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The solid electrolyte interphase (SEI) is formed in various energy storage batteries, including lithium (Li), sodium (Na), potassium (K), and magnesium (Mg) ion batteries. It is the main factor causing low Coulombic efficiency of anode and the key to controlling ion diffusion on the anode surface. Enhancing the electronic insulation and ionic conductivity of SEI can effectively address these issues and improve the electrochemical performance of metallic anode energy storage batteries. This review provides a comprehensive summary of advanced electrolytes employed to modulate the structure and phase composition of the SEI. Additionally, it addresses a key question: is the inorganic-rich interface or the organic-rich interface more favorable for lithium metal anodes, thereby offering a promising pathway for designing SEIs that can effectively mitigate lithium dendrite formation in future applications.

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ARTICLE

Advanced Research on Electrolyte for Regulating SEI in High Performance LMBs

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Rechargeable lithium metal batteries (LMBs) with lithium anode have attracted wide attention as next-generation energy storage due to the high specific energy density and wide working voltage. Electrolytes not only bear the responsibility of transporting lithium ions, but also play an important role in the formation of solid electrolyte interphase (SEI) on the lithium anode surface, which effects the Coulombic efficiency of LMBs. Up to now, extensive research of electrolyte modification has been devoted to adjusting the structure and composition of SEI for the purpose of inhibiting the growth of dendrites in rechargeable lithium anode. In order to guide the further research of electrolyte, this paper summarizes the latest advances of the electrolytes for lithium metal anode with the emphasis to build stable SEI on the lithium anode surface. Finally, a perspective for the development direction of LMBs is proposed, which is helpful to guide researchers in desiging excellent LMBs in the future.

Introduction

The lithium-ion batteries (LIBs) with the highest energy density currently still cannot meet the growing demand for power density and capacity density in power batteries due to the low energy density (372 mAh g^{-1}) of graphite negative materials.[1] On the contrary, rechargeable lithium metal batteries (LMBs) with metallic lithium (Li) anode have been regarded as the “holy grail” for energy storage.[2] Li metal is considered the most ideal anode material due to the high theoretical specific capacity (3860 mAh g^{-1}) and lowest redox potentials (-3.04 V vs SHE).[3] However, Li metal anode suffers from substantial challenges in cycle life, safety and sustainability which hinders practical applications.[4] The main reason for the low lifespan of Li metal anode (LMA) is uncontrolled dendrite growth during repeated deposition/stripping processes, which causes complex side reactions and the risk of puncturing the diaphragm.[5] Therefore, in order to achieve practical LMBs, it is urgent to suppress the growth of Li dendrites.

Various methods have been proposed to suppress the Li dendrites such as current collection modification, alloy array, solid state electrolyte, electrolyte engineering and electrochemical artificial SEI.[6] After extensively research and discussion, it is widely recognized that electrolyte engineering paly an important role to stabilize LMA.[7] That is because the physicochemical properties of the electrolyte not only control the migration behaviour of Li ions, but also affect the properties of the solid electrolyte interphase (SEI) formed by the reaction between electrolyte and Li metal on the anode surface.[8] SEI as a protective layer can block further parasitic reactions between electrolytes and Li metal, and be capable of preventing the growth of Li dendrites.[9] Constructing a suitable SEI is necessity for LMA to achieve long cycle-life and safety.[10] Ideal SEI should satisfy the following requirements: (1) it must be ion conducting and electron insulating; (2) it should have high surface energy and mechanical strength; (3) it can tolerate the huge volume changes of LMA; (4) it should have homogeneously morphology and structure. [11] Regulating the structure and composition of SEI through electrolyte engineering to meet the above requirements is the simplest and most efficient method.

In this review, we have summarized recent advanced research work in electrolytes engineering. Firstly, we briefly introduced the formation mechanism of SEI on the surface of LMA and the application history of liquid electrolytes in Li battery systems. Then, we summarized the electrolyte chemistry on the surface of LMA, as well as the mechanism for regulating the structure and components of SEI to suppress Li dendrites. Finally, we discuss and forecast the future development direction of liquid electrolytes. We hope that this review can promote the investigation of advanced electrolyte for high electrochemical performance LMBs.

