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PERSPECTIVE

Electronic and Ionic Channels in Working Interfaces of Lithium Metal Anodes

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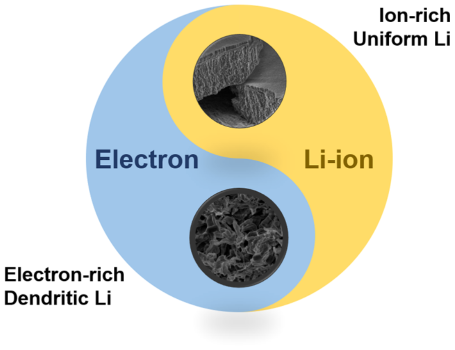
ABSTRACT: Lithium metal batteries have been considered as a promising choice to satisfy rising energy requirements for upmarket consumer electronics and electric vehicles due to the high theoretical specific capacity and most negative equilibrium potential of Li metal anodes. With regards to practical and safe batteries, interfaces in the batteries are required to be clearly perceived, especially related to Li metal anodes. In this Perspective, we describe the interfaces in the anode of Li metal batteries, mainly focusing on the electronic and ionic behavior of the solid−electrolyte interphase and mixed conducting interphase. The features of these interfaces are comprehensively recapitulated. Current and future strategies to fabricate the mixed conducting interphase are anatomized. The efficient fabrication of a composite electrode with prestored Li metal and rational ionic and electronic networks is still challenging, which further requires interdisciplinary collaboration from surface chemistry, structured materials, computation, and engineering science.



The commercialization of rechargeable lithium-ion batteries (LIBs) in the early 1990s is considered as the most significant milestone in the development of battery technologies. Since then, batteries have achieved great success in portable electronic devices, electric vehicles, and smart grids. In recent decades, however, the escalating speed in the energy density of LIBs remains rather sluggish, which severely falls short of the requirements of upmarket electronics and advanced electric vehicles. For a good rechargeable battery, the improvement in energy density has primarily driven the overall technological progress over the past 150 years—from lead−acid cells in the 1850s (40 Wh kg^{-1}), nickel−cadmium cells in the 1890s (60 Wh kg^{-1}), and nickel metal hydride cells in the 1960s (100 Wh kg^{-1}) to, finally, LIBs in the present day (170−250 Wh kg^{-1}).[1,2] Advanced next-generation battery systems are critically required.[3]

In the battery realm of beyond LIBs, Li metal batteries (LMBs) have been strongly considered due to the high theoretical specific capacity (3860 mAh g^{-1}) and the most negative equilibrium potential (−3.040 V versus standard hydrogen electrode) of the Li metal anode.[4,5] Generally, the energy density of a rechargeable battery is determined mainly by the specific capacities and operating voltages of the electrode materials. Therefore, LMBs are optimistically able to have an energy density 3−5 times higher than that of conventional LIBs.[6] However, the development of LMBs is fraught with many difficulties. Since their first appearance in the 1970s, low efficiency, poor lifespan, and battery fires related to dendritic Li deposition have accompanied LMBs. To realize the practical applications of LMBs, prominent strategies have been proposed to suppress dendritic Li deposition and protect the Li metal anode from corrosive electrolytes, such as nonaqueous electrolyte additives,[7] solid-state electrolyte (SSE),[8] and three-dimensional (3D) host materials, etc.[9]

Recently, several outstanding reviews in the scope of the strategies to suppress Li dendrite growth have been released.[10−14] However, fundamental understandings and summaries on the transport behaviors of Li ions and electrons in different interfaces are rarely involved. Actually, there is a real possibility that the future high-energy-density batteries operate as hybrids that serially combine liquid and solid electrolytes to suppress unwanted redox shuttles. This leads to additional interfaces that might significantly decrease the cycling-rate capability and lifespan.[15] In this Perspective, we focus on the interfaces of the Li metal anode and try to describe the different transport behaviors of Li ions and electrons. By decoupling the intricate relations between the cell performance and interfacial proprieties, more fundamental understandings can be proposed to shed fresh light on the design principles of high-energy-density, long-lifespan, and high-security LMBs.

