

Recent Advances in Electrolyte-Mediated Interfacial Regulation for Lithium Metal Batteries: From Fluorinated Design to Localized High-Concentration Electrolytes

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Abstract. Lithium metal anodes, with their high theoretical specific capacity and low electrode potential, are considered promising anode materials for next-generation high-energy-density batteries. However, their practical application is severely limited by uneven lithium deposition, continuous electrolyte consumption, dead lithium formation, and repeated rupture of the solid electrolyte interphase during cycling. As a key component directly involved in interfacial reactions, the electrolyte can regulate lithium plating/stripping behavior and cycling stability by tailoring the Li^+ solvation structure, electrolyte reduction pathway, and SEI composition. This review focuses on electrolyte-mediated interfacial regulation strategies for lithium metal batteries. First, the formation mechanism, compositional features, and stabilizing role of the SEI are discussed. Then, fluorinated electrolyte design is summarized, with emphasis on its ability to construct LiF -rich interphases and enhance the electronic insulation and chemical stability of the SEI. Furthermore, localized high-concentration electrolytes are reviewed in terms of their design logic, including the preservation of high-concentration-like local solvation structures, promotion of anion participation in interfacial reactions, and formation of inorganic-rich SEI layers. Finally, the challenges of fluorinated localized high-concentration electrolytes are analyzed, including cost, environmental impact, ion transport properties, and validation under practical operating conditions. This review provides useful guidance for the rational design of electrolytes toward high-Coulombic-efficiency, long-life, and safe lithium metal batteries.

Keywords: Lithium metal batteries, Electrolyte design, Fluorinated strategy, Localized high-concentration electrolytes

1. Introduction

With the rapid development of electric vehicles, portable electronic devices, and large-scale energy storage systems, higher requirements have been placed on the energy density, safety, and cycling life of rechargeable batteries [1]. Conventional commercial lithium-ion batteries mainly use graphite as the anode material, whose theoretical specific capacity is 372 mAh g^{-1} and is gradually approaching its performance limit, making it difficult to meet the demands of next-generation high-energy-

density energy storage systems [2]. Therefore, developing new anode materials with higher capacity and lower electrode potential has become an important direction for improving battery energy density.

Lithium metal anodes possess a theoretical specific capacity of approximately 3860 mAh g⁻¹ and a low electrode potential of approximately -3.04 V, making them important candidate anodes for high-energy-density battery systems [3]. Unlike intercalation-type graphite anodes, lithium metal can directly serve as an active lithium source in electrochemical reactions, and is therefore theoretically more favorable for improving battery energy density. However, the high reactivity of lithium metal also leads to complex interfacial failure issues in liquid electrolytes. The failure of lithium metal anodes is mainly associated with two aspects. First, Li⁺ deposition on the anode surface is often non-uniform. Local electric-field enhancement, uneven ion flux, and concentrated current density can induce dendritic or porous lithium formation, thereby reducing the reversibility of lithium plating/stripping and even causing separator penetration and internal short circuits [4]. Second, metallic lithium continuously reacts with organic electrolytes, consuming active lithium and electrolyte while forming a solid electrolyte interphase, namely the SEI, on the anode surface [5].

Among various modification strategies, electrolyte regulation offers advantages such as good process compatibility, broad applicability, and relatively high scalability, making it an important approach for improving the interface of lithium metal anodes. However, the core of electrolyte design for lithium metal batteries is not merely to improve the intrinsic stability of the electrolyte, but to reduce continuous electrolyte decomposition and dead lithium formation by regulating the Li⁺ solvation structure, preferential interfacial reduction reactions, and SEI composition. This review focuses on the formation mechanism of the SEI, fluorinated strategies, and localized high-concentration electrolyte design. Fluorinated strategies mainly induce the formation of LiF-rich SEI through fluorinated components, while localized high-concentration electrolytes promote greater anion participation in interfacial reactions by regulating the solvation structure. Although these two strategies differ in their design principles, both aim to construct a stable, uniform, and inorganic-rich SEI.

