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Interfacial Issues and Modification of Solid Electrolyte Interphase for Li Metal Anode in Liquid and Solid Electrolytes

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Interfacial Issues and Modification of Solid Electrolyte Interphase for Li Metal Anode in Liquid and Solid Electrolytes

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*Oh B. Chae and Brett L. Lucht**

The high energy density required for the next generation of lithium batteries will likely be enabled by a shift toward lithium metal anode from the conventional intercalation-based anode such as graphite. However, several critical challenges for Li metal originate from its highly reactive nature and the hostless reaction of deposition and stripping impede the practical use of Li metal as an anode. The role of the solid electrolyte interphase (SEI) is very important for the Li metal anode where the SEI must protect the dynamically changing surface of the Li metal. Since the SEI-generating reaction mechanisms for the two different electrolyte systems, liquid and solid, are considerably different, the SEI layers formed between the Li metal and the electrolytes in the two electrolyte systems have substantially different properties, causing different interfacial issues. Inhibition of the interfacial problems requires different strategies to reinforce the SEI layer for each of the electrolyte systems. However, the differences in the two electrolyte systems have not been clearly compared in the prior literature. In this report, the interfacial issues for the two different electrolyte systems are compared and different strategies for SEI modification are provided to overcome the issues.

1. Introduction

Lithium-ion batteries (LiBs) have revolutionized energy storage systems over the past several decades and have become an indispensable and important item in the modern era. With high energy density and stable cycling, LiBs have gradually replaced traditional energy storage devices such as nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), and lead-acid batteries.[1,2] LiBs have recently become widely used for portable electric devices, electric vehicles, and grid-scale energy storage. The current system of LiBs based on Li transition metal oxide cathodes, graphite anodes, and carbonate-based electrolytes allows an energy density of around 800 Wh L^{-1}. However, the intercalation-based chemistry of LiBs has an intrinsic capacity limitation and the increasing demand for higher energy storage systems is driving the development of new battery chemistries.[3,4]

Among the various anode materials such as transition metal oxides ($Li_4Ti_5O_{12}$, TiO_2, V_2O_5, Fe_2O_3, etc.)[5–8] and Li-alloy materials (Si, Sn, Ge, Zn, etc.),[9–13] it is generally accepted that Li metal is the ultimate anode material to achieve high energy density due to the highest theoretical capacity (3860 mAh g^{-1}) and lowest redox potential (−3.04 V vs the standard hydrogen electrode).[14,15] The energy density can be significantly increased above 1000 Wh L^{-1} when the graphite anode is replaced by Li metal in the current system. However, critical issues derived from the high reactivity to environmental conditions and non-uniform Li dendrite formation result in serious safety concerns including fire and explosion.[16–17] Thus, in order to commercialize Li metal anodes, these problems must be overcome.

Contrary to the graphite anode which requires intercalation and de-intercalation for the storage and release of Li (**Figure 1**a),[3] the Li metal anode can store and release Li based on deposition and stripping reaction as a hostless anode (Figure 1b).[18] Thus, the morphology of deposited Li metal can be varied by many factors such as current density,[19,20] solid electrolyte interphase (SEI),[21–26] temperature,[27,28] electrolyte mass transfer,[29–33] crystallography of current collector,[34–36] mechanical pressure,[37–39] and so on. The different reaction mechanisms between graphite and Li metal lead to a different SEI formation process. Most of the graphite surface is covered by reductive decomposition products of electrolyte components during the initial few cycles (Figure 1c).[40] The small volume change of graphite during the charge and discharge (<10%) mitigates SEI crack generation, which minimizes the exposure of the fresh graphite surface during cycling, preventing continuous electrolyte decomposition. On the contrary, the initial SEI of Li metal is generated as soon as the Li metal is exposed to the electrolyte since the electrochemical potential of Li metal is lower than the stability window for most of the electrolyte components. The uncontrolled Li deposition causes inhomogeneous exposure of fresh Li surface to the electrolytes, resulting in continuous electrolyte decomposition during the cycling

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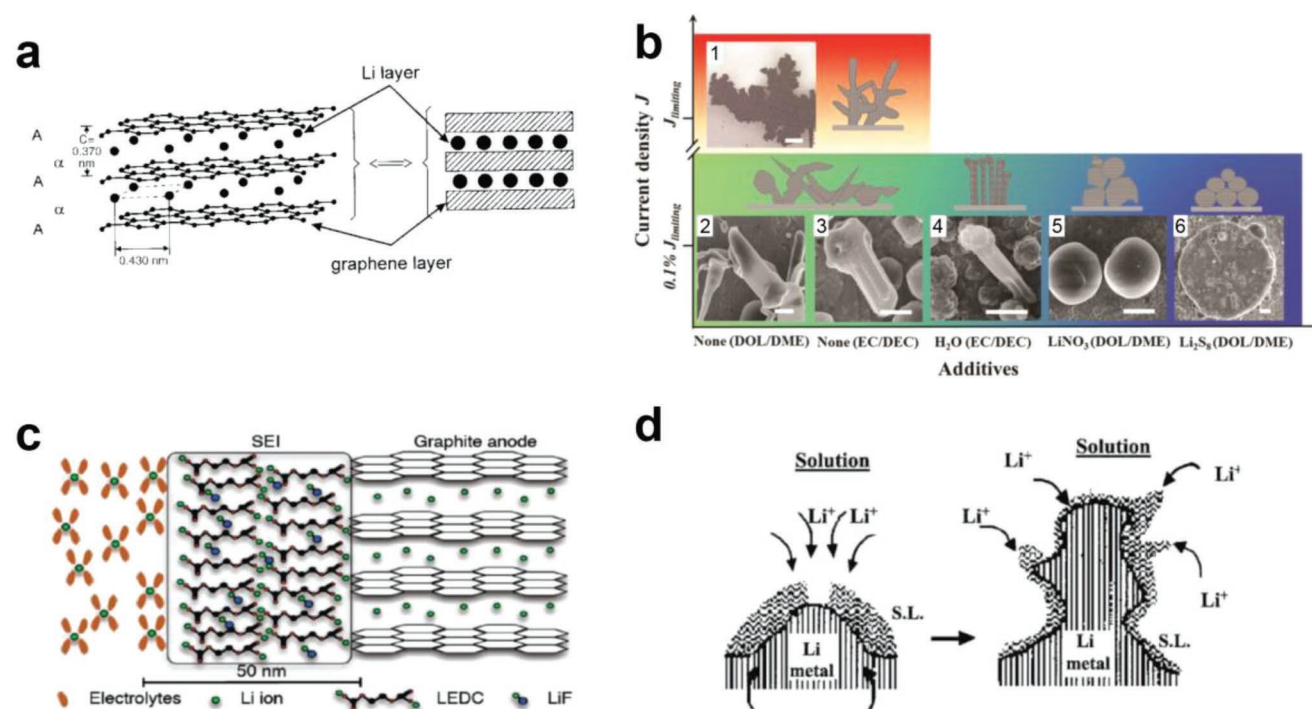
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Figure 1. a) Structure of LiC$_6$. Schematic drawing showing the AA layer stacking sequence and the $\alpha\alpha$ interlayer ordering of the intercalated lithium (left). Simplified representation (right). Reproduced with permission.[3] Copyright 1998, Wiley-VCH. b) Growth of lithium electrodeposits as a function of current density J and additives in electrolyte. Reproduced with permission.[18] Copyright 2017, National Academy of Sciences USA. c) Schematic figure of SEI formed on graphite anodes during the first cycle. Reproduced with permission.[40] Copyright 2013, American Chemical Society. d) A schematic illustration of Li dendrite formation and electrolyte decomposition on Li surface during Li deposition. Reproduced with permission.[41] Copyright 2002, Elsevier.