Formation Mechanism of SEI on LMA Surface

Electrolyte is an important component of LMBs, which is not only used to connect the anode and cathode, but also serves as a medium for dissolving Li ions. However, it faces serious challenges on the surface of LMA. Due to the high reducibility, a spontaneous reduction reaction occurred when LMA contact with liquid electrolytes and forming of a passive layer on the LMA surface which are known as SEI.[12] The composition, structure, and physicochemical properties of SEI are closely

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related to the electroplating morphology of Li ions on the LMA surface. Goodenough et al. put forward the formation mechanism of SEI formed on LMA. As shown in Figure 1, Assuming the electrochemical potentials of the anode and cathode are μ_a and μ_c, respectively, when the lowest unoccupied molecular orbital (LUMO) of the electrolyte molecules is lower than the anode electrochemical potential μ_a, electrons tend to transfer to the unoccupied orbitals of the electrolyte, causing reduction reaction on the LMA surface. This reaction will only terminate when the obtained SEI can completely passivate the LMA.[13] In fact, due to the lowest reduction potential of LMA, the side reaction between LMA and electrolyte is always unavoidable, so SEI layer will spontaneously formed on the surface of LMA. In contrast, the SEI on the graphite anode can only form after charging due to the high potential which cause different structures and component distributions of SEI.[14] To obtain long-life LMBs, it is necessary to understand the structure, composition, and physicochemical properties of SEI and the way they influence the growth of Li dendrites.

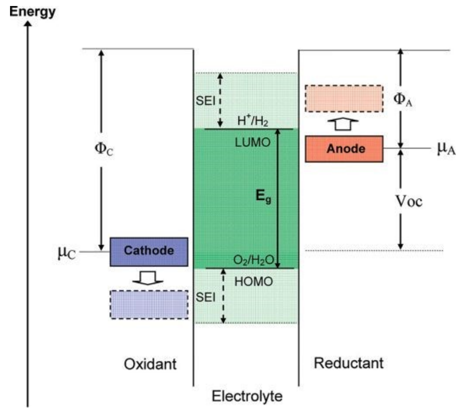

Figure 1. Formation mechanism of SEI on Li metal surface.[13]

Electrolyte Derived SEI Suppressing Li Dendrite in LMA

Mechanism of SEI suppressing Li dendrites

The SEI plays an important role in the repeated charging and discharging process of LMBs. As shown in Figure 2, the SEI generated from the electrolyte decomposition is usually fragile and easily punctured by the initial nucleation of Li, leading to new metal reduction sites thus promoting the growth of filamentous, mossy, and dendritic Li metal. Moreover, the inherent physical and chemical properties of SEI also easily cause dendrite growth.[15] During the charging and discharging process of LMA, Li ions need to pass through the SEI. However, the non-uniform Li ion channels in the SEI resulting in non-uniform initial Li nucleation. Subsequently, they will puncture the SEI, grow along the axial direction with the tip effect, and eventually form dendritic morphology.[16]

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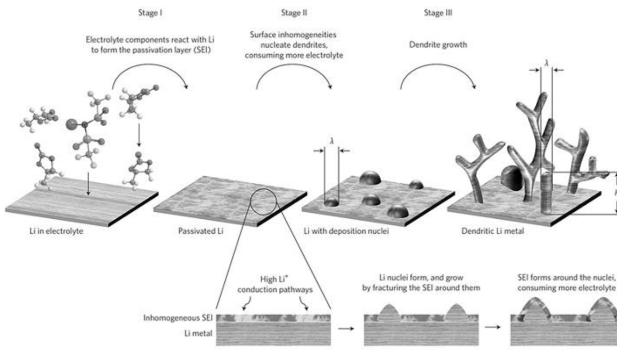

Figure 2. Schematic diagram of SEI controlling Li dendrite growth.[16]

With the continuous growth of Li dendrites, the decomposition reaction between Li metal and electrolyte also continues to occur, causing a rapid increase of overpotential. In addition, for each charging and discharging process, the growth of Li dendrites consumes a large amount of active Li metal, which inevitably leads to a decrease of capacity and low Coulomb efficiency (CE).[17] Therefore, altering the SEI structure and composition to regulate the physical and chemical properties of SEI is a key method for suppressing Li dendrites.[18]

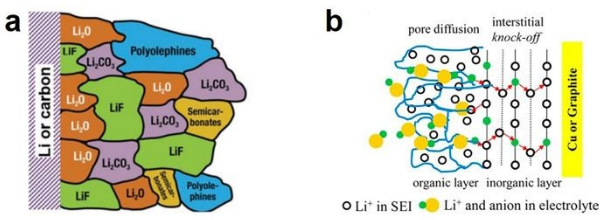

Figure 3. (a) The thermodynamic [19] and (b) kinetics of SEI repressing the growth of Li dendrites.[20]

