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Review

Recent Advancements in Li-ion Batteries Electrolytes: A Review

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Lithium-ion batteries (LIBs) have emerged as important power sources in recent years, and their improved performance is accelerating the adoption of electric vehicles (EVs) as viable alternatives to internal combustion engines. A focal point for the international community of materials scientists, computational physicists, and chemists is the exploration of innovative materials for LIBs, with an overarching emphasis on addressing concerns related to safety, durability, energy density (ED), and affordability during the developmental stages. The electrolyte, serving as a solvent containing conducting salt and additional substances, plays a critical role, while the incorporation of additives is explored to enhance security, performance, and recyclability. To meet the multifaceted demands of automotive and grid applications, batteries necessitate advancements in power, durability, safety, environmental sustainability, and cost-effectiveness. Overcoming challenges associated with current LIBs, primarily those crafted from flammable and volatile organic solvents, becomes imperative. Addressing issues such as large electrochemical windows (Ews), a broad working temperature range, appropriate safety measures, and optimal surface reactions on electrodes for controlled passivation without compromising low impedance are formidable tasks. This review aims to comprehensively diverse LIB electrolyte types, facilitating the development of enhanced electrolytes for high-performance LIBs. Furthermore, it advocates for the design and implementation of safer electrolytes in future LIB iterations. The exploration of electrolyte additives is also a subject of investigation. The conclusion underscores the imperative to consider cell longevity when devising electrolytes for applications requiring rapid charging.

Keywords: Li-ion battery; Electrolytes; Electrolyte classes; Electrolyte filling; Li-ion batteries safety

1 Introduction

The performance of anodes, cathodes, and electrolytes influences the functionality of Li-ion batteries (LIBs). A promising LIB can be designed with materials that are inexpensive, non-hazardous, safe, and abundant[1,2]. The impact of LIB electrolytes on the macroscopic electrochemical characterizations of batteries contains their effect on battery capacity, internal resistance, the performance of discharge and magnification charge, operating temperature range, battery storage and cycle life, safety, self-discharge performance, and overcharging and over-discharge. Several methods have been put forth for creating new electrolytes for LIBs that can charge quickly. The life spans of cells are often only considered secondarily in the reports cited. To be economically feasible, electrolyte innovations must be compatible with applicable cell chemistries and deliver equivalent lives to cutting-edge electrolyte systems[3]. The LIBs give specific energy and energy density exceeding 270 $Wh.kg^{-1}$ /650 $Wh.L^{-1}$, which are continuously developed through progress in materials and manufacturing techniques[4].

The LIB is a type of rechargeable battery that is widely used in various electronic devices, including smart phones, laptops, electric vehicles, and many others. The main parts of a LIB include a cathode, anode, electrolyte, separator, current collectors, and housing. The cathode is the positive electrode of the battery and is typically made of a lithium metal oxide compound, such as lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMn_2O_4$), lithium nickel manganese cobalt oxide ($Li(NiMnCo)O_2$)[5], or lithium iron phosphate ($LiFePO_4$)[6]. The cathode material is responsible for storing and releasing Li-ions during the battery's charge and discharge cycles. The anode is the negative electrode of the battery and is usually made of graphite. During charging, Li ions move from the cathode to the anode and get intercalated into the graphite structure. The anode stores the lithium ions when the battery is charged and releases them

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during discharge[7]. The electrolyte is a conductive solution or gel that allows the movement of lithium ions between the cathode and the anode while preventing direct contact between them. It usually consists of a Li salt dissolved in an organic solvent[8]. The electrolyte acts as a medium for the transport of ions and ensures the overall functioning of the battery.

The separator is a thin, porous material that is placed between the cathode and the anode to prevent short circuits. It allows the flow of lithium ions while restricting the movement of electrons. The separator is typically made of a polymer material that provides mechanical support and prevents direct contact between the electrodes. It can be enhanced using nanoporous materials. Nanoporous separators provide a larger surface area for ion transport, allowing for faster diffusion of lithium ions between the electrodes. This can improve the battery's power density and reduce internal resistance. The current collectors are conductive plates or foils that collect the current generated during the battery's charge and discharge processes. They are usually made of materials like copper for the cathode and aluminum for the anode. The current collectors provide a pathway for the flow of electrons to and from the external circuit. The housing, or the battery cell casing, is a protective container that holds all the components of the battery together. It is typically made of metal or plastic and provides mechanical support and protection to the internal components. The housing also plays a role in preventing the leakage of electrolytes and protecting the battery from external impacts. These are the main parts of a typical LIB. It's important to note that there can be variations in the specific designs and materials used depending on the application and requirements of the battery. When the LIB is charged, electrons move from cathode material to anode material through electrolytes when voltage is applied between two electrodes. While the electron moves in reverse from the anode material to the cathode material from the electrolyte, the LIB is discharged[9]. The general representation of LIB is shown in Fig. 1.

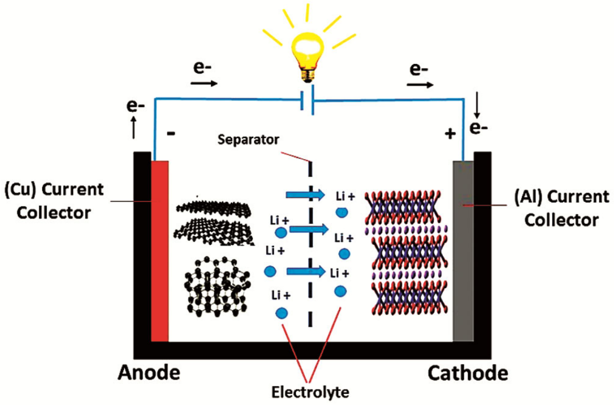

Fig. 1 — Schematic drawing of LIB's structure.

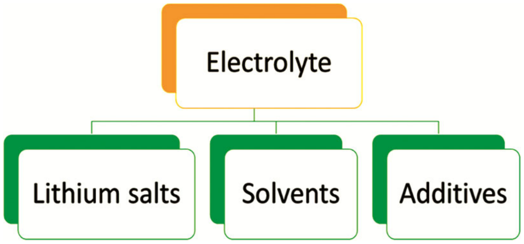

Fig. 2 — Electrolyte materials.

