



Lithium Metal Anode Materials Design: Interphase and Host

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Abstract

Li metal is the ultimate anode choice due to its highest theoretical capacity and lowest electrode potential, but it is far from practical applications with its poor cycle lifetime. Recent research progresses show that materials designs of interphase and host structures for Li metal are two effective ways addressing the key issues of Li metal anodes. Despite the exciting improvement on Li metal cycling capability, problems still exist with these methodologies, such as the deficient long-time cycling stability of interphase materials and the accelerated Li corrosion for high surface area three-dimensional composite Li anodes. As a result, Coulombic efficiency of Li metal is still not sufficient for full-cell cycling. In the near future, an interphase protected three-dimensional composite Li metal anode, combined with high performance novel electrolytes might be the ultimate solution. Besides, nanoscale characterization technologies are also vital for guiding future Li metal anode designs.

Keywords Lithium metal anode · Interphase · Host · Electrolyte · Cryo-EM

1 Introduction

Secondary battery systems based on lithium (Li)-ion chemistries have achieved great success with their broad applications in portable electronics, electric vehicles and grid storage during the past few decades [1]. However, future development of Li-ion batteries is reaching their limit primarily due to the intrinsically low specific capacities of both the anodes and cathodes.

Li metal, with its lowest electrode potential (-3.04 V vs. the standard hydrogen electrode) and highest theoretical specific capacity (3860 mAh g^{-1}), is the ultimate anode choice that can satisfy the increasing demand for high energy density secondary batteries [2]. But practical applications of Li metal anodes have been plagued by its notoriously poor cycling capability. This is originated from many reasons, two among which are the most critical. Firstly, Li metal spontaneously reacts with electrolytes, forming an unstable solid electrolyte interphase (SEI). Cracks on the nanometer-thick

SEIs during Li metal cycling expose fresh Li metal with concentrated local Li-ion flux, leading to dendritic growth and continuous loss of active material and electrolyte. Secondly, Li metal shows huge volume fluctuation during cycling compared with graphite anodes with well-defined frameworks accommodating Li species [3]. This greatly aggravates the fracture and reconstruction of the SEI, leading to accelerated electrolyte consumption and capacity decay.

Numerous works have been reported focusing on these two most critical issues of Li metal. For Li metal/electrolyte interphases, researchers attempted to stabilize the SEI via various approaches, including SEI formation by electrolyte additive decomposition as well as artificial interphase material engineering. With respect to the volume changing issue, we recently introduced the idea of artificial “host” structures to accommodate the Li metal and minimize the thickness fluctuation during cycling. After continuous progress on Li cycling performance, materials design for interphases and hosts has been widely acknowledged as a promising approach to realize the practical applications of Li metal, although further breakthroughs are still demanded. In this perspective, we will first summarize representative research advancements on the materials designs for Li metal/electrolyte interphases and host structures and then outline the challenges that still remain. Finally, we will offer insights for possible future solutions that can address these challenges.

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2 Li Metal Interphase Design

2.1 Interphases Tuned by Electrolyte Additives

Interphase quality is crucial for Li metal anodes. A chemically stable, mechanically strong interphase can effectively prevent Li metal from excess reaction with electrolytes, suppressing corrosion and capacity loss. An intuitive idea is to tune the SEI composition through electrolyte additives. This methodology facilitated numerous success in Li-ion battery chemistries [4], thus being considered as an

important approach also for Li metal anodes. LiNO_3 is one of the most effective and widely used additives [5, 6]. It is capable of tuning SEI compositions with its high reduction potential around 1.7 V versus Li^+/Li [6] (Fig. 1a). With LiNO_3 additives, Li metal grew into uniform pellets instead of dendrites (Fig. 1b, c), and high Coulombic efficiency (CE) over 98% can be achieved. With further added Li polysulfide, even more homogeneous Li deposition morphology and cycling performance were achieved [7, 8]. Other additives, such as fluoroethylene carbonate (FEC) [9, 10], halogenated salts [11, 12] and CsPF_6 [13], are also vigorously studied.