When bare Li is exposed to electrolytes, immediate reactions occur between Li and solution species with time constants of milliseconds or less, forming an interface between them. The interface was first proposed by Dey in 1970[16] and named as solid−electrolyte interphase (SEI) by Peled in 1979.[17] Besides the nonaqueous electrolyte, reactions can occur between Li

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The most negative equilibrium potential of Li leads to incredible chemical activity; thus, multiple interfaces are generated due to the redox reactions between Li and electrolytes.

metal and air, as well as between Li metal and certain SSEs. The SEI films are also regarded as anode−electrolyte interphases (AEIs) and electrode−electrolyte interphases (EEIs) in some literature reports (Figure 1). On the cathode side, the EEI has the same meaning as the cathode−electrolyte interphase (CEI), which will not be emphasized herein. We focus on the substance interchange near the interfaces of anodes. Therefore, the best-known SEI is adopted to refer to the interfaces between the Li metal anode and electrolytes.

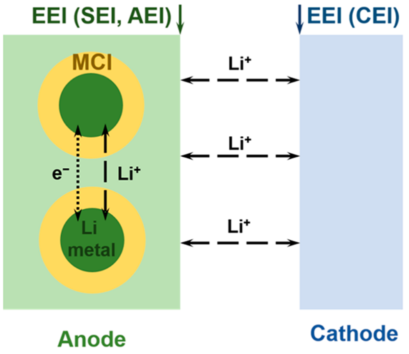

Figure 1. Schematic diagram of interfaces in the LMBs. EEI is a generic term to describe the interfaces between an electrode and electrolyte. EEI is identical to CEI on the cathode side, while it is referred to as AEI or SEI on the anode side. MCI refers to the mixed conducting interphase within the electrode and a transition layer of the SEI film.

In an electrochemical battery, the rapid transport of electrons and ions is critically important to realize a high energy density and long lifespan.[18,19] The SEI is designed to conduct Li ions rather than electrons to maximumly avoid the side reactions, and an ideal SEI film can effectively improve the cycling efficiency. Another interface within the anode framework has recently been valued, the mixed conducting interphase (MCI), which is dual-functional to transfer electrons and Li ions. Fundamental research as well as applications of the MCI in energy storage materials has been well demonstrated by Maier and co-workers.[20] These interfaces naturally coexist in a battery and synergistically determine the battery performance.

Ideally, the SEI is designed to conduct Li ions, rather than electrons, while the MCI is dual-functional to transfer electrons and Li ions. Practically, the SEI and MCI are always tightly coupled with each other.

The SEI can be formed by spontaneous chemical and electrochemical reactions of Li metal and solutions/gases. Previously, we contributed a comprehensive review on the SEI formation mechanism, their structure features, and applications in LMBs.[21] For an ideal SEI, there are two primary features: high Li ionic conductivity and electronic insulation. The ionic conductivity renders the ionic channels between the cathodes and anodes, while the electronic insulation can stop the continuous reactions between the Li metal anodes and electrolytes (Figure 2a).

There are two extensively accepted models to describe the SEI structure: the mosaic model[22] and multilayer model,[23] both of which have been experimentally confirmed.[24] In the mosaic model (Figure 2b),[22] several reductive decompositions of the electrolytes are proceeding on the negatively charged anode surface simultaneously, and a mixture of insoluble multiphase products deposits on the anode. In contrast, the SEI layer in the thickness direction is not homogeneous as well in the multilayer model (Figure 2c). The layer close to the Li metal surface contains species of low oxidation states, such as Li_2O, Li_3N, LiF, LiOH, and Li_2CO_3, labeled as the inorganic layer. The outer part of surface films is comprised of species with higher oxidation states, such as $ROCO_2Li$, ROLi, and $RCOO_2Li$ (R is an organic group related to the solvent), labeled as the organic layer. These components have an electronic transfer barrier of LiF > Li_2CO_3 > Li_2O > Li_3N and an ionic migration barrier of LiF > Li_2CO_3 > Li_2O > Li_3N (Table 1). These two models are not contradictory. An overall image for the SEI film is proposed as multilayers on the surface of Li anodes with material build blocks in each layer distributed in a mosaic form. The outer porous organic layer can take off the solvation sheath of Li ions to realize rapid Li ion diffusion in the inorganic layer and provide a SEI with flexibility as well. The inner dense inorganic layer offers electronic insulation. Most of the inorganic materials have an ultralow electronic conductivity and can inhibit the transfer of electrons from the anode to the outer electrolytes. The mechanism of ionic transfer in the inorganic layer has not been explained clearly. The pathways through the grain boundary[25] and crystal phase[26,27] both have their supporters.