In principle, an ideal SEI should have the following properties: SEI should have high mechanical strength, which can prevent further side reactions caused by initial Li nucleation and puncture; SEI should be conducive to Li ion conduction, thereby promoting uniform Li ion flow and achieving uniform initial Li nucleation; The SEI should be as uniform as possible to reduce heterogeneous nucleation during Li metal deposition; SEI should have high electronic insulation to reduce excessive electrolyte decomposition and the consumption of Li metal. In order to achieve the above properties, regulating the structure and composition of SEI such as introducing LiF to improve the mechanical strength of SEI has been proven effective.[19] With the increase of SEI mechanical strength, it can effectively prevent SEI from being punctured by Li metal nucleation thus reduce the growth sites of Li dendrites (Figure 3a). On the other hand, introducing components with good Li ion conductivity into the SEI can improve Li nucleation homogeneity. As more Li ions can simultaneously reach the LMA surface during the deposition process, the uniformity of initial Li nucleation is

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improved, and subsequent dendrite growth is suppressed (Figure 3b).[20] Therefore, regulating the SEI components to improve the mechanical stability, Li ion conductivity, uniformity, and other physical and chemical properties can effectively suppress the growth of Li dendrites, and improve the electrochemical CE of LMA.[21]

Inorganic-rich SEI to repress dendrites

The electrolyte is the main component involved in the formation of SEI on the LMA surfaces so that the main method to change the structure and composition of SEI is regulating the components the electrolyte solvents, Li salts, and additives.[22] Generally, inorganic-rich SEI generated by the decomposition of anions is widely regarded as having high stability and surface energy, which can effectively inhibit the growth of Li dendrites.[23] In this section, we summarized the recent researches on engineering liquid electrolyte to regulate inorganic-rich SEI in LMBs.

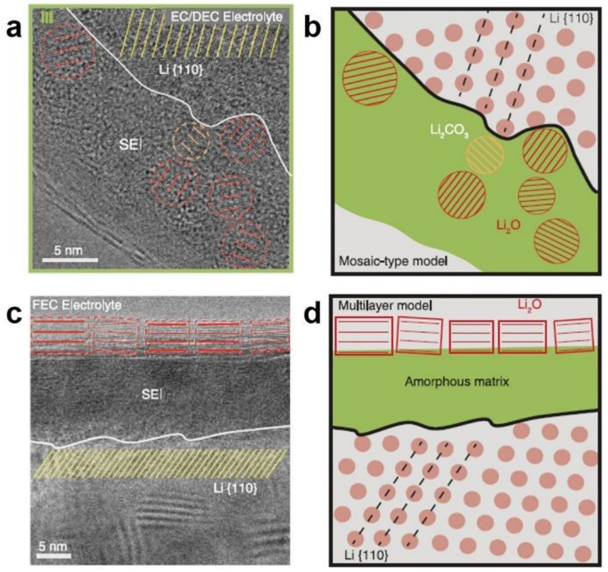

Figure 4. SEI (a, b) mosaic and (c, d) multilayer structure model.[26]

Carbonate electrolyte is widely used in Li-ion batteries in the past few decades, which usually has excellent physical and chemical properties such as high dielectric constant, high Li salt solubility, high oxidation resistance and so no. Therefore, it can provide high ionic conductivity and low resistance. However, its stability is poor on LMA surface and it cannot effectively inhibit the growth of Li dendrites. In contrast, ether electrolytes exhibit high compatibility for LMA but cannot tolerate high voltages. In order to suppress Li dendrites and improve electrochemical performance of LMBs, many studies on electrolytes have been conducted by researchers including electrolyte additive strategies, high concentration electrolytes (HCE), localized high concentration electrolytes (LHCE), and so on.[24]

Usually, the Li salt concentration in electrolytes is 0.8-1.2 M, which exhibits high ionic conductivity, lower viscosity, and low cost so that it is widely used in LIBs. However, it exhibits poor compatibility and high safety risks in LMBs. Due to the formation of more Li dendrites, the CE of LMA in dilute carbonate electrolyte is usually lower than 90.0%, resulting in poor cycling performance. That is because the SEI formed in carbonate electrolyte mainly contains heterogeneous organic alkyl carbonate lithium ($ROCO_2Li$), inorganic lithium carbonate (Li_2CO_3), lithium oxide (Li_2O), lithium fluoride (LiF), and so on.[25] Generally, those components are unevenly distributed in SEI, which is depicted by the mosaic model (Figure 4).[26] There are two distinct migration pathways for Li^+ in SEI: through the inorganic species crystals or along the grain boundaries of different components, ultimately result in the deposition of Li^+ on the anode surface (Figure 5).[27] The more complex of migration path, the more uneven of Li deposition morphology. Therefore, many studies have been devoted to improving the uniformity of species distribution in SEI to enhance the uniformity of Li metal deposition. In addition, it is also possible to improve the mechanical stability, chemical stability, and Li-ion conductivity of SEI by increasing the content of inorganic species in SEI to suppress the growth of Li dendrites.

