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The Challenge and Perspective of Li-ion Battery Electrolytes

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Abstract. The development of lithium-ion batteries (LIBs) is essential for electric vehicles and renewable energy. It makes them a key technology to achieve global “dual carbon” goals. Among all components, the electrolyte plays a central role—not only in ensuring safety but also in determining wide-temperature performance and fast power delivery. Today’s commercial electrolytes, usually based on organic carbonates like EC or DMC with $LiPF_6$ salt, have supported large-scale applications. However, they still face major problems: they are volatile and flammable, creating safety risks; their performance drops sharply at both low and high temperatures due to viscosity or decomposition issues; and their ionic conductivity is not enough for ultra-fast charging. On top of that, PFAS and toxic byproducts raise environmental and health concerns. This work takes a close look at these fundamental challenges and highlights emerging solutions, such as solid-state electrolytes for safer operation, new liquid systems like localized high-concentration electrolytes, ionic liquids, and fluorinated solvents for better stability and ion transport, as well as synergistic strategies including advanced salts (LiFSI, LiTFSI), functional additives, and solvation structure design. Collectively, these advances aim to address the safety, temperature resilience, and fast charging requirements of next-generation energy storage systems.

Keywords: Lithium-ion batteries, Electrolytes, Ionic liquids

1. Introduction

The global transition toward electric vehicles and renewable energy sources necessitates advancements in lithium-ion batteries (LIBs). While cathode and anode materials have garnered significant research attention, the electrolyte is equally pivotal. This is attributable to its role in facilitating ion transport between electrodes, directly influencing battery safety, operational stability across a broad temperature range, and power output capabilities. Electrolytes are the core pillar of lithium-ion batteries' "safety, efficiency, and durability." Their technological breakthroughs are key to promoting the commercialization of next-generation lithium-ion batteries with high safety, wide temperature range applicability, and ultra-fast charging capabilities. Furthermore, they are an important guarantee for accelerating the global energy transition and achieving the "dual carbon" goals.

Current liquid electrolytes predominantly consist of organic carbonates (e.g, ethylene carbonate, dimethyl carbonate) and lithium salts (e.g. $LiPF_6$). However, these formulations are plagued by critical limitations: poor thermal stability, flammability risks, and inadequate ionic conductivity under demanding conditions such as fast charging or extreme temperatures. To address these problems, researchers have explored new lithium salts, solvents, and additives, as well as new systems such as high-concentration and solid-liquid hybrid electrolytes. However, these solutions still face challenges like high costs and complex preparation processes, and there is a gap from large-scale commercial application. The primary challenges facing such electrolytes are addressed by two main types of solutions. The first category involves modifications to traditional liquid electrolytes; this strategy regulates electrolyte composition through the introduction of functional modifiers. These include functional additives that enhance the stability of both the solid electrolyte interphase (SEI) and the cathode electrolyte interphase (CEI), while also adjusting the solvation structure to reduce free solvent content and promote the formation of anion-derived interphases. The second category involves the development of alternative electrolyte systems, such as solid-state electrolytes, gel polymer electrolytes, and deep eutectic electrolytes. These systems utilize materials with high thermal stability and non-flammability to replace traditional low-flash-point, flammable organic solvents, thereby enhancing both the electrochemical performance and safety of lithium-ion batteries [1, 2].

In this context, the present work systematically analyzes the fundamental challenges in contemporary LIB electrolytes and critically evaluates cutting-edge research directions. The overarching objective is to develop electrolytes with enhanced safety profiles, expanded temperature adaptability, and superior high-power performance to address the evolving demands of next-generation energy storage systems.

2. Critical challenges in conventional electrolytes

2.1. Safety concerns: flammability and thermal runaway

Commercial electrolytes typically employ organic solvents that are highly volatile and flammable. Under conditions of excessive heating—such as those induced by overcharging, external thermal exposure, internal short circuits, mechanical damage leading to leakage, or prolonged operation at elevated temperatures—these solvents are prone to ignition. This fire risk is exacerbated in large-format battery packs, such as those utilized in electric vehicles (EVs). While flame-retardant additives (e.g., phosphates or fluorinated compounds) offer partial mitigation, they often compromise ionic conductivity or electrochemical stability. Consequently, the development of inherently non-flammable electrolytes—particularly solid-state electrolytes or highly concentrated liquid systems—remains a paramount research objective. Oxide inorganic solid-state electrolytes represented by LLZO, LLTO, and LATP exhibit complete non-volatility and non-flammability, remaining combustion- and decomposition-resistant even at elevated temperatures without generating flammable substances. Locally concentrated electrolytes represent an improvement over conventional electrolytes by incorporating inherently flame-retardant diluents to reduce the proportion of free solvent. This approach leverages high salt concentration to decrease the proportion of flammable solvents, thus lowering electrolyte combustibility [3].

