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Review

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Modulating the lithiophilicity at electrode/electrolyte interface for high-energy Li-metal batteries

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Abstract

Lithium-metal anodes show significant promise for the construction of high-energy rechargeable batteries due to their high theoretical capacity (3860 mAh g^{-1}) and low redox potential (-3.04 V *vs.* a standard hydrogen electrode). When Li metal is used with conventional liquid and solid electrolytes, the poor lithiophilicity of the electrolyte results in an unfavorable parasitic reaction and uneven distribution of Li^+ flux at the electrode/electrolyte interface. These issues result in limited cycle life and dendrite problems associated with the Li-metal anode that can lead to rapid performance fade, failure and even safety risks of the battery. The lithiophilicity at the anode/electrolyte interface is important for the stable and safe operation of rechargeable Li-metal batteries. In this review, several factors that affect the lithiophilicity of electrolytes are discussed, including surface energy, roughness and chemical interactions. The existing problems and the strategies for improving the lithiophilicity of different electrolytes are also discussed. This review helps to shed light on the understanding of interfacial chemistry *vs.* Li metal of various electrolytes and guide interfacial engineering towards the practical realization of high-energy rechargeable batteries.

Keywords: Rechargeable batteries, Li-metal anodes, lithiophilicity, electrode/electrolyte interface

INTRODUCTION

Rechargeable lithium-ion batteries based on intercalation electrodes are now able to deliver a cell-level specific energy of > 300 Wh kg^{-1} to meet the power requirements of consumer electronics and automobiles. For further improving the energy density, rechargeable batteries that operate based on the use of metallic lithium as an anode material have shown promise, yet the practical realization of rechargeable Li-metal batteries is hindered by rapid failure and safety issues regarding the Li-metal anode. The unsatisfactory performance of Li-metal anodes originates from the unstable structural and chemical evolutions at the anode/electrolyte interface, which include infinite volume variation, the formation of unstable solid electrolyte interphases (SEIs) and the growth of Li dendrites. To improve the performance of Li-metal anodes, efforts have been made to regulate the chemical compositions and structures of the electrolyte[1-3] and the Li-metal anode[4] to reshape the SEI[5,6] and to rebuild the current collector[4,7-9]. The lithiophilicity of electrolytes at the anode/electrolyte interface was studied as it significantly affects the uniformity of Li deposition/dissolution at the interface. In the case of non-uniform Li deposition/dissolution, dendrite nucleation/formation occurs and can leads to severe performance decay[10-12]. To improve the electrochemical stability at the interface, researchers have turned to lithiophilic materials with the purpose of facilitating uniform Li nucleation[13].

For a given material, its lithiophilicity can be modulated by adjusting the surface energy, surface roughness and chemical interactions with Li metal. Surface energy has a major impact on the lithiophilicity of the electrolyte and is highly correlated with the chemical compositions of the SEI. Surface roughness, according to the Wenzel model, can significantly influence the lithiophilicity[14]. This model follows the concept of super-wetting materials according to Su *et al.*[15]. Although the actual surface often deviates from the Wenzel model, modulating the surface roughness has proved to be an effective method to tune the lithiophilicity in recent decades[16]. For practical applications, roughness can be modulated by forming hierarchical micro-/nanoscale structures. Wang *et al.*[17] reported that Ni foils and foams exhibit different lithiophilicity for liquid Li due to their different surface morphologies. In addition to the surface energy and roughness, lithiophilicity can be regulated by introducing additional chemical interactions at the interface. For example, in solid-state Li-metal batteries, an interlayer capable of alloying with metallic Li is effective in improving the interfacial contact between the Li anode and the solid electrolyte[18-23].

The creation of a lithiophilic anode/electrolyte interface is desirable for the stable operation of a rechargeable Li-metal battery. In liquid-electrolyte-based Li-metal batteries, poor lithiophilicity often leads to inhomogeneous Li-ion distribution and dendrite formation[24]. A lithiophilic electrolyte helps to improve its wetting on the Li metal surface, promotes the formation of a homogeneous SEI and reduces continuous electrolyte consumption during battery cycling[25]. In solid-state Li-metal batteries, a lithiophobic interface leads to high interfacial resistance and rapid dendrite nucleation and propagation through the solid electrolyte, and therefore, accounts for the low critical current density[18-23]. To achieve optimal battery performance, the study of lithiophilicity enhancement between the Li anode and electrolytes is crucial.

This review aims to enrich the current understanding of lithiophilicity at the anode/electrolyte interface in liquid electrolyte-based and solid-state rechargeable Li-metal batteries [Figure 1], as well as its impact on battery performance. For liquid electrolyte-based batteries, strategies are provided to improve the interfacial

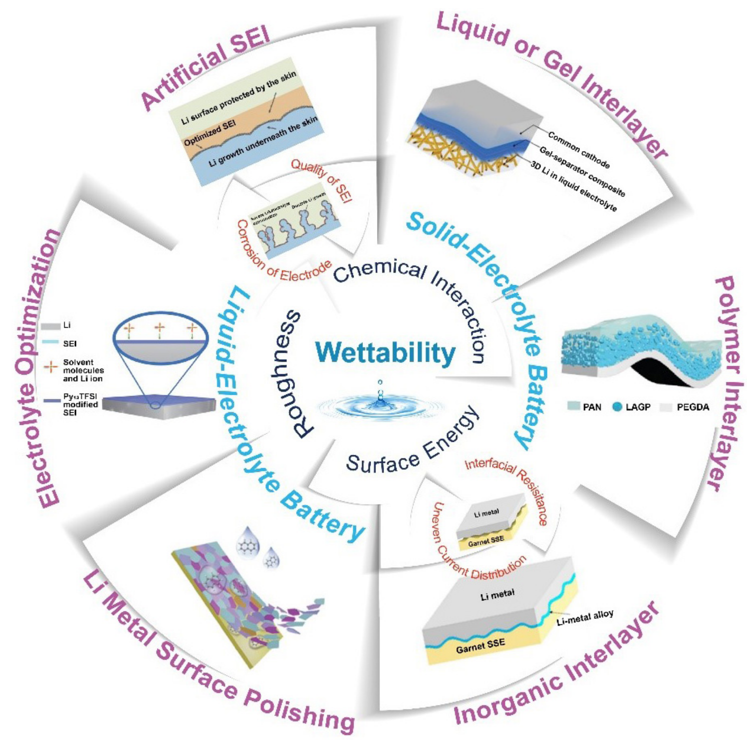

Figure 1. Schematic diagram illustrating the lithiophilicity-related studies in rechargeable Li-metal batteries with both liquid and solid electrolytes. Reproduced with permission from Ref.[23] (Copyright 2017, American Association for the Advancement of Science), Ref.[26] (Copyright 2016, Wiley-VCH), Ref.[36] (Copyright 2017, American Chemical Society), Ref.[45] (Copyright 2018, Elsevier), Ref.[64] (Copyright 2019, Wiley-VCH) and Ref.[72] (Copyright 2019, Wiley-VCH).

wetting, such as optimizing the compositions of the SEI and modifying the Li metal surface or the structures of the host materials. For solid-state batteries, we provide effective strategies to ameliorate the lithiophilicity of solid electrolytes so that we can address the interfacial challenges and offer insights to improve the battery performance.

LITHIOPHILICITY OF LIQUID ELECTROLYTES

The high reactivity of Li metal with electrolytes and the formation of SEI layers represent driving forces to help improve the interfacial contact between Li and electrolytes. However, the continuous reaction during the cycling process leads to excessive SEI formation and severe electrode corrosion. The construction of a stable SEI layer that possesses good lithiophilicity to Li, strong mechanical properties and stable electrochemical stability is vital to enhancing the interface and battery performance. In this section, we discuss various strategies, including the introduction of *in-situ* and reactive SEIs and polishing of the Li metal surface for homogeneous SEI formation. Taking advantage of the host structure with good lithiophilicity to Li, the suppressed Li dendrites and volume change show a positive effect in improving the electrochemical stability of Li metal.

Building lithiophilic and (electro)chemically stable SEIs

The high reactivity of metallic Li inevitably results in the decomposition of the electrolyte and SEI formation on the Li metal surface. The generated SEI is easily cracked due to the hostless volume variation of Li metal, which results in the continuous consumption of electrolytes/Li and performance fade of the anode with long-term cycling. Therefore, a lithiophilic SEI layer constructed on the surface of Li metal, which helps homogenize the distribution of nucleation sites for Li deposition and suppresses continuous electrolyte decomposition, is vital for boosting battery performance. At present, the strategies of SEI optimization are mainly focused on the manipulation of electrolyte chemistry and reactive artificial SEI design. The evaluation of the effectiveness of building lithiophilic and (electro)chemically stable SEIs is summarized in Table 1.