Materials for the electrolytes are revealed in Fig. 2. Electrolytes are the method of ionic conductivity in electrochemical cells. While they do not engage actively in the redox processes of the cell, they allow for charge compensation. The electrolyte must meet six basic requirements[10]. The redox reaction occurs at the electrode-electrolyte interface,characterized by high ionic conductivity and electronic insulation. While the ions must migrate among the electrolyte and separator to react at the opposing electrode, the resulting electrons must not enter the electrolyte but rather be routed via the external circuit. The electrolyte must be inert within the cell's redox potential and operate within a broad EW. This allows for the execution of a wide range of desired redox reactions without the electrolyte degrading, for instance, because of over potentials. The desired redox reaction should be the only internal reaction in the cell, with all other cell components remaining inert. Degradation of the electrolyte, electrodes, separator, current collectors, and housing should be prevented. During operation, slight changes in the cell's environment should not impair its functionality due to safety against abuse. This refers explicitly to system modifications that are electrical, mechanical, and thermal. The cell should suffer from damage. There should be little to no harm to the environment. For production and commercialization, affordability and low prices are crucial[10].

The electrolyte is the main barrier preventing the next-generation LIBs'progress[11]. This is typically the result of unwanted side reactions, sometimes impaired by nanoscale reactive materials. Insight, treating, and minimizing side effects is challenging[12]. There have been major attempts in recent years to introduce novel salts, solvents, and additives that may improve the functioning of these systems. Organosulfur compounds, such as fluorine-substituted, propylene sulfite, and organophosphorus compounds, are novel solvents. At the same time, $LiPF_3(C_2F_5)_3$ and Li bis(oxalate)borate (LiBOB) are examples of new salts. In addition to these salts, the report should highlight efforts to develop new additives for electrolyte solutions, such as organoborane complexes, organic nitrates, phosphates, ssulphates, active gases like CO_2 and SO_2, surface polymerizable agents like olefins and vinylene carbonate[13].

1.1 Lithium Salts

In LIBs, a wide range of Li-salts have been tested, most of which contain mixtures of complex anions and Li+-cations. Lithium hexafluorophosphate ($LiPF_6$), which is almost exclusively used in commercial LIBs, is the most well-known and cutting-edge example. $LiPF_6$ offers an above-average behavior but does not excel in any characteristic essential for good conducting salts compared to most other possible salts. Most other salts exhibit an unbalanced distribution of their characteristics, with one feature standing out while others are below average. They partially show toxicity, some are explosive, and others aid the electrode's passivation. To prevent undesirable side effects, particularly hydrolysis leading to the formation of HF, $LiPF_6$ must be produced with a very high degree of purity. However, the intricate synthesis includes extremely hazardous hydrofluoric acid and several halides. As a result, it significantly impacts how much electrolytes cost. $LiPF_6$ also exhibits poor high-temperature stability, which causes capacity fading and decomposition above about 50 °C. These elements result from fluorine's high reactivity, binding to Li and the solvent or impurities[10]. To solve these issues, new salts are currently being researched. They might function as a conducting salt or an additive, enhancing overall performance. Lithium bis(oxalate)borate (LIBOB) exhibits at least the same performance as $LiPF_6$ while improving high-temperature stability and reducing capacity fading. Lithium difluoro(oxalate)borate (LiDFOB)indicates higher solubility and lower resulting viscosity, which maybe a better version of this salt. Utilizing Li-fluoroalkyl phosphates is another choice. Their anions are more resistant to impurities. So, during decomposition, no hazardous or explosive byproducts are produced. In addition to performing better, both chemicals require less energy than the typical $LiPF_6$[10].

An electrolyte must contain salt to function. Salt is added to water or another organic solvent. The conductivity of electricity is due to the cations mobility and anions in a solution. Electrolytes are essential to all electrochemical devices. Salts dissolved in solvents represent various commonly employed electrolytes and exist in liquid form within the operational temperature ranges. The selection of the optimal electrolyte is a crucial aspect of an efficient LIB. The salt's effectiveness depends on the type and concentration of solvent employed. The delocalization of large anion radii causes ion mobility and dissociation; as the active electrode material is commonly carbon, this anion's insertion and interaction characteristics are like those of the active electrode in many batteries. A compromise between viscosity and charge carrier concentration, improved to achieve the best conductivity and electrochemical characterizations, is an additional essential factor for ionic conductivity. Maximum conductivity occurs at a salt concentration of 1 M. When dissolved in different organic solvents, salts used as electrolytes in LIBs must have high ionic conductivity and enhanced thermal and chemical stability[14,15]. The physical properties of lithium salts are tabulated in Table 1[8].

1.1.1 Lithium hexafluorophosphate ($LiPF_6$)

$LiPF_6$ is a commonly utilized salt in LIB because it rapidly dissolves in various solvents containing widely evaluated dipolar aprotic organic solvents, such as cyclic carbonates such as ethylene carbonate or linear carbonates such as diethyl-, dimethyl-, and ethyl methyl carbonate with high ionic conductivities[14,16]. $LiPF_6$ has a conductivity range of 10.7 mScm1 when dissolved in ethylene carbonate/dimethyl carbonate (1:1), and its anionic size of 0.255 nm is needed for ionic conductivity. Additionally, an excellent electrochemical property, high electrochemical inertness, the ability to create a passivation layer on the Al current collector that shields it from corrosion, and noticeable anionic mobility all contribute to an increase in ionic

Table 1 — Physical properties of different Li salts[8.]

Salt	Mol. Wt.	Melting Point (Tm), °C	$T_{decomposition}$ (°C) in Solution	Al Collector Corrosion
$LiPF_6$	151.9	200	~80 (EC/DMC)	No
$LiBF_4$	93.9	293	>100	No
$LiAsF_6$	195.9	340	>100	No
$LiClO_4$	106.4	236	>100	No
LiTFSI	286.9	234	>100	Yes

conductivity. $LiPF_6$ has a low thermal stability above 55 °C and decays among the reaction (1), which results in the production of highly toxic chemicals when (PF_5) reacts with solvents[17].

$$LiPF_6 \rightarrow LiF\ (s) + PF_5\ (g) \qquad ...(1)$$

The stability of Li-salts affects the cyclability and capacity of LIBs greatly. It may not be easy to precisely evaluate and interpret the voltage-capacity reports of discharge-charge processes if the side reactions generated by Li-salts are not electrochemical reactions. Moreover, the interaction between the solvent and Li-salts that happens during the discharge/charging of LIBs may have a major effect on their electrochemical performance. As a result of LiPF6 breakdown, LiF forms a significant layer atop Li_2O_2. The $LiClO_4$ is discovered to be more stable than Li_2O_2. However, its oxidation may be less stable. It has been recommended that Lithiumbis (trifluoromethane sulfonyl)imide (LiTFSI) and LIFSI be used as more stable salts in LIBs. In addition, the interaction between the solvent and Li-salts during the discharge/charging of LIBs may have a significant impact on their electrochemical performance. In addition, the interaction between the solvent and Li-salts that takes place during the discharge/charging of LIBs may have a substantial effect on their electrochemical performance[12]. Computer simulations are an excellent tool for studying chemically highly unstable substances.

