Perspective on solid-electrolyte interphase regulation for lithium metal batteries

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Abstract
The solid-electrolyte interphase (SEI) generated between the electrode and the electrolyte strongly influences the performance of batteries. As the most attractive next-generation energy storage system with ultrahigh energy density, the development of lithium metal batteries (LMBs) has been greatly plagued by the uncontrollable lithium (Li) dendrite and serious electrolyte decomposition resulting from the self-derived unstable SEI with poor properties. In this perspective, the recent progress of regulating the nature and composition of the SEI to stabilize the Li metal in LMBs is summarized, followed by a discussion of the formation mechanism and the property of the SEI. The strategies for constructing a stable SEI are summarized, for example, design of a compatible electrolyte with the anode, adding self-sacrificing additives or solvation control additives, and the regulation of nonfaradaic electric adsorption and desorption progress. Finally, the guideline for the rational design of the SEI is proposed.

KEYWORDS
additive, electrolytes, lithium metal batteries, metallic lithium anode, solid electrolyte interphase

1 | INTRODUCTION
Because of the high working voltage, high energy density, and long cycle life, lithium ion batteries have attracted tremendous attention and been extensively studied in recent decades.¹ However, with the great development of electric vehicles and the continuous expansion of portable electronic devices market, development of next-generation high energy batteries is urgently needed.² Lithium (Li) metal, with its ultrahigh theoretical capacity (3860 mAh/g) and low redox...
potential (−3.04 V vs. SHE), is considered as the ultimate anode material; therefore, lithium metal batteries (LMBs) that employ Li metal as the anode have been studied in detail recently. However, the practical application of LMBs is still greatly plagued by the uncontrollable Li dendrite growth and the continuous electrolyte decomposition during the repeated Li plating and stripping process. The uncontrollable Li dendrite growth mainly results from the inhomogeneous distributions of current on the surface of the anode and the heterogeneous compositions of the solid-electrolyte interphase (SEI). Therefore, the physicochemical properties of the SEI formation on the anode strongly influence the electrochemical performance of LMBs. Thus, it is of great importance to clearly identify the nature and composition of the SEI in LMBs. The composition and nature of the SEI is highly influenced by the anode and composition electrolyte. In recent years, great efforts have been devoted to the rational design of the electrolyte to control the formation of the SEI with desirable properties for LMBs. Strategies such as employing solid-state electrolytes/solid-state electrolytes, introducing film-forming additives, and regulating anions in the Li+ solvation sheath, have been widely reported. In this perspective, the following topics are summarized: (1) focal points related to the formation mechanism and properties of the SEI in LMBs and (2) the major challenges and perspectives regarding the prospects for the rational modification of SEI in LMBs.

2 | FORMATION MECHANISM AND NATURE OF THE SEI

The SEI model, first proposed by Peled in 1979, involves the passivation layer between the electrode and electrolyte acting as a solid electrolyte. Currently, it is generally accepted that SEI formation is caused by the thermodynamic instability of the electrolyte in contact with the anode electrode. Specifically, because of the low Li+ intercalation potential of most anode materials (i.e., 0 eV for Li and 0.1 eV for graphite vs. Li/Li+), the working voltage of the device will exceed the decomposition potential of most electrolytes; therefore, the electrolyte will be reduced on the surface of anode and lead to the formation of the SEI. The as-formed SEI allows Li+ diffusion while featuring low electronic conductivity; therefore, with increasing thickness, inhibition of electron tunneling will be achieved and further decomposition of the electrolyte will be halted. The functionality of an ideal SEI could be summarized as follows: (1) the SEI should feature high Li ion conductivity to allow fast Li+ kinetic behavior; (2) the electronic conductivity of the SEI should be as low as possible because a lower electronic conductivity would lead to the earlier establishment of the electron tunneling and thus result in the formation of a thinner SEI, thereby consuming less electrolyte and active Li+; (3) the SEI should possess high chemical stability and strong mechanical stability to endure the attack of radicals and huge volume expansion of the anode during cycles. On one hand, the formation of an even and stable SEI could act as the protection layer for the anode to prevent the corrosion of electrolyte by anode; on the other hand, the SEI formation also consumes electrolyte and active Li+ to some extent (Figure 1). Therefore, it is of great importance to study the nature of the SEI in detail and find effective methods to rationally modify the SEI.