Manipulation of electrolyte chemistry

The chemical compositions of the SEI layer derived from *in-situ* electrolyte decomposition are highly dependent on the electrolyte components. Reasonable optimization of these components to achieve desirable strength and stability of the SEI is thus important for improving the interfacial lithiophilicity.

In-situ SEIs

It has been reported that a hybrid electrolyte consisting of an N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide (Py_{13}TFSI) ionic liquid and ether solvents assists the formation of a stable SEI on the Li-metal anode. As a result, the Li anode shows a high coulombic efficiency (CE) of 99.1% after 360 cycles at 1 mA cm^{-2}, which indicates the effective suppression of Li dendrites and corrosion, as shown in Figure 2A[26]. Using pure fluoroethylene carbonate (FEC) as the solvent, Yan *et al.*[27] constructed a dual-layered SEI consisting of compact organic components ($ROCO_2Li$ and ROLi) and inorganic components (Li_2CO_3 and LiF). It protected the Li-metal anode from electrolyte corrosion and helped to regulate the Li deposition behavior. In addition, Yan *et al.*[27] reported that a passivation layer could be formed via immersing Li metal in the FEC solvent. After treatment, the Li/Li-symmetric cells showed stable cycling for over 1500 h at 0.1 mA cm^{-2} in a 1 M $LiPF_6$/acetonitrile electrolyte. Different from the pure FEC solvent, Fan *et al.*[28] proposed an all-fluorinated electrolyte composed of 1 M $LiPF_6$ in a mixture of FEC, 3,3,3-fluoroethylmethyl carbonate and 1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether (HFE) (2:6:2 by weight). The all-fluorinated electrolyte formed a highly fluorinated interface with a thickness of 5-10 nm to prevent the electrolyte oxidation and transition metal dissolution and therefore ensure stable cyclability of the battery (when paired with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ and $LiCoPO_4$, the CEs are 99.93% and 99.81%, respectively).

The SEI layers derived from electrolyte decomposition naturally have a benign affinity with Li metal. However, the *in-situ* SEIs are too fragile to adapt to the volume change of Li and prevent dendrite growth. Furthermore, they are less efficient in regulating the nucleation of Li metal. Therefore, *in-situ* generated SEIs are suggested to accompany other interfacial modification strategies to improve battery performance.

Reactive artificial SEIs

As a result of the poor electrochemical stability of SEIs derived from the decomposition of conventional electrolytes, artificially designed SEIs that show favorable lithiophilicity has been proposed. However, these coating layers must be chemically/electrochemically stable and mechanically strong to achieve the effect of "1 + 1 > 2"[29].

With the merits of high mechanical strength and ionic conductivity and good lithiophilicity, some inorganic protective layers (such as P-based protective layers[30,31]) have been widely studied as protective artificial layers to inhibit Li dendrites and regulate the Li-ion transport. To acquire a stable inorganic SEI layer, Li *et al.*[32] proposed an inorganic Li_3PO_4 layer by the *in-situ* reaction of polyphosphoric acid with Li metal. On the one hand, this layer could quickly spread on the electrode surface to form a smooth and uniform coating. On the other hand, the uniform Li_3PO_4 SEI layer exhibits high chemical stability without breakage/repair during the Li deposition/dissolution process [Figure 2B][32]. Using the same soaking method, Guo *et al.*[33] prepared a Li_3PO_4 layer on the Li-metal anode of a Li-oxygen battery. With the

Table 1. Summary of the improvement of lithiophilicity in liquid electrolytes

			Lithiophilic and (electro)chemically stable SEI				
Strategy	**Ref.**	**Method**	**Interfacial resistance (before cycling)**	**Interfacial resistance (after cycling)**	**Polarized potential (after cycling)**	**Li-Cu efficiency**	**Cycle life**
***In-situ* SEI**	[26]	Ionic liquid assisted SEI	~24 Ω after resting 2 h	~32 Ω after resting 48 h	-	~99.1% after 360 cycles (1.0 mA cm^{-2}, 3 mA h cm^{-2})	360 cycles at 0.5 mA cm^{-2}, 1 mA h cm^{-2}
	[27]	Dual functional SEI	186 Ω (after a 52 h standing)	174 Ω (after a 52 h standing)	360 mV after 25 h (5.0 mA cm^{-2}, 0.5 mA h cm^{-2})	98.3% (1.0 mA cm^{-2})	90 h at 5.0 mA cm^{-2}, 0.5 mA h cm^{-2}
	[28]	FEC derived passive SEI	-	-	~20 mV after 700 h (1.0 mA cm^{-2}, 0.5 mA h cm$^{-2)}$	-	700 h at 0.1 mA cm^{-2}, 1 mA h cm^{-2}
	[29]	All fluorinated electrolyte SEI	-	-	~78 mV after 500 h (0.2 mA cm^{-2}, 1 mA h cm^{-2}) Li|Cu battery	> 99% after 500 cycles (0.5 mA cm^{-2}, 2 mA h cm^{-2})	500 h at 0.2 mA cm^{-2}, 1 mA h cm^{-2} Li|Cu battery
Reactive artificial SEI	[33]	Inorganic Li_3PO_4 SEI	-	80 Ω after 24 h in Li|Li battery	-	-	600 h at 0.5 mA cm^{-2}, 1 mA h cm^{-2}
	[35]	Single-ion-conducting Li_3PS_4 SEI	20 Ω cm^{-2}	5 Ω cm^{-2} after 10 cycles	~120 mV 400 h (4 mA cm^{-2}, 1 mA h cm^{-2})	-	400 h at 4 mA cm^{-2}, 1 mA h cm^{-2}
	[36]	Skin-grafting SEI	~90 Ω	130 Ω after100 cycles	~30 mV after 300 h (0.5 mA cm^{-2}, 1 mA h cm^{-2})	98.3% after 200 cycles (0.5 mA cm^{-2}, 1 mA h cm^{-2})	Over 300 h at 0.5 mA cm^{-2}, 1 mA h cm^{-2}
	[37]	LiPAA SEI	~160 Ω	~90 Ω after 50 cycles	-	-	700 h 0.5 mA cm^{-2}
	[38]	PECA-based artificial SEI	~60 Ω after resting 1 day	~70 Ω after resting 7 days	-	-	Capacity retention of 93% at 2 C for 500 cycles in $LiFePO_4$|Li
	[39]	Li_xSiS_y/Nafion film	-	-	46 mV initial 30 mV after 1400 h 1 mA cm^{-2}, 1 mA h cm^{-2}	-	1400 h at 1 mA cm^{-2}, 1 mA h cm^{-2}
	[40]	LixSiSy protection layer	-	-	~25 mV at 0.1 mA cm^{-2}, 1 mA h cm^{-2}	-	2000 h at 0.1 mA cm^{-2}, 1 mA h cm^{-2}
	[41]	Armored MCI film	55 Ω	67 Ω after resting 300 h	180 mV initial 80 mV over 830 h at 2.5 mA cm^{-2} 0.5 mA h cm^{-2}	-	830 h at 2.5 mA cm^{-2}, 0.5 mA h cm^{-2}
	[42]	PTMEG-Li/Sn alloy hybrid layer	14 Ω after resting 0.5 h	22 Ω after resting 24 h	30 mV after 1000 h at 0.1 mA cm^{-2} 1 mA h cm^{-2}	-	1000 h at 0.1 mA cm^{-2}, 1 mA h cm^{-2}

synergistic effects of DMSO, $LiNO_3$ and LiI, the Li_3PO_4-protected Li anode exhibited excellent electrochemical stability and no mossy or dendritic Li was found during the cycling process. To create a uniform SEI that binds tightly with Li metal, Pang *et al.*[34] developed a single-ion-conducting Li_3PS_4 SEI layer formed by soaking Li foil in a dimethoxyethane (DME) solution with a trace amount of electrolyte additive complex (Li_2S_6-P_2S_5). This thin amorphous Li_3PS_4 layer had a high Li^+ transference number of 1, which effectively promoted Li^+ transport and avoided the presence of a strong electric field to obtain a dendrite-free morphology.