1.1 Solvents

Lithium hexafluorophosphate (LiPF6) salt is dissolved in organic carbonates in most non-aqueous electrolytes used in commercial lithium-ion batteries. These include mixtures of ethylene carbonate (EC) with dimethyl carbonate (DMC), propylene carbonate (PC), diethyl carbonate (DEC), and/or ethyl methyl carbonate (EMC). The physicochemical characteristics of these typical solvents are listed in Table 2[18].

1.2.1 Organic carbonates

The reactions between the solvent and Li-salts that take place during the discharge/charging of LIBs may substantially affect their electrochemical performance. However, the instability of organic carbonates remains a severe issue. The most prevalent non-aqueous organic solvents include ethyl-methyl-carbonate (EMC), diethyl-carbonate, dimethyl-carbonate, propylene-carbonate, and ethylene-carbonate. Because of its stability at the anode surfaces in LIBs, ethylene-carbonate (EC) plays a prominent role among these electrolytes. The LEs of these batteries involve a Li-salt dissolved in an organic solvent, like $LiPF_6$, $LiBF_4$, $LiClO_4$, or $LiAsF_6$. Combining two or more electrolytes is more convenient because it optimizes important properties like ionic diffusion, viscosity, ionic transport, chemical stability, salt dissociation, dielectric constants, *etc*., resulting in improved stability and performance in LIBs under varying operating conditions. Understanding the process of molecule adsorption needs knowledge of the Li^+ ions improvements in the electrolyte[12].

The powerful influence of Li^+ ions may also influence neighboring electrolytes' structural and kinetic properties. In addition, the interaction between the solvent and Li-salts that occurs during the discharge/charging of LIBs might significantly impact their electrochemical performance. Due to EC's relatively high melting point, creating goods with a stable SEI may be feasible. Since the combination of the high dielectric permittivity of dimethylene carbonate (DMC) or Diethyl carbonate (DEC) with the low viscosity of EC or PC outcome in an electrolyte with high ionic conductivity, linear carbonate mixtures, including DMC or DEC with a high concentration of EC, are frequently evaluated in LIBs. To construct the most effective batteries, knowing the ionic diffusion processes in solid phases and anticipating transport coefficients is necessary[12].

1.2.2 Ethers

They are suitable electrolyte solvents for LIBs due to their compatibility with Li metalanodes, resistance to high oxidation potentials of more than 4.5 V vs. Li/Li^+, affordability, safety, and low volatility in the case of large molecular weights, such as tetraglyme.

Table 2 — The physicochemical properties of some common solvents[18].

Solvent	FW	d, $g.cm^{-3}$ (25 °C)	ε_r (25 °C)	η, mPa.s (25 °C)	E_{homo}, eV	E_{lumo}, eV	mp, °C	bp, °C	fp, °C
Ethylene carbonate (EC)	88	1.32 (40 °C)	90 (40 °C)	1.9 (40 °C)	-12.86	1.51	36	238	143
Propylene carbonate (PC)	102	1.20	65	2.50	-12.72	1.52	-49	242	138
Dimethyl carbonate (DMC)	90	1.06	3.1	0.59	-12.85	1.88	5	90	17
Ethyl methyl carbonate (EMC)	104	1.01	3.0	0.65	-12.71	1.91	-53	108	23
Diethyl carbonate (DEC)	118	0.97	2.8	0.75	-12.59	1.93	-74	127	25

Triglyme and dimethoxyethane are additional notable ethers. Choi and Freunberger observed that ethers are more stable than organic carbonates in terms of O_2 reduction and the generation of Li_2O_2 at around 2.7 V, at least during the first discharge. However, the ether electrolyte continued to degrade, yielding HCO_2Li, Li_2CO_3, and CH_3CO_2Li[19-22].

1.2.3 Ionic liquids (Ils)

The hydrophobic character, low flammability, large potential window, low vapor pressure, and strong thermal stability of hydrophobics at room temperature (RT)- ILs make them attractive electrolyte solvents for LIBs. ILs are more hydrophobic than conventional aprotic solvents, effectively insulating the Li-metal anode from moisture. The hydrophobicity and low vapor pressure of ILs made them attractive electrolytes for LIB systems. Some studies have considered ILs as electrolyte systems in LIBs, such as Kuboki *et al.*[23], utilized 1-alkyl-3-methylimidazolium-bis(trifluoromethyl-sulfonyl) imide (EMITFSI) in LIBs. Allen *et al.*[24] also explored the oxygen electrode rechargeability in an RT of IL-EMITFSI and observed that the electrode type influences the reaction process. Gold proved the capacity to effectively recharge oxygen without requiring electrode passivation. Future research on LIBs using Li metal and oxygen electrodes may consider ILs stable electrolytes. Mizuno et al. found that LIBs using ionic LEs have a shallow capacity[25,26].

1.2.4 Solid-state electrolytes

Abraham and Jiang were the first to describe utilizing polymer-based electrolytes in non-aqueous rechargeable LIBs[27]. Kumar *et al.*[28] established the glass and polymer-ceramic electrolytes soli-state. Due to the unique qualities of these electrolytes, including great stability when faced with moisture, a large EW, and exceptional thermal stability, they discovered that LIB systems could be recharged across a broad temperature range. Because of the limited ion conductivity of solid-state electrolytes, it is essential to improve their poor electrochemical performance[3]. Nanocomposite electrolytes combine nanoparticles with a polymer or ceramic matrix to create hybrid electrolyte materials. These nanocomposite electrolytes can offer a balance of properties, such as high ionic conductivity, mechanical flexibility, and improved stability. They can be tailored to meet specific requirements for different battery applications.

Other teams have recently used ester co-solvents to enhance the Li-ion cells'performance at low temperatures (LTs) or high charge rates[29]. Methyl butyrate (MB) performed better at low and high temperatures than a typical electrolyte blend when combined with electrolyte additives[30]. Methyl propionate (MP) provides the optimal agreement between ionic conductivity and stability in complete cells, according to studies conducted by Smart and coworkers[31], who evaluated an even wider variety of ester co-solvents. Hall *et al.* examined the performance of a range of co-solvents comprising esters and other co-solvent types such as forms, amides, and nitriles in an EC: EMC: DMC solvent mixture in NCA/graphite (Gr)-SiO cells employing ultra-high precision coulometry and high-temperature storage[32,33]. Numerous of these co-solvents were incompatible with the chemistry of the cell. Poor coulombic efficiency (CE) and storage performance were observed; however, MF was a co-solvent with decreased cell performance and a remarkable rise in conductivity[34].