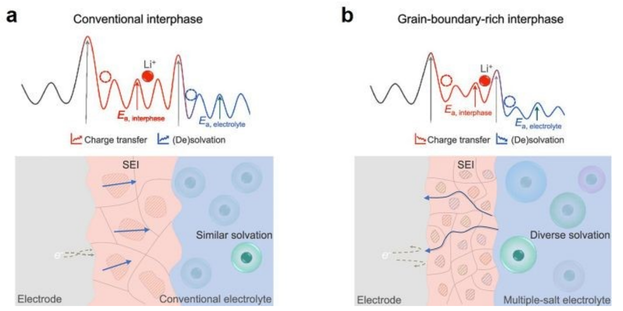

Figure 5. The migration pathway of Li ions in SEI (a) intracrystalline migration model, (b) grain boundary migration model.[27]

It is an effective method to increase the content of inorganic components in SEI through the strategy of electrolyte additives.[28] Although additives are usually present in very low amounts in electrolyte, they can effectively regulate the components of SEI. Among all additives, lithium nitrate ($LiNO_3$) exhibits excellent inhibitory effects on Li dendrites even at lower concentrations.[29] $LiNO_3$ can decompose into lithium oxide (Li_2O) and lithium nitride (Li_3N) on the LMA surface, which are the components with ultra-high ion conductivity that accelerates the transport of Li ions in SEI.[30] For example, Zhang and his colleagues increased the solubility of $LiNO_3$ in traditional carbonate electrolytes by using $LiNO_3$ as additive and CuF_2 as co solvent, promoting $LiNO_3$ participation in the formation of Li_3N-rich SEI. Compared to the blank electrolyte, the LMA with this SEI exhibits high CE and cycling stability (Figure 6a).[31] Except increasing the solubility of $LiNO_3$ in the electrolyte, integrating $LiNO_3$ into the separator or polymer molecular array can result in sustained slow release of $LiNO_3$, thus supporting $LiNO_3$ continuous participation in the formation of SEI, ultimately improve the CE and cycle life of LMA (Figure 6b, c).[32] Except

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$LiNO_3$, other nitrates also used to form Li_3N-rich SEI and inhibit the growth of Li dendrites (Figure 6d).[33] These results indicate that the method of using additives to form inorganic-rich SEI to improve its Li ion conductivity can effectively inhibit the growth of Li dendrites.

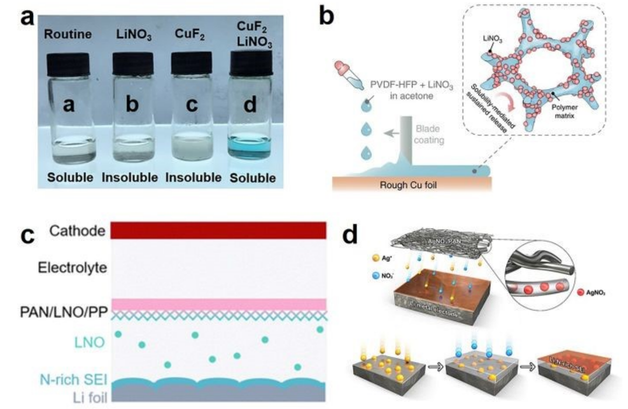

Figure 6. The methods to product Li_3N-rich SEI in carbonate electrolytes. (a) Increase the solubility of $LiNO_3$ in electrolyte, [31] (b, c) solubility mediated sustained release, [32] (d) add high solubility nitrates.[33a]

Molecular additives are also important components in forming stable SEI.[34] For example, new carbonate solvents such as fluorinated ethylene carbonate (FEC) can decomposed to produce lithium fluoride (LiF). LiF is a recognized substance that can improve the mechanical stability of SEI, which has a positive effect on the cycling performance of LMA and LMBs.[35] LiF has various positive effects on SEI, including high bandgap (13.6 eV) which can improve the electronic insulation of SEI and reduce the thickness of SEI formation, high mechanical strength can improve the mechanical and electrochemical stability of SEI, the high interfacial energy of LiF is beneficial to Li metal deposition along the interface between SEI and LMA thereby reducing dendrite growth. In addition, the formation of heterojunctions between LiF and other inorganic components can enhance the Li-ion conductivity of SEI.[36] The ability of SEI in suppressing Li dendrites based on high content of LiF can be further improved by designing high fluorine electrolyte. For example, Wang's team designed a perfluorinated electrolyte (FEC/FEM/HFE (2:6:2)) to construct a LiF-rich SEI, which induced the growth morphology of large Li particles and low porosity. This highly dense arrangement of large Li particles greatly reduces the specific surface area of the LMA and reduces the side reactions between the electrolyte and Li metal.[37] Therefore, a high CE of 99.2% was achieved in this system.