The U.S. Federal Aviation Administration documented 74 lithium battery leakage incidents in 2022 where $LiPF_6$ hydrolysis ($LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF$) released toxic HF gas, causing chemical pulmonary injuries in workers [4].

According to statistics from the Fire and Rescue Bureau of the Ministry of Emergency Management, there are approximately 2000 electric vehicle fires across the country each year, and 80% of these fires are related to the lithium batteries of the electric vehicles. The Federal Aviation Administration of the United States also reported that there were 74 accidents caused by lithium batteries in 2022 (Figure 1).

According to the National Big Data Alliance for New Energy Vehicles, compared to 2019, the number of fire accidents increased by 47% starting from 2020, with a total of 124 incidents. In the first half of 2021, there were reports of 56 incidents of electric vehicle fires and explosions. As the promotion of new energy vehicles continues, the public's anxiety over lithium-ion battery explosion accidents has been increasing.

2.2. Temperature performance limitations

Lithium-ion batteries exhibit suboptimal performance outside the temperature range of 15 °C to 35 °C. At low temperatures, electrolyte viscosity increases significantly, impeding ionic mobility and reducing charge acceptance, while also promoting lithium dendrite formation on the anode. At elevated temperatures (>60–80 °C), electrolyte components undergo rapid degradation: $LiPF_6$ salts hydrolyze in the presence of trace moisture to generate toxic hydrogen fluoride (HF), which corrodes electrode materials, and organic solvents decompose, releasing gaseous byproducts. This degradation compromises the integrity of the critical solid electrolyte interphase (SEI) on the anode, potentially triggering cascading thermal runaway [5].

Low-temperature failure: Viscosity surge (>200 mPa·s at -20 °C) impedes Li^+mobility, accelerating Li dendrite growth. High-temperature degradation: $LiPF_6$ decomposes ($LiPF_6 \rightarrow LiF + PF_5$), and PF_5 catalyzes solvent (EC/DEC) decomposition ($C_3H_4O_3 \rightarrow CO + C_2H_4\uparrow$), rupturing the SEI layer. Thermal decomposition of cathode material:

$$LiCoO_2 \rightarrow xLiCoO_2 + 1/3(1-x)Co_3O_4 + 1/3(1-x)O_2 \tag{1}$$

Onset temperature: ≈180 °C (fully charged $LiCoO_2$) Released oxygen (O_2) acts as an oxidizer for subsequent combustion. Oxygen further reacts with the electrolyte:

$$EC + 3O_2 \rightarrow 3CO_2 + 2H_2O \tag{2}$$

$$DEC + 6O_2 \rightarrow 5CO_2 + 5H_2O \tag{3}$$

$$DEC + 7/2O_2 \rightarrow 5CO + 5H_2O \tag{4}$$

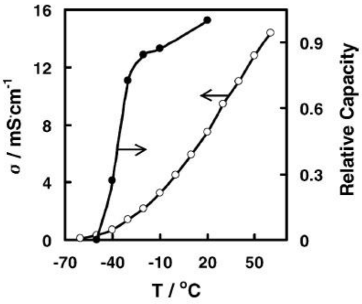

Figure 1. Relationship between battery capacity and electrolyte conductivity at different temperatures [6]

2.3. Rate capability constraints

Fast charging imposes stringent demands on electrolyte performance, primarily due to limitations in ionic transport kinetics. Key bottlenecks include (1) insufficient ionic conductivity of the electrolyte itself under high-current conditions; (2) increased viscosity at elevated current densities, which slows ion diffusion; (3) impeded ion transport across the electrode-electrolyte interface; and (4) degradation of the protective interphases (SEI on the anode, CEI on the cathode) under high current densities, leading to increased interfacial resistance and accelerated battery aging. The primary challenge lies in enabling rapid charging without sacrificing cycle life or energy density.