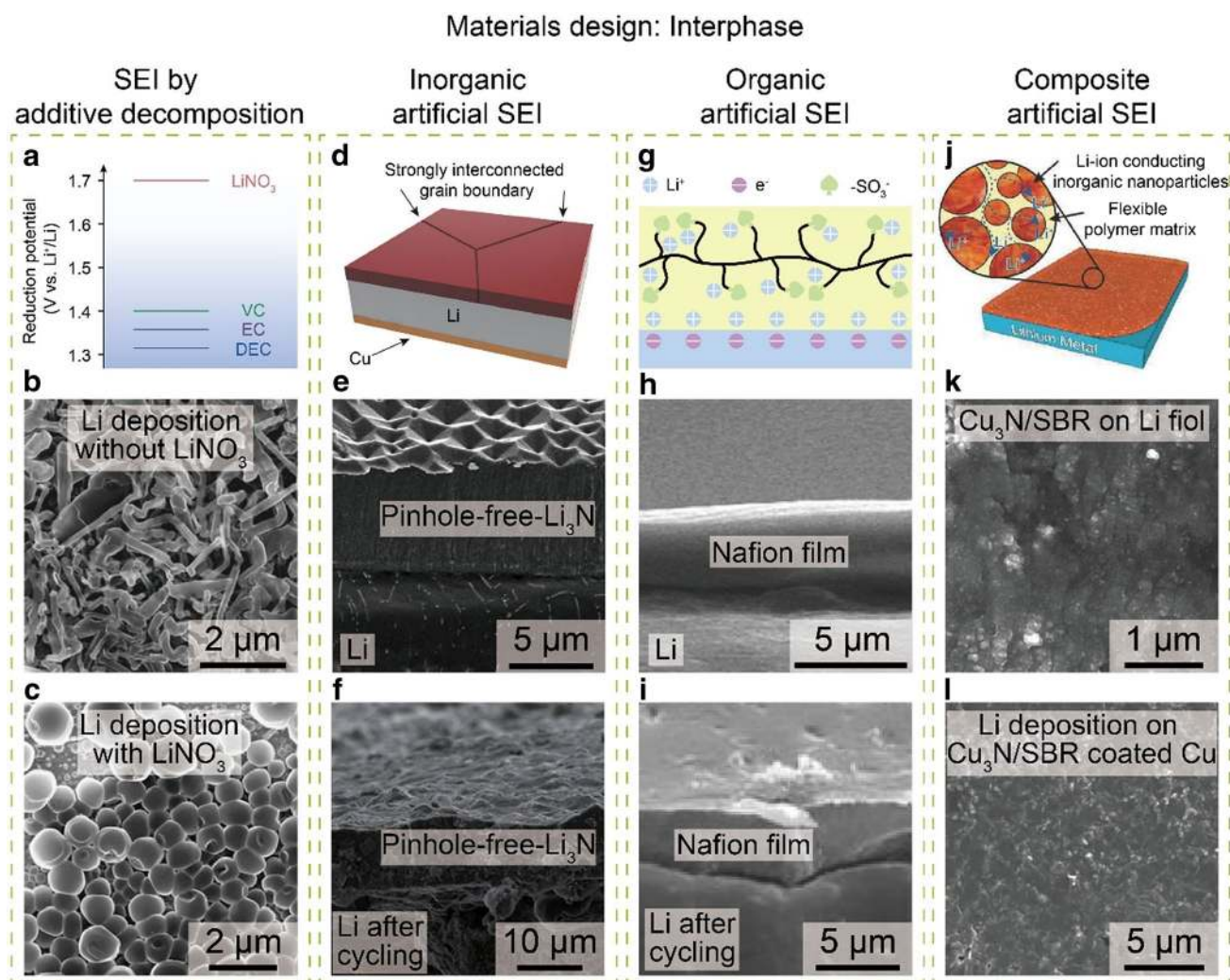


Fig. 1 Materials design for Li metal interphases. **a** Reduction potential comparison between LiNO_3 and various solvents. **b** Li deposition morphology in electrolytes without LiNO_3 . **c** Li deposition morphology in electrolytes with LiNO_3 . **d** Schematic illustration of large grain Li_3N artificial SEI. **e** SEM image of pinhole-free Li_3N on Li metal. **f** SEM image of Li metal with Li_3N after 100 cycles in a Li/LTO cell.

g Schematic illustration of Nafion coated on Li metal. **h** SEM image of the interphase between Li foil and the Nafion film. **i** Morphology of Li protected by Nafion after ten cycles at 10 mA cm^{-2} . **j** Schematic illustration of a composite SEI composed of Cu_3N and SBR. **k** Morphology of the composite SEI coated on Li foil. **l** Morphology of Li deposited onto artificial SEI coated Cu foil

2.2 Artificial SEIs

Besides tuning SEIs through electrolyte additive decomposition, researchers also fabricated various kinds of artificial SEIs onto Li metal before battery assembly [14]. These artificial SEIs usually possess better chemical or mechanical properties than SEIs formed through electrolyte decomposition, leading to improved cycling lifetime. Inorganic artificial SEIs such as hollow carbon spheres [15], BN and graphene [16], LiF [17–19], Li₃N [20], Li₃PO₄ [21] and Al₂O₃ [22] have been reported. In particular, a highly oriented pinhole-free Li₃N was introduced serving as artificial SEIs [20] (Fig. 1d). This layer of Li₃N showed excellent mechanical strength and Li-ion conductivity, leading to homogeneous Li metal plating (Fig. 1e, f) and prolonged cycling. Organic artificial SEIs also attracted broad interests with their good flexibility. Kim et al. used a few-micrometer-thick Li-Nafion coatings as artificial SEIs [23] (Fig. 1g), achieving compact Li metal morphology after cycling (Fig. 1h, i). Numerous other organic