In addition to the above-mentioned additives, many additives that can produce special components such as Li_2S, LiBxOy, and LiSxOy during SEI formation have been widely studied in carbonate electrolytes.[38] For example, Zheng's team designed a new additive of vinyltrimethylsilane (VTMS) that can construct excellent SEI, greatly improving the electrochemical performance of LMBs.[39] Methyl methanesulfonate (MMDS) and 1,3-propanesultone can generate Li_2S components with high Li ion conductivity in SEI, thereby improving the uniformity of Li metal deposition and reducing dendrite growth.[40] The introduction of these additives improved the stability of SEI and Li ion conductivity, which effectively repressed the growth of Li dendrites. In addition, additives containing unique elements such as silicon, boron, and magnesium can form special SEI alloys on LMA and also exhibit inhibitory effect for Li dendrites.

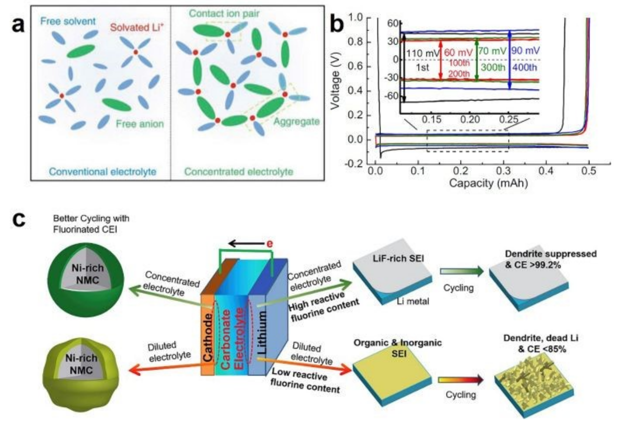

Figure 7. (a) The schematic diagram of HCEs[42] and (b) it repressing the growth of Li dendrites[43]. (c) High concentration Li salt forms inorganic-rich SEI in HCEs.[44]

High concentration electrolytes (HCEs) is a system relative to dilute electrolytes with a salt concentration exceeding 3.0 M. Due to the high Li salt concentration, it exhibits high thermodynamic stability as well as promote the Li salt participate in the formation of SEI.[41] The composition of Li ion solvation sheaths is completely different from that in dilute electrolytes in HCEs. In dilute electrolytes, Li ions are completely surrounded by solvents, but in HCE, the solvation structure of Li ions contains more anions (Figure 7a).[42] As the number of anions in the Li ions solvation sheath increases, which tends to form a highly stable anions-driven SEI and reduce electrolyte decomposition thus suppress Li dendrites. For example, in a 7.0 M LiFSI-FEC solution, the LMA exhibited a high CE of 99.6% (Figure 7b).[43] In the 10.0 M LiFSI-EC/DMC (1:1) electrolyte, more FSI anions involved in the formation of SEI with more LiF and Li_2S components, resulting in a high CE of 99.2% for the LMA (Figure 7c).[44] It is worth noting that not all high concentrations of Li salts can improve the dendrite suppression effect of LMA, and more work is needed to clarify the differences in SEI formation among different Li salts in HCEs.

Although HCEs contribute to the formation of highly inorganic SEI and effectively repress the Li dendrite growth, this electrolyte often showed low Li ion conductivity, high viscosity, poor electrode wettability and high price due to high Li salt concentration. To address these issues, localized high concentration electrolytes (LHCEs) have been proposed as alternative electrolyte systems.[45] LHCEs are typically composed of electrolytes and diluents that do not dissolve Li salts. Since diluents do not participate in Li ion solvation sheath but more anions into the Li ion solvation, achieving anion-driven inorganic-rich SEI. This high concentration effect, which does not require high salt concentration but is achieved through diluents, is called LHCEs. The commonly used diluents are fluorinated ethers such as 1,1,2,2-tetrafluoroethyl-2,2,3-tetrafluoropropyl ether (TTE) and bis (2,2,2-trifluoroethyl) ether (BTFE).[46]