A stable and mature SEI requires good electronic insulation.[30] However, not all SEI films can adequately stop electron transfer. Sometimes, the substandard SEI film exhibits some features of electronic conductivity of MCI. There are two models to describe the electronic transfer behavior of a substandard SEI. The first is the electron tunneling model.[17] When the SEI film is ultrathin (several atoms thick), electrons can tunnel through it. If its thickness evolves beyond the electron tunneling regime, the growth of SEI film stops, where MCI can be regarded as a transition stage of a robust SEI film. The SEI film formed on the Li electrode has a practical thickness ranging from a few to several hundreds of nanometers. The second is the porous model. The practical SEI does not have a homogeneous and dense structure. The unqualified SEI film can realize direct contact of electrons and electrolyte and transfer electrons through it. There are two reasons for the transformation from a good and mature SEI film to a poor and substandard one in nonaqueous electrolyte: water attack and stress release during Li plating/stripping. While dry O_2 and N_2 (99.9999 vol %) form a uniform SEI film on Li, trace water vapor (~1 mol %) disrupts this passivation and forms a porous film on Li metal that allows gas and electrolyte to penetrate and continuously react with Li.[31] Another destructive power is from stress during repeated Li plating/stripping.[32] After Li plating, the initially flat current collectors all wrinkle and the wrinkle patterns evolve from 1D to 2D patterns, which generates large stress in the Li metal anode. The naturally formed SEI film is fragile and cannot bear the compressive stress. It becomes

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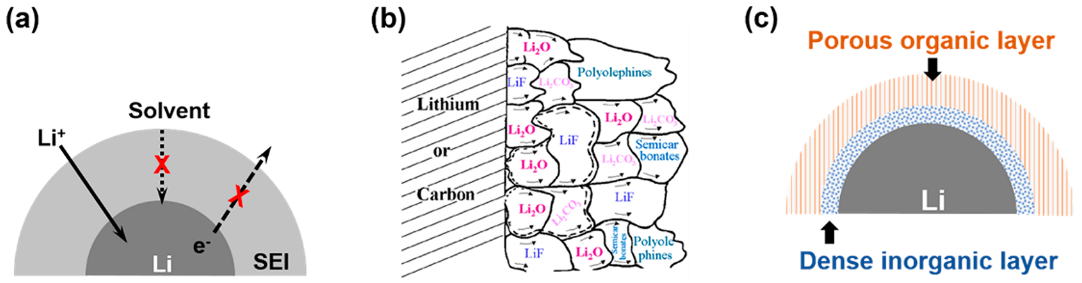

Figure 2. Features of SEI film. (a) An ideal SEI presents two primary features: high Li ionic conductivity and electronic insulation. (b) Mosaic model of SEI components. (Copyright Elsevier, reproduced with permission from ref 22). (c) Multilayered structure of the SEI film.

Table 1. Ionic and Electronic Properties of Species in a SEI Film

species	energy barriers of Li migration (eV)	band gap (eV)
Li_2O[28]	0.15	4.7
Li_3N[29]	0.007−0.038	1.1
LiF[28]	0.73	8.9
Li_2CO_3[28]	0.23−0.49	5.0

cracked and allows direct contact of the electrode/electrons with electrolyte. However, research on the relation between the structure of SEI/MCI on the Li metal surface and the stress accumulation during Li plating/stripping is less involved. Advanced characterization methods and modeling strategies are required to boost the understanding and reduce stress generation during Li plating/stripping.[33,34]

MCI can act as a transition state of the SEI, not only in the nonaqueous electrolyte but also in the SSE.[35] Due to the highly negative nature of the Li metal anode, most of the SSE (such as the solid sulfide electrolyte) can react with the Li metal anode to form an interfacial layer. Some of them are SEIs, while others are MCIs (Figure 3a). When investigating detailed information on the chemical reactions at the $Li/Li_{10}GeP_2S_{12}$ interface, an interface composed of Li_3P, Li_2S, and Li−Ge alloy is discovered.[36] However, the formed MCI film is not stable and will further transfer electrons to the SSE. For these SSEs, interfacial coating with a stable SEI film between them are necessary for a robust LMB.

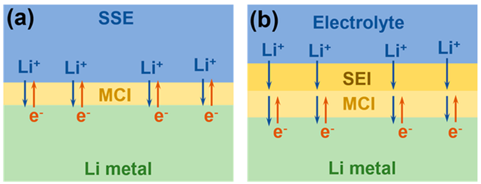

Figure 3. Role of MCI in the interfacial film of the Li metal and electrolyte. (a) MCI between the Li metal and SSE. (b) MCI as an inner layer between the SEI and Li metal.