(Figure 1d).[41] Thus, stabilization of the interface between the electrolyte and the Li metal is a key factor for the improvement of electrochemical performance for Li metal anode since the continuous electrolyte decomposition on Li metal brings about a decrease of Coulombic efficiency, an increase of interfacial resistance and acceleration of electrolyte depletion.

To overcome the issues derived from the instability of Li metal in the liquid electrolytes, solid-state electrolytes (SSEs) have emerged as promising alternatives.[42–46] The SSEs act as a separator that physically separates the cathode and anode in addition to functioning as an electrolyte that conducts Li ions. Thus, the SSEs can replace both the polymer separators and the organic liquid electrolytes which are currently used in the conventional LiBs. Ultimately, the safety concerns could be effectively mitigated by replacing flammable organic liquid electrolytes with solid-state electrolytes.[47,48] In addition, the high stiffness of SSEs can suppress internal short circuits by preventing the Li dendrite formation during the cycling, leading to a lower risk of fire and explosion.[49–51] Moreover, unlike the liquid electrolytes, the SSEs do not permeate into the pores of deposited Li metal, preventing the continuous electrolyte decomposition on the newly generated Li surface. Despite these advantages, several critical issues such as low ionic conductivity, high interfacial resistance, and poor chemical/electrochemical stability impede the practical application of SSEs.[52,53]

The use of Li metal in commercial battery systems faces many challenges. One of the fundamental sources of these

challenges comes from the interfaces between the Li metal and the electrolytes. Since Li deposition and stripping reactions are mainly governed by the properties of the interface, a stable and uniform interface is essential for good electrochemical properties such as high Coulombic efficiency, low resistance, and stable cycling performance. When the interface is unstable and non-uniform, inhomogeneity of Li deposition and parasitic side reactions are accelerated, resulting in critical safety issues as well as poor electrochemical performance. Meanwhile, each electrolyte system has a completely different interface between the Li metal and the electrolytes where the liquid electrolyte system has a solid/liquid interface and the solid electrolyte system has a solid/solid interface. The difference of interface inevitably affects the interfacial phenomena such as the wettability of electrolyte with Li metal, Li$^+$ ion transfer, and generation of the SEI, causing different interfacial issues. Thus, a deep understanding of interfacial phenomena is vital for solving these problems and will provide inspiration to develop strategies for the commercial application of Li metal anodes. In particular, different strategies for SEI modification on Li metal are necessary for the liquid and solid electrolyte systems since the interfacial phenomena in the two electrolyte systems are completely different. However, the interfacial characteristics and strategies for SEI modification in the liquid and solid electrolyte systems have not been clearly compared in prior literature. Herein, we review the generation of the SEI and the critical challenges of the interface between the Li metal and electrolytes

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in both liquid electrolyte-based batteries and solid electrolyte-based batteries. In addition, different strategies for SEI modification to overcome the interfacial issues in two electrolyte systems are compared, and future research directions for practical applications of the Li metal anode will be discussed.

2. Generation of SEI and Interfacial Issues for Li Metal Anode

In both liquid electrolyte-based batteries and solid electrolyte-based batteries, the interface between the Li metal anode and the electrolyte is one of the most important factors in determining the performance of the Li metal-based batteries. However, the interfacial problems in both battery systems are not completely understood even though much effort has been devoted to understanding the reaction mechanisms and structure of the interfaces.

Due to its highly reactive nature, pristine Li metal is covered by a native surface film composed of an outer layer of Li_2CO_3 and LiOH and an inner layer of Li_2O.[54,55] Once Li metal contacts the liquid or solid electrolytes, the high reactivity results in an immediate reaction with the electrolyte components and the formation of an SEI layer between the Li metal and the electrolyte. Moreover, many aspects of the conditions can alter the chemical and physical properties of the SEI layer. In addition, the Li deposition morphology during cycling can also modify the interface. Fundamentally, liquid and solid electrolytes have completely different chemical and physical properties. Thus, the interfacial challenges facing liquid and solid electrolytes are

considerably different. A detailed understanding of different interfacial issues between the two electrolyte systems is essential to solving the problems associated with the use of lithium metal anodes.