2. SEI formation as the central interfacial problem

The SEI is a solid interfacial layer formed after the lithium metal anode comes into contact with the electrolyte. It can essentially be understood as the corrosion and passivation product of lithium metal in non-aqueous electrolytes [5, 6]. Because lithium metal has an extremely low electrochemical potential, its Fermi level is higher than the lowest unoccupied molecular orbital of most electrolyte components. Therefore, electron transfer occurs after contact with the electrolyte, inducing the reductive decomposition of solvent molecules and lithium salt anions [7]. This process occurs not only during cycling, but also rapidly at the initial contact between lithium metal and the electrolyte, and it continues to reconstruct during subsequent lithium plating/stripping processes.

The SEI is generally composed of both inorganic and organic components. The inorganic components mainly include LiF, Li₂CO₃, Li₂O, Li₂S, and decomposition products derived from nitrogen- and sulfur-containing lithium salts, while the organic components include lithium alkyl carbonates, polycarbonates, polyethers, and other solvent-reduction products [5]. Different electrolyte systems can induce SEIs with markedly different structures. Conventional carbonate-based electrolytes tend to continuously decompose on the lithium metal surface, forming SEIs with a high proportion of organic components and non-uniform thickness and spatial distribution. Ether-based electrolytes are generally more compatible with lithium metal anodes, but their stability still depends on the synergistic regulation of lithium salts, additives, and solvation structures [8, 9].

The stability of the SEI directly determines the reversibility of lithium plating/stripping. During cycling, the surface morphology of lithium metal continuously changes, and the SEI attached to its surface is subjected to stresses such as stretching, compression, and local delamination. When the SEI has insufficient mechanical strength, non-uniform spatial distribution, or uneven Li^+ transport, the interfacial layer can easily rupture, exposing fresh lithium metal to the electrolyte and triggering new side reactions and SEI regeneration [10]. This repeated rupture and repassivation continuously consume electrolyte and active lithium, increase interfacial impedance, and ultimately lead to capacity decay.

An ideal SEI should simultaneously possess high electronic insulation, appropriate Li^+ conductivity, good chemical stability, and a certain degree of mechanical adaptability [11, 12]. Electronic insulation helps prevent electrons from further passing through the SEI and reducing the electrolyte; Li^+ conductivity ensures that ions can smoothly migrate through the interfacial layer and deposit uniformly; and mechanical stability helps the SEI accommodate the dynamic changes of the lithium metal surface. Therefore, constructing a stable SEI is not simply a matter of increasing interphase thickness, but requires a balance among composition, thickness, spatial uniformity, electronic blocking capability, and Li^+ transport.

From the perspective of electrolyte design, the key issue of the SEI lies in its origin. Solvent-dominated decomposition usually tends to form organic-rich SEIs, whereas the participation of lithium salt anions in interfacial reduction is conducive to the formation of inorganic-rich SEIs containing LiF , Li_2S , LiN_xO_y , and related species. The latter generally exhibits stronger electronic blocking capability and higher interfacial stability [13]. Therefore, regulating the Li^+ solvation structure to promote the preferential participation of anions and specific film-forming components in interfacial reactions is the fundamental logic of current electrolyte design for lithium metal batteries. The fluorinated strategies and localized high-concentration electrolytes discussed below can both be understood within this design logic.

3. Fluorinated electrolyte design

Fluorinated strategies are among the most representative interfacial regulation approaches in electrolyte design for lithium metal batteries. Their core purpose is not simply to increase the fluorine content in the electrolyte, but to regulate the interfacial reduction sequence through fluorinated additives, fluorinated solvents, and fluorinated lithium salts, thereby inducing the formation of LiF -rich SEI and improving the reversibility of lithium plating/stripping [14, 15]. LiF possesses a wide band gap, high electronic insulation, and good chemical stability, which help suppress continuous electrolyte decomposition and, to some extent, improve the uniformity of lithium deposition [16].

