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Review on the Development of Lithium-Ion Batteries Electrolytes

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Abstract

This paper systematically reviews the technological evolution of Lithium-Ion Batteries battery (LIB) electrolytes, from traditional liquid systems to innova-tive solid/gel composite systems, with a focus on advances in high-voltage, wide-temperature-range, and flame-retardant electrolytes. By analyzing the synergistic optimization mechanisms of solvents, lithium salts, and additives, the study elucidates the critical role of electrolytes in determining battery en-ergy density, safety, and environmental adaptability. Integrating recent break-throughs in solid-state electrolytes (e.g., sulfide/oxide electrolytes) and green manufacturing trends, it outlines key challenges and future directions for elec-trolytes in pairing with advanced materials such as high-nickel cathodes and silicon-based anodes, providing theoretical support for next-generation LIB de-sign.

Keywords

Lithium-Ion Batteries; Electrolyte; Solid-State Electrolyte; High-Voltage; Flame-Retardant

1. Introduction

As a core energy storage technology in the carbon-neutral era, the performance ceiling of LIBs is increasingly constrained by electrolyte systems[1]. Electrolytes fulfill a threefold mission: ion transport, interface stabilization, and safety protection, earning their reputation as the "lifeblood" of batteries. With the energy density of power batteries advancing from 250 Wh/kg toward 500 Wh/kg[2], electrolytes must maintain stability under multiple harsh conditions, including high voltage (>4.5 V), wide temperature ranges (40–80°C), and fast charging (10C). Concurrently, the industrialization of solid-state batteries is reshaping the technological paradigms of electrolytes. This paper aims to review the developmental trajectory of LIB electrolytes, analyze current research hotspots, and forecast future trends, providing valuable references and insights for related fields.

2. Overview of Lithium-Ion Batteries Electrolytes

2.1. Composition and Functions of Electrolytes

The electrolyte is composed of a ternary system comprising lithium salts, organic solvents, and functional additives. Its design must meet the following core metrics[3]: ionic conductivity (>1 mS/cm at 25°C), electrochemical window (>4.5 V vs. Li+/Li), thermal stability (decomposition temperature >200°C), and interface compatibility (formation of stable SEI/CEI films).

Regarding lithium salts, lithium hexafluorophosphate ($LiPF_6$) dominates 80% of the market share due to its high dissociation degree (>90%) and moderate cost. However, its poor thermal stability (decomposition at 60°C) has driven the development of novel lithium salts such as lithium bis (fluorosulfonyl) imide (LiFSI). The solvent system primarily employs carbonates (EC/DMC/EMC), but their low flash points (<40°C) pose flammability risks. Fluorinated solvents (e.g., FEC)[4] reduce combustibility through hydrogen atom substitution, though increased viscosity compromises low-temperature performance. Emerging localized high-concentration electrolytes (LHCE)[5] utilize inert diluents (e.g., TTE) to maintain high lithium salt concentration (>3 M) while reducing viscosity, achieving 0.5 mS/cm ionic conductivity at 30°C.

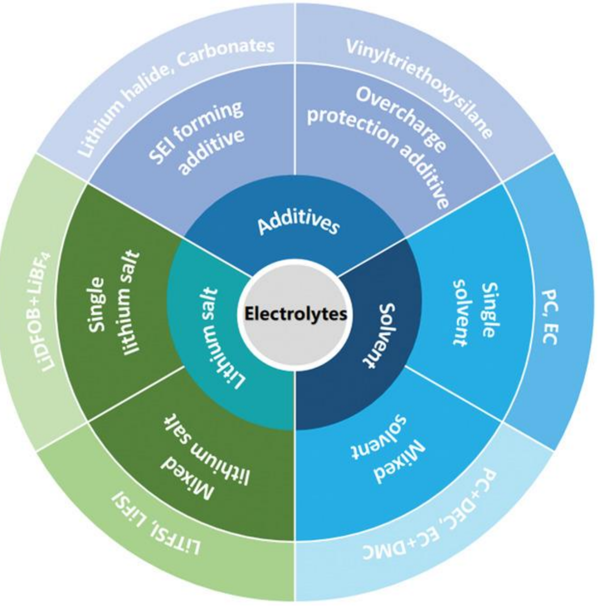

Figure 1. Lithium-Ion Batteries factors related to electrolyte performance improvement.[3]

Additives serve as the "precision control switches" of electrolytes. Over 20 commercial additives are categorized by function:

1) Film-forming additives (VC, FEC)[6, 7]: Preferentially reduced to form dense SEI films, inhibiting solvent decomposition.

2) Flame-retardant additives (trimethyl phosphate, ionic liquids): Delay combustion

chain reactions via radical scavenging mechanisms.
3) Overcharge protectants (biphenyl, cyclohexylbenzene): Undergo electro-polymerization under high voltage to form passivation layers.
Recent advancements include novel additives: Kang et al.[8] reported dimethyl ether sulfide (DMS) for high-voltage batteries. Its electron-donating groups deactivate reactive superoxide radicals released from cathodes under high voltage while inducing sulfur-rich cathode electrolyte interfaces, suppressing side reactions and metal dissolution. Ka et al.[9] demonstrated lithium difluoro(oxalate)borate (LiDFOB) as an additive to inhibit $LiPF_6$ hydrolysis and scavenge its decomposition byproducts. Shaik et al.[10] investigated methyl vinyl sulfone (MVS), a sulfur-based additive that suppresses lithium dendrite growth by reorganizing sulfur atom alignment to alter lithium crystal growth orientation and inhibit nucleation.