2.1. SEI and Interfacial Issues for Li Anode in Liquid Electrolytes

A schematic illustration of Li deposition behavior in the liquid electrolytes is provided in **Figure 2**a. Compared to conventional anode materials such as graphite and Si, Li metal is extremely reactive to organic liquid electrolytes. Thus, the solvents and salts in the electrolytes are rapidly reduced upon contacting the Li metal, generating an SEI layer on the Li metal surface. Generally, the SEI layer consists of $ROCO_2Li$, ROLi, Li_2CO_3, and/or LiF, which can be altered by the electrolyte composition.[56] Inorganic species such as Li_2CO_3, Li_2O, and LiF are primarily in the inner layer while the outer part of SEI is mainly comprised of organic species including ROLi, $ROCO_2Li$, and $RCOO_2Li$.[41,57,58] The SEI has electrically insulating and ionically conductive properties which prevent direct contact between the electrolytes and Li metal but allows Li^+ ions to migrate through the SEI layer. Ideally, the SEI layer would avoid continuous electrolyte decomposition on the Li metal surface and afford homogeneous distribution of Li^+ ion flux, leading to uniform Li deposition.[59] However, the actual SEI layer is uneven, inflexible, and brittle. In addition, the components of the SEI layer are not robust enough to accommodate the large volume change of Li metal during Li deposition and stripping.[60,61] Thus, the SEI layer on Li metal can be easily
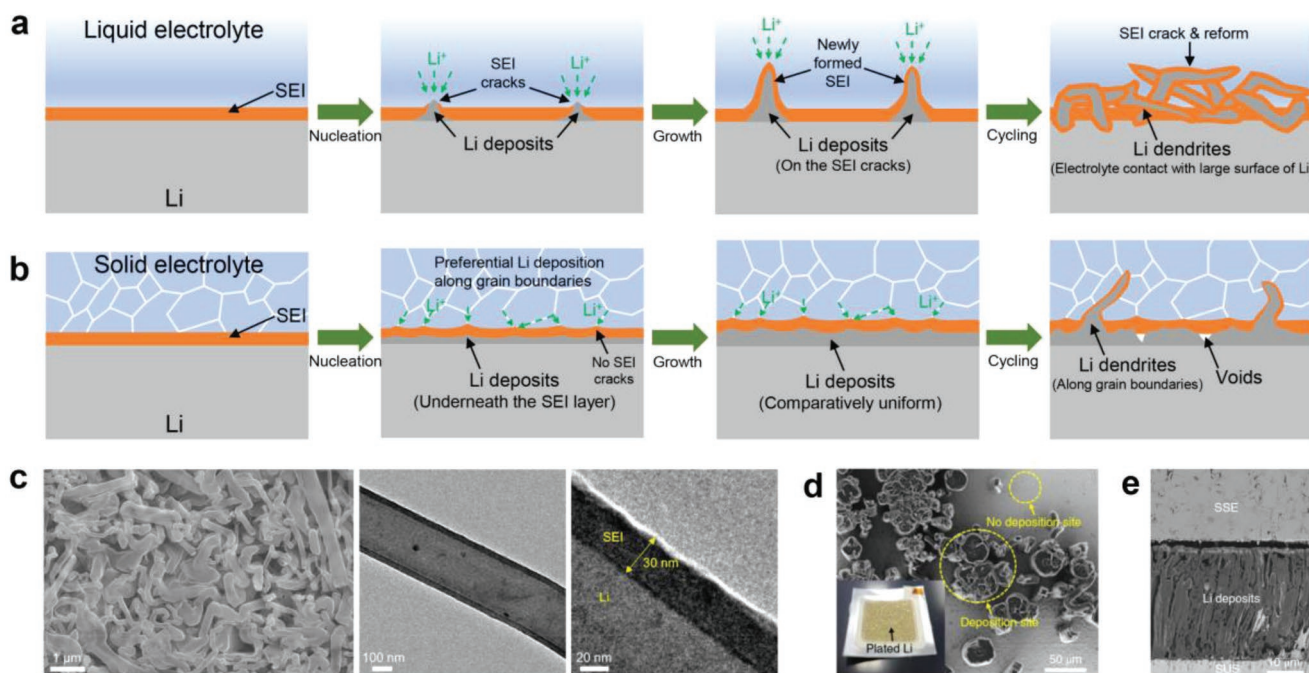
Figure 2. a) Schematic illustration of Li deposition behavior in liquid electrolytes. b) Schematic illustration of Li deposition behavior in solid-state electrolytes. c) FE-SEM and cryo-TEM images of the deposited Li at 1 mA cm^{-2} for 1 mAh cm^{-2} in liquid electrolyte. Reproduced with permission.[25] Copyright 2021, American Chemical Society. c) Top view of plated Li after 0.05 C charging at 50% SOC in solid-state electrolyte. d) Cross-sectional view of plated Li after 0.05 C charging at 100% SOC in solid-state electrolyte. Reproduced with permission.[44] Copyright 2020, Nature Publishing Group.

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broken during both volume expansion during the Li deposition and volume contraction during Li stripping, causing the generation of severe cracks in the SEI layer. Li+ ions are preferentially deposited and the applied current density is localized at these cracks since the interfacial resistance of the newly exposed Li surface at the crack is much lower than that of the Li surface covered by the intact SEI. Therefore, Li metal protrusions grow non-uniformly out of the cracks, leading to heterogeneous Li deposition.[41,62,63] In addition, the newly deposited Li metal inevitably creates a fresh Li surface. Due to the highly reactive nature of the surface of fresh Li, the electrolytes decompose on the surface, forming a new SEI layer on the surface of newly deposited Li.[64,65] The repeated destruction and reformation of the SEI layer originating from inhomogeneous Li deposition and stripping brings about a continuous consumption of the electrolyte and Li metal, resulting in increased interfacial resistance and poor Coulombic efficiency.[24,66,67]

The main reason for the continuous parasitic reactions on the Li metal can be attributed to the liquid nature of the electrolytes. In the liquid electrolyte-based batteries, all the Li dendrites generated during cycling are immersed in the liquid electrolytes. Thus, all of the surfaces of the Li dendrites can be active sites for electrolyte decomposition and the parasitic reactions between the Li metal and the electrolytes inevitably occur on all surfaces of the Li metal immersed in the electrolyte, generating irreversible electrolyte decomposition products. It is clearly shown in Figure 2c where all Li deposits are covered by an SEI layer which originates from the interfacial side reaction between the Li metal and the liquid electrolyte.[25] The surface area of Li dendrites is gradually increased as the cycling progresses which rapidly accelerates the parasitic reactions, resulting in cell failure.