FEC is one of the most widely studied fluorinated film-forming additives in early research. The C–F bond in the FEC molecule makes it prone to reduction on the anode surface, generating LiF while also undergoing radical polymerization and ring-opening reactions, ultimately forming a composite SEI composed of both LiF and organic polymers [17]. In lithium metal batteries, FEC can improve the SEI structure and lithium deposition morphology, thereby enhancing the stability of lithium plating/stripping [18]. However, the reduction products of FEC are not limited to LiF , but also include polycarbonates and other organic components. When the organic phase is excessive or unevenly distributed, the SEI may still undergo cracking, thickening, and reconstruction during cycling [19]. Therefore, FEC is more suitable as a representative additive for understanding fluorinated film-forming mechanisms, rather than representing the entire scope of fluorinated strategies.

Fluorinated lithium salts are another important source for constructing LiF-rich SEI. Fluorinated anions in lithium salts such as LiPF_6 , LiFSI, and LiTFSI can enter the Li^+ solvation sheath and migrate with Li^+ to the anode interface, where they participate in reductive decomposition to generate LiF, Li_2S , LiN_xO_y , and other sulfur- or nitrogen-containing inorganic species [9, 20]. Among them, FSI^- in LiFSI exhibits relatively high interfacial reactivity and is more likely to induce the formation of an inorganic-rich SEI. By contrast, the trifluoromethyl groups in LiTFSI are relatively stable, and its film-forming effect depends more strongly on the specific solvent environment and salt concentration [21]. Therefore, the role of fluorinated lithium salts is determined not only by the presence of fluorine, but also by the anion structure, solvation state, and interfacial reduction pathway.

In recent years, fluorinated solvents have become an important direction in the development of fluorinated strategies. Compared with conventional ether- or ester-based solvents, fluorinated solvents can simultaneously regulate electrolyte safety, oxidative stability, wettability, and interfacial film-forming behavior [22]. For example, fluorinated ether solvents can improve the compatibility of electrolytes with both high-voltage cathodes and lithium metal anodes, and enable prolonged cycling life through molecular structure regulation [23, 24]. Fluorinated orthoformate-based electrolytes can form a more monolithic SEI on the lithium metal surface, thereby reducing lithium consumption and electrode pulverization [25]. Fully fluorinated ester electrolytes and other fluorinated ether-based electrolytes have also been used to construct high-voltage and wide-temperature lithium metal batteries, demonstrating the value of fluorinated molecular design in improving interfacial stability and safety [26, 27].

Therefore, the development of fluorinated strategies has evolved from "introducing fluorinated film-forming components" to "regulating the reaction pathways of fluorinated components." Early studies mainly focused on whether additives such as FEC could provide LiF, whereas later studies further emphasized the combined effects of fluorinated lithium salts, fluorinated solvents, and solvation structures on preferential interfacial reactions. It should be noted that a LiF-rich SEI does not mean that the SEI should be composed entirely of LiF. An excessively thick or overly continuous and dense LiF layer may increase interfacial impedance and hinder rapid Li^+ transport. Therefore, a more ideal SEI should be a composite structure in which inorganic phases such as LiF provide electronic blocking and chemical stability, while an appropriate amount of organic phase is retained to enhance interfacial flexibility.

Overall, fluorinated strategies can directly regulate the chemical composition of the SEI and represent an important direction for stabilizing lithium metal anodes. However, they still face several challenges, including the high cost of fluorinated molecules, unsatisfactory viscosity or low-temperature kinetics of some fluorinated components, non-uniform spatial distribution of decomposition products, and environmental persistence. Future fluorinated electrolyte design should move from single-component screening toward the synergistic regulation of solvents, lithium salts, additives, and solvation structures, aiming to achieve controllable decomposition and uniform interphase formation of fluorinated components at the interface while maintaining sufficient ion transport capability.