2.2. Evolution of Electrolytes

The development of lithium-ion battery electrolytes represents a technological journey from fundamental chemical exploration to engineered innovation. In the 1970s, as research on lithium metal anodes gained momentum, scientists began seeking compatible ion-transport media. Early electrolytes relied on highly reactive lithium salts (e.g., $LiClO_4$) paired with ether-based solvents. However, practical applications were hindered by short circuits and explosions caused by lithium dendrite growth.
A pivotal milestone arrived in 1991 with Sony's launch of the first commercial lithium-ion battery[11], establishing the liquid electrolyte system: lithium hexafluorophosphate ($LiPF_6$) as the lithium salt, blended with ethylene carbonate (EC) and dimethyl carbonate (DMC) as co-solvents. This system demonstrated robust ionic conductivity (~10 mS/cm) and interfacial stability at 4.2 V, enabling the widespread adoption of consumer electronics. Yet, the inherent flammability of liquid electrolytes limited their use in demanding applications. Researchers shifted focus to solid-state electrolytes. Oxide-based systems (e.g., garnet-type LLZO[12]) emerged with room-temperature conductivity on the order of 10^{-3} S/cm, but rigid interfaces resulted in electrode contact impedance as high as 3000 $\Omega\cdot cm^2$. Polymer electrolytes (e.g., PEO-based[13]), while processable, faced limitations due to ion transport activation only above 60°C.
Looking ahead, electrolyte development will prioritize functional integration and environmental sustainability. From liquid to solid-state systems, and from single-ion conductors to smart responsive architectures, each breakthrough in electrolyte technology continues to redefine the performance frontiers of lithium-ion batteries.

3. Research Progress on Novel Electrolyte Systems

In recent years, the development of novel electrolyte systems has focused on overcoming the performance bottlenecks of traditional carbonate-based liquid systems.

The academic community has driven the evolution of electrolytes towards high voltage tolerance, wide temperature range adaptability, and intrinsic safety through molecular design, interface regulation, and multi-scale structural optimization.

In the field of high-voltage electrolytes, Zheng et al.[14] proposed a new electrolyte additive, 4-fluorophenyl isocyanate (4FBC), containing isocyanate and phenyl functional groups. This additive can form a robust and uniform nitrogen-rich and phenyl ring skeleton CEI film on the cathode surface, thereby alleviating electrolyte decomposition and suppressing the dissolution of transition metals in the cathode material, enhancing electrochemical performance under high voltage.

For extreme temperature applications, Xie et al.[15] used a dual electrolyte additive containing B, lithium tetraborate (Li2TB), and 2,4-difluorobiphenyl (FBP). This combination preferentially oxidizes to form a unique double-layer CEI on the cathode surface, enabling the battery to adapt to a wide temperature range while retaining the high thermal stability of the FBP-derived CEI and the low interfacial impedance of the Li2TB-derived CEI.

Research on flame-retardant electrolytes has shifted from passive addition to intrinsic safety design. For example, Xu and his colleagues[16] synthesized a series of partially fluorinated alkyl phosphates and found that the presence of fluoride not only improved reduction stability but also enhanced the effectiveness of FR. Xia et al.[17] reported the use of PFPN as a flame-retardant additive. This process combines the good electrochemical stability of cyclophosphazene with the high flame-retardant efficiency of organic fluorine structures, achieving highly synergistic flame-retardant effects and good electrochemical compatibility on graphite anodes. Experiments showed that an electrolyte containing only 5 wt.% PFPN completely suppressed the flammability of the electrolyte without affecting the electrochemical performance of the electrode. Moreover, this additive significantly improved the cycling performance of LiCoO2 at a high cutoff voltage of 4.5V, making it a suitable flame-retardant additive for high-voltage lithium-ion battery applications.

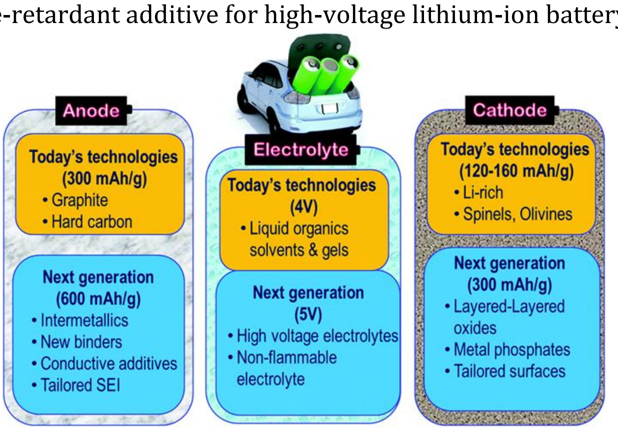

Figure 2. Schematic diagram of current and future technologies for lithium-ion batteries.[18]

These innovative achievements not only deepen the understanding of the structure-activity relationship of electrolytes but also lay a theoretical foundation for the next generation of high-energy-density, high-safety lithium-ion batteries

Conclusion

The evolution of lithium-ion battery electrolytes has transitioned from liquid to solid-state systems and from single-function to multifunctional composites. In the future, electrolyte research will advance towards higher energy density, enhanced safety, broader operating temperature ranges, and environmental friendliness. The development of novel lithium salts, solvents, and additives, along with the application of new materials such as nanotechnology and ionic liquids, will provide fresh opportunities for further improvements in electrolyte performance. Concurrently, the synergistic optimization of electrolytes with cathode and anode materials, as well as the application of intelligent manufacturing technologies, will propel the overall progress of lithium-ion battery technology. As these research efforts deepen, lithium-ion batteries are expected to play an even more significant role in electric vehicles, smart grids, and other fields, making a substantial contribution to the sustainable development of human society.

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