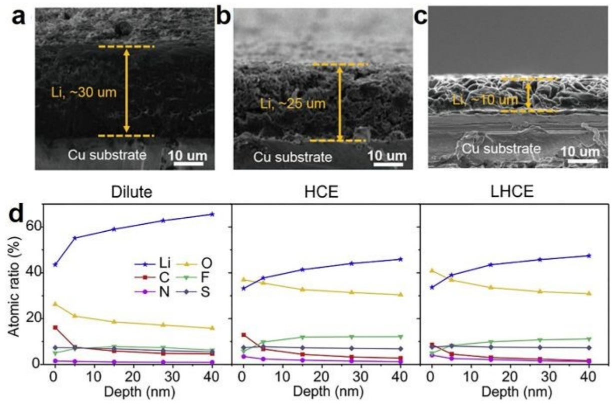

Figure 8. The thickness of Li deposition in (a) 1.0 M $LiPF_6$/EC-EMC (4:6), (b) 1.2 M LiFSI/DMC, (c) 1.2 M LiFSI/DMC-BTFE (1:2) electrolytes, respectively.[48] (d) The element distribution of SEI formed in different electrolytes.[49]

Fluorinated ethers have ultra-low viscosity, which not only reduces electrolyte viscosity and improve Li ion conductivity, but also increases the participation of anions in Li ion solvation groups thus improving the content of inorganic species in SEI.[47] Through LHCE strategy, the LMA can achieve high CE of over 99.0%. At such a high CE, it means that the LMA is deposited in the form of dendrites but in the form of large particles. For example, the 1.2 M LiFSI-DMC-BTFE (1/2) LHCEs designed by Zhang's team exhibited high CE of 99.5% for LMA, indicating the growth of Li dendrite was significantly inhibited. The deposition layer formed in the designed LHCEs is shown in Figure 8a-c, a dense Li deposition layer with a thickness of only 10 μm was achieved in LHCEs, while the deposition layer of the LMA reached 30 μm in dilute electrolyte, indicating the strategy of LHCEs effectively inhibits the growth of Li dendrites and improves the cycling stability of the LMA.[48] The high CE in these LHCEs is mainly attributed to the formation of anion-driven inorganic-rich SEI. As shown in Figure 8d, a SEI with higher Li_3N and LiF content was formed on the surface of LMA in LHCEs which enhanced the Li ion conductivity and reduced the growth of Li dendrites, thus exhibiting a high CE of 98.2%.[49] It should be noted that the inorganic-rich SEI can inhibit the growth of Li dendrites, but the current system is still difficult to achieve practical LMBs so that further research is needed. It is worth noting that the cathode material significantly influences the SEI of the Li metal anode. The properties of cathode materials, particularly the degradation products of transition metal ions, can significantly impact the formation and stability of the SEI. For example, certain transition metal ions such as Mn^{2+} form a thick, soft, and unstable SEI, which ultimately results in the degradation of battery performance. Furthermore, nickel-rich cathode materials may also cause instability of the SEI due to increased reactivity with the electrolyte, thereby affecting the cycling life and stability of the battery.

Inorganic-polymerized organic hybrid SEI to repress dendrites

Recent research has shown that highly inorganic SEI may not necessarily be beneficial, as an excessive inorganic component can lead to poor mechanical stability due to inadequate interconnection between inorganic particles. Polymerized organic components are usually flexible and can accommodate significant volume changes during the Li metal deposition process.[50] High molecular weight polymerized organic materials also exhibit high viscosity, which can strongly adhere the fine inorganic nanoparticles to the Li anode surface.[51] Consequently, the inorganic-polymerized organic hybrid structure of SEI demonstrates high stability due to the high mechanical strength of inorganic components and high toughness of organic components. This combination allows it to withstand Li metal volume expansion and inhibit the growth of Li dendrites.[52] Furthermore, the inorganic-polymerized organic hybrid SEI structure can easily form a double-layer structure, which offers greater uniformity than the "mosaic" structure and maximizes the avoidance of functional interference between different layers (Table 1). Therefore, the hybridization of inorganic and polymerized organic components is essential for achieving the ideal uniformity, flexibility, and mechanical stability of the SEI.[51b, 53]

Table 1. Comparison of Li||Cu battery performance with inorganic-rich SEI or Inorganic-polymerized organic hybrid SEI.

	Current ($mA\ cm^{-2}$)	Cycle number	CE (%)	SEI type
Ref.28b	0.5	100	94.0	inorganic-rich
Ref.29a	0.5	100	98.5	inorganic-rich
Ref.33a	1.0	160	97.5	inorganic-rich
Ref.37	0.2	500	99.2	inorganic-rich
Ref.51	0.5	300	98.1	hybrid
Ref.56b	2.5	50	97	hybrid
Ref.57	1.0	900	99.2	hybrid
Ref.59	1.0	400	99.5	hybrid