Table 1. Representative fluorinated electrolyte components and their roles in regulating SEI chemistry for lithium metal batteries

Category	Representative components	Main interfacial role	Typical SEI species	Advantages	Limitations
Fluorinated additive	FEC	Preferential reduction and film formation	LiF, organic polymers, polycarbonates	Improves Li deposition and SEI stability	Organic products may still cause SEI thickening
Fluorinated lithium salt	LiFSI, LiTFSI, LiPF ₆	Promotes anion-derived SEI formation	LiF, Li ₂ S, LiN _x O _y	Forms inorganic-rich SEI	Depends on salt concentration and solvent environment
Fluorinated ether solvent	TTE, HFE, BTFE or related fluorinated ethers	Regulates solvation structure and interfacial reaction	LiF-rich and salt-derived SEI	Improves anode/cathode compatibility	Cost, volatility, possible transport limitation
Fluorinated ester or orthoformate	Fluorinated esters, fluorinated orthoformates	Builds more stable interphase on Li surface	LiF-containing compact SEI	Supports high-voltage or wide-temperature systems	Molecular design and cost remain issues

4. Localized high-concentration electrolyte design

The concept of localized high-concentration electrolytes (LHCE) arises from the contradiction between conventional dilute electrolytes and high-concentration electrolytes. In conventional dilute electrolytes, the lithium salt concentration is usually around 1 mol L⁻¹. Li⁺ is mainly coordinated by abundant solvent molecules, forming a solvation structure dominated by solvent-separated ion pairs, while anions are generally located outside the first solvation sheath of Li⁺ [28]. In this case, interfacial reactions at the anode are usually dominated by solvent decomposition, which tends to form organic-rich SEI. High-concentration electrolytes significantly increase the lithium salt concentration, reduce the number of free solvent molecules, and strengthen the interaction between Li⁺ and anions, thereby forming contact ion pairs and aggregate structures [29, 30]. This anion-involved local solvation structure can alter the reduction pathway on the anode surface, promote the preferential decomposition of salt anions, and generate an inorganic-rich SEI. Although this strategy improves interfacial stability, the high salt concentration also leads to high viscosity, reduced ionic conductivity, poor wettability, and increased cost [31].

Table 2. Comparison of conventional dilute electrolytes, high-concentration electrolytes, and localized high-concentration electrolytes

Electrolyte type	Li ⁺ solvation structure	Main interfacial reaction	SEI feature	Advantages	Main problems
Dilute electrolyte	Li ⁺ mainly coordinated by solvent molecules	Solvent-dominated decomposition	Organic-rich SEI	Low viscosity, good wettability	Unstable SEI, continuous side reactions
High-concentration electrolyte	More contact ion pairs and aggregates	Anion-involved decomposition	Inorganic-rich SEI	Better Li metal compatibility	High viscosity, high cost, poor wettability

Table 2. (continued)

LHCE	Maintains HCE-like local structure with diluent	Anion- or fluorinated-component-involved decomposition	Inorganic-rich and more stable SEI	Lower viscosity and cost than HCE, improved wettability	Diluents may be costly, volatile or environmentally concerning
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The core idea of LHCEs is to introduce non-solvating or weakly solvating diluents into high-concentration electrolytes, thereby reducing the overall salt concentration, viscosity, and cost while retaining, as much as possible, the local solvation structure rich in contact ion pairs and aggregates found in HCEs [32, 33]. Therefore, LHCEs are not simply diluted HCEs, but electrolyte systems that maintain localized high-concentration characteristics at a relatively low overall salt concentration. An ideal diluent should be uniformly miscible with the high-concentration electrolyte, while interacting only weakly with Li^+ and not significantly disrupting the original first solvation sheath of Li^+ [34]. The role of the diluent should not be understood as completely inert. Recent studies have shown that diluents can not only reduce viscosity and improve wettability, but may also influence Li^+ transport, the desolvation process, and the interfacial electric-field distribution [35]. At the lithium metal anode interface, Li^+ must first undergo desolvation before being reduced and deposited as metallic lithium. In LHCEs, the participation of anions in Li^+ coordination can alter the interfacial desolvation process and preferential reduction pathway, shifting the interfacial reaction from solvent-dominated decomposition to anion-dominated or anion/fluorinated-component co-dominated decomposition, thereby forming a salt-anion-derived inorganic-rich SEI [31].