Others have explored the different electrolyte solvent's effects on the Li-ion cells'performance at high rates and LTs. Cho et al. evaluated the behavior of propionitrile (PN), acetonitrile (AN), and butyronitrile (BN) when standard electrolytes failed in NCA/Gr cells. At -20 °C, they could attain cycle speeds of 3C[35]. Recent research indicates that highly concentrated electrolyte solutions may enhance rate capability. Yamada and coworkers exhibited enhanced rate performance with a 1,2-dimethoxyethane (DME) electrolyte of 3.6 M LiN(SO2F)2. Electrolytes in DME do not permit Li+ in graphite electrodes reversible intercalation at conventional salt concentrations (1.0 M) but employing the highly concentrated electrolyte resolved this issue[36]. Recent research has revealed a potential electrolyte for Li-metal reversible cycling in a family of electrolytes called localized high-concentration electrolytes (LHCEs). These electrolytes are "diluted" with a solvation-inactive, low-viscosity solvent[37,38]. Despite their reduced solution viscosity, these LHCEs have the same solvation structure as highly concentrated electrolytes[39]. While research on this electrolyte system intends to allow Li metal anodes, several investigations have shown that it performs similarly to more typical, highly concentrated electrolytes[40]. The main target of this review article is to recognize the classifications of electrolytes in LIBs and electrolyte additions, performance, fillings, and their future work and challenges.

2 Electrolytes classification

Based on their physical condition, electrolytes may be categorized as liquid, solid, or solid liquid, as seen in Fig. 3[41]. Typically, solid electrolytes (SEs) are divided

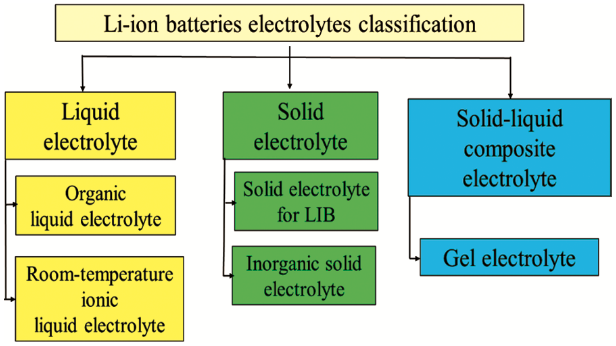

Fig. 3 — The electrolytes classification.

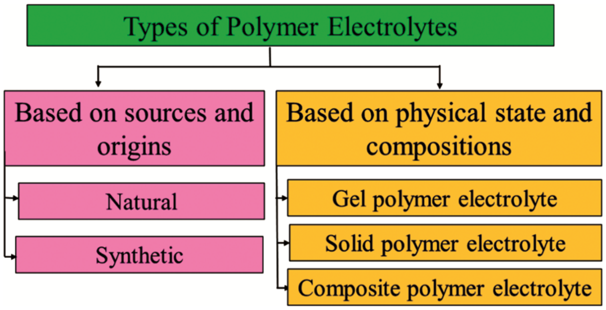

Fig. 4 — Types of polymer electrolytes.

into two subtypes: organic (based on polymer) and (ii) inorganic. Alternatively, polymer electrolytes (PEs) may be separated into gel-polymer electrolytes (GPEs) and solid-polymer electrolytes (SPEs), as exists in Fig. 4. In the former case, the polymeric matrix is a solid ionic conductor. The latter improves the characteristics of a polymer by incorporating a LE into it. Moreover, the addition of fillers results in a new class of electrolytes recognized as "composite-polymer electrolytes" (CPEs)[42]. CPEs comprise inert-oxide-ceramic-based SPEs, and metal-organic frameworks (MOF)-based composite electrolytes[43-45].

2.1 Liquid Electrolyte (LE)

LE is one of the most crucial materials for commercial LIBs[46,47]. The solvent, a conducting salt (like lithium hexafluorophosphate ($LiPF_6$)), and additives can make up all three of its components[48]. The LEs in LIBs are less safe when employed, particularly at high temperatures that might trigger an explosion. High temperature and voltage present in LIBs cause complex chemical reactions. High energy densities and power demands can cause LIBs to undergo intricate reactions that harm users[49]. Because Li-all-solid batteries (ASSLB) have higher stability and safety than LIBs, they solve the LIB problem[50]. ILs are materials of significant relevance in LIB technology, particularly in resolving safety problems, owing to their unique temperature and transport capabilities and high design adaptability[51,52]. ILs are typically created by reacting to a flexible anion like N, N-bis(trifluoromethane sulfonyl)imide (TFSI) with a large, weakly interacting cation of the imidazole type. Li transport is ensured by a Li-salt being dissolved in the mixture. (*e.g.*, LiFTSI)[53].

2.1.1 Organic liquid electrolyte

Li-salt electrolytes may be dissolved in a polar aprotic organic solvent to provide an electrolyte with excellent electrochemical stability, a low freezing point, a high boiling point, and the capacity to work across a broad temperature range. Where organic solvents of LEs have the disadvantages of a small dielectric constant, a high viscosity, poor ability to dissolve inorganic salt electrolytes, especially sensitivity to trace amounts of water, and a tendency to leak, low electrical conductivity. The products must employ a solid metal shell, the shell model and size are set, resulting in a lack of adaptability, and organic solvents are combustible, resulting in inadequate safety. Consequently, battery protection measures must be impeccable[41].

2.1.2 Room-temperature ionic liquid electrolyte

Large organic cations in RT-ILs are characterized by strong electrostatic interactions linking them to small inorganic or organic anions. They can also be combined with a variety of organic solvents. By adding fluorine atoms, Zugmann *et al.*[54] examined the characteristics of Li bis (oxalato)borate (LiBOB). Excellent Al corrosion protection, no hydrofluoric acid (HF) formation by hydrolysis, excellent cycling behavior of $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ cathode, lithiated carbon anodes, and high solubility in the dipolar aprotic solvent were identified[12]. One of the most significant applications is the flammability of organic solvents like cyclic and linear carbonates that may produce thermal runaway[55,56]. It is good knowledge that linear carbonates like DEC and DMC have lower flash points than cyclic carbonates like EC[57]. The flash point is the temperature at which the vapors of a substance ignite when exposed to an ignition source[43]. The electrochemical stability window (ESW) change caused by the hydrogen chemical substitution with extra electronegative elements has two benefits. First, the increased stability toward oxidation makes these solvents advantageous in terms of cell overcharge. Second, the decreased stability toward decrease might have a positive effect on SEI formation, thereby enhancing safety and cyclability[58]. Ionic liquids show promise for high-energy-density LIBs, although challenges related to their viscosity and cost need to be addressed.