End-of-life battery disposal and improper waste management further exacerbate environmental concerns, as electrolytes and degradation products can leach into ecosystems. Persistent organic pollutants known as per- and polyfluoroalkyl substances (PFAS)—often derived from binders or fluorinated additives—are particularly problematic due to their bioaccumulative and non-biodegradable nature, leading to long-term ecological and human health impacts. Despite incremental improvements in electrolyte safety, commercial formulations continue to rely on numerous hazardous components.

3. Research directions for advanced electrolytes

3.1. Enhancing safety

Solid-state electrolytes (SSEs) hold tremendous promise as the safest electrolyte alternative, owing to their non-flammable nature and potential to mitigate hazardous lithium dendrite growth. Three primary classes dominate research: (1) brittle ceramic electrolytes (e.g., LLZO, LATP) with high ionic conductivity; (2) flexible polymer electrolytes (e.g., PEO) with limited room-temperature ionic mobility; and (3) composite electrolytes integrating ceramic and polymer phases. Critical challenges include achieving ionic conductivities comparable to liquid electrolytes, ensuring robust electrode-electrolyte interfacial stability, and enabling cost-effective large-scale manufacturing [7].

Alternative strategies focus on non-flammable liquid systems, such as fluorinated carbonates, ionic liquids (ILs), or deep eutectic solvents (DES). ILs offer non-flammability and thermal robustness but suffer from high cost and viscosity. DES provides a lower-cost alternative but requires further optimization for electrochemical compatibility. Researchers are also exploring novel additives that promote the formation of robust protective interphases or quench combustion reactions [8].

Chen et al. from Beijing University of Chemical Technology proposed a flame-retardant quasi-solid-state electrolyte based on a ternary molecular synergy strategy [9]. The cross-linked network formed by pentaerythritol tetraacrylate (PETA) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) provides the structural framework for ion migration. The ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BmimTFSI), acts as a plasticizer, softening the polymer chains by weakening intermolecular interactions between them. This simultaneously provides additional ion transport channels and imparts flame retardancy. Furthermore, the highly electronegative fluorine atoms in the additive, 2-(perfluorohexyl)ethyl methacrylate (PFMA), promote the dissociation of LiTFSI through electron cloud migration. Concurrently, strong PFMA-$Bmim^+$ coordination immobilizes the $TFSI^-$ anions, suppressing their competition with lithium ions. Through this synergy, the resulting F-PIL electrolyte achieved a high lithium-ion transference number (tLi^+) of 0.72 and a room-temperature ionic conductivity of 1.84×10^{-3} S cm^{-1}.

Ghafari et al. developed a composite electrolyte by coating NASICON-type LATP ceramics with a thin LiF/PVDF-HFP protective membrane [10]. The LiF nanophase provided a hard, ionically conductive scaffold that effectively suppressed dendrite penetration, while the PVDF-HFP polymer improved flexibility, wetting, and interfacial compatibility, thereby lowering resistance. This interfacial buffer also prevented the undesirable reduction of LATP by lithium metal. In symmetric Li|Li cells, the composite electrolyte enabled highly stable plating/stripping for over 1000 hours at 0.5 mA cm^{-2} without short circuit. In full $LiFePO_4$|Li cells, remarkable durability was demonstrated: at 0.2C, the cell operated for nearly 8 months with 86.4% capacity retention; at 1C, ~2000 cycles were achieved with only ~12.5% loss. Structural analysis further confirmed the integrity of the LATP and interfacial layers during cycling. This work shows that ceramic–polymer synergy not only enhances mechanical robustness and dendrite resistance but also preserves electrochemical stability at room temperature. Importantly, the fabrication route—solution casting and coating—offers potential for cost-effective large-scale processing. Together, these advances highlight composite strategies as a practical pathway toward safer, longer-lived solid-state lithium-metal batteries.