2.2. SEI and Interfacial Issues for Li Anode in Solid Electrolytes

Although the replacement of the liquid electrolytes with SSEs suppresses the interfacial reactions between the Li metal and the electrolytes, several serious issues including narrow electrochemical stability window, poor wettability with Li metal, and inhomogeneous ionic conductivity between the grain interior and the grain boundary hinder their practical application. A schematic illustration of Li deposition behavior in the SSEs is provided in Figure 2b. Even though SSEs are more electrochemically stable than liquid electrolytes, most SSEs are reductively decomposed by contact with Li metal before electrochemical cycling begins since most SSEs have a narrow electrochemical stability window.[68,69] Thus, an SEI layer is generated as a decomposition product of the SSEs. It is noteworthy that the SEI layer generated in solid electrolytes is considerably stronger and more rigid compared to the SEI layer formed in liquid electrolytes because the SEI layer formed in the SSEs originates from a structural transformation of the solid electrolytes.[70–72] Previous studies have revealed that the properties of the SEI layer are altered depending on the electronic conductivity and ionic conductivity of the SEI. When the SEI exhibits high ionic conductivity and low electronic conductivity, the most stable SEI is formed and the interface between the Li metal and the SSEs becomes comparatively stable.[71,73] However, the interface between the Li metal and the SSEs often has electronic conductivity which

acts as a mixed ionic electronic conductor. Thus, the transferred electrons across the interface cause a continuous consumption of the SSEs and volume growth of the unstable SEI layer, resulting in an increase in interfacial resistance.[71,74] Among the various SSEs, the sulfide-based SSEs are more easily decomposed than the other SSEs due to a narrower stability window. Previous studies have shown that Li_6PS_5X (X = Cl, Br, I) decomposes upon contact with Li metal which generates an interphase layer consisting of Li_3P, Li_2P, and LiX, increasing the interfacial resistance and decreasing the electrochemical performance.[75,76] Similarly, NASICON-type SSEs exhibit a spontaneous reduction of the metal (Ti or Ge) in contact with Li metal which causes the formation of an unstable SEI layer, leading to severe resistance increases.[77,78] Meanwhile, SSEs, in particular the garnet-type SSE, have poor wettability with Li metal since the solid has poor solid-solid contact between the Li metal and the SSEs.[79,80] The poor wettability of Li metal onto the SSEs leads to microscopic gaps between the Li metal and the SSEs during the curing of the molten Li metal, resulting in increased interfacial resistance and acceleration of dendritic Li growth.

Once the electrochemical Li deposition reaction occurs, Li+ ions transfer across the SSEs and Li metal is deposited underneath the SEI layer. Since there is a comparatively higher ionic conductivity along the grain boundary than the grain interior, Li is preferentially deposited along the grain boundaries of SSEs.[81–83] Thus, inhomogeneous Li deposition occurs as depicted in Figure 2d.[44] The non-uniform volume expansion during the Li deposition can possibly damage the SSEs and SEI. However, the comparatively stiff nature of SSEs can accommodate the stress derived from the non-uniform volume expansion, suppressing the generation of cracks.[51,84] Therefore, the fresh Li metal is not significantly exposed to the SSEs which mitigates the parasitic reactions between the fresh Li and the SSEs. Due to the advantageous nature of the rigid solid form of SSEs, more uniform Li deposition occurs with less consumption of both the electrolytes and the Li metal compared to the liquid electrolyte systems (Figure 2e).[44] In addition to the stiff nature of SSEs, previous studies reported that the SEI layer between the Li metal and the SSEs plays an important role in alleviating the growth of Li dendrite.[70,71] However, even though it is not as severe as the liquid electrolyte systems, the repeated cycling of Li deposition and stripping unavoidably brings about the generation of Li dendrites and voids with the SSE system. In particular, the non-uniform Li+ ion flux originating from the different ionic conductivity between the grain boundaries and the grain interior accelerates the heterogeneity of Li deposition.[81–83] The inhomogeneous Li deposition leads to Li dendrites and voids resulting in crack formation in the SSEs, electrolyte decomposition, and loss of connection between the Li metal and the electrolytes, resulting in a dramatic decrease in cycling performance and safety problems.

3. Strategies of SEI Modification for Li Anode in Liquid and Solid Electrolytes

As shown above, the Li metal anode encounters severe interfacial problems with both liquid electrolytes and solid electrolytes. The unstable interface between the Li metal and the electrolytes
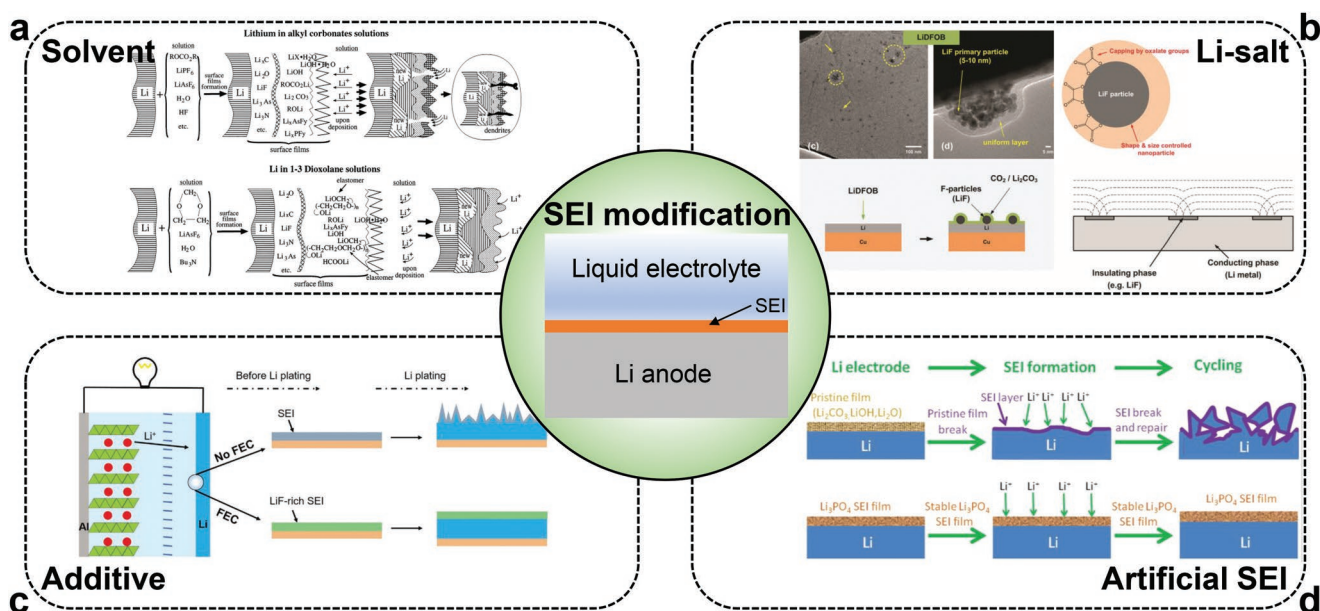
Figure 3. Schematic illustration of SEI modification strategies for Li anode in liquid electrolytes. a) Schematic illustration of surface film formation on lithium electrodes in alkyl carbonates and in 1–3 dioxolane solutions. Reproduced with permission.[63] Copyright 2000, Elsevier. b) TEM images of lithium plated from 1.2 M LiDFOB in EC:EMC = 3:7, schematic illustration of LiF particle and SEI model with diffusion fields. Reproduced with permission.[92] Copyright 2018, Royal Society of Chemistry. c) Schematic illustration of the effect of FEC additives on a Li metal anode. Reproduced with permission.[21] Copyright 2017, Wiley-VCH. d) Schematic illustration of the general Li metal and Li_3PO_4-modified Li metal anodes during SEI formation and cycling. Reproduced with permission.[119] Copyright 2016, Wiley-VCH.