2.2 Solid Electrolyte (SE)

Traditional LiBs use liquid or gel electrolytes. However, researchers have been working on developing solid-state electrolytes, which are composed of solid materials that conduct ions[59]. Solid-state electrolytes offer several advantages, including improved safety, increased energy density, and wider operating temperature ranges. The SEs are one of the best-suggested alternatives since they may provide the fabrication of safer and lighter solid-state batteries with more design flexibility[60]. The SEs comprise crystalline inorganic compounds, gelled (or wet) polymers, inorganic glasses, and solvent-free polymers[12]. Since they are theoretically compatible with the Li-metal electrode, they are of current interest. The most significant downside of these materials is their ionic conductivity, which, at RT, is much lower than that of liquid solutions, except for $Li_{3.25}Ge_{0.25}P_{0.75}S_4$[61]. However, the high cost of the germanium component associated with this electrolyte somehow precludes its practical use[62]. Finally, it must be noted that creating smooth electrode interfaces is a significant barrier to using SEs in batteries. The SEs do not spontaneously wet the electrodes, but LEs do. The powdered electrolyte and electrode material can be combined to create an intimate, reciprocal contact as a potential solution to this problem. This approach, though, isn't always practical in real life[53].

Two types of inorganic SEs are utilized in all-solid LIBs: glass and ceramic. They have benefits because SEs can replace the diaphragm in the battery and act as electrolytes. This prevents leakage and allows for further miniaturization of the battery, despite the high number of Li-ion migrations in this material. When such materials are used in LIBs, the interface impedance between the material and electrolyteis high, and the conductivity of the electrolyte is much less than that of a LE[12]. Ceramic electrolytes can enable higher-voltage operation, prevent the formation of dendrites (which can cause short circuits), and enhance the overall stability and lifespan of the battery.

2.3 Solid-Liquid Electrolyte

2.3.1 Gel electrolytes

Despite its appropriateness for electric cars (EVs), the poor RT conductivity of poly(ethylene oxide) (PEO)--based PEs restricts their application in LIBs. Then, one must investigate different, more conductive mediums[18]. GPEs have potential[63,64]. Theoretically, GPEs are hybrid systems with a liquid component entrapped in a polymer matrix by physical and chemical linkages (for example, one based on PEO, polyethylene oxide, or polyvinylidene difluoride, PVDF). The conductivity of GPEs is like to that of typical organic liquid solutions. Because of this property, GPEs are extensively employed for manufacture[53]. Recent proposals have been made to create innovative liquid, semi-solid, and SEs with improved durability, safety, and electrochemical performance like biomimetic electrolytes[65], ionogels/ eutectogels[66,67], and patterned membranes created by 3D printing and/or photo- or stereolithographic methods [68], and (iv) super-concentrated solutions[69], some of which also contain self-extinguishing properties[70]. Numerous reviews on solid-state electrolytes have been published. Still, novel liquid-like or quasi-solid ion conductors, which may contribute to technical advances in battery development, have not[71,72] received little consideration. It was defined as "quasi-solid" electrolytes in systems where a liquid phase is chemically or physically restricted inside a solid matrix, typically nanostructured, such as MOFs or ionogels[43,44,45].

Because of its restricted EW of organic LEs, high-voltage electrodes always produce unsatisfactory electrode-electrolyte interfaces. In addition, the primary contributor to the safety risks associated with current LIBs is the flammability of conventional organic LEs. In this situation, the best action is to change the flammable organic LEs with high-tech nonflammable electrolytes, primarily fluorinated varieties, and phosphate ester solvents[73]. Aqueous batteries are highly competitive regarding safety, affordability, and environmental friendliness. However, their insufficient ED and constrained output voltages prevent their large-scale application. Contrary to solid-state electrolyte-based all-solid-state lithium batteries (ASSLBs), has lately garnered increased interest because of their better advantages of high ED and exceptional safety[74].

LIB requires electrolytes with melting temperatures, low vapor pressure, and boiling points. Essential qualities include rapid Li-ion transit between the cathode, and anode, chemical stability, and electrochemical stability, which protects the electrolyte throughout the charge-discharge process. Salt solubility/crystalline solvates (particularly for LT cells), ionic conductivity (high Li-ion cation rate to produce high power), and formation of SEI (preventing further electrolyte-electrode interactions) are also crucial. Lithium-ion batteries rely mostly on inorganic LEs. Even though they are well-established,

Table 3 — The famous non-aqueous conductive salt characterization in LIBs[42].

Salt	$T_{decomposition}$ In the solvent/°C	Al-Corrosion	Conductivity (1M, Ec/DMC, 25 °C)/ $mS.cm^{-1}$	Electrochemical stability Vs. Li/Li+	Characteristics
$LiClO_4$	>100	No	8.4	4.5 V	• Insensitive to hydrolysis. • No HF is formed. • Explosive. • Favorable SEI developing properties. • High thermal/electrochemical stability.
$LiAsF_6$	>100	No; Al passivates (current collector)	11.1	4.5 V	• Good SEI formation. • Toxic. • Degradation products. • Improve the efficiency of Li metal plating/stripping
$LiBF_4$	>100	No	4.9	--	• Strong Lewis base. • Break down and form HF. • Less susceptible to hydrolysis. • More thermal stability than $LiPF_4$.
$LiPF_6$	>70	Inhibits Al corrosion	10.7	4.8V	• Very sensitive to hydrolysis. • Stable SEI formation with graphite electrodes. • Low thermal stability.
$LiN(SO_2F)_2$	>100	Yes, small corrosion of Al	>10	4.8 V	• Insensitive to hydrolysis. • Doesn't form HF. • Expensive in production.

they do not meet many standards for commercial battery electrolytes. Table 3 illustrates the greatest general salts. $LiPF_6$ is a commonly used salt in commercial batteries, and one of the concerns with its usage is that the existence of HF in the salt substantially influences the performance of the cell[42].

The separator and the LE can be swapped out for PEs. Peter V. Wright and Fenton reported ionic conductivity in polymers containing complex alkali salts for the first time in 1973[75,76]. The electrolyte of PEs, which dissolve in a polymer matrix, is a Li-salt with low lattice energy and abundant anions. In PEs, ionic conduction is supported by covalent bonds between polymer backbones and ionizing groups. The polymer's electron donor group first forms a solvation bond with the cation component of the dopant salt before permitting ion separation and an ionic hopping process. Therefore, ionic conductivity is produced. In a conventional battery, the electrolyte and separator facilitate the flow of ions between the two electrodes. The separator is crucial in increasing the electrochemical characteristics and significantly impacts performance. In a solid-state design, PEs may change the separator and electrolyte. The concept of PEs has garnered significant interest from both electrochemists and polymer scientists due to its unique features[77,78]. The PEs are better compared to others due to their ability to compensate for volume changes of electrodes via elastic and plastic deformation, increased current density, wettability because of their particle-free and more flexible nature, safety compatibility, thermal stability, and decreased dendrite formation with a variety of emerging technologies. However, at RT, the Li-ion conductivity of PEs is poor for battery operation. SPEs have improved their capacity to boost conductivity by mixing, modifying, and generating PEO derivatives, among other approaches. These qualities differentiate PEs from LEs[14]. The ion transport mechanism in PEs happens in two ways such as percolation theory and space theory[42].