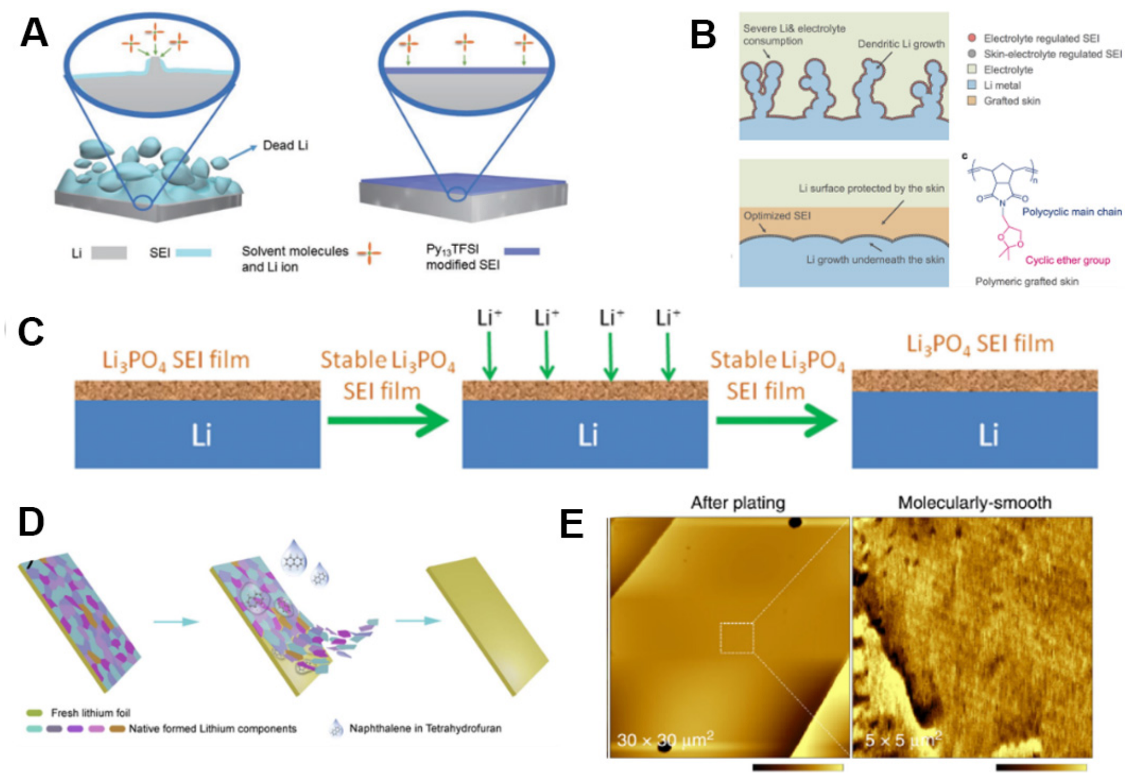

Figure 2. (A) Surface structure of Li metal in a 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) ether-based electrolyte and an optimized hybrid electrolyte by using hybrid N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide (Py13TFSI) and ether electrolyte in rechargeable Li-metal batteries[26]. Copyright 2016, Wiley-VCH. (B) Li_3PO_4-modified Li metal anode exhibiting a smooth and uniform surface after Li plating/stripping[32]. Copyright 2015, Wiley-VCH. (C) Different interfacial structural characteristics of bare Li metal and Li metal coated with polymer skin[35]. Copyright 2017, American Chemical Society. (D) Preparation process of polished Li foil in a naphthalene solution[44]. Copyright 2018, Elsevier. (E) AFM characterization showing the morphology of polished Li metal surfaces after plating in the electrolyte of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of dimethoxyethane/1,3-dioxolane (DME/DOL, v/v=1:1)[45]. Copyright 2018, Nature Publishing Group.

Organic protective layers are favored for their high flexibility and lithiophilicity to resist volume changes and maintain the integrity of the SEI. A skin-grafting strategy was proposed to prepare chemically and electrochemically active poly((N-2,2-dimethyl-1,3-dioxolane-4-methyl)-5-norbornene-exo-2,3-dicarboximide) on Li metal [Figure 2C][35]. The polymer layer showed a high volume fraction of cyclic ether groups, which had good lithiophilicity and could avoid an excessive parasitic reaction between the Li metal and electrolyte. Furthermore, Li *et al.*[36] designed a Li polyacrylic acid (LiPAA) SEI layer via an *in-situ* reaction between Li metal and PAA. Due to the high binding ability and stretchability of the LiPAA polymer, the formed SEI could effectively address the dynamic volume change of Li metal during Li plating/stripping by adapting and regulating the interface. Therefore, the side reactions and Li dendrite growth could be avoided and stable cycling of 700 h could be obtained in Li/Li-symmetric cells. Wang *et al.*[13] reported a porous and lithiophilic polymer coating induced by the phase separation of polyvinylidenefluoride-polyacrylonitrile (PAN) blends, which promoted uniform Li deposition and rapid Li^+ diffusion.

Organic-inorganic hybrids not only have high mechanical strength (inorganic layer) but also high flexibility and lithiophilicity (organic layer), so that they provide a promise and feasible strategy to improve the interfacial stability. Based on this concept, an artificial SEI layer prepared from the *in-situ* polymerization of ethyl α-cyanoacrylate (ECA) monomer precursors in the presence of $LiNO_3$ additives was proposed[37]. The CN^- groups from ECA and the NO_3^- groups from $LiNO_3$ could react with the Li metal to generate an inner inorganic nitrogenous interface layer, combined with the outer poly(ethyl α-cyanoacrylate) (PECA) layer. This organic-inorganic protective layer could facilitate ionic conductivity and restrain the volume change caused by the Li plating/stripping process. Additionally, for Li-S batteries, Jin *et al.*[38] proposed a double-layered artificial SEI-Li_xSiS_y/Nafion composite layer, consisting of an organic lithiated Nafion layer facing towards the electrolyte and an inorganic Li_xSiS_y layer facing towards the Li metal. The soft Nafion layer provided flexibility to maintain the structural integrity of the SEI and to prevent the shuttling of polysulfide anions. The rigid Li_xSiS_y layer showed high ionic conductivity and mechanical strength to inhibit Li dendrite growth. It is noteworthy that the Li_xSiS_y layer was directly grown on the Li metal surface, based on the following two *in-situ* reactions, so that it ensures intimate contact with the electrode[39]:

$$Li + Li_2S_8 = Li@Li_2S_x \tag{1}$$

$$Li@Li_2S_x + SiCl_4 = Li@Li_xSiS_y \tag{2}$$

In particular, it has been reported that materials with a high bulk diffusion coefficient of Li^+, such as LiF/Cu[40] and Sn[41], are able to facilitate rapid Li^+ transport and protect Li metal from dendrite formation. In a recent work by Yan *et al.*[40], a mixed ionic-electronic conducting interphase (MCI), consisting of LiF and Cu, was formed on the Li metal surface through an *in-situ* displacement reaction between copper fluoride (CuF_2) and Li. The MCI showed excellent Li storage ability at the grain boundaries of LiF/Cu and a high Li^+ conductivity, as well as high mechanical strength to suppress Li dendrite growth. The $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$|Li cell with the MCI film was able to deliver an extremely high CE of 99.5% with a long lifespan of 500 cycles. Jiang *et al.*[41] proposed a facile method to construct an artificial hybrid SEI consisting of poly(tetramethylene ether glycol) (PTMEG) and a Li/Sn alloy, which provided abundant Li^+ diffusion channels due to the Li vacancies in the Li/Sn alloy and a strong affinity for Li because of the abundant C-O bonds in the polymer. The treated Li-metal anode showed a much smaller contact angle (27°) with ether electrolytes than that for water (70 °C). Therefore, the treated Li maintained good activity and capacity retention in Li-S and Li-$LiFePO_4$ (LFP) full cells.

Artificial SEIs constructed on the surface of Li metal can combine the advantages of organic and inorganic materials to regulate Li-ion transport and inhibit Li dendrites and therefore exhibit better battery performance than *in-situ* SEIs. However, artificial SEIs still express a deficiency in flexibility and mechanical strength. More importantly, artificial SEIs do not solve the fundamental problems of Li metal, such as the huge volume change and formation of dead Li.