artificial SEIs such as Li polyacrylic acid (LiPAA) [24] and polyacetylene [25] were also reported. Combining the advantages of inorganic and organic species, the composite artificial SEI simultaneously has excellent mechanical strength and considerable flexibility. For example, Cui et al. mixed Cu₃N nanoparticles with styrene–butadiene rubber (SBR), achieving an artificial SEI which is simultaneously Li-ion conductive, mechanically strong and flexible [26] (Fig. 1j–l).

3 Li Metal Host Design

Despite the advancements in interphase engineering, the importance of maintaining constant Li anode dimensions has long been overlooked. Large volume fluctuation induces aggravated SEI cracking issues even with well-designed artificial interphases. Pioneered by Cui's group at Stanford University, artificial “host” frameworks are brought up as an efficient approach to minimize the Li metal anode volume change during cycling.

3.1 Hosts with Pre-stored Li

Molten Li infusion is commonly used for the synthesis of host structures with pre-stored Li before battery assembly. Cui et al. firstly found that reduced graphene oxide (rGO) [27] (Fig. 2b, e), fabricated through the spark reaction between GO (Fig. 2a, d) and molten Li metal, possessed excellent lithophilicity, and molten Li was able to infiltrate in between the nanogaps of an rGO film driven by capillary force. Using this composite Li anode (Fig. 2c, f), thickness fluctuation was effectively reduced to only ~20% without severely diminishing its specific capacity (Fig. 2h,

i). And homogenous Li deposition (Fig. 2g) and prolonged cycling stability especially under high current densities were realized. Inspired by this work, a series of host structure designs based on carbon [28], polymer [29], ceramic [30] and numerous other types of frameworks was developed and reported by utilizing the melt infusion method and achieved exciting improvements on Li anode performance.