causes continuous electrolyte decomposition, uneven Li deposition, and continuous consumption of electrolyte and Li metal. This results in an increase in interfacial resistance and consequent decay of electrochemical cycling. These critical problems originate from a combination of the highly reactive nature of Li metal and the narrow electrochemical stability window of electrolytes. While the SEI layer, which is generated by the electrolyte decomposition reaction with Li metal, can suppress the parasitic side reactions, the physical and chemical properties are insufficient to tolerate the stress derived from repeated cycling. Thus, the SEI layer needs to be modified to overcome the interfacial issues between the Li metal and the electrolytes. Since liquid and solid electrolytes have intrinsically different properties, different strategies are required for better electrochemical performance for each system.

3.1. SEI Modification for Li Anodes with Liquid Electrolytes

Compared to the solid electrolytes, the SEI generated on the Li anode from liquid electrolytes is weaker and more fragile since the SEI is composed of heterogeneous components derived from the decomposition of inorganic salts and organic solvents while the SEI formed by the structural transformation of solid electrolytes is intrinsically stiff. Thus, the SEI generated from liquid electrolytes can be easily broken during the volumetric change of the Li anode during cycling, leading to the generation of more Li dendrites. To suppress the damage to the SEI layer, the physical and chemical properties of the SEI layer need to be improved. Since the SEI layer is generated by the decomposition of electrolytes, the properties of the SEI can be

modified by modification of the electrolyte components such as solvents, Li-salts, and additives.

As shown in **Figure 3**a, the SEI layer on Li metal is significantly altered by electrolyte solvents.[63] In recent decades, carbonate-based electrolytes have been most commonly used for LiBs. Thus, most studies for lithium metal batteries (LMBs) have been conducted with carbonate-based electrolytes. In general, carbonate-based electrolytes are composed of a mixture of cyclic carbonates and linear carbonates as solvents. Linear carbonates such as dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) generate comparatively short-chain compounds (CH_3OCO_2Li or $CH_3CH_2OCO_2Li$).[85] Thus, a stable and strong SEI layer cannot be formed by these short-chain compounds and the generation of Li dendrites is rarely suppressed.[86] In contrast, the cyclic carbonates such as ethylene carbonate (EC) and propylene carbonate (PC) generate relatively longer chain semi-carbonate products such as $CH_3CH(OCO_2Li)CH_2OCO_2Li$ or $(CH_2OCO_2Li)_2$ via a ring-opening reaction and form a stronger and more flexible SEI layer.[85,87] The favorable feature of the SEI layer plays an important role in suppressing inhomogeneous Li growth.[86] However, the cyclic carbonates must be used as a mixture with the linear carbonates due to their high viscosity and poor wettability. In addition, the lithium alkyl carbonates have relatively poor thermal and mechanical stability and thus decompose on the surface of the Li metal anode upon cycling.[88,89] Thus, more studies of carbonate-based electrolytes will be necessary to solve the interfacial issues. Alternatively, considerable research on ether-based electrolytes has been devoted to understanding the SEI formation mechanisms and solving the interfacial problems.[18,63,90,91] The ether-based electrolytes including 1,3-dioxolane (DOL), 1,2-dimethoxyethane

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(DME) and tetraethylene glycol dimethyl ether (TEGDME) generate oligomers of polydioxolane in addition to HCOOLi and $CH_3CH_2OCH_2OLi$ by reductive decomposition reactions on Li metal. In particular, the insoluble polydioxolane oligomers can easily adhere to the surface of Li metal and form a flexible SEI layer. Thus, the flexible SEI layer can facilitate more stable cycling by accommodating the large volume change during the Li deposition and stripping.[90] However, the ether-based electrolytes are difficult to use at high potential since they are incompatible with high voltage cathodes (e.g., LCO, NCM) due to the low oxidative stability of ethers (<4 V vs Li/Li+).

The properties of the SEI layer are also dependent upon the structure of the Li-salts. Lithium hexafluorophosphate ($LiPF_6$) which is the most commonly used Li-salt in LiBs is not suitable for LMBs since $LiPF_6$ salt generates a highly porous film and a low concentration of LiF in the SEI. Therefore, many investigations have been conducted to develop a better Li-salt for the Li anode. Previous investigations compared the effect of various Li-salts on the generation of the SEI layer, the effect on the morphology of the deposited Li and the Coulombic efficiency.[86] Surface analysis via X-ray photoelectron spectroscopy (XPS) suggests that LiF is the most prominent Li compound generated in the electrolytes with ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) while lithium bis(oxalate)borate (LiBOB), lithium difluoro(oxalate)borate (LiDFOB), lithium hexafluoroarsenate ($LiAsF_6$), and lithium triflate ($LiCF_3SO_3$) generate Li_2CO_3 as the dominant Li compound. In addition, the XPS data indicate that electrolytes consisting of lithium perchlorate ($LiClO_4$) and Lithium iodide (LiI) generate more Li_2O. Investigations of the Coulombic efficiency revealed that electrolytes containing $LiAsF_6$ salt exhibit the highest Coulombic efficiency. The authors claimed that the AsF_3 formed by the reduction of $LiAsF_3$ suppresses further electrolyte decomposition on Li metal, improving Coulombic efficiency. In addition, the Li-salt can modify the physical properties of the SEI layer. Our group reported that an electrolyte comprised of LiDFOB salt improves the cycling stability of lithium metal anodes (Figure 3b).[92] Comprehensive surface analysis via cryogenic-TEM and XPS revealed that the SEI formed by the reductive decomposition of LiDFOB salt has uniformly distributed LiF nanoparticles (5–10 nm). Due to the electronically insulating nature of LiF and its low cation diffusivity, LiF can act as an inactive area for Li deposition and stripping. Thus, the SEI layer on Li metal has both active and inactive areas, leading to uniform diffusion field gradients and uniform Li deposition and stripping. Another approach for building a stable SEI layer is to apply a high concentration of Li-salt.[93–95] A previous study utilized a highly concentrated lithium bis(fluorosulfonyl)imide (LiFSI) solution in DME solvent for the Li anode.[93] Surface and electrochemical analysis revealed that the highly concentrated LiFSI generates a highly conductive and compact SEI layer which leads to stable voltage profiles during the cycling and suppression of further corrosion of the Li metal below the SEI layer.