Chemical treatment of Li metal surface

The high reactivity of Li metal with an electrolyte easily gives rise to the formation of various surface contaminants, such as Li_2O, Li_2CO_3 and LiOH, which usually lead to poor lithiophilicity, inhomogeneous surface morphology and SEI growth. Since these contaminants are poor electronic/ionic conductors, their accumulation on the surface of Li metal inevitably leads to high interfacial impedance[42]. Therefore, it is necessary to remove the surface contaminants from the Li metal foil before using them in rechargeable batteries.

The chemical polishing of Li metal foil has proved to be an effective method to remove the surface contaminants. For example, a macroscopically flat surface of Li metal could be obtained after pure acetone[43] or naphthalene solution[44] [Figure 2D] treatment based on the Li-solvent reactions. However, the above strategies failed to provide desirable smoothness at the microscopic scale and the formed SEI was too fragile to inhibit the growth of Li dendrites. To address this problem, the electrochemical polishing method has been proposed to smooth the Li metal surface and modulate the SEI composition simultaneously. A multi-step electrochemical polishing procedure was carried out in a conventional ether electrolyte, 1 M LiTFSI-DME/DOL (v:v = 1:1), by a potentiostatic stripping and galvanostatic plating process. A primarily smooth foil surface and the initial stage of SEI formation were achieved by Li-metal dissolution and electrolyte reduction. The metallic Li deposition and further reduction of the electrolyte then worked together to heal the remaining defects and complete the SEI formation [Figure 2E][45]. During the electrochemical polishing process, the ultra-smooth and ultra-thin SEI with alternating laminated inorganic- and organic-rich mixed multilayer structures was obtained. It is noted that fine control of the anodic stripping and cathodic plating potentials and electrolyte components and a high current density in the stripping process are necessary for determination of the smoothness of the Li metal surface and the structure of the SEI[46].

The chemical polishing of Li could help remove the surface contaminants, such as LiOH, Li_2CO_3 and Li_2O, homogenize the lithium deposition and reduce the interfacial impedance. However, these strategies could not solve the issues generated during Li cycling. Other modification strategies conducted on polished Li foils could help optimize the cycling performances of Li-metal batteries.

Modulating the lithiophilicity of anode host materials

A Li host material with a large specific surface area and sufficient pore volume is desired to suppress Li dendritic growth and accommodate Li volume change during the Li stripping/plating process. However, most host materials exhibit poor affinity to Li, which leads to uneven Li deposition. Therefore, tuning the lithiophilicity of the host materials from lithiophobic to lithiophilic is vital for the realization of next-generation Li-metal batteries.

Chemical strategies for improving lithiophilicity

At present, the methods for improving the lithiophilicity of host materials are mostly operated under a high vacuum, which is time-consuming and costly. Recently, a new chemical strategy has been proposed by Wang *et al.*[47], which employed functional groups, such as -COOH, -OH, $-SO_3H$, $-NH_2$, -NH-,-Si-O, -F, -Cl, -Br and -I, or elemental additives, such as Mg, In, Ca, Sr, Ba, Sc, Y, Rh, Ir, Pd, Pt, Au, Cd, Hg, Ga, Tl, Ge, Pb, As, Sb, Bi, S, Se and Te, to alter the lithiophilicity of host materials. This strategy was applied based on negative Gibbs formation energies ($\Delta_r G$) and newly-formed chemical bonds. Notably, they summarized the lithiophilic properties of different elements for a better understanding of the wetting behavior of molten Li on various substrates [Figure 3A][47]. For example, molten Li does not react with the elements in red (like Ti and Fe) at 180-300 °C; however, lithiophilic organic coatings with functional groups, such as -N, -F, -P and -Br (given in blue) wet well with molten Li and the addition of lithiophilic elements in green (like In and Mg) in molten Li also helps to improve the lithiophilicity. Therefore, it is important to understand the lithiophilicity of various substrates for molten Li, through which one can prepare ultrathin Li-metal anodes. In addition, layered reduced graphene oxide (rGO), after a spark reaction, exhibits a high lithiophilicity due to the strong binding energy between the organic functional groups of rGO (such as carbonyl and alkoxy groups) and Li metal, which helps to promote the infusion of molten Li into the rGO interlayers [Figure 3B][48].

Lithiophilic coatings on host materials

Lithiophilic coating of the host materials represents another effective strategy to improve the anode performance, as the modified host plays an excellent role in regulating Li stripping/plating and provides

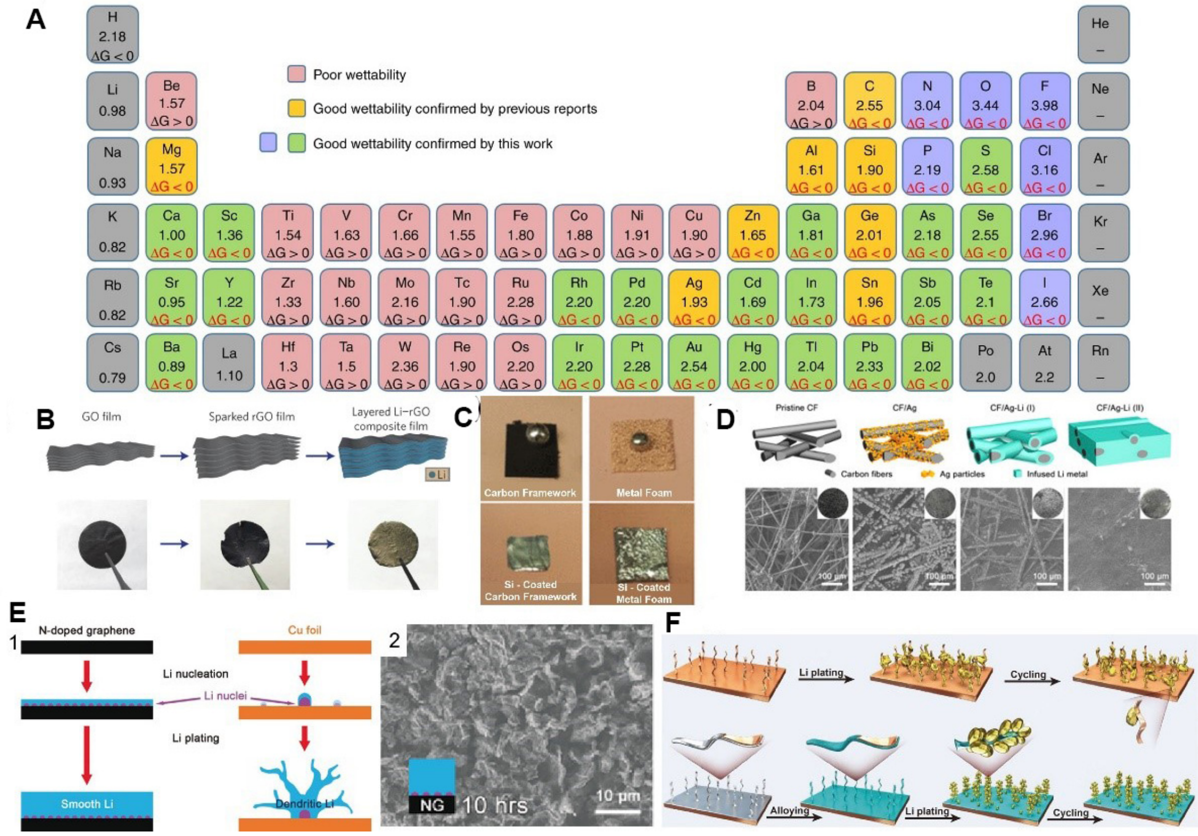

Figure 3. (A) Electronegativities and $\Delta_r G$ of various elements that are able to react with molten Li in the periodic table. The elements in green and blue represent those that could react with molten Li by forming new chemical bonds, which is responsible for the improved wettability, while red represents the elements that could not react with the molten Li[47]. Copyright 2019, Nature Publishing Group. (B) Fabrication of a layered Li-rGO composite film that consists of a GO film (left), a sparked rGO film (middle) and a layered Li-rGO composite film (right)[48]. Copyright 2016, Nature Publishing Group. (C) Comparison of lithiophilicity of different substrates with and without the Si coating[49]. Copyright 2016, National Academy of Sciences. (D) Schematic of synthesis process of carbon fiber CF/Ag-Li. The CF with electroplated Ag layer (CF/Ag), only the surface of CF is covered with molten Li [CF/Ag-Li(I)] and the CF framework is completely covered by molten Li [CF/Ag-Li(II)][54]. Copyright 2018, Elsevier. (E) Different Li nucleation and plating processes on N-doped graphene and Cu-foil electrodes and the SEM image of Li deposits at a low current density of 0.05 mA cm^{-2} for 10 h[57]. Copyright 2017, Wiley-VCH. (F) Thin Al layer reacted with Li to generate a binary Li-Al alloy phase, which functioned as the lithiophilic sites to ensure homogeneous growth of Li[60]. Copyright 2017, American Chemical Society.