Recently, the MCI film is found to act as an inner layer of the SEI film to improve the stability and ionic conductivity (Figure 3b). Yu et al. reported that Li can be stored at the grain boundary regions reversibly. This type of interfacial storage is an intermediate state between the insertion capacity and storage in supercapacitors, which is beneficial to realize rapid Li ion transfer and storage.[37] MCI can work similarly as a temporary reservoir for Li interfacial storage. Different from the classical SEI film without electronic conductivity, these interfacial films, such as a Sn−Li hybrid layer,[38] $Li_{13}In_3$ layer,[39] Cu/Li_3N layer,[40] Ni/LiF layer,[41] $Li_{0.35}La_{0.52}[V]_{0.13}TiO_3$/Li hybrid layer,[42] and copper acetate additive-induced SEI film,[26] can conduct some electrons while still render superior cell performance. In this regard, the MCI film has a little overlap with the inorganic layer of the SEI film. Some viewpoints for this MCI layer are that it can buffer the Li ion concentration gradient and level secondary current distribution on the Li metal surface. However, the exact functional mechanism and structure features of the MCI film underneath of the SEI are not clearly known.

Therefore, the issues of electronic and ionic channels in the interfacial film on a Li metal surface are extremely complicated. It is generally acknowledged that the interfacial film must not be with electronic conductivity, while some films with inner electronic channels can also render superior cycling performance. A mixed conducting interfacial film introduces Li metal anode protection. A clear understanding of its roles and elaborate fabrication of a functional film are very helpful to achieve efficient LMBs.

> Electronic conductivity is not favorable for the interface between Li metal and electrolyte, while both the electronic and ionic channels are required to finish the electrochemical redox within the electrode materials.

During cell discharge, electrons and Li ions are requested to reach the electrode surface to finish the electrochemical redox and provide energy (Figure 4a).[43] Therefore, within the electrode materials, a mixed conducting framework with electronic and ionic channels is indispensable to allow electron and Li ion diffusion. This is critically applicative for graphite anodes and routine cathodes. For the traditional Li metal anode, the pathways for electrons and Li ions are separate: Li ion diffuses at the interface between the Li metal and the electrolyte, while electron transfer occurs in the interface between the Li metal anode and the current collector (Figure 4b). However, recent investigations have demonstrated that common Li foils are almost impossible to plate/strip uniformly, and the host is a prerequisite for a safe and efficient Li metal anode. When introducing a host to the Li metal anode, the electronic and ionic channels are not separated and always connected with each other (Figure 4c).

For a stable and long-lifespan LMB, a mixed conducting framework is critically required, where the ionic and electronic channels are nearly tightly associated. Ionic supply is realized by the bulk electrolyte (nonaqueous electrolyte or SSE) and the interfacial film (refer to SEI) of electrode materials in the mixed

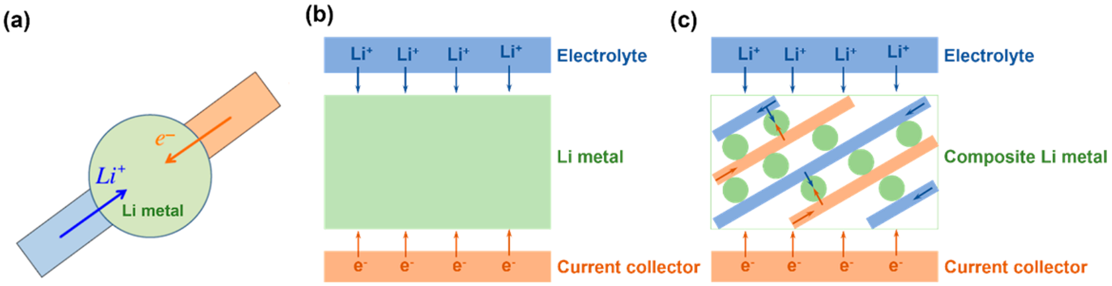

Figure 4. Electronic and ionic channels in the mixed conducting framework. (a) Electrons and Li ions are a must for electrochemical redox (Copyright Science, reproduced with permission from ref 43). Electronic and ionic channels in the (b) common Li foil and (c) 3D composite Li metal electrode.

conducting framework, while the electronic supply is accomplished by the conductive additive agents. The electron pathways can be achieved easily, while the ionic supply is always insufficient, especially in the SSE. In the nonaqueous electrolyte, the mixed conducting framework can easily be realized due to the superior wettability of nonaqueous electrolyte on the anode surface. There is a huge problem for solid-state batteries whether the interconnected ionic pathways within the interior electrode are in the cathode or anode part.