Since 2020, numerous studies have demonstrated the significance of electrolyte polymerization in the SEI, with "film-forming" serving as a fundamental mechanism to inhibit Li dendrite growth in non-aqueous electrolytes. For example, Guo et al. and Archer et al. utilized anion-induced ring opening polymerization of 1,3-dioxolane (DOL) to form pDOL polymer which exhibited high Li metal tolerance thus mitigate the adverse reactions between Li metal and electrolyte, thereby enhancing the utilization rate of active Li metal (Figure 9a).[54] However, polymer molecules typically exhibit low Li ion conductivity and poor Li affinity. To address these limitations,

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various additives such as $LiNO_3$ and AlF_3 have been introduced into pDOL to build an inorganic-polymerized organic hybrid SEI to improve its Li ion conductivity and Li affinity, facilitating uniform Li metal deposition.[54b]

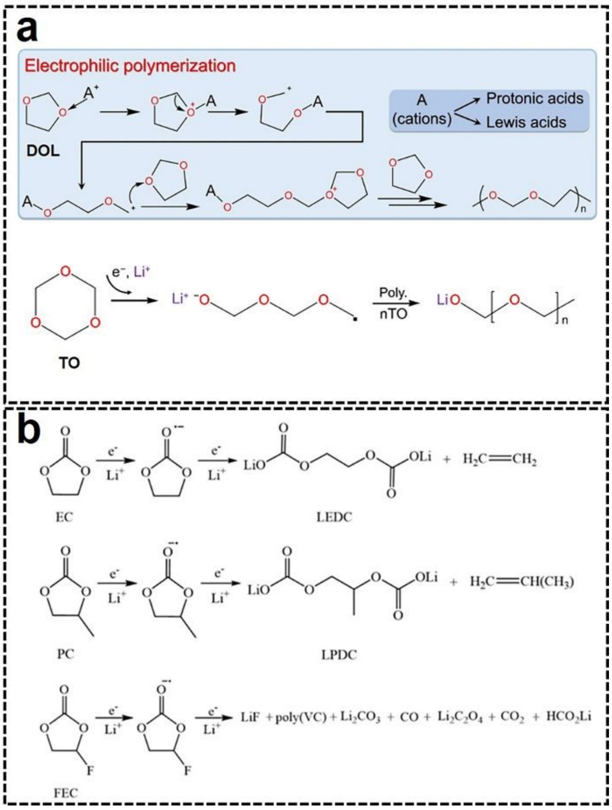

Figure 9. (a). In situ polymerization pathway of ether solvents in LMA surface.[54] (b) In situ polymerization pathways of carbonate solvents in LMA surface.[55]

For liquid electrolyte systems in LMBs which can achieve high CE, it is evident that a general common component of the electrolyte is a film-forming agent that readily undergoes polymerization. For example, cyclic carbonates in traditional carbonate electrolyte are the main components of SEI formation to produce a large number of glycol based Li decarbonate and poly-lithium carbonate by ring-opening polymerization (Figure 9b).[55] In this type of SEI, the CE of LMA can reach 95%. Chen's group developed a 1.0 M LiTFSI-VC electrolyte, which formed a stable SEI due to the polymerization of VC on the surface of LMA (Figure 10).[56] This SEI exhibits high Li-ion conductivity (1.39×10^{-6} S cm^{-1}) and high mechanical strength (34 GPa), resulting in a high CE (97.0%). it also maintains low polarization and high cycling stability even at high current densities of 5 mA cm^{-2} and 10 mA cm^{-2}. Zhao et al. utilized lithium difluorooxalate borate (LiDFOB) as additive to alter the decomposition pathway of difluoroethylene carbonate (DFEC) molecules, ensuring the formation of inorganic LiF by inducing direct defluorination of DFEC. The defluorinated DFEC is prone to polymerization into polyvinyl carbonate, which enhances the elasticity of the SEI. This polymer-interleaved LiF-dominated hybrid SEI shows high ionic conductivity and mechanical stability, effectively accelerating the kinetics of electrode reactions and facilitating more efficient reversible deposition and stripping of LMA.

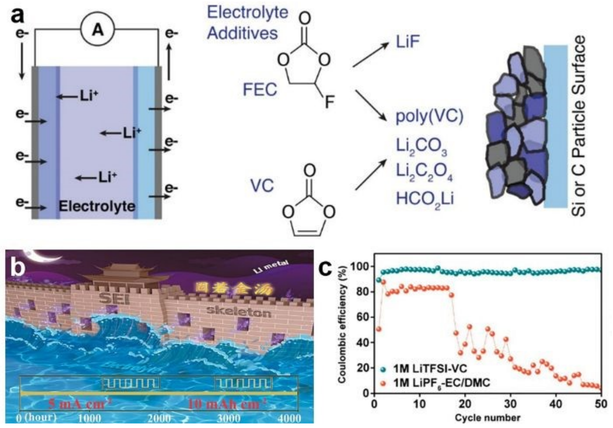

Figure 10. (a) The polymerization pathway of VC and FEC to form SEI. (b, c) Polymerization of VC effectively repressed the growth of Li dendrites and improved CE of LMA.[56]