confinement for the suppression of the anode volume change. By coating lithiophilic Si on a three-dimensional (3D) porous carbon matrix, the molten Li is quickly infused into a surface-modified 3D matrix[49]. Interestingly, a binary alloy phase of lithium silicide was created by the spontaneous reaction of Si and Li metal and therefore the low contact angle with molten Li was easily obtained [Figure 3C][49]. Derived from natural wood, Zhang *et al.*[50] demonstrated that a lithiophilic ZnO-coated carbon matrix with unique well-aligned channels showed advantages in uniformizing Li nucleation and growth, as well as alleviating dendrite growth. In addition to Li/C-wood composites, Liu *et al.*[51] found that by coating a layer of ZnO on a polyimide (PI) matrix, the molten Li can be quickly infused into the PI matrix. Such a design enables uniform Li stripping/plating and contributes to improved cycling stability over 500 cycles at a current density of 5 mA cm^{-2}. In addition to ZnO, Al_2O_3[52] and SnO_2[53] also show good affinity to Li metal. For example, Zhang *et al.*[54] electroplated Ag on a carbon fiber (CF) framework and produced a lithiophilic coating layer that guided molten Li into the matrix and accounted for the dendrite-free morphology [Figure 3D]. Xu *et al.*[55] developed a graphitic carbon nitrite layer (g-C_3N_4) that was evenly coated on carbon cloth (CC). Because of the high lithiophilicity of N in g-C_3N_4 and the high specific surface area of CC, metallic Li could be uniformly deposited into the interlayer between the g-C_3N_4 layer and CC fibers. Li|Li symmetric cells with g-C_3N_4/CC operated stably for over 1500 h with a small overpotential of ~80 mV at 2 mA cm^{-2}.

Doping of host materials with lithiophilic species

Because of the weak lithiophilic properties of most carbon materials, many dopants have been adopted to improve the lithiophilicity between the molten Li and the host material. For example, bromide and bromide intermediates (Br, CuBr and LiBr) show high lithiophilicity, which can promote homogenous Li nucleation[56]. When paired with a $LiFePO_4$ cathode, the full cells exhibit significantly improved cycling performance and a high capacity retention of 98% after 200 cycles. Furthermore, pyridinic and pyrrolic nitrogen in N-doped graphene have been demonstrated to be effective in guiding uniform Li nucleation [Figure 3E][57]. Chen *et al.*[58] demonstrated that O- or O/B-co-doped carbon materials also help to guide uniform Li nucleation. N/P-co-doped CC is easily wetted by molten Li due to the significantly improved binding energy between Li and the CC[59]. A Li-I_2 full battery with such a 3D electrode exhibited an ultralong cycle life with a high capacity of 197 mAh g^{-1} over 4000 cycles at 10 C.

Alloying of anode materials

Materials that form alloys with Li metal, such as Li/Al[60] and Mg-doped Li-LiB alloys[61], have been demonstrated to strongly bind with Li metal and therefore represent promising host materials. In particular, the Li-Al alloy can be generated through an *in-situ* electrochemical reaction and exhibits high lithiophilicity towards Li metal, so that it regulates Li nucleation and growth to enable dendrite-free plating [Figure 3F][60]. More importantly, the Li-Al alloy can compensate for the irreversible Li loss and extend the lifespan of the battery. The addition of Mg into a LiB alloy not only reduces the volume variation and local current density but also increases the adsorption energy of Li and therefore contributes to homogeneous Li^+ flux at the interface[61]. The proposed 3D Li-B-Mg composite anode displays a long and stable cycle life for more than 500 h at 0.5 mA cm^{-2} without a short circuit in the Li|Li symmetric cell. Wei *et al.*[62] recently studied the 3 °C GaInSnZn liquid metal that is able to react with Li metal and a Li-based alloy framework can be formed on the surface of Li metal. The Li-based alloy framework tightly attaches to Li metal to provide fast Li^+ diffusion, lower chemical reactivity and better lithiophilicity than pure Li.

Improving the lithiophilicity of host materials can effectively reduce the local current density and nucleation overpotential for Li deposits. The effectiveness of different anode host materials formed from different lithiophilic modulation strategies is listed in Table 2. Nevertheless, the dispersion uniformity of dopants is hindered by the complicated host structure and alloying anodes face significant synthetic difficulties due to the sensitivity of Li to temperature and atmosphere. Therefore, the performance of Li anodes has not been greatly improved in batteries at scale.

LITHIOPHILICITY OF SOLID ELECTROLYTES

Although numerous efforts have been made to improve the lithiophicility in liquid Li-metal batteries, the existence of liquid electrolytes that are highly reactive with Li metal still raises safety hazards. Replacing liquid electrolytes with solid electrolytes that possess good mechanical strength presents significant potential in addressing such safety problems and inhibiting Li dendrites. However, the poor lithiophilicity of solid electrolytes towards Li metal induces high resistance and blocks effective ion transport, which has restricted the development of solid-state Li-metal batteries. Taking advantage of the excellent lithiophilicity of liquids, gels and polymers with Li metal, the poor solid-solid contact can be changed into a benign liquid-solid or a soft solid-solid contact, which resolves this interfacial dilemma. The strategies for improving lithiophilicity in solid electrolytes are summarized in Table 3.

Table 2. Summary of the improvement of lithiophilicity of anode host materials

Modulating the lithiophilicity of anode host materials							
Strategy	**Ref.**	**Method**	**Interfacial resistance (before cycle)**	**Interfacial resistance (after cycle)**	**Polarized potential (after cycling)**	**Li-Cu efficiency**	**Cycle life**
Chemical strategies for improving the lithiophilicity	[49]	rGO layered reduced graphene oxide	20 Ω	25 Ω after 10 cycles	-	-	1000 h at 1 mA cm^{-2}, 1 mA h cm^{-2}
Lithiophilic coatings on the host material	[50]	Coating lithiophilic Si	~60 Ω	~40 Ω after 1 cycle	-	-	80 cycles under a high current rate of 3 mA cm^{-2}, 1 mA h cm^{-2}
	[51]	ZnO-coated carbon matrix	60 Ω	40 Ω after 3 cycles	20 mV at 0.5 mA·cm^{-2}, 1 mA h·cm^{-2}	65 mV at 0.5 mA·cm^{-2}, 1 mA h·cm^{-2}	Over 200 h at 0.5 mA·cm^{-2}, 1 mA h·cm^{-2}
	[52]	ZnO coated polyimide (PI) matrix	-	-	35 mV at 1 mA cm^{-2}, 1 mA h cm^{-2}	40 mV after 100 cycles at 1 mA cm^{-2}, 1 mA h cm^{-2}	100 cycles at 1 mA cm^{-2}, 1 mA h cm^{-2}
	[55]	Electroplated Ag on the carbon fiber (CF) framework	-	-	-	~60 mV after 200 cycles	400 h at 1 mA cm^{-2}
	[56]	Graphitic carbon nitrite layer coated carbon cloth	~60 Ω	~30 Ω after 100 cycles	-	~80 mV over 1500 h at 2.0 mA cm^{-2}, 1 mA h cm^{-2}	Over 1500 h at 2.0 mA cm^{-2}, 1 mA h cm^{-2}
Lithiophilic dopants on the host materials	[57]	CuBr- and Br-doping Cu Current Collectors	~24 Ω	12.7 Ω after 60 cycles	Less than 25 mV over 800 h at 1 mA cm^{-2}, 1 mA h cm^{-2}	98.8% over 300 cycles at 2.0 mA cm^{-2}, 2.0 mA h cm^{-2}	850 h at 2.0 mA cm^{-2}, 2.0 mA h cm^{-2}
	[58]	N-doped graphene	-	-	-	98% near 200 cycles at 1.0 mA cm^{-2}, 1.0 mA h cm^{-2}	Over 140 cycles at 2.0 mA cm^{-2}, 0.042 mA h cm^{-2}
Alloying anode materials	[61]	Li-Al alloy	-	-	-	98.6% for 85 cycles at 0.5 mA cm^{-2}, 2 mA h cm^{-2}	1700 h at 0.5 mA cm^{-2}, 1 mA h cm^{-2}
	[62]	Mg doped Li-LiB alloy	-	15 Ω after the first cycle	Less than 50 mV after 500 h at 0.5 mA cm^{-2}, 0.5 mA h cm^{-2}	-	500 h at 0.5 mA cm^{-2}, 0.5 mA h cm^{-2}
	[63]	GaInSnZn liquid metal	-	-	Less 0.15 V after 300 h at 1.0 mA cm^{-2}, 0.5 mA h cm^{-2}	-	400 h at 1.0 mA cm^{-2}, 0.5 mA h cm^{-2}