The electronic pathways in the mixed conducting framework are contributed by the conductive host. During plating, heterogeneous deposition of Li ions results in dendritic growth of Li metal, while heterogeneous dissolution of Li dendrites leads to dead Li, which is out of the electronically conductive matrix. Xiao and co-workers claimed that a dead Li layer gradually grew inward toward the bulk (fresh) Li metal, which evolved into a messy and highly resistive layer.[44,45] Before the cell failure of the dendrite-induced short circuit, the impedance of the battery escalates sharply and the service life is terminated early. The powdery dead Li significantly increases the possibility of fire and largely raises the danger. To reduce the evolution of dead Li, an interconnected conductive matrix is required within the Li metal anode. Additionally, these porous matrices are demonstrated to play roles in relieving the volume changes[46] and suppressing dendrite growth.[47,48] Similar to graphite anode, it can be nearly alleged that the Li metal anode is not able to be practically applied until there is an efficient host material.

The so far reported hosts with the electronic channels can be divided into two categories: nanostructured and microstructured materials. (1) The nanostructured hosts have a high specific surface area, which can largely reduce the areal current density and render the uniform deposition of Li metal.[48] The nanoscale platform is also convenient to achieve a uniform distribution of lithiophilic sites by element doping (such as nitrogen).[49] The lithiophilic doping must be homogeneous within the host framework; otherwise, Li ions tend to deposit and accumulate in these sites, leading to dendritic Li growth. Guo and co-workers pioneeringly proposed that Li prefers to deposit on the mouth of channels, and the situation becomes intractable in the areas with high curvature at high rates (Figure 5a).[50] The preferential deposition behavior is caused by two factors: (i) The current density on the mouth of the microchannels is obviously larger than that on the upper surface and inside of channels of the porous Cu; (ii) the nanoscale pores exhibit a large resistance of Li ion diffusion from the pore mouth to the inside pores. This preferential deposition of Li ions results in a low utilization rate of interior space of the host materials, which limits the areal capacity confined in the nanopores. (2) The microstructured host has a relatively large pore and matrix size at 50−200 μm. Li ions are more inclined to deposit in the pores, which can effectively relieve the volume change and dendrite growth issues (Figure 5b). However, the present microstructured hosts generally have a heavy weight and a large thickness, which reduce the specific capacity based on the whole electrode.[51] Its excess capacity versus the cathode dwindles the energy density as well.[52] An efficient conductive host is required for practical applications of a Li metal anode, which cannot only primarily transfer electrons but also suppress the dendrite growth, dead Li formation, and volume change and not reduce the high-capacity feature much as well.

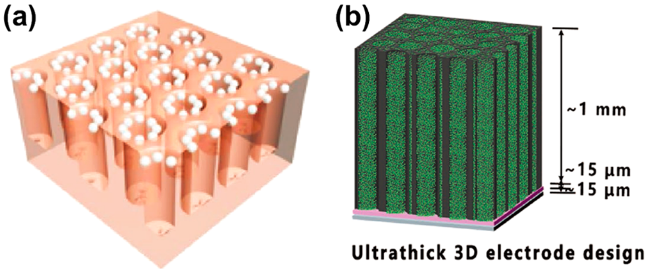

Figure 5. Conductive hosts for Li metal. (a) Li preferential deposits on the mouth of channels (Copyright Wiley-VCH VerlagGmbH&Co. KGaA, reproduced with permission from ref 50). (b) Thick electrode of the Li metal anode; 1 μm of Li is equal to a specific capacity of ∼0.2 mAh cm^{-2}, while 1 mm of Li is ∼200 mAh cm^{-2} (Copyright Wiley-VCH VerlagGmbH&Co. KGaA, reproduced with permission from ref 52).