3 | STATUS OF SEI REGULATION

As the interface between the electrolyte and the electrode, the composition of the SEI is highly dependent on the thermodynamic stability of the electrolyte and the nature of the anode materials. Recently published works have demonstrated that, by the rational adjustment of electrolyte components, the reaction pathway and kinetics of the SEI formation change; as a result, the desired nature of the SEI could be achieved. Lee et al. reported a locally concentrated ionic liquid electrolyte with hydrofluoroether as additives to be used as a fire-retardant electrolyte. The low viscosity and much-improved thermal stability of the electrolyte result in the formation of a SEI with improved transport properties.

Besides the adjustment of the electrolyte solvents, the use of self-sacrificing additives is another method to effectively regulate the SEI. Theoretically, if the additives possess higher reduction potential than the electrolyte solvents, it will be reduced earlier than the solvents on the anode, thereby forming an ideal environment for Li deposition. Yang et al. reported the use of a boron additive to effectively passivate carbonate electrolytes for LMBs. The as-used tris(pentafluorophenyl)borane (TPFPB) additive with lower LUMO energy level than ethylene carbonate/ethyl methyl carbonate possess early reduction tendency on Li metal; as a result, a thin and uniform SEI can be produced on the anode (Figure 2A). The decreased poly(CO3) peaks of C1s in additive-contained electrolyte demonstrated the effective suppression of electrolyte decomposition. The increased B signals in the X-ray photoelectron spectroscopy (XPS) on the anode further demonstrated the earlier reduction of TPFPB (Figure 2D). The much-improved capacity retention and the high coulombic efficiency (99%) of LNMO/Li batteries with the additive proved the practicality of the TPFPB additive. Although self-sacrificing additives are useful, due to the inherent low concentration of additives, the passivation effect will decrease with the
consumption of additives; therefore, it is important to develop a more reliable approach to intrinsically suppress the high reaction tendency of electrolytes with Li metal. For this consideration, Cui reported the study of the solubility-mediated sustained release of LiNO₃ in traditional carbonate electrolytes for providing stable Li metal in LMBs. LiNO₃ is an effective additive widely used in ether electrolytes for Li-sulfur batteries; however, its application in carbonate electrolytes is greatly hindered by the poor solubility of LiNO₃ in carbonates. By the construction of a solubility-mediated sustained release structure for LiNO₃, the solubility limitation of LiNO₃ in carbonates was overcome. The easy reduction of NO₃⁻ than electrolyte was confirmed by cyclic voltammetry, the decisive role of NO₃⁻ reduction in the electrochemical properties of the SEI was demonstrated by scanning electron microscope, XPS, and...
cryogenic electron microscopy. The unique bilayered structure of the SEI in the LiNO$_3$-contained electrolyte was achieved, in which the outer layer was mainly consistent with ordered crystalline Li$_2$O and the inner layer featured an amorphous matrix structure. This unique SEI with low-resistance and better ion-transport lead to the even deposition of Li and the prevention of dendrite formation.$^{30}$

Apart from the use of self-sacrificing additives, another useful method to adjust the SEI is to introduce additives that do not participate in the formation of the SEI directly but influence the formation process of the SEI by controlling the coordination of electrolyte solvents with Li$^+$. Yu and his coworkers reported the fabrication of a polar polymer network (PPN) with rich polar C≡N groups to effectively reduce the reactivity of carbon solvents (Figure 3A). According to a Raman spectra survey, the dipole-dipole interaction between solvent and polar polymers was confirmed. The increased number of inorganic components of the SEI induced by anion decomposition improves the electrochemical stability of the SEI. The nonconsumed PPN could provide a sustainable environment for the electrolyte to form the SEI with thin and compact structure during the whole cycle process (Figure 3B,C). The much improved electrochemical performance of Li|NCM batteries with additives demonstrated the reliable and sustainability of this strategy. Another method to stabilize the electrolyte is to adjust the concentration of Li salt in the solvent. The recent published works demonstrated that the anion in the salt can influence the reduction of the electrolyte and the formation of the SEI. In the concentrated electrolyte, because of the scarcity of the solvent molecules that coordinate with Li$^+$, the salt anions will enter into the first solvation layer of Li$^+$; thus, the SEI formation will shift from the solvent decomposition phase to the salt anion decomposition phase. The as-formed LiF-rich SEI features significantly improve both Li$^+$ ion