At present, commonly used LHCE diluents include fluorinated ethers, fluorinated cyclic ethers, fluorinated alkanes, fluorinated aromatics, phosphazenes, and some halogen-free diluents. Among them, fluorinated ether diluents such as BTFE, TTE, and HFE are among the earliest studied and most widely applied types. They generally exhibit low Li^+ coordination ability, good chemical stability, and certain flame-retardant characteristics, enabling reduced viscosity and improved wettability without significantly disrupting the localized high-concentration structure [32, 36]. Subsequently, researchers began to screen diluents based on parameters such as donor number, dielectric constant, electrostatic potential, boiling point, viscosity, and oxidative stability. Functionalized diluents and additives have also been developed to simultaneously optimize the SEI, CEI, safety, and wide-temperature performance [37-39].

Unlike fluorinated additives, which regulate the SEI mainly from the perspective of film-forming components, LHCEs place greater emphasis on altering interfacial reactions at the solvation-structure level. By regulating the spatial distribution of solvents, anions, and diluents around Li^+ , LHCEs promote greater anion participation in interfacial reactions, thereby forming a more stable inorganic-rich SEI. The recently proposed concept of generalized localized high-concentration electrolytes further indicates that the key to LHCE design is not a fixed salt concentration or a specific type of diluent, but the ability to balance relatively low overall salt concentration, favorable transport properties, and stable interfacial reactions [40].

Nevertheless, LHCEs still face practical application challenges. Some fluorinated diluents are costly, have low boiling points, or exhibit high volatility, which is unfavorable for large-scale application and high-temperature operation. Some fluorinated diluents may also raise environmental and sustainability concerns. Meanwhile, the mechanisms by which diluents affect Li^+ transport, desolvation, and the spatial structure of the SEI still require further clarification. Future LHCE design should move from single-formulation optimization toward the synergistic regulation of salts, solvents, diluents, and additives, and should be validated under more practical conditions, such as high areal capacity, low N/P ratio, lean electrolyte, and long-term cycling.

5. Conclusion

Lithium metal batteries, with their high theoretical specific capacity and low electrode potential, represent an important direction for next-generation high-energy-density batteries. However, lithium metal anodes are prone to dendrite growth, continuous electrolyte consumption, repeated SEI rupture, and increasing interfacial impedance during cycling, which severely limits their practical application. Electrolyte design can regulate the composition, structure, and formation pathway of the SEI from the origin of interfacial reactions, and is therefore a key strategy for stabilizing lithium metal anodes.

With SEI stabilization as the central theme, this review summarizes two representative electrolyte design strategies: fluorinated strategies and localized high-concentration electrolytes. Fluorinated strategies mainly induce the formation of LiF-rich SEI through fluorinated additives, fluorinated solvents, and fluorinated lithium salts, thereby enhancing the electronic insulation and chemical stability of the interface. LHCEs regulate the local Li⁺ solvation structure, allowing more anions to participate in interfacial reduction and thus forming inorganic-rich SEI. The common feature of these two strategies is that they alter the preferential decomposition pathway of the electrolyte on the lithium metal surface, shifting the interphase from a solvent-derived, organic-rich structure toward an anion-involved, inorganic-rich composite structure.

It should be emphasized that stabilizing the lithium metal interface is not equivalent to simply increasing the LiF content, nor is it equivalent to merely increasing the salt concentration. An ideal SEI should simultaneously possess electronic blocking capability, Li⁺ conductivity, mechanical adaptability, and chemical stability. Therefore, the future development of fluorinated LHCEs should focus on the molecular design of fluorinated components with low cost and low environmental risk, low-fluorine or fluorine-free alternative systems, quantitative relationships between solvation structure and SEI composition, and battery validation under practical operating conditions. Through the synergistic optimization of molecular structure design, solvation structure regulation, and interphase construction, fluorinated LHCEs are expected to become an important electrolyte system for promoting the practical application of high-energy lithium metal batteries.

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