One of the frequently reported strategies to modify the SEI layer is the use of electrolyte additives. Many studies have focused on the development of electrolyte additives since the incorporation of electrolyte additives into electrolyte formulations is a straightforward method to improve electrochemical

cycling performance. Among the many electrolyte additives, fluoroethylene carbonate (FEC)[21–23,96,97] and lithium nitrate ($LiNO_3$)[98–101] are the most effective electrolyte additives for the Li metal anode. FEC is a well-known electrolyte additive that generates a LiF-rich SEI layer. Generally, LiF is considered an important SEI component due to its attractive physical properties including high mechanical strength,[102,103] low solubility,[104] and wide electrochemical stability window[68,105] in addition to its favorable electrochemical features such as low resistance[106,107] and homogeneous regulation of Li+ ions flux.[23,92] Therefore, the LiF-rich SEI layer formed on Li metal affords significantly improved cycling performance. In previous work, 5 wt.% of FEC was incorporated into carbonate-based electrolyte as an electrolyte additive. The first-principles calculations suggest that FEC is easily reduced on the Li metal surface to form LiF due to a low-lying lowest unoccupied molecular orbital (LUMO) level (–87 eV) of FEC. The electrochemical observations showed that the LiF-rich SEI layer mitigates Li dendrite formation and leads to stable polarization and improved Coulombic efficiency of 98% within 100 cycles in Li/Cu cells (Figure 3c).[21] Meanwhile, it has been reported that $LiNO_3$ is reduced at 1.8 V (vs Li/Li+) and Li_3N and LiN_xO_y are generated by the reductive decomposition of $LiNO_3$.[108,109] Since the Li_3N and LiN_xO_y have good ionic conductivity (up to 10^{-3} S cm^{-1}) and high mechanical strength, they can enhance the Li+ ion diffusivity across the SEI layer and suppress the dendritic Li growth.[109–113] In addition, the incorporation of $LiNO_3$ in electrolytes allows homogeneous spherical Li deposition without non-uniform Li dendrites, improving Li deposition and stripping cycling.[91,98,101] However, since $LiNO_3$ is largely insoluble (≈800 ppm) in carbonate-based electrolytes,[100] it has primarily been investigated in ether-based electrolytes which are incompatible with high-voltage cathode materials. Although several approaches using solubilizing agents such as triethyl phosphate (TEP), $LiBF_4$, CuF_2, and γ-butyrolactone have been reported to improve the poor solubility of $LiNO_3$ in carbonate-based electrolytes, further improvement is required to use $LiNO_3$ in practical battery systems with carbonate-based electrolytes.[101,114–116]

In addition to the electrolyte components such as solvents, Li-salts, and additives, the SEI layer on Li metal can be modified by pre-treatment of the Li metal surface prior to cell fabrication to generate an "artificial SEI". The artificial SEI can reinforce the physical and chemical properties of Li metal surface, leading to uniform Li deposition and stripping. Among the many strategies, the most effective ways can be divided into inorganic or polymer artificial SEIs. Inorganic materials such as LiF,[117] Li_3AlF_6,[118] Li_3PO_4,[119] Al_2O_3,[120] Li_3N,[121] $LiBO_2$,[122] and 3-methacryloxypropyltrimethoxysilane (MPS)[123] can enhance mechanical properties of the SEI layer and physically suppress crack formation during repeated cycling. A previous investigation reported that a Li_3PO_4 layer formed by a simple reaction of polyphosphoric acid (PPA) with Li metal functions as an artificial SEI and exhibits highly stable chemical properties and a high Young's modulus. Therefore, the Li dendrite growth and continuous electrolyte decomposition reaction were significantly mitigated, resulting in considerably improved cycle performance (Figure 3d).[119] Artificial SEIs using polymers such as poly(vinyl alcohol),[124] poly(vinylidene difluoride),[125] supramolecular polymer[126] and Li polyacrylic acid (LiPAA)[127] have

many advantageous properties including high elasticity, robustness, and durability. In particular, the highly flexible nature of a polymer can address the issues derived from the large volume change of Li metal, mitigating the non-uniform Li growth and parasitic electrolyte decomposition. As shown above, pre-treatment of Li metal can enhance the rigidity and flexibility of the SEI layer which can suppress some interfacial problems. However, more studies are necessary since the current artificial SEIs do not address issues originating from newly exposed Li metal surfaces during dynamic Li deposition and stripping cycling.

3.2. SEI Modification for Li Anodes with Solid Electrolytes

Since the SSEs have more favorable properties including stronger mechanical strength and higher electrochemical stability than the liquid electrolytes, the generation of Li dendrites and the continuous electrolyte decomposition which are encountered in liquid electrolyte-based battery systems are significantly suppressed in the solid electrolyte-based battery systems. However, several issues originating from their rigid structure, low wettability with Li as well as the electrochemically unstable nature of the surface are still encountered at the interface between the Li metal and the SSEs. The completely different properties of the SSEs from the liquid electrolytes require different strategies for SEI modification to suppress the interfacial problems between the Li metal and the electrolytes. Since the SEI layer is formed by interfacial reactions between the Li metal and the surface of SSEs, surface treatments of the SSEs and tuning of the Li metal in addition to buffer layer coatings on SSEs can be used to modify the SEI layer.