As discussed above, the factors affecting lithiophilicity include surface energy and chemical interactions. Following these principles, the surface energy can be tuned by increasing the temperature and effective surface modifications. Li melts into a molten state above 180.5 °C. This temperature increase is beneficial for improving the lithiophilicity due to the entropy increase, viscosity decrease and surface tension decline of molten Li[17]. The addition of alloying additives (like Sn, In and Mg) and organic coatings (such as -COOH, -OH and -F) into molten Li can also significantly improve the lithiophilicity via reducing the surface energy and Gibbs formation energy[47]. Li-reactive coatings on solid electrolytes, such as Au, Al or Al_2O_3 interlayers, can enhance the lithiophilicity between Li and solid electrolytes via chemical interactions with Li[17]. To date, various strategies have been proposed to ameliorate the lithiophilicity of solid electrolytes. These strategies are mainly focused on physical contact improvement, surface energy adjustment and chemical interaction exploration. With improved

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Table 3. Summary of the improvement of lithiophilicity of solid electrolytes

			Lithiophilicity of solid electrolytes				
Strategy	**Ref.**	**Method**	**Interfacial resistance (before cycling)**	**Interfacial resistance (after cycling)**	**Polarized potential (after cycling)**	**Li-Cu efficiency**	**Cycling life**
Improving physical contact	[64]	IL interlayer (N-propyl-N-methylpyrrolidiniumbis (trifluoromethanesulfonyl) amide)	6000 Ω	320 Ω	40 mV at 0.1 mA cm^{-2}, 0.2 mA h cm^{-2}	-	100 cycles at 0.5 C for Li|LFP
	[65]	IL interlayer (1-ethyl-3-methylimidazolium$_{0.8}$Li$_{0.2}$) (TFSI)	-	-	70 mV at 0.2 mA cm^{-2}, 0.2 mA h cm^{-2}	-	100 cycles at 0.1 C for Li|LFP
	[66]	IL interlayer (BMP)-TFSI	-	-	17 mV at 0.1 mA cm^{-2}, 0.1 mA h cm^{-2}	-	200 cycles at 0.5 C for Li|NCM811
	[67]	Gel interlayer containing Al-(oxy)fluorides	-	-	345 mV at 4 mA cm^{-2}, 2 mA h cm^{-2}	-	200 cycles at 1 C for Li|LFP
	[68]	Gel interlayer (LiTFSI-$LiPF_6$)	-	-	-	-	300 cycles at 0.5 C for Li|LFP
	[69]	Gel interlayer with $LiNO_3$	-	-	-	~97% after 100 cycles	100 cycles at 0.1 C for Li|LFP
	[70]	Polymer interlayer poly(ethylene glycol) methyl ether acrylate	-	-	-	99.8%-100% over 640 cycles for Li|LFP	640 cycles at 0.6 C for Li|LFP
	71	Polymer interlayer PEGDA	-	-	40 mV at 2 mA cm^{-2}, 2 mA h cm^{-2}	99.8% after 270 cycles for Li|NCM622	270 cycles at 0.5 C for Li|NCM622
Chemical interaction	[76]	Li-Sn anode	-	7 Ω cm^2	-	-	-
	[77]	Li-C anode	381 Ω cm^2	11 Ω cm^2	-	-	-
	[20]	Li-Mg anode	1000 Ω cm^2	70 Ω cm^2	-	-	-
	[23]	Li-Al anode	-	75 Ω cm^2	-	-	-
	[22]	Li-Zn anode	2000 Ω cm^2	20 Ω cm^2	-	-	-
	[81]	Mg_3N_2 interlayer	-	-	-	-	200 cycles at 0.5 C for Li|LFP
	[83]	Graphite interlayer	1078 Ω cm^2	58 Ω cm^2	-	-	100 cycles at 0.1 mA cm^{-2} for Li|NCM111
	[86]	HFE interlayer	127.4 Ω cm^{-2}	48.4 Ω cm^{-2}	90 mV at 0.5 mA cm^{-2}, 0.1 mA h cm^{-2}	-	100 cycles at 0.1 mA cm^{-2} for Li|LCO

lithiophilicity, interfacial problems like poor contact and huge interfacial impedance can be addressed, thereby furthering the application of advanced solid-state Li-metal batteries.

Improving physical contact

The introduction of liquid interlayers enables improved physical contact between solid-solid interfaces. Among the various liquid electrolytes species, ionic liquid (IL) electrolytes show advantages in terms of safety and good compatibility with Li metal anodes. Using an IL, N-propyl-N-methylpyrrolidiniumbis(trifluoromethanesulfonyl) amide, mixed with LiTFSI as an interlayer, Ma *et al.*[63] proposed an electrolyte design with cellulose acetate/polyethylene glycol/$Li_{1.4}Al_{0.4}Ti_{1.6}P_3O_{12}$ [Figure 4A] that exhibited a high Li^+ transference number of 0.61 and reduced interfacial resistance from 6000 to 320 Ω. Taking advantage of its high viscosity and poor flammability, the IL interlayer showed satisfactory viscoelasticity and excellent safety, as well as facilitating the uniform deposition of metallic Li. Furthermore, Wang *et al.*[64] demonstrated a metal-organic framework-based electrolyte impregnated with an IL [1-ethyl-3-methylimidazolium$_{0.8}$Li$_{0.2}$-bis(trifluoromethylsulfonyl)amide]. Featuring a nano-wetting interfacial mechanism, the electrolyte exhibited excellent compatibility with a Li metal anode and led to a small polarization voltage of ±70 mV in Li|Li symmetric cells under 0.2 mA cm^{-2}. Similarly, Zhang *et al.*[65] introduced a 1-butyl-1-methylpyrrolidinium (BMP)-TFSI interlayer on the surface of a garnet electrolyte and the obtained hybrid electrolyte showed an ultrahigh Li^+ transference number of 0.99 and a critical current density larger than 0.74 mA cm^{-2}. Benefiting from its good lithiophilicity, the obtained electrolyte enabled continuous ionic transport at the interface and allowed for a stable voltage polarization of 0.17 V for more than 300 cycles in Li|Li symmetric cells.

The introduction of gel interlayers to construct intimate soft solid-solid contacts is another method to improve the physical contact between two solid interfaces. The construction of *in-situ* interlayers represents an alternative used to tighten contact and reduce interfacial resistance. For example, via an *in-situ* electrochemical lithiation reaction, nanosized $AlPO_4$ particles dispersed in the quasi-solid electrolyte can turn into repellent containing Al-(oxy)fluorides, which have been proved to stabilize the electrode interface. With the repellent transitional interlayer as a Li anode safeguard, the constructed Li-$LiFePO_4$ batteries can maintain a capacity retention of over 85% for 200 cycles at 55 °C without Li dendrites detected[66]. A dual-salt (LiTFSI-$LiPF_6$) gel polymer electrolyte with a robust SEI interlayer was constructed through the *in-situ* polymerization of poly(ethylene glycol) diacrylate (PEGDA) and ethoxylated trimethylolpropane triacrylate. In the formation of the SEI for the Li metal anode, COR and COOR could be detected in the gel electrolyte and after cycling, the COR and COOR signals were still strong. CO_3^{2-} and CF_3 signals were not detected, indicating a lack of decomposition of the solvent and salts. Therefore, the SEI in the gel system was sufficiently stable and robust to inhibit the growth of Li dendrites, allowing for a capacity retention of 87.93% after 300 cycles in $LiFePO_4$|gel|Li cells[67]. A double polymer network gel electrolyte design with $LiNO_3$ additives also offers a method to steady the interface via the *in-situ* formation of a stable SEI layer containing ROLi, ROCOOLi and LiN_xO_y species. $LiNO_3$ can react with electrolytes and form a robust SEI, which enables symmetric cells to cycle for 400 h with a dendrite-free morphology[68].

