around the cation in first solvation shell were well represented by the DOM. Schmollngruber *et al.* [95] compared the effect of IPD and DOM polarization methods on IL with EMIM⁺ cation and CF₃SO₃⁻ anion. In cases of smaller values of polarizability, both the model predicts similar trends for properties such as ion-pair polarizabilities, mean squared displacement values and the coordination of anions around the cation. At high polarizable levels the models tend to deviate and the IPD model have higher impact on the properties of the simulated ionic liquid.

5.3.3 Fluctuating charge model (FCM)

In all the above cases the dipoles are induced using drude particles or atoms that have induced dipole moment while the actual charge on the atom remains fixed throughout the simulation. In the FCM the charge on each atom in the molecule is changed every timestep in such a way that the potential energy is minimized. The Lagrangian multiplier method is used to find the minimal combination of partial charges on the atom based on the constraint that the sum of charges on the atoms in a molecule is constant. This indirectly specifies that in this model the electronegativity

of every atom in the molecule is considered as constant, thus also referred as charge equilibration or chemical potential equilibration model [97]. Cavalcante *et al.* [98] have studied the effect of FCM polarization in the structural rearrangement of anions (PF_6^- and Cl^-) around the cations (1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium). The cations were simulated as non-polarizable molecules while the polarizability model was applied to the anions. The parameters such as electronegativity and hardness used in FCM was calibrated using Mulliken charges obtained by quantum chemical calculations at the MP2 level, with the basis function 6-311G*. The fixed charge model placed the anions around the C2 carbon atom in imidazolium ring. After introducing polarizability in the anions, the high probability region for the position of the anions shifts off-plane (away from the plane of the ring) and is further placed above and below the ring center. This position of PF_6^- ions are in accordance with the experimental results. Apart from structural aspects it could also reproduce the natural trend of diffusion coefficients with increase in their melting point.

5.4 Monte Carlo (MC) simulations

The main difference between the MD and MC simulation is that the former method tries to trace the exact trajectory of the atoms while the latter deals with only the equilibrium states and the simulation proceeds by sampling microstates following different functions depending upon different ensembles being used. MC simulation involves performing the metropolis algorithm. A lattice is chosen for defining the sites, on which the events of the process to be simulated, are performed. The events are chosen in such a way that the probability of acceptance of any event P_{acc} is given by Eq. (15)

$$P_{acc} = \min \{1, x\} \quad (15)$$

where, x is the ratio of probabilities of the new and the old state. The function used to calculate x depends mainly on the type of ensemble being used.

Phase equilibrium of the electrolytes is one of the factors that decides the operating range of the electrolyte in terms of operating temperature [99]. For phase equilibrium calculations using MC, NPT, Grand Canonical (GC) and Gibbs ensemble MC simulations are found to be suitable ensembles rather than canonical ensembles. In the grand canonical model, a generalized form of canonical ensemble is developed by keeping the system in an ideal gas reservoir in such a way that the system volume is kept constant while the number of particles within the system is allowed to change by accepting or donating particles to the ideal-gas reservoir. The events in this ensemble involve all the events in the canonical ensemble (particle displacements within the system) along with insertion and rejection of particles from the system.

In a study by Rane *et al.* [100] the standard GCMC method is extended for ionic liquids by considering separate ideal gas reservoirs for cations and anions and to maintain neutrality the insertion of ion-pair took place simultaneously. In order to eliminate low acceptance probability, instead of choosing the insertion sites randomly, it is based on distance biasing insertion/deletion methods. In this method, the first ion insertion site is randomly chosen while the site for the counter ion is chosen with a probability which decreases exponentially with increasing interionic distance. Restrictive Primitive Model (RPM), a simple model, which assumes ions as small spheres was used to simulate the liquid-vapor phase change of the ILs and the above GCMC method was found to be efficient for this study.

The temperature at which the phase transformation in RPM occurs does not provide enough driving force for the single ions to move from one lattice site to the other, making the equilibration of the system a time-consuming process. Orkoulas *et al.* [101] added new MC multi-particle movements for canonical ensemble steps, where a low density induces a ion-pair movement in contrast to the cluster movement at high density regime along with the distance biased insertion and destruction of the ion pairs for GCMC Simulations. The dipole and cluster movement led to equilibration of the system within 5×10^5 MC steps with smaller total energy compared to the normal simulation with single ion movements which could not converge.