Moisture on the surface of SSEs adsorbed by exposure to the ambient atmosphere reacts with the SSEs to form byproducts. Previous studies reported that the reaction of the sulfide-based SSEs with moisture generates toxic H_2S and the reaction of the garnet-based SSEs with moisture and CO_2 forms passivation films comprised of Li_2CO_3 and $LiOH$. [128-132] Since the byproducts can cause an increase in the interfacial resistance between the Li metal and SSEs, it is necessary to remove these byproducts to afford better electrochemical performance. Previous investigations suggest three primary methods to remove the contaminants including dry polishing, wet polishing, and heat treatments. The contaminants such as Li_2CO_3 and $LiOH$ on $Li_7La_3Zr_2O_{12}$ (LLZO) cause poor wettability of Li metal, resulting in high interfacial resistance. However, the contaminants can be mostly removed by surface treatment including the above-mentioned methods and the Li wettability is significantly increased, resulting in a decrease of the interfacial resistance (**Figure 4**a). [130] In addition to physical surface treatment, chemical treatment of the surface of SSEs using H_2PO_4 has been reported. The strategy uses phosphoric acid (H_3PO_4) which reacts with the passivation film including Li_2CO_3 and $LiOH$ on the $Li_7La_3Zr_2O_{12}$ (LLZTO) to generate a Li_3PO_4 layer. Surface and electrochemical analyses reveal that the Li_3PO_4 layer improves the interfacial wettability of Li metal and suppresses dendritic Li growth, resulting in a decrease in interfacial resistance (7.0 Ohm cm^{-2}) of the symmetric cell and stable cycling performance for over 1600 h at 0.1 mA cm^{-2} and over 450 h at 0.5 mA cm^{-2}. [131]

In contrast with the liquid electrolytes, the rigid nature of SSEs causes insufficient contact between the Li metal and the SSEs due to their poor wettability with the Li metal anode. The

Figure 4. Schematic illustration of SEI modification strategies for Li anode in solid electrolytes. a) Surface of LLZO and contact angle of melten metallic Li before and after surface control. Reproduced with permission.[130] Copyright 2017, American Chemical Society. b) The synthesis process of Li-C$_3$N$_4$ composite and the interfacial contact comparison of Li/garnet and Li-C$_3$N$_4$/garnet. Reproduced with permission.[133] Copyright 2019, Royal Society of Chemistry. c) Schematic diagrams of Li/Li$_7$P$_3$S$_{11}$ interface and modified interface with a uniform thin LiF (or LiI) interphase layer and HFE (or I solution) infiltrated sulfide electrolyte. Reproduced with permission.[139] Copyright 2018, Elsevier. d) Schematic illustration of the conventional solid-state battery and solid polymer electrolyte layer-applied solid-state battery. Reproduced with permission.[147] Copyright 2019, Elsevier.

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high interfacial resistance originating from the poor contact can accelerate the generation of dendritic Li, resulting in poor electrochemical performance. One method to resolve the problem is to modify the Li metal to improve the wettability between the Li metal and the SSEs. A commonly used method is to form a Li-alloy or Li-composite which can regulate the surface energy and the viscosity of Li metal, improving the wettability against SSEs. Previous investigations reported that the wettability of the garnet-based SSEs can be significantly improved by the addition of g-C_3N_4 into Li metal because the addition of g-C_3N_4 promotes both a viscosity increase of molten Li and a decrease in the surface tension of molten Li. Furthermore, the study showed that the Li-C_3N_4 composite, which is made by mixing molten Li with g-C_3N_4, forms a highly Li$^+$ ion conducting and good electrically insulating Li_3N layer between the Li metal and the SSEs, enabling low interfacial resistance (Figure 4b).[133] Similarly to the Li-C_3N_4 composite, it was reported that lithium-graphite (Li–C) and lithium-boron nitride (Li–BN) composites enhance the wettability of Li metal with garnet-based SSEs, leading to low interfacial resistance. The studies suggest that the enhanced wettability can be ascribed to the increased viscosity of Li-composites.[134,135] In addition, similar strategies were reported in which the wettability of SSEs was improved by adding Sn,[136] Sr,[137] and Si_3N_4.[138]

Among the various strategies to suppress the electrochemical and chemical instabilities of SSEs, buffer layer coatings on the surface of SSEs are one of the most frequently used methods. The buffer layers can protect the surface of SSEs and suppress the deformation of the SSEs resulting from contact with reactive Li metal and function as an artificial SEI between the Li metal and the SSEs. Moreover, the buffer layer can improve the wettability of Li metal with the SSEs which ultimately mitigates Li dendrite formation and improves the electrochemical stability. The buffer layers can be roughly classified into inorganic and polymer layers.

Since Li-halides have an extremely wide electrochemical stability window, they are the most widely used as inorganic buffer layers between the Li metal and SSEs.[68] Previous work reported that the use of Li-halides (LiF and LiI) as a buffer layer effectively blocks the parasitic decomposition reaction between the Li metal and the SSEs due to their low electronic conductivity. Moreover, the work also revealed that the high interfacial energy with Li metal mitigated the dendritic Li growth (Figure 4c).[139] Several related investigations concluded that the favorable features of the Li-halide buffer layers such as high interfacial energy with Li metal and strong modulus play a key role in the remarkable improvement of electrochemical performance.[139–141] Meanwhile, Si, Al, Mg, ZnO, and Sn which can be alloyed with Li metal have been used as the inorganic buffer layers to modify the SEI layer between the Li metal and the SSEs.[142–146] A thin layer of these materials coated on the SSEs forms an interphase layer of Li metal alloy when the materials are in contact with Li metal. The SEI layer comprised of Li metal alloy modifies the surface of SSEs to lithiophilic which promotes increased Li wettability of SSEs. Thus, the physical contact between the Li metal and the SSEs is significantly improved and interfacial resistance is considerably reduced, resulting in stable Li deposition and stripping.