The PEs are especially intriguing since they may function as electrolytes and separators between the anode and cathode. A solid PE was produced using TiO_2 or Al_2O_3 nanoparticles as solid plasticizers in PEO. These electrolytes' conductivity rose, and crystallization ended. In combination with the potential structural vibrations and conductivities of plastic crystal matrices, Li-ion doped plastic crystal matrices are stable beyond 5 V and well suited for battery applications[12]. Based on physical state and content, there are three basic kinds of PEs for LIBs: solvent-free PEs like SPEs, GPEs, and CPEs. Plasticized PEs with good conductivity but low mechanical and chemical durability constitute an essential subclass of PEs. The GPEs comprise polymer matrices, liquid plasticizers (solvents), Li salts, and other components like inorganic fillers. GPEs cannot be used in large-scale batteries because of their expensive cost and limited mechanical strength. Nonporous GPEs and PVDF are manufactured using the techniques of casting, in situ polymerization, dip coating, hot pressing, and screen printing[42]. GPEs and SPEs typically include just polymer matrices and Li salts as solutes, with no liquid solvents added as plasticizers. They must meet requirements for high molecular weight, type of cation solvation, dielectric constant, and backbone flexibility[42]. The separator comprises carbonic acid ester compounds such as EC, PC, and DMC. Although LE has strong ionic conductivity and great wettability on electrode surfaces, electrochemical instabilities, safety issues, possible hazards, and inadequate ion selectivity have prevented its application in LIB, paving the way for SEs[14]. Polymer electrolytes offer flexibility, good processability, and potential cost advantages compared to ceramic electrolytes. Researchers are actively exploring various polymer electrolyte formulations to improve their ionic conductivity and stability.

3 Improving the transport number

The t+ and t- define the percentage of ionic current transported by a specific ion in an electrolyte; it equals the sum of the positive and negative transference numbers. To enable Li^+ to absorb as much ionic current as feasible in LIBs, the transference number of Li^+ should be as near to 1 as possible. In carbonate electrolytes, t+ is nevertheless typically between 0.35 and 0.4. The electrolyte's Li-ion transference number has been proven to impact the rate capability[79,80] substantially. Carbonate-based electrolytes' generally low transference numbers are due to the huge solvation shells that develop around Li^+, forming ions with highly effective radii. The most used methods to increase t+ are toconcentrate electrolytes briefly earlier[81]; or increase t+ by restoring common Li salts like $LiPF_6$and $LiBF_4$ with salts that have larger 'bulky' anions; nonetheless, this procedure will likely reduce the conductivity of the solution[82-85].

In several studies discussing electrolytes for high rate charging in LIBs, including some previously cited, only the ionic conductivity and seldom the viscosity of these electrolytes are discussed. The conductivity and viscosity of an electrolyte influence whether or not it can enhance the performance of high rate charging. As a result of their inability to correctly define ionic transport in the electrolyte, they cannot accurately predict high-rate performance in a cell. Conductivity and diffusion coefficients of the ionic species in solution (D+/-), transference numbers (t+/-), and the mean molar activity coefficient are required to describe bulk ionic transport comprehensively. Doyle *et al.*[80] showed via simulations that substantial concentration gradients arise in electrolytes with high conductivity but low Li-ion transference number t+, restricting cell performance at high discharge rates. There is no data on the diffusivity, transference number, and activity coefficients of relevant electrolyte systems. However, there has been a renewed emphasis on developing methodologies for determining these transport characteristics, and it is essential to continue developing these approaches if electrolytes for high-rate charge applications are to progress. Hou and Monroe[86] have recently tested and described the whole range of transport parameters of the LiPF6-PC system using custom-built cells. Farkhondeh *et al.*[87] measured the transport characteristics using a four-electrode cell configuration. This approach is not electrochemical. However, Forster *et al.*[88] employed confocal Raman spectroscopy paired through a microfluidic device to produce concentration gradients and quantify the diffusion coefficient.

4 Improvement of electrolyte functions by additions

Additives are substances consciously added to the electrolyte to change its characteristics. The concentrations used are relatively low (0.5-10%),not to change the solution's general nature. Nano additions to LIB electrolytes have been an area of active research and development. The incorporation of nanomaterials into the electrolyte can offer several benefits, including improved conductivity, enhanced safety, and increased stability. The three primary issues that are being addressed by using additives are listed below:

4.1 Durability

Each cell charging cycle should be highly reversible (99.99%) to ensure durability. In this way, the battery life of a mobile device, like a phone, could be extended from the current 2 years to 10 years or more. The stability of the various parts of the cell is the main factor affecting durability. For instance, it was previously discussed to substitute other salts for the relatively reactive $LiPF_6$. It is crucial to guarantee a stable SEI formation and prevent exfoliation to prevent ongoing electrode degradation. It uses co-precipitation to create a more stable SEI by adding vinylene carbonate, catechol carbonate, and substances from the succinimide family. They exhibit a reduction potential slightly below the electrolytes and deposit onto the anode upon the initial charge. As it has been formed, the SEIresists the ensuing charging cycles. The alternative method stops exfoliation by preventing solvent molecules from entering the multilayer graphene lattice. By binding Li+ with oxidation-resistant additives like crownethers, whose affinity for Li is higher than that of solvent molecules, this can be accomplished through preferential salvation[12].

4.2 Performance

Enhancing the ionic transport of the Li-ion can improve a cell's performance, which is directly related to its ionic resistance. Ions move through solutions more efficiently and effectively the better they are solved. Thus, the goal is to increase salts' solubility in the organic solvent. Although crown ethers are toxic to the environment, they effectively dissolve Li. Aza- and boron-based ethers, particularly tris (penta- fluorophenyl) borane (TPFPB), hold partial positive charges due to their electron-drawing substituents, making them efficient anion coordinators. Since Li+ is not constrained in a relatively large coordination sphere and is instead free to move, their use results in higher dissolved salt concentrations and increases conductivity[12]. Certain nanoparticles, such as metal oxides (*e.g.*, titanium dioxide, tin oxide) or carbon-based nanomaterials (*e.g.*, carbon nanotubes, graphene), can be added to the electrolyte to improve its ionic conductivity. These nanoparticles provide a conductive network that facilitates the movement of Li ions within the electrolyte, leading to improved battery performance.