In situ polymerization of ether solvents in can significantly inhibit the growth of Li metal dendrites.[57] Wang et al. proposed dipropylene glycol dimethyl ether, a non-toxic and non-flammable ether solvent, in Li-S@pPAN battery. [58] This solvent undergoes in situ electrochemical polymerization during the cycling process, effectively addressing the low-polarization interphase and alleviating interfacial side reactions. The electrochemical polymerization of this non-flammable electrolyte exhibited excellent stability over 3000 hours of LMA. Huang et al. also introduced an in situ polymerization of trioxane additive on the surface of LMA, which is easier to polymerize than DOL (Figure 11), customizing a dual-layer SEI structure.[59] The inner layer is dominated by LiF to enhance mechanical stability, while the outer layer contains lithium polyformalin to improve uniformity. Together, these layers synergistically facilitate reversible Li deposition/stripping with ultra-high CE of 99.4%. Above discussion indicates that the in-situ polymerization of electrolyte in LMA surface is also important for suppressing Li dendrites.[60]

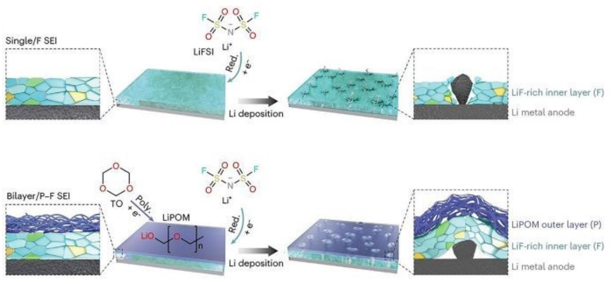

Figure 11. Schematic diagram of the bilayer SEI structure formed by the in-situ polymerization of trioxane.[60]

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The latest research suggests that the structure and composition of the SEI are usually controlled by the potential of the anode. High potential conditions tend to preferentially form organic-dominated SEI, while low potential conditions typically generate inorganic-dominated SEI.[61] Therefore, understanding the underlying mechanisms of SEI formation enables the rational design of inorganic-polymerized organic hybrid SEIs, which can more effectively suppress the growth of dendrites on lithium metal anode. This may offer a viable approach to achieving lithium anodes with Coulombic efficiency exceeding 99.5%.

Conclusions and Perspectives

Since the birth of LIBs in 1990, the accessible capacity of graphite anodes has reached its theoretical limit. Pursing higher energy density forces us to explore the possibility the LMA. However, the highly reactive nature of LMA and the associated electrolyte has faced enormous challenges for practical applications. A spontaneously formed SEI on the surface of LMA significantly influences the growth morphology of deposited Li metal and ultimately leading to the growth of Li dendrites. Therefore, the main method for suppressing Li dendrite formation entails the establishment of a stable and homogeneous SEI, which helps mitigate the non-uniform nucleation of Li metal and the subsequent rupture of SEI. Although the fundamental mechanisms by which SEI suppressed Li dendrites remain elusive, several related connections have been established:

(1). High ionic conductivity of SEI can accelerate the migration rate of Li ions, allowing more Li ions to reach the anode surface simultaneously, thereby reducing the non-uniform nucleation caused by concentration polarization. Uniform initial Li nucleation promotes subsequent uniform deposition thus reducing the growth of Li dendrites.

(2). The thermodynamic and mechanical properties of SEI mitigate the disordered growth of LMA. On one hand, the significant expansion in volume and surface area during the growth of Li dendrites results in high surface energy. So, the trend of dendrite growth can be alleviated by the enhanced thermodynamic surface energy of SEI. On the other hand, the high mechanical strength of SEI can suppress the intense stress generated by Li dendrites, thereby suppressing the growth of dendrites.

Based on the aforementioned considerations, the most pressing task in electrolyte design is to enhance the thermodynamic stability, mechanical strength, and ionic conductivity of SEI. In summary, an inorganic-polymer hybrid SEI with a dual-layer structure is likely to meet all these requirements simultaneously thus effectively suppressing Li dendrites. This approach offers a promising pathway for the development of practical LMBs in the future.

Author contributions

We strongly encourage authors to include author contributions and recommend using CRediT for standardised contribution descriptions. Please refer to our general author guidelines for more information about authorship.

Conflicts of interest

There are no conflicts to declare.

Data availability

A data availability statement (DAS) is required to be submitted alongside all articles. Please read our full guidance on data availability statements for more details and examples of suitable statements you can use.

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