3.2 Hosts Without Pre-stored Li

This category of host structures can also be considered as three-dimensional current collectors. In this scenario, Li metal is deposited into a well-designed high surface area scaffold instead of the planar Cu foil. Local current density can be effectively reduced, and better Li plating morphology can be achieved. In a representative work, submicron size amorphous carbon hollow spheres with gold nanoparticles inside were fabricated [31] (Fig. 2j). Li metal can first alloy with the gold seeds forming Li_xAu (Fig. 2k) [32, 33] and then precipitate out into the spheres as Li metal (Fig. 2l). In this way, electrode volume was well maintained, and deposited Li metal was also protected from corrosion with electrolytes by the carbon shell. As a result, a high CE of ~98% in carbonate electrolytes was realized (Fig. 2m). Other high surface area host structures based on copper fiber [34], graphene [35–39], carbon fiber [40], graphite [41] and carbon nanotubes [42] were also reported.

4 Challenges

4.1 Deficient Robustness of Interphase Materials

Despite the engineering efforts on the Li metal interphases, they seem insufficient to function consistently during long-term cycling. For Li-ion insulating materials such as LiF [17], it is most likely Li-ion transfers through the pinholes on the interfacial layer during deposition. In this scenario, the electrolyte will also be likely to leak through the coatings, reacting with fresh Li metal beneath. For Li₃N and other highly Li-ion conductive materials, Li-ion can transfer through the coating easily [20]. However, a typical 3 mAh cm⁻² Li metal plating equals to 15 μm thickness fluctuation, which the brittle inorganic materials cannot sustain. As a result, the intact coating will possibly crack after continuous cycling, losing its protection for Li metal. Polymeric interphase designs seem to be able to accommodate the thickness fluctuation with their excellent flexibility [14]. But they usually either swell or slowly dissolve into the electrolyte. In either case, Li metal is still exposed to the solvent molecules, leading to reduced but non-negligible material loss. Further innovations are necessary to address long-term cycling robustness of Li interphases and more detailed