4.3 Safety and stability

Regarding using additives to increase safety, the main emphasis has been preventing battery explosions and fires during charging. The limitation of the Li-amount in LIBs causes overcharging. No more Li+ can be intercalated into the anode after full charging, and the electrolyte breaks down. There are two overcharge defense mechanisms: a reversible (redox shuttle) and a final (Shut down). Some electrolyte solvents, like sulfites and EC or vinylene,use electrolyte additions to improve cycling performance[12]. Several additives may be putinto the electrolyte to increase LIB performance by influencing, among other things, the production of intercalation SEI at anode surfaces and the electrolyte's characteristics as a function of operating circumstances. However, if these additives are used in large amounts in specific solvents or are chemically mixed with other substances, they may have adverse effects. Due to the difficulty of observing the electrode-electrolyte interface in situ in LIBs, it is unknown what microscopic mechanism is responsible for the reductive decomposition and subsequent growth of the SEI electrolyte additives, which has a significant impact on the SEI formation mechanism and its functionality. Adding 5–10 percent vinylene carbonate (VC) to the EC solvent boosts Li-ion polymer cells' irreversible capacity and cycle life[89,90]. Additives in non-aqueous electrolytes may enhance the performance of LIBS by raising the solubility of phases in the electrolyte owing to an increase in oxidation kinetics and charging rate[12].

During the first charging phase, film-forming electrolyte additives are largely decreased on the graphite anode surface, constituting an efficient approach. Among these additions are ethylene sulphite (ES), vinyl ethylene sulphite (VES), VC, and vinyl ethylene carbonate (VEC). These additives impede both the decrease of salt anion and solvent. Han and Lee have investigated the potential reaction products and thermodynamic stability of Li+-EC and Li+-VC through nucleophilic addition with CH_3O. Electrolyte additives have been used in this context to boost the durability of nanomaterial-based anodes by avoiding the exfoliation/ destruction of the graphite anode by PC[91]. Using relatively large quantities of electrolyte additives that generate extremely resistant SEI layers on graphite electrodes resulted in a substantial capacity loss at high charge rates.

An inverse association was identified between the impedance at the negative electrode and the initial charging rate at which Li plating was seen. Recent research has revealed novel Li salts and other additions, such as difluorobis(oxalato) phosphate (LiDFBOP)[92,93], 4-chloromethyl-1,3,2-dioxolane 2-oxide (CMDO)[94], $LiPO_2F_2$[95], and fluoro sulfonyl isocyanate (FI)[96], that generate advantageous SEI layers for rapid charging. To accelerate the development of electrolyte additives for high-rate applications, it has been determined that a more profound comprehension of SEI production and Li+ movement in the SEI is essential[97,98].

In Si-based anodes, reductive chemicals containing fluorine-donating or vinyl groups have been employed to generate SEI. FEC has been used extensively[99-102] owing to its exceptional capacity to create a mechanically stable LiF-containing SEI and maintain the interfacial stability of Si-based anodes. Despite this, the unforeseen defluorination of FEC by Lewis acidic PF_5 in $LiPF_6$-containing electrolytes, which produces corrosive HF, has been observed [103], and gaseous species, such as CO_2, are seento substantially degrade the storage capacity of LIBs under high-temperature circumstances[104,105]. The excellent effect of FEC in LIBs may be obtained by combining complementing additives when using FEC-containing electrolytes[106]. The introduction of lithium borate electrolyte salts motivates the scientific community to study how lithium borate may be employed as an electrolyte additive to influence the morphology of Li deposition[107]. Many electrolyte adjustments that boost rate capacity decrease cell life span[108]. Harlow and coworkers recently announced cycling findings for single crystal NMC/Gr cells with highly tuned electrolyte compositions. In addition, it was shown that adding as little as 20% MA to these electrolyte formulations shortened their longevity, and these cells had a low propensity to deteriorate after many thousands of cycles[109].

The stability of the electrode material, the rate and depth of charge/discharge, the temperature, and proper use and maintenance are only a few of the numerous factors that affect the cycle life of LIBs. The electrolyte deteriorating at voltages of more than 4.2 V Li/Li+ is one of the critical issues with high-voltage cathodes and LIBs[110-116]. Therefore, the substance stability that substitutes the electrolyte may be a significant electrochemical characteristic for implementing next-generation devices with a greater cell potential to grow Li-ion conductivity. Rapid advancements in the safety and ED of EVs and power plants create new difficulties for LIBs[117-120]. Understanding the battery components' electrical, chemical, and structural modifications that impact the charge-discharge cycle is crucial to developing LIB technology. Each LIB component enhancement greatly improves the performance of LIB[121]. During discharge and charging, lithium ions in LIBs migrate from the negative electrode, commonly composed of graphite, to the positive electrode. During the discharging/cycling operation, the SEI layer continually cracks due to the mass fluctuation of active material during the oxidation reaction[122,123]. The active material's interface stability boosts the battery's retention capacity during cycling and lengthens its energy storage lifetime[124,125]. Focus has been made on modifying the mechanical properties and composition of the surfaces of active materials[126]. Immediate requirements for electroactive materials to be regarded as latent candidates for LIBs include reversible capacity, great ionic conductivity, long life duration, and outstanding Li diffusion rate into active materials[121].

LIB safety is mainly governed by the stability of the electrode material, the manufacturing process, the composition of the electrolyte, and the battery's working conditions. LIB safety is mainly governed by the stability of the electrode material, the manufacturing process, the composition of the electrolyte, and the battery's working conditions. However, the greatest contributor to safety concerns about liquid LIBs is the organic LE's high flammability and volatility. Therefore, organic solvents' combustibility must be eliminated to eliminate battery safety risks. A battery thermal management system (BTMS) is necessary to keep battery temperatures within a safe range and eliminate temperature changes between cells, increasing battery safety[127].

Various additives are being investigated to enhance the stability and performance of LIB electrolytes. For example, the addition of certain salts, such as lithium bis(fluorosulfonyl)imide (LiFSI) or lithium difluoro (oxalate)borate (LiDFOB), can improve the electrolyte's thermal stability, reduce side reactions, and enhance the battery's cycle life. Nanoscale encapsulation of the electrolyte components can enhance the safety of LIBs. For instance, coating the electrolyte with a thin layer of polymer or nanostructured materials can prevent direct contact between the electrodes and suppress the formation and growth of dendrites. This helps to mitigate the risk of short circuits and improve the overall safety of the battery. It's worth noting that the successful integration of nano additions into LIB electrolytes requires careful consideration of factors such as nanoparticle size, dispersion, stability, and compatibility with other battery components. Moreover, the scalability, cost-effectiveness, and long-term stability of these nano-enhanced electrolytes remain important considerations for their practical implementation in commercial LIBs.