In the NPT model, the system to be simulated is kept isolated but in thermal and mechanical contact with an ideal gas reservoir. A study was done by Shah [102] on 1-n-butyl-3-methylimidazolium hexafluorophosphate using NPT ensemble. Apart from the combined displacement of ion pair movement described in the Canonical ensemble a volume change Monte Carlo move was also carried out for every two cycles. The molar volume calculated was within 5% of the experimental values. The method also shows good agreement for values such as isothermal compressibility and cubic expansion coefficient with experimental results.

One of the widely used MC methods for phase equilibrium calculation is the Gibbs Ensemble Monte Carlo (GEMC) simulation. Here a constant volume is divided into two regions with each region allowing particle transfer interaction, volume change and particle movement within each other thus having events belonging to both NPT and GCMC simulations. However, the method used for ionic liquids involves transfer of single ions with a background charge to maintain neutrality [103]. Orkoulas *et al.* [101] extended the distance biased ion-pair insertion method to GEMC and found that the results produced were in agreement with the conventional GEMC for RPM with increased efficiency.

6. Future perspectives

Rechargeable LIBs are the suitable systems to store energy for powering electric or hybrid vehicles. They have very high energy density, capacity and efficiency among all commercially available electrochemical storage systems. The technologies of LIBs have reached a very advanced stage [104]. The safety concerns towards the flammable nature of conventional electrolytes may be tackled to a great extent by using ILs as additive to them. There is a great future scope and a dream to use ILs as a sole electrolyte (ILs-based gels or polymer electrolytes) containing lithium salts in combination with the advanced electrode materials to provide high thermal stability. In order to fulfill this dream, one needs to exploit the underlying thermodynamic and kinetic stabilities of these ILs with respect to electrode materials. Some task specific ILs may be designed which will facilitate the formation of SEI layer to protect the electrodes during the charge discharge cycle of the battery cell. Customizing the cations and anions of the ILs used in LIBs, one may fine tune the SEI formation during charge -discharge cycle. Also, there is a need for the development of an alternative to the aluminum as current collectors because it has tendency to corrode at high operating voltage of LIBs. Although the typical ILs used in LIBs are hydrophobic, the dissolved lithium salt makes them very water sensitive. To tackle this problem, new salts may be designed as an alternative to the presently used lithium salts. ILs presents plausible future solutions to the problems encountered during the high-power demand at the start-up and acceleration in electric or hybrid vehicle technology.

7. Conclusion

ILs are very attractive candidates for electrolyte and electrolyte-additive owing to their highly customizable configurations leading to unique electrochemical properties that are of great importance for high performance LIBs. ILs have many desirable properties such as (i) very negligible vapor pressure, (ii) high thermal stability, (iii) wide electrochemical window, (iv) tunability, (v) non flammability, and (vi) environment friendly. Some of the representative ILs used as electrolytes in rechargeable batteries with corresponding electrochemical systems have been tabulated. Schematic open-circuit-diagram of an electrolyte and SEI formation in a thermodynamically stable cell has been discussed from the viewpoint of electronic energy levels. Simulations of the ILs to understand and exploit the solvation effect is of paramount importance in imparting performance enhancement in LIBs and their properties. The first principle methods have been widely used to study the effect of cation and anion used, on its ESW, Lithium oxidation/reduction rate at the anode/cathode, Lithium ion conductivity, viscosity, solvation shell constituents. An iterative SCRF can be used to calculate the actual charge distribution in the solute cavity. Typical error in ESW estimation by thermodynamic cycles method is $\sim 15\%$ while that for HOMO/LUMO is $\sim 50\%$. Non-polarizable model predicts slower dynamics for IL in comparison to the experimental results. A scaling factor, accounting for partial charge, is determined for a specific IL therefore, it lacks transferability between different ILs and it fails to produce good results in case of IL mixtures. The Drude oscillator model incorporates anisotropy in the polarization of the atom, which is advantageous over the IPD method. Phase equilibrium calculations using NPT, Grand Canonical and Gibbs ensemble MC simulations are found to be suitable rather than canonical ensembles. The ion-pair and cluster movement leads to equilibration of the system within reasonable (5×10^5) MC steps with smaller total energy compared to the normal simulation. GCMC and GEMC simulation can also be modified with the ion-pair and cluster movement and are more efficient for phase transformation simulation.

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Conflict of interest

The authors declare no conflict of interest.

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