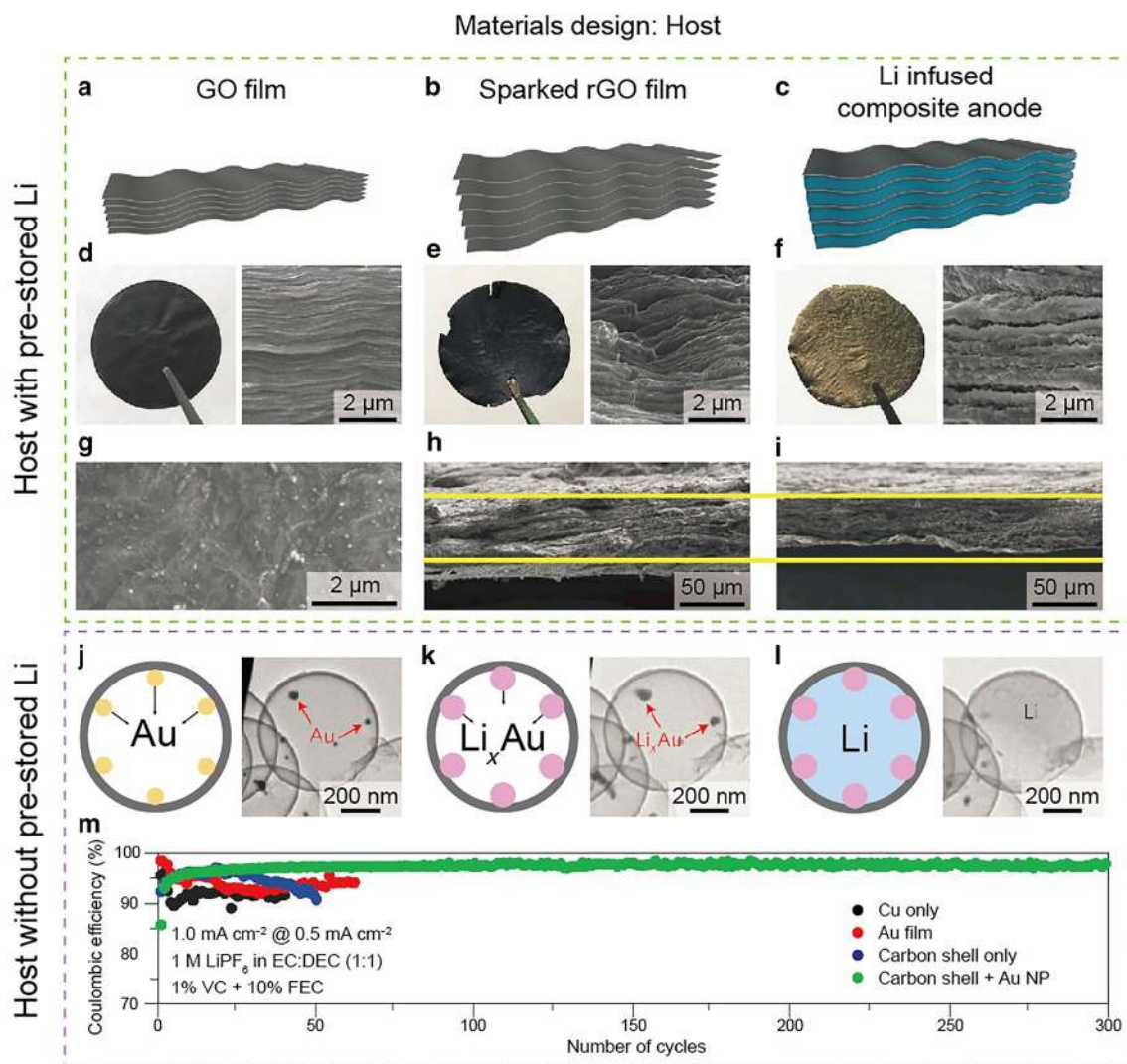


Fig. 2 Materials design for the Li metal host. **a–c** Schematic illustration of the pristine GO film (**a**), the sparked rGO film (**b**) and the Li-infused composite anode (**c**). **d–f** Digital photographs and SEM images of the pristine GO film (**d**), the sparked rGO film (**e**) and the Li-infused composite anode (**f**). **g** Morphology of Li/rGO after ten cycles under 1 mA cm⁻² and 1 mAh cm⁻². **h** Cross-sectional image

of the Li/rGO film. **i** Cross-sectional image of the Li/rGO film after stripping all the Li metal away. **j–i** Schematic and TEM images of pristine seeded hollow carbon spheres (**j**), carbon spheres after Li alloys with the Au seeds (**k**) and carbon spheres after filled with Li metal (**i**). **m** Coulombic efficiency result under 0.5 mA cm⁻² and 1 mAh cm⁻²

characterizations need to be done for interphase compositions after cycling to determine whether the designed materials still function as expected.

4.2 Exposure of Li Metal to Electrolytes in Host Structures

Host scaffolds are indeed capable of reducing volume fluctuation during cycling and suppressing SEI breakdown, while simultaneously boosting the fast charging capability with their high surface areas [2]. However, this increased surface area also introduces several key issues. In particular, many host frameworks have an open structure, exposing the high

surface area Li to electrolytes and causing accelerated corrosion. As a result, Li capacity decay might not be slowed down to a great extent even with the minimized thickness fluctuation. Some of the host designs, such as amorphous carbon spheres, provide certain amount of protection for Li metal inside the nanocapsules [31]. In an ideal scenario, SEIs should only form on the outer surface of the carbon spheres and do not reform during subsequent cycling. However, this ideal scenario is difficult to achieve, due to the fracture of some of the spheres attributed to their brittle nature. Clearly, better host designs with broadened functionalities still need to be engineered. Not only do electrode dimensions need to remain constant within the host framework, such framework

also needs to be mechanically strong and chemically stable enough to offer continuous protection for Li metal deposited from corrosion with electrolytes.