Soft solid-solid contact can also be achieved through the introduction of polymer electrolyte interlayers. The group of Goodenough proposed a polymer/ceramic/polymer sandwich structure, in which the crosslinked poly(ethylene glycol) methyl ether acrylate polymer interlayer wets well with the Li metal anode and triggers a homogenous Li^+ flux at the interface. Therefore, Li dendrites were significantly inhibited and full cells with $LiFePO_4$ electrodes exhibited a high CE of 99.8%-100% over 640 cycles[69]. Additionally, a heterogeneous multilayered solid electrolyte was proposed, in which PEGDA adheres to the Li anode while PAN faces the cathode and PAN@$Li_{1.4}Al_{0.4}Ge_{1.6}(PO_4)_3$ (LAGP) functions as an electrolyte interlayer in the middle [Figure 4B][70]. The introduced PEGDA has good compatibility with Li metal and stands as a soft interlayer to avoid direct contact between LAGP and the Li metal anode, which enables the construction of Li|Li symmetric cells with a stable polarization of less than 40 mV for more than 1000 h at 2 mA cm^{-2}. The multilayer structure exhibits good compatibility at both the cathode and anode sides, thereby broadening

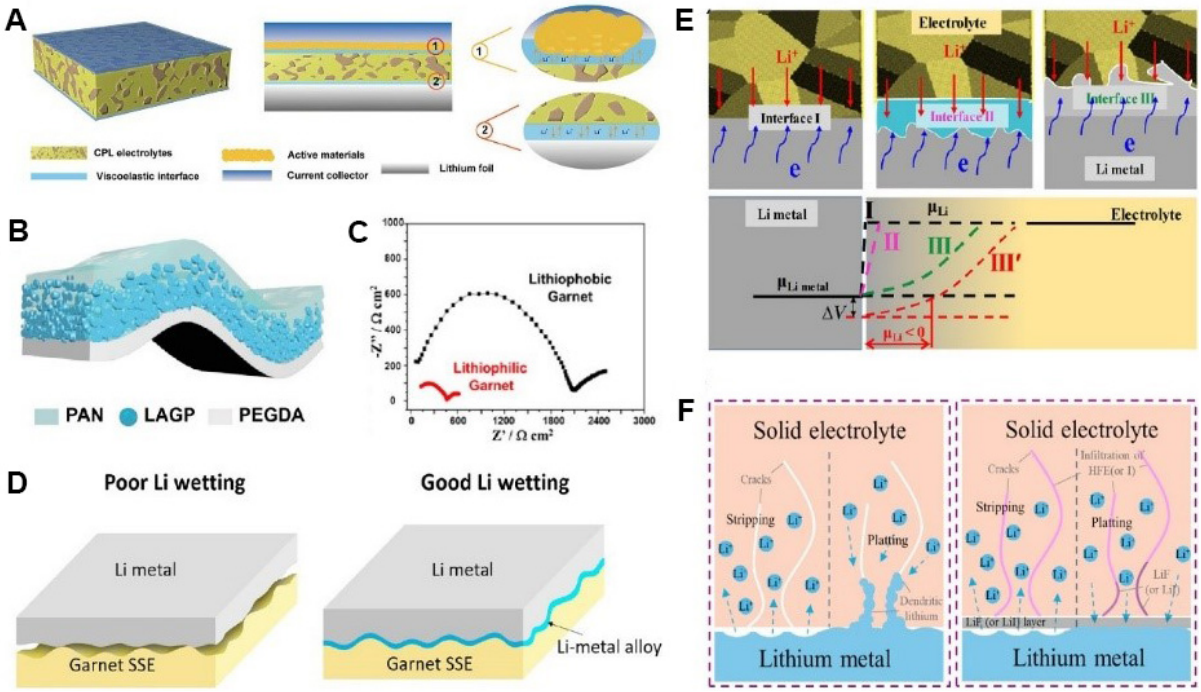

Figure 4. (A) Schematic of electrolyte design with viscoelastic ionic liquid (IL) as interlayers. In Li-metal batteries, the IL interlayers can buffer the interfacial contact and their viscoelasticity can efficiently facilitate the homogeneous deposition of Li ions[63]. Copyright 2019, Wiley-VCH. (B) Schematic of a heterogeneous multilayered solid electrolyte. When the electrolyte is applied in Li-metal batteries, polyethylene glycol diacrylate (PEGDA) is on the Li anode side and poly(acrylonitrile) (PAN) faces the cathode side. The middle layer is the electrolyte $Li_{1.4}Al_{0.4}Ge_{1.6}(PO_4)_3$(LAGP) mixed with PAN[71]. Copyright 2019, Wiley-VCH. (C) The Li-alloy interlayer can turn the surface from lithiophobic to lithiophilic. From the electrochemical impedance spectroscopy (EIS) measurements, the interfacial resistance of symmetric cells with lithiophilic garnet is much lower than that of lithiophobic garnet[78]. Copyright 2016, American Chemical Society. (D) Comparison of interfaces with and without Li-metal alloy interlayer. The pristine garnet electrolyte exhibits poor wetting behaviors with Li. After coating a metal interlayer, a Li metal alloy will form at the interface and improve the contact, therefore improving the lithiophilicity and decreasing the interfacial resistance[23]. Copyright 2017, American Association for the Advancement of Science. (E) Classifications of interfaces between Li metal and solid electrolyte along with the changes of Li potentials at different interfaces. Interface I indicates the thermodynamically stable interface. Interface II refers to the electronic isolating interface and interface III refers to the electronic conducting interface. The Li potential drops abruptly from the electrolyte to Li metal in interface II, which can effectively block side reactions[84]. Copyright 2018, American Association for the Advancement of Science. (F) Comparison of Li stripping/plating behaviors in pristine solid electrolyte and methoxyperfluorobutane (HFE) treated electrolyte. Li dendrites can easily form in the pristine solid electrolyte. The introduced HFE can react with Li and form a LiF interlayer, which can efficiently inhibit dendrite growth. If the Li dendrites break the interlayer, the HFE in electrolytes can still consume the Li and repair the interlayer[85]. Copyright 2018, Elsevier.

the electrochemical window to 5 V and allowing the application of high-voltage cathodes like $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622) and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811), which are rarely used in solid-state Li-metal batteries[71]. Inspired by this design, many other strategies using polymer interlayers have also been reported, such as asymmetric solid electrolytes[72], Janus structures[73] and thio-LiSICON/polymer composite electrolytes[74].

IL and gel interlayers can improve the lithiophicility of solid electrolytes; however, the leakage of liquid components from the electrolyte|Li interface leads to safety concerns. Increasing the polymer ratio of the interlayer can decrease leakage risks, while the poor ionic conductivity of polymers harms the workability of batteries at ambient temperatures. The exploration of high-conductivity and lean-electrolyte systems could shed light on building interlayers with better safety.

Surface energy and chemical interactions

Additives can effectively manipulate the surface energy of molten Li and therefore improve the lithiophilicity on different substrates. The group of Hu added alloying elements (like Sn, Zn and Si) into molten Li and the Li alloys exhibited outstanding lithiophilicity against various substrates. The Li alloys contacted tightly with garnet electrolytes and the interfacial resistance of Li-Sn alloy symmetric cells was decreased to only 7 Ω cm^2, demonstrating remarkable electrochemical stability[75]. Using graphite as an additive, a paste-like Li-C composite anode was obtained, which exhibits excellent lithiophilicity against garnet electrolytes and reduced interfacial resistance from 381 to 11 Ω cm^2[76].