5 Electrolyte filling

Before the initial charge can be applied to the cell, all the pores and cavities of the cathode, anode, and separator must be filled with an electrolyte, a process called formation[128,129]. This stage of manufacturing is very labor- and quality-intensive. During the electrolyte filling and subsequent wetting stages, poro, US electrode materials, and separators are saturated with a lithium-conducting salt solution in a solvent. This is especially important in terms of quality since gas accumulation in the pores of the active ingredient affects cell efficiency[130]. During manufacture, more costly electrolytes are added to the battery cell to guarantee full wetting. The outcome is a reduction in ED and an increase in cell weight[131]. In addition, the wetting time after filling is evaluated experimentally using a manufacturing technique with large safety margins. Currently, inline control of the wetting state is impossible due to the phenomenon's limited accessibility[132]. Lanz *et al.*[133] state that LIB must be completely wet before initiating the forming process. First, charging promotes the formation of the SEI, a passivation layer on the anode active material, after the initial wetting. Wetting and shaping take three to seven days, making them a production bottleneck for batteries[134].

Recent experimental research has used in-situ approaches to explore the filling process. These techniques included thermography, wetness balancing tests, focused ion beam coupled with scanning electron microscopy, neutron radiography, X-ray measurements, and electrochemical impedance spectroscopy[135-138]. Unfortunately, most of these techniques are difficult and time-consuming. They all suffer from insufficient spatial or temporal resolution, erroneous wetting front localization, or an inability to distinguish the interdependencies between the contributing factors[139]. Consequently, there is a shortage of comprehensive knowledge during the filling procedure, especially of pore-scale processes. Given the broad diversity of electrochemical systems and cell types available[140], the optimal method for optimizing this operation is still debatable. During the electrolyte filling process, vacuum and overpressure conditions may be used to ensure uniform and rapid wetting of the electrode sheets. Material changes in the electrodes, electrolytes, and process temperatures can also affect the wetting conditions. Wetting on electrodes or separator sheets can also be measured using wetting balance tests[141,142]. The wetting balance test simplifies the wetting process for each test object and makes it possible to monitor the electrode's wetting development visually or gra-vimetrically. Visual measurement makes small-scale quantification of the electrolyte movements possible[143].

6 Future work and challenging

Due to the elevated temperature, the limited thermal stability of the combustible organic LE may provide fire or explosion threats. Furthermore, the uneven deposition of Li-ions on the electrode/electrolyte interface may result in the formation of Li-dendrites[144]. This results in a penetrating effect, an internal short circuit, a significant heat impact, and the deterioration of battery components, such as SEI film disintegration, anode/solvent reactions, and separator melt. In addition to the internal chemical reaction variables, external factors like overheating, overcharging, and short circuits resulting from mechanical stress may produce thermal runaways in LIBs. Therefore, electrolytes with high conductivity, nontoxicity, noncombustibility, and great interfacial compatibility with electrodes to avoid the formation of Li-dendrites are required to prevent thermal runaway[145]. For safer LIBs, technical innovation and rational electrolyte design are necessary. Numerous research initiatives, including nonflammable fluorinated organic solvents, developing solid-liquid mixed electrolytes, high-concentration electrolytes, and flame-retardant (FR) additives, have been founded on this notion[146].

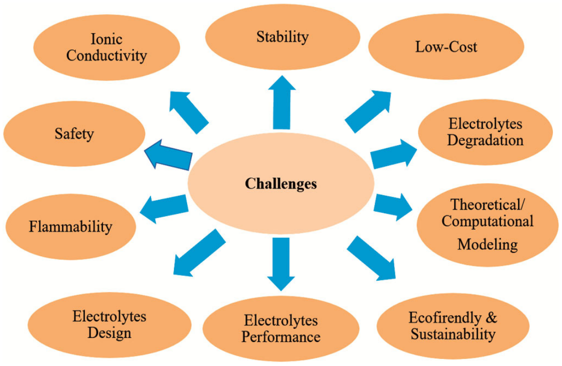

Fig. 5 — The main challenges of electrolytes in LIBs.

The chemical makeup of the cathode and anode of a battery determines its energy output. During the charge and discharge operation, the electrolyte has a key effect on the flow of ions and mass. This controls the mass flow rate inside the battery, defining the maximum energy discharge rate. Additionally, the choice of anode and cathode is constrained by the voltage window of the electrolyte. Selecting an electrolyte for LBs requires a quick ion transfer without self-discharge. The electrolyte must possess excellent ionic conductivity and electronic insulating characteristics, excellent electrochemical stability, and no electrolyte deterioration. Electrolytes and cell components must not react negatively, including cell separators, electrode substrates, and packaging materials[107]. The materials with a higher ED, higher power density, higher safety, longer cycle life, larger capacity, rate performance, and cycling durability were enhanced[147]. The computational approach best analyzes, anticipates, and filters novel electrolytes and their thermodynamic and electrochemical characteristics to guide investigation and testing[12]. Theoretical or computational modeling, as effective tools necessary to contemporary materials and energy storage research, may aid in the significant improvements needed for new and existing battery materials. Pioneered by computer models, data-driven materials design allows the analysis of innovative and current materials and the construction of improved materials[12]. The main challenges of electrolytes in LIBs are provided in Fig. 5.

7 Conclusion

Lithium-ion batteries (LIBs) stand out as an outstanding energy source, boasting higher energy density (ED) compared to most other battery types. Despite notable advancements in electrolyte materials, achieving a LIB characterized by elevated energy density, cost-effectiveness, and comprehensive safety control remains a pending challenge. This underscores the imperative for concurrent improvements in both energy content and safety features, coupled with advancements in materials for practical development. While LIBs have found extensive application in portable electronic devices, electric vehicles, and energy storage, safety concerns have impeded their widespread adoption. The presence of volatile solvents in electrolytes (LEs) can lead to rapid oxidation under extreme heat conditions, resulting in heightened heat build up and thermal runaway. To overcome these challenges, designing a safe electrolyte is essential to mitigate volatility and flammability, prevent thermal runaway, and ultimately ensure the risk-free and fireproof operation of LIBs. Strategic modifications in electrolyte design aim to enhance safety, paving the way for the secure utilization of LIBs in diverse applications. Therefore, further research endeavors are warranted to optimize the performance of LIBs, effectively address existing challenges, and guarantee their commercial viability in the ever-expanding landscape of energy storage solutions.

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Data availability statement:

The data supporting this study's findings are available from the corresponding author upon reasonable request.

Conflict of interest:

The authors declare that they have no conflicts of interest.

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