The ionic pathways in the mixed conducting framework are contributed to by the bulk electrolyte (nonaqueous electrolyte or SSE) and the interfacial film (SEI). The nonaqueous electrolyte and SSE both can adequately transfer Li ions, and some advanced SSEs can indicate a high room-temperature ionic conductivity approaching that of the nonaqueous electrolyte (10^{-2} S cm^{-1}).[53] For the SSE, its issue is mainly in the fabrication of a uniformly distributed ionic framework within a 3D electronic matrix because SSE cannot facilely wet the interior pores of the conductive matrix as the nonaqueous electrolyte does. Though some flowable interfaces of ionic channels have been achieved by poly(ethylene glycol) gel electrolyte (Figure 6a),[54] it is really tough to obtain an interconnected and uniformly distributed inorganic ceramics SSE in the mixed conducting framework. It is a wise method to presynthesize a porous SSE framework and melt Li metal into its pores to obtain a composite Li metal anode. Hu's group has pioneered the work to design a porous SSE by a tape-casting strategy, which sheds fresh insight on the composite Li metal anodes and all-solid-state LMBs.[55]

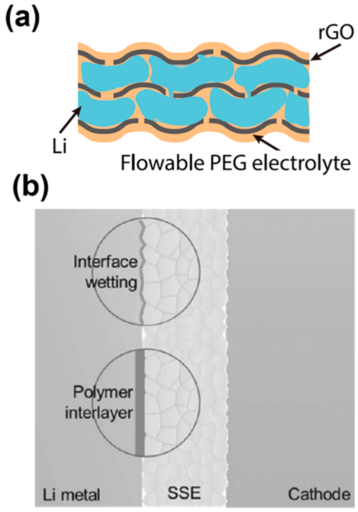

Figure 6. Mixed conducting framework in the solid-state Li metal anode. (a) Flowable interface contributed by a polymer electrolyte.[54] (b) Lithiophilic modification to the SSE surface to render tight contact with a Li metal anode (Copyright Wiley-VCH VerlagGmbH&Co. KGaA, reproduced with permission from ref 59).

Due to the highly reactive nature of the Li metal anode, nearly all electrolytes (whether nonaqueous electrolytes or SSEs) form an interfacial film (SEI) on the anode surface. High ionic conductivity and long-term stability are the primary requirements for the SEI film. There are extensive experiences of SEI design in nonaqueous electrolytes, such as electrolyte additives,[56] highly concentrated electrolytes,[57] nanostructured electrolytes,[58] etc. On the contrary, research on the design of this SEI film between a Li metal anode and the SSE is extraordinarily rare. The research focuses on the lithiophilic coating on SSE to render tight contact with the Li metal anode to reduce interfacial impedance (Figure 6b).[59] Though the bulk SSE is able to achieve high room-temperature ionic conductivity, it is challenging to run a superior room-temperature solid-state LMB due to the high interfacial impedance between the Li metal and SSE. Much expertise on the SEI design principles for SSEs can be learned from nonaqueous electrolytes.

Though proposed for more than 50 years, the Li metal anode lost the opportunity to the public because the graphite anode achieved better safety and long-term cycling performances in the 1990s. Nanoscience and nanotechnology in the current century provide emerging possibility in practical applications for the Li metal anode, while they introduce more interfaces in the electrode materials relative to the macroscopic materials. An interface with extraordinary stability on the time and space scales is critically required to render rapid electron or ion transfer, finally realizing uniform deposition of Li metal and superior cycling performances.

A MCI can be found in the inner layer of a SEI film and a mixed conducting framework can be found within the electrode materials to realize an excellent electronic and ionic pathway. The role of MCI in the SEI has not been clearly investigated, while mixed electronic and ionic channels within the electrode materials are indeed required. Each electronic and ionic pathway can be productively fabricated by conductive host materials, electrolytes, and SEI designs. However, an anode network with Li metal materials and unblocked electronic and ionic pathways is still a hurdle for researchers in the field of energy storage materials. There are several points should be strongly concerned: (1) The electronic framework should be realized on a proper scale, which cannot only fully use the pore volume for a Li metal host during Li plating but also not increase the futile weight much. (2) The all-SSE (such as the ceramic) has poor operability due to its mechanical fragility, and it alone is really tough to run a long-term Li metal anode. The compositing strategy of the ceramic with a polymer or nonaqueous electrolyte seems capable for practical LMBs. (3) The molten Li infusion and hot-pressing at high temperature are relatively practical methods to fabricate a composite Li metal anode with a mixed conducting framework. However, there are many safety concerns and operational complexity. Novel strategies are required to fabricate the composite electrode. (4) The additional mixed conducting framework must not increase the weight of the composite electrode much to preserve the high-capacity feature of the Li metal anode. Not only for the anodes, these principles are also suitable for the cathodes of LMBs. The composite electrode framework requires novel surface electrochemistry and engineering attempts, which will shed new light on material design for next-generation energy storage systems.

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