3.2. Broadening temperature adaptability

For low-temperature operation, electrolytes require tailored formulations: low-viscosity solvents (e.g., specific esters or ethers), optimized salt concentrations (avoiding excessive viscosity from oversaturation), and anti-freezing lithium salts (e.g., LiTFSI, LiFSI). For high-temperature stability, thermally resilient salts (LiFSI and LiTFSI as replacements for $LiPF_4$), robust solvents (e.g., sulfones or nitriles), and additives that stabilize SEI/CEI layers under heat stress are critical. Emerging formulations such as liquid hybrid concentrated electrolytes (LHCEs) show potential for broad temperature adaptability [11].

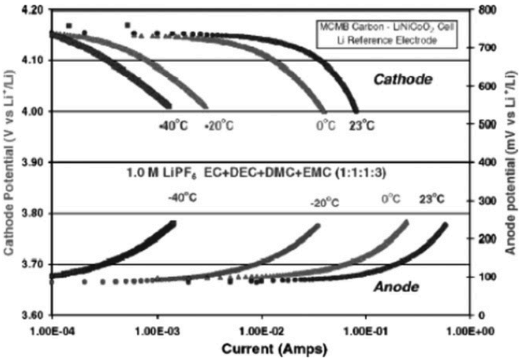

Figure 2. Tafel polarization measurement at different temperatures carried out on mesocarbon microbeads (MCMB) and $LiNiCoO_2$ electrodes in 1.0 m $LiPF_6$/EC/DEC/DMC/EMC (1:1:1:3) [2]

According to the temperature dependences of the limiting current densities, as temperature decreases, the gap between the polarizations at the anode/electrolyte and cathode/electrolyte interfaces rapidly closes (Figure 2). Formulating electrolytes with solvents of low freezing points and high dielectric constants is a direct approach to extending the service-temperature range of lithium batteries. However, the SEI formed by the decomposition products of common electrolytes cannot satisfy the electrochemical properties at ultralow temperature. Many efforts have been made to optimize interphase property, including the adjustment of solvents, salts, additives, and so on [2].

Holoubek et al. engineered a DEE–LiFSI electrolyte to enable ultra-low-temperature cycling, addressing crystallization and sluggish ion transport in conventional systems. DEE, with low viscosity and weak Li^+ coordination, forms looser solvation cages that reduce desolvation barriers at the electrode interface, while LiFSI salt promotes the formation of a stable, LiF-rich SEI [12]. In Li SPAN full cells with high-loading 3.5 mAh cm^{-2} cathodes, the electrolyte delivered excellent performance: 84% capacity retention at –40 °C and 76% at –60 °C after 50 cycles, compared to DOL/DME-based cells that short-circuited immediately. Electrochemical impedance spectroscopy confirmed lower charge-transfer resistance at low temperature, and XPS revealed an SEI enriched in inorganic fluorides, maintaining ionic conductivity in deep-cold conditions. Importantly, the DEE–LiFSI formulation also preserved reasonable ionic conductivity (>1 mS cm^{-1} at –60 °C), ensuring both bulk transport and interfacial stability. This work demonstrates how rational solvation engineering can extend the operating window of lithium-metal batteries to extreme environments such as polar regions, aerospace, and defense applications, without relying on external heating or bulky thermal management systems.

3.3. Enhancing rate capability through advanced electrolyte engineering

Ultra-fast charging (e.g., reaching 80% capacity within 15 minutes) requires electrolytes that can overcome multiple kinetic barriers [13, 14]. The main challenges include: (1) insufficient bulk ion diffusion under high current densities (>4 mA cm^{-2}); (2) sluggish interfacial ion transfer at polarized electrodes; (3) instability and degradation of SEI/CEI layers, which increase resistance; and (4) lithium dendrite growth driven by concentration polarization. To tackle these issues, recent studies focus on improving bulk ionic transport, optimizing electrode–electrolyte interfacial kinetics, and stabilizing interphases.