4.3 Coulombic Efficiency

Coulombic efficiency (CE) is the key indicator for the long-term cycling capability for an electrode material. CE of bare Li foil usually stays at ~90% or even lower in baseline carbonate-based electrolytes, and that has long been preventing it from commercialization in secondary batteries. In Table 1, we summarize some of the CE results reported in

recent works. We can see that with novel designs for interphase and host structures, CE can be effectively improved. However, most of current CE over 98.5% is achieved with ether-based electrolytes, which are highly flammable and usually not compatible with high voltage cathodes [43]. CE in carbonate-based electrolytes can still hardly surpass 98.5%. These results are still far from sufficient for practical usage. Even with excess Li sources, we expect the average CE of Li anodes to be at least 99.5% for 300 cycles to be commercially practical. It is without doubt that grand advancements are called for to further boost the CE of Li metal anodes in the near future.

Table 1 Coulombic efficiency for representative works on Li metal anodes

	CE (%)	Current density (mA cm ⁻²)	Areal capacity (mAh cm ⁻²)	Cycle numbers	Electrolyte	
Interphase design	98.10	1	1	200	1 M LiPF ₆ in EC/DEC (1:1) with saturated LiNO ₃ [6]	
	99.10	2	1	400	1 M LiTFSI in DOL/DME (1:1) with 5 wt % LiNO ₃ and 0.18 M Li ₂ S ₈ [7]	
	98.30	1	1	–	1 M LiPF ₆ in FEC [9]	
	92.00	2	1	100	1 M LiTFSI in DOL/DME (1:1) [11]	
	97.50	1	1	150	1 M LiTFSI in DOL/DME (1:1) with 1% LiNO ₃ and 0.1 M Li ₂ S ₈ [15]	
	97.00	0.5	1	50	1 M LiPF ₆ in EC/DEC [16]	
	96.30	0.5	1	100	1 M LiPF ₆ in EC/DEC (1:1) [19]	
	97.40	1	1	100	1 M LiPF ₆ in EC/DEC (1:1) with 10 wt % FEC [26]	
	Host design	96.50	1.5	3	75	1 M LiPF ₆ in EC/DEC (1:1) with 2 wt % VC [27]
		99.10	1	2.2	120	1 M LiTFSI in DOL/DME (1:1) with 1 wt % LiNO ₃ [28]
96.40		1.5	3	65	1 M LiPF ₆ in EC/DEC (1:1) [29]	
98.00		0.5	8	~80	1 M LiTFSI in DOL/DME (1:1) with 1 wt % LiNO ₃ [30]	
98.00		0.5	1	300	1 M LiPF ₆ in EC/DEC (1:1) with 10 wt % FEC and 1 wt % VC [31]	
98.50		0.5	1	50	1 M LiTFSI in DOL/DME (1:1) with 1 wt % LiNO ₃ and 0.005 M Li ₂ S ₈ [34]	
93.00		0.5	0.5	50	0.5 M LiTFSI and 0.5 M LiFSI in DOL/DME [35]	
98.00		0.5	1–10	–	1 M LiPF ₆ in EC/DEC (1:1) with 10% FEC and 1% VC [36]	
99.10		0.5	3	100	10 M LiFSI in DMC [36]	
98.00		1	1 mA cm ⁻²	200	1 M LiTFSI in DOL/DME (1:1) with 5% LiNO ₃ [37]	
Host + interphase design	98.40	–	–	50	1 M LiPF ₆ in EC/DEC (1:1) [41]	
	92.40	1	2	80	1 M LiPF ₆ in EC/DEC (1:1) [42]	
	97.40	1.65	3.3	150	1 M LiPF ₆ in EC/DEC (1:1) with 10 wt % FEC and 1 wt % VC [44]	
	96.00	2	1	100	1 M LiPF ₆ in EC/DEC (1:1) with 10 wt % FEC and 1 wt % VC [45]	
	99.00	0.5	1	500	1 M LiTFSI in DOL/DME (1:1) with 5 wt % LiNO ₃ [45]	
	Novel electrolytes	98.50	1	1	500	4 M LiFSI in DME [46]
		99.20	0.5	1	–	1.2 M LiFSI in TEP/BTFE (1:3) [47]
		99.30	0.2	1	250	10 M LiFSI in EC/DMC (1:1) [48]
		99.60	0.25	0.5	400	7 M LiFSI in FEC [49]