Inorganic solid electrolytes show promise in high-safety Li-metal batteries due to their desirable mechanical strength and poor flammability. Among the various inorganic solid electrolytes, garnet-type solid electrolytes show considerable potential in applications, owing to their excellent chemical/electrochemical stability and relatively high ionic conductivity. However, due to their poor lithiophilicity with Li-metal anodes, garnet-type solid electrolytes exhibit high interfacial resistance and low critical current density, leading to the possible formation and penetration of Li dendrites. $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZT) is a representative garnet-type electrolyte. Impurities, like Li_2O and Li_2CO_3, are very easy to generate at the interface between LLZT and Li metal, causing poor lithiophilicity and high interfacial resistance. Li_2O has a positive formation energy (0.23 J cm^{-2}) and therefore LLZT covered by Li_2O cannot wet well with Li. By rubbing LLZT pellets into molten Li, the superficial impurities are polished and the exposed LLZT becomes sufficiently wetted by Li, which is consistent with the negative Li/LLZT formation energy (-6.14 J cm^{-2}). Benefiting from the intrinsic lithiophilicity, the interfacial impedance of Li|Li symmetric cells decreased to 6.95 Ω cm^2, accompanied by an increased critical current density of 13.3 mA cm^{-2} and a stable cycling performance over 950 h at room temperature[77].

To improve the wettability, the polishing strategy is only applicable to planar surfaces other than geometric surfaces and is not scalable based on current technology. Therefore, various interfacial engineering methods have been explored, mainly focusing on high electronic conducting, mixed ionic-electronic conducting and ionic conducting but electronic insulating interlayers. Recently, coating metals, such as Si[78], Mg[20], Al[23,79] and Ge[19], or metal oxides, like Al_2O_3[19] and ZnO[22], can trigger an alloying reaction with Li and form high electronic conducting Li-metal alloy interlayers. Li-metal alloy interlayers exhibit excellent lithiophilicity with Li and significantly improve the physical contact, leading to an even current distribution and low interfacial resistance [Figure 4C]. Taking Mg as an example, the Mg atoms diffuse into the Li metal anode during the alloying process and then form as a transient layer, leading to enhanced solid-solid contact that significantly decreases the interfacial resistance from 1000 to 70 Ω cm^2[20]. Similarly, the formation of a Li-Al alloy transforms the garnet surface from lithiophobic to lithophilic with a decreased interfacial resistance of 75 Ω cm^2 [Figure 4D][23]. When a metal oxide interlayer, like ZnO, is introduced via atomic layer deposition, Li atoms tend to diffuse into the interlayer and reduce ZnO into a Li-Zn alloy, which effectively tightens the contact and reduces the interfacial resistance from 2000 to 20 Ω cm^2[22].

Modulating the surface energy via Li alloying additives can improve the lithiophilicity of solid electrolytes, which offers a promising solution from a chemical perspective. However, these strategies still face problems in all battery systems and long cycling situations, owing to the consumption of additives and deterioration of the chemical environment. The stability of alloyed interfaces at operating conditions is reliant on future research.

In terms of improving lithiophilicity, high electronic conducting interlayers can significantly boost physical contact and reduce interfacial resistance, contributing to decreased overpotentials during cycling. However, with enhanced ionic conductivity, mixed ionic-electronic conducting interlayers, like Mg_3N_2[80], Li_3PO_4[81] and graphite[82], present remarkable potential for inhibiting Li dendrites. Via an *in-situ* reaction with the Li metal anode, the introduced Mg_3N_2 layer transforms into electronic conducting Mg and ionic conducting Li_3N, with Mg leading to an even current distribution and Li_3N contributing to a homogeneous concentration gradient of Li^+, therefore prohibiting the formation and growth of Li dendrites[80]. In addition, the group of Maruga reported that, as well as reducing the interfacial resistance from 1078 to 58 Ω cm^2, Li|Li symmetric cells with graphite as a mixed ionic-electronic conducting interlayer could also afford a high critical current density (750 μA cm^{-2})[82].

Although high electronic conducting interlayers can improve contact and mixed ionic-electronic conducting interlayers exhibit the ability to prohibit Li dendrites, their electronic conducting properties make it difficult for them to block side reactions. As shown in Figure 4E, interface I represents a thermodynamically stable contact between the electrolyte and Li metal anode, which is unrealistic. Interface III refers to high electronic or mixed ionic-electronic conducting interlayers, which can conduct electrons. The potential in interface III gradually changes from the electrolyte to the Li anode and therefore continuous side reactions cannot be easily avoided in the above two interlayers. The ionic conducting but electronic isolating interlayers are classified as interface II, in which Li ions can easily transport. The electronic isolating properties of interface II lead to an abrupt potential drop from the electrolyte to Li metal, which can efficiently prohibit parasitic reactions.

Therefore, various kinds of electronic insulating interlayers, including LiF[83-85], Li_3N[86] and Li_3OCl[87], have attracted significant interest, among which LiF is mostly researched. LiF possesses the properties of a low surface diffusion barrier and high interfacial energy, which makes the Li ions wet the interface planarly instead of forming needle-like dendrites[83]. A robust LiF-rich interlayer can be formed via an *in-situ* reaction between the LiFSI-coated solid electrolyte Li_3PS_4 and the Li metal anode, which can effectively block side reactions and inhibit Li dendrites, thereby contributing to an increased critical current density of more than 2 mA cm^{-2} and an enhanced CE of 98%[84]. Similarly, the added HFE in the solid electrolyte $Li_7P_3S_{11}$ can react with the Li metal anode and produce a LiF interlayer, which can protect the electrolyte from penetrating dendrites. If the dendrites pierce the LiF interlayer, the HFE in the electrolyte immediately reacts with the Li in dendrites and forms new LiF to repair the broken interface, therefore ensuring a steady interface structure and stable cycling over 200 cycles in Li|Li symmetric cells [Figure 4F][85]. Therefore, interface II with poor electronic conductivity shows a better ability to inhibit side reactions compared to interface III. Constructing an electronic isolating interface instead of a mixed ionic-electronic conducting interlayer might be a reasonable method to address interfacial problems and boost lithiophilicity.

CONCLUSION AND OUTLOOK

A lithiophilic electrode/electrolyte interface is vital for the stable operation of rechargeable Li-metal batteries. Due to the different physiochemical properties of liquid and solid electrolytes, the cases of lithiophilicity vary significantly in liquid and solid-state batteries. In this review, we have summarized the challenges and strategies for improving the interfacial lithiophilicity in different types of rechargeable Li-metal batteries.

For liquid electrolyte-based batteries, the precise manipulation of the structure and chemical compositions of the SEI on the Li metal surface is required to enable improved wetting and (electro)chemical stability at the anode/electrolyte interface. A smooth anode surface via chemical treatment (e.g., polishing) is favorable for homogenizing the ion distribution at the anode surface and contributes to dendrite-free plating/stripping. Host materials with suitable porous structures have received attention as they can suppress dendrite evolution and lithium volume change, and various strategies, including elemental additives, surface coatings, dopants and alloying materials, were proposed to improve the lithiophilicity of host materials via reducing the surface and Gibbs formation energies.

Solid electrolytes usually show poor lithiophilicity and high interfacial resistance *vs.* the Li metal anode, which account for the rapid performance degradation of the battery. To address these issues, one approach is to improve the contact at the Li/electrolyte interface. *In-situ* formed polymers can improve the interfacial contact due to their high flexibility against the anode surface. In the case where the interlayer consists of electronically conductive materials, such as metals or metal oxides, the alloying/conversion reaction with Li that occurs at the interface acts as the driving force for wetting and contributes to improved interfacial Li^+ mobility. A mixed ionic-electronic conductive interlayer is able to trigger homogeneous distribution of Li ions and therefore effectively inhibit the growth of dendrites. In contrast, an ionically conductive but electronically isolative interlayer (e.g., LiF) is applied to suppress parasitic reactions as it brings an abrupt potential drop at the interface. An interlayer with multiple sublayers or a composite design would be desired to achieve optimal storage performance.

It is noteworthy that, despite the progress made so far in improving the interfacial contact of electrolytes against Li metal, there are still many challenges toward the realization of high-energy Li-metal batteries, including:

1. Although the initial state of interfacial lithiophilicity can be improved, it remains difficult to maintain contact upon the hostless evolution of interface/volume at the anode side during the repeated cycling process.

2. The dynamic evolution of morphology, structure, chemical compositions and their physiochemical properties at the anode/electrolyte interface requires further investigation.

3. A deep understanding of the interfacial lithiophilicity within a wide temperature range is required for the safe operation of batteries.

4. Advanced characterization tools and theoretical calculations are required to resolve the interfacial wetting behavior and the science behind it.

DECLARATIONS

Authors' contributions

Preparing the manuscript draft: Li CC, Zhang XS, Zhu YH
Writing - review and editing, funding acquisition, supervision: Zhang Y, Xin S, Wan LJ, Guo YG

Availability of data and materials

Not applicable.

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Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
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