As a polymer buffer layer, Li$^+$ ion conducting polymers such as polyethylene oxide (PEO) have been widely studied to address the poor solid-solid contact between the Li metal and the SSEs.[147–151] Generally, the PEO has blended with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) which is deposited onto SSEs by spin coating or spray coating methods as a polymer buffer layer. The soft nature of PEO provides soft-to-hard contact between the Li metal and the SSEs which improves the Li wettability of the SSEs. In addition, the physical protection of a polymer on the SSEs can block the parasitic decomposition reaction between Li metal and the SSEs. Figure 4d contains a previous example using a soft polymer electrolyte (SPE) as a buffer layer between the Li metal and the LLZTO.[148] LLZTO is a well-known garnet-type SSE which has a particularly hard nature resulting in poor solid-solid contact with the Li metal anode. However, in the previous report, the insufficient wettability was overcome by coating the soft SPE buffer layer on the surface of the LLZTO which allows soft-to-hard contact between the Li metal and the LLZTO, resulting in a decrease of interfacial resistance, improved Coulombic efficiency and superior cycling performance. However, using the polymer buffer layers often requires elevated temperatures for cell cycling because of the poor ionic conductivity of the polymer layer.

4. Conclusion and Perspectives

In this article, the differences in SEI layers on Li metal anodes, interfacial issues, and strategies for SEI modification in both the liquid and solid electrolyte systems have been reviewed. For the two electrolyte systems, the SEI layer plays an important role in electrochemical Li deposition and stripping reactions since the SEI layer is generated between the lithium metal anode and the electrolyte and has a large influence on the interfacial reaction. Thus, enhancement of the physical and chemical properties of the SEI layer can be an effective method to improve the electrochemical performance. However, the different physical and chemical nature between the liquid electrolytes and the solid electrolytes generates entirely different SEI layers in each electrolyte system since the SEI layer is formed by the reductive decomposition reaction of the electrolytes. In liquid electrolyte systems, a weak and fragile SEI layer is generated by the decomposition of liquid electrolytes while in solid electrolyte systems, the SEI layer has comparatively strong and rigid properties since the SEI layer is formed by the structural transformation of solid electrolytes. Since the weak SEI layer does not properly suppress the dendritic Li growth in the liquid electrolyte systems, the strategies of SEI modification in the liquid electrolyte systems are mostly focused on the reinforcement of physical rigidity and chemical stability of the SEI layer. In the liquid electrolyte systems, tuning the electrolyte components such as solvents, Li-salts, and additives is the most effective method to modify the SEI layer because the SEI layer is derived from the decomposition of electrolytes and the surface of dynamically transformed Li metal is in contact with the liquid electrolytes. Alternatively, even though Li dendrite formation can be suppressed by the high strength of the SEI formed in SSEs, repeated cycling causes dendritic Li growth along

Table 1. Characteristics of SEI modification strategies for Li anode in liquid electrolytes and solid electrolytes.

Electrolyte systems	SEI modification strategies	Methods	Characteristics	Ref.
Liquid electrolyte	Solvent	Cyclic carbonates (EC, PC)	Generation of longer chain compounds	Ref. [85,87]
		Ether-based electrolytes (DOL, DME, TEGDME)	Formation of adhesive and flexible SEI	Ref. [63,90,91]
	Li-salt	$LiAsF_6$	Generation of AsF_3	Ref. [86]
		LiDFOB	Generation of uniformly distributed LiF nanoparticles	Ref. [92]
		Highly concentrated LiFSI	Generation of highly conductive and compact SEI	Ref. [93]
	Additive	FEC	Generation of LiF-rich SEI	Ref. [21–23,96,97]
		$LiNO_3$	Generation of Li_3N and LiN_xO_y	Ref. [98–101]
	Artificial SEI	Inorganic materials (LiF, Li_3AlF_6, Li_3PO_4, Al_2O_3, Li_3N, $LiBO_2$, MPS)	Enhancing mechanical properties of SEI	Ref. [117–123]
		Polymers (PVA, poly(vinylidene difluoride), supra-molecular polymer, LiPAA)	High elasticity, robustness and durability	Ref. [124–127]
Solid electrolyte	Surface treatment of SSEs	Physical treatments (dry polishing, wet polishing, heat treatment)	Removing contaminants such as Li_2CO_3 and LiOH	Ref. [130]
		Chemical treatments (H_3PO_4)	Improving interfacial wettability of Li metal	Ref. [131]
	Li metal tuning	Addition of g-C_3N_4, graphite, BN, Sn, Sr, Si_3N_4 into Li-metal	Increasing surface energy and viscosity of Li metal	Ref. [133–138]
	Inorganic buffer	Li-halides (LiF, LiI)	Generation of electrochemically stable layer	Ref. [139–141]
		Li-alloys (Si, Al, Mg, ZnO, Sn)	Surface modification of SSEs to lithiophilic	Ref. [142–146]
	Polymer buffer	PEO	Providing soft-to-hard contact between the Li metal and the SSEs	Ref. [147–151]

the grain boundaries of SSEs. Moreover, the physically rigid and chemically unstable nature of SSEs leads to severe problems such as poor Li wettability with the SSEs and large interfacial resistance between Li metal and the SSEs. In the solid electrolyte systems, surface treatments of the SSEs and the Li metal or the generation of a buffer layer coating on SSEs are the most widely used methods for SEI modification since the SEI layer is derived from the interfacial reaction between the Li metal and the surface of the SSEs. Although various strategies of SEI modification have been investigated to overcome the critical challenges of Li metal anodes in both the liquid and solid electrolyte systems as presented in **Table 1**, using highly reactive Li metal as an anode material remains problematic. In order to achieve the practical application of Li metal, a better understanding of the SEI generation mechanisms on Li metal must be uncovered and innovative strategies for each electrolyte system must be developed. It is absolutely crucial that each electrolyte system should be applied with different strategies for SEI modification on Li metal since each electrolyte system has completely different interfacial phenomena. However, future research directions are similar and should be focused on generating a chemically stable, physically strong, and uniform SEI in each electrolyte system. These favorable features are essential due to the significant challenges associated with the Li metal anode such as low reaction potential, large volume change, and non-uniform Li-ion flux, resulting in uniform Li deposition and stripping. In addition, the method for SEI modification must be simple so it can be practically usable. Meanwhile, similar to the Li metal anode, the Na metal anode has similar interfacial issues to be addressed. Its highly reactive nature and the host-less deposition/stripping-based reaction results in an unstable interface between the Na metal and the electrolytes, resulting in critical interfacial problems including inhomogeneous Na deposition and high interfacial resistance in both liquid electrolytes and solid electrolytes. Thus, modification of the SEI is also important for the practical application of the Na metal anode and this article can provide insight into the best research directions for solving the interfacial issues of the Na metal anode in addition to the Li metal anode.

Conflict of Interest

The authors declare no conflict of interest.

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