3.3.1. High-conductivity lithium salts & solvent design

Conventional $LiPF_6$ suffers from limited dissociation and poor thermal stability. Lithium bis(fluorosulfonyl)imide (LiFSI) offers significant advantages, including a higher dissociation constant ($\sim 10^{-5}$ vs. $\sim 10^{-6}$ for $LiPF_6$), lower activation energy for ion migration (≈0.15 eV), and enhanced anion stability above 4.5 V. For example, Kang et al. demonstrated that a ternary electrolyte of 1.8 M LiFSI in EC/EMC/EPE (3:5:2 vol%) achieved an ionic conductivity of 12.3 mS cm^{-1} at 25 °C (vs. 9.2 mS cm^{-1} for $LiPF_6$), a 70% higher Li^+ transference number ($t_+ = 0.53$), and stable cycling in symmetric cells at 5 mA cm^{-2} for 500 cycles [15]. Mechanistically, the branched ether EPE disrupted strong EC–Li^+ coordination, lowering solvation energy by 35% (DFT). In NMC811|Graphite full cells, this electrolyte enabled 80% capacity retention within 10 minutes even at –20 °C [16].

3.3.2. Localized High-Concentration Electrolytes (LHCEs)

LHCEs address the viscosity drawback of conventional high-concentration electrolytes by introducing inert diluents (e.g., hydrofluoroethers) that maintain the desired solvation structure while improving fluidity. Zhang et al. reported that LHCEs not only preserved the advantages of concentrated electrolytes in suppressing side reactions but also enhanced low-temperature ionic conductivity, thereby supporting high-rate operation without compromising interfacial stability [17]. Jiang et al. demonstrated that a localized high-concentration electrolyte (LHCE) composed of 1.5 m LiFSI in dimethoxyethane (DME) with bis(2,2,2-trifluoroethyl) ether (BTFE) as an inert diluent can effectively suppress solvent co-intercalation into graphite while enabling fast charging [18]. In this formulation, BTFE does not coordinate with Li^+ but maintains the favorable solvation structure of a concentrated electrolyte while lowering bulk viscosity. This dual effect preserved high Li^+ transport and stability of the interphase. In graphite Li cells, the LHCE delivered ~220 mAh g^{-1} at 4C, and capacity retention remained at 85.5% after 200 cycles, in sharp contrast to conventional dilute DME electrolytes that degraded rapidly. Mechanistic studies showed the formation of a robust LiF-rich SEI with low charge-transfer resistance, as confirmed by XPS and electrochemical impedance spectroscopy. Moreover, the electrolyte's localized solvation environment minimized solvent decomposition and improved Coulombic efficiency during high-rate cycling. These advances highlight LHCEs as a powerful strategy to balance ionic conductivity, interfacial stability, and dendrite suppression, enabling practical 10–15 min charging of lithium-ion batteries. This work provides not only a validated formulation but also a theoretical framework for electrolyte design targeted at ultrafast charging applications.

4. Conclusion

Advanced electrolytes are pivotal to the development of next-generation lithium-ion batteries. Addressing the interconnected challenges of safety, temperature tolerance, and fast-charging capability requires a multifaceted approach. Solid-state electrolytes represent a highly promising long-term solution for safety but face significant hurdles in interfacial compatibility and scalability. For the near term, enhanced liquid electrolytes (and semi-solid hybrid systems) offer a more pragmatic advancement, leveraging novel salts (LiFSI, LiTFSI), thermally stable solvents (e.g., tailored esters, sulfones), non-flammable components (ionic liquids, functional additives), and interphase modifiers (FEC, LiDFOB, $LiPO_2F_2$). Emerging strategies such as high-concentration electrolyte blends and solid-liquid hybrids also show potential for achieving balanced performance metrics.

Among them, semi-solid hybrid systems are one of the most promising solutions. They combine the advantages of solid and liquid electrolytes: the solid component provides good safety by reducing the amount of flammable liquid, while the liquid component ensures high ionic conductivity and good interface contact. This balance makes it more likely to be commercialized in the short term.

Progress in this field hinges on a deeper understanding of (1) the degradation mechanisms of electrolyte components over cycling, (2) the interfacial interactions and dynamics (e.g., SEI/CEI formation and evolution), and (3) ionic transport behavior under diverse operational conditions. Cross-disciplinary collaboration between chemists, materials scientists, and engineers will be critical to translate promising lab-scale discoveries into industrially viable, cost-effective electrolyte formulations. Such advancements will accelerate the development of safer, higher-performance EV batteries with extended range and faster charging, more reliable renewable energy storage systems, and longer-lasting consumer electronics—ultimately driving the global transition to clean energy.

Authors contribution

All the authors contributed equally and their names were listed in alphabetical order.

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