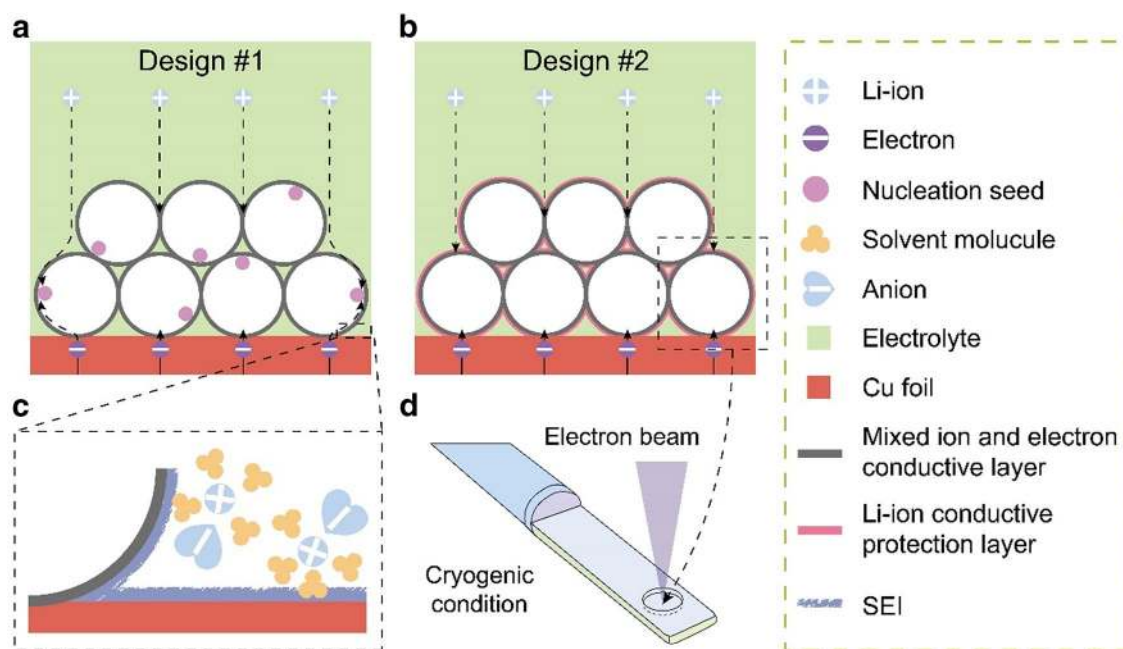


Fig. 3 Future possibilities for Li metal. **a, b** Ideal designs for Li metal with host frameworks and interphase protections. **c** Schematic of higher-quality SEI formation by using novel electrolyte designs.

d Schematic showing the importance of microscopy technology for future designs of Li metal