![Figure 3](image-url)
transport and adhesion to the electrode surface. Liu et al. reported a high concentration Li salt electrolyte with enhanced reductive/oxidative tolerance and good compatibility with the electrodes. With the concentrated electrolytes, the coating layer on the electrode shifts from being thick and rough to being thin and dense. An XPS survey demonstrated that, on the surface of the electrode with high Li concentration, the P element content decreased and the S and F element contents increased, indicating the effective suppression of solvent decomposition and the presence of a stable SEI resulting from the decomposition of FSI\(^{−}\).

A computational calculation based on density functional theory demonstrated that, in a high concentration electrolyte, the anion participates in the Li primary solvation shell, resulting in the improved kinetic behavior of Li\(^{+}\) (Figure 3D–G).

It was reported that, before the formation of the SEI, the electrical double layer will form between the electrolyte and the Li metal anode. In the charging/discharging states, nonfaradaic electric adsorption and desorption will also affect the composition and structure of the SEI. Zhang and his coworkers reported the study of the regulation of the inner Helmholtz plane (IHP) for a stable SEI on Li metal in LMBs. In this study, LiNO\(_3\) and CuF\(_2\) were added to electrolytes to construct a robust electric double layer. The preferential initial competitive adsorption of Cu-NO\(_3\)\(^{−}\) complexes in the IHP was then demonstrated. Fresh insights into the correlation between the initial competitive adsorption in the IHP with the interfacial chemistry of the SEI formation were proposed. The significantly improved electrochemical performance with CuF\(_2\) and LiNO\(_3\) indicated the integrated SEI formation on the Li anode and the inhibition of the electrolyte decomposition. The better Li\(^{+}\) transport in the SEI film and the lower desolvation energy of Li\(^{+}\) verified by EIS according to the law of Arrhenius confirmed the significant effect of the IHP regulation on the SEI formation (Figure 4A,B). The much larger binding energy of the Li slab with anions than that of Li\(^{+}\) demonstrated by first-principles calculations indicates that the anions adsorption was dominant in the IHP. The larger binding energy of NO\(_3\)\(^{−}\) with the Li slab results in the formation of the SEI with a unique property (Figure 4D,E).

**Conclusion and Perspectives**

Current studies related to the efforts to address the main problems of LMBs (i.e., Li dendrite growth and electrolyte decomposition) based on the rational regulation of the SEI were briefly reviewed. To improve a self-derived unstable
SEI with low Li\(^+\) conductivity, low mechanical strength, and inhomogeneous composition, the following strategies were proposed: (1) design an electrolyte compatible with the anode to avoid the formation of an unstable SEI on the electrodes; (2) add specific self-sacrificing additives that reduce earlier than electrolyte solvents to form the SEI with desired properties to prevent the corrosion of Li caused by the electrolyte; (3) use additives that do not decompose but can regulate the solvation structure of Li\(^+\) to stabilize the electrolyte and inhibit the decomposition of the electrolyte; (4) employ a concentrated electrolyte to stabilize the electrolyte and form the SEI that forms mainly by the reduction of salts anions; (5) construct a unique IHP to achieve unique preferential initial competitive adsorption to generate a robust SEI with fast Li\(^+\) transport. To achieve the construction of an ideal SEI featuring high Li ion conductivity, low electronic conductivity, and high chemical/mechanical stability, the interdependent and correlated factors that influence the SEI should be considered together in a future study. Advanced characterization technology should be applied to characterize the composition of the SEI and clearly identify the functionality of the different compositions of the SEI (such as LiF, LiH, and LiCO\(_3\)). The relationship between Li dendrite growth and the nature of the SEI should be clearly identified.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

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