5 Future Opportunities

5.1 Combining Interphase and Host Engineering

As discussed above, interphase engineering cannot accommodate the thickness fluctuation during cycling, while host scaffolds cannot offer surface protection for Li metal. So the synergy of interphase design on a three-dimensional host structure appears to be a most reasonable approach to ultimately solve the issue. Recently, there have been some attempts along this line of thinking. For example, an over-lithiation method was used for the AlF_3 template to form a composite Li anode [44]. With this design, nearly no volume change can be observed during Li stripping. Meanwhile, LiF nanoparticles at the interphase promote homogeneous Li deposition. However, there is no complete protection for Li metal and it can still be partly exposed to electrolytes. In another work, Al_2O_3 was uniformly coated onto carbon spheres by using atomic layer deposition (ALD) to further prevent electrolyte leakage into the spheres [45]. In this way, Li metal can be basically isolated from contact with electrolytes during cycling and maintains a constant volume as well. Nevertheless, Al_2O_3 is unstable to Li metal and will gradually decompose, so that the CE in carbonate-based electrolytes is still not satisfying. For future research work, we here outline two ideal structural designs for Li metal anodes (Fig. 3a, b). In both cases, a well-designed and compact mixed ion and electron conductive interfacial layer

(for example, graphene) is needed for Li metal protection to prevent it from direct exposure to electrolytes. During cycling, it is most vital to guarantee that Li metal deposits inside the host structure. In the first design, Li nucleation seeds are dispersed inside the structure to lower the nucleation overpotential for Li metal (Fig. 3a). In this way, Li can be preferentially plated inside the framework. In the second design, a layer of Li-ion conductive but electron-insulating material is uniformly coated to prevent electrons being conducted to the outer surface (Fig. 3b). Note that the adhesion between the two protection layers must be robust to prevent Li deposition in between. Comparing these two approaches, the latter one seems to be more promising. This is because in the first design, when Li metal is not totally stripped during previous cycling, the nucleation site will not function as expected. So it will be crucial to search for a Li-ion conductive but also stable material serving as the protection layer in the future. One more critical issue that needs to be addressed is that when electrolytes cannot penetrate the interfacial layer, there will be a significant pressure drop when Li metal is stripped away from the scaffold. This requires: (1) the mechanical strength (i.e., Young's modulus) of the interphase layers to be good enough; (2) certain structural configuration design to guarantee that the scaffold does not collapse. These requirements call for elaborative explorations on various material synthesizing methods to optimize the host properties.

5.2 Electrolyte Optimization

The commercialized carbonate-based electrolytes are still being widely used in the testing of Li metal. However, these electrolytes are optimized for graphite anodes but not for Li metal. Li metal shows improved cycling lifetime in ether-based electrolytes, which are plagued by the low oxidation potential and flammability. An optimized electrolyte offers high-quality SEI and better protection for Li metal. Recently, a series of novel electrolytes has been reported [46–49]. Most of them are composed of highly concentrated fluorinated molecules, providing an SEI with much amplified ratios of inorganic fluorine species on the SEI of Li metal. Further studies are demanded focusing on the innovation of electrolytes to boost the cycling capability of Li metal. Note that the ultimate realization of Li metal anodes might need a collaborative strategy. This means that the better electrolytes can also be combined with artificial interphase and host designs, providing reinforced SEI protection for the composite Li anodes (Fig. 3c).

5.3 Nanoscale Characterizations

Despite the vigorous research on SEIs, their nanoscale compositions have never been clearly resolved until the recent application of cryogenic transmission electron microscopy (Cryo-EM) on battery materials [50]. For the emerging high performance electrolytes and artificial SEIs, we should not only know that they improve Li metal performance, but also the reason why they are effective. Therefore, it will be meaningful to characterize the interphases in these works with Cryo-EM technology (Fig. 3d), along with electrochemical and spectroscopic analysis. Only in this way, common structural features can be concluded to be beneficial for Li metal cycling, guiding future innovation and designs for the Li metal interphase.

In conclusion, material designs for Li metal interphase and host structures are two effective ways addressing the existing issues of Li metal anodes. They have proved to be effective but still face several challenges yet to be overcome. Collaborative, instead of unitary, strategies are needed to solve the complex problems of Li metal. Combining artificial interphase design with host frameworks as well as better electrolyte innovations might be the ultimate approach for the realization of its practical application in secondary batteries.

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