Inhibiting Lithium Dendrite Growth for Lithium Batteries: Challenges and Strategies

Qian Sun and Xiangbo Meng*
Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR, the United States

ABSTRACT

With the continuous depletion of fossil fuels and environmental issues, modern societies have an ever-aggravating concern on transportation relying on the combustion of gasoline. Simulated by the great success of lithium-ion batteries (LIBs) in the 21st century, nowadays battery-powered electric vehicles have become one premier pursuit for future transportation and are undergoing intensive development. To power electric vehicles, a minimum energy density of 300 Wh/kg is required. State-of-the-art LIBs are dominating portable electronics, but can only enable an energy density of 100-220 Wh/kg in practice to date. Apparently, LIBs need new electrodes with higher capacities. In this aspect, metallic lithium is highly regarded as promising next-generation anodes, ascribed to its extremely high theoretical capacity of 3860 mAh/g versus 372 mAh/g of the commercial graphite anodes. With the adoption of metallic lithium as anodes, on the other hand, lithium-sulfur (Li-S) batteries can realize a theoretical energy density of 2600 Wh/kg, five to ten times higher than those of LIBs. In addition, non-aqueous lithium-oxygen (Li-O_2) batteries excluding oxygen mass can deliver a specific energy of 12000 Wh/kg theoretically and even 1700 Wh/kg at cell level has been achieved. Therefore, metallic lithium has become one of the most ideal anodes for new battery systems enabling higher energies to meet our pursuit in electric vehicles. However, the dendrite growth of lithium anodes during charge-discharge processes poses serious safety risks and should be fully addressed technically. In this context, a number of research efforts have been conducted for gaining a better understanding on the dendrite growth mechanisms and for developing feasible strategies. In this Chapter, we focus on clarifying the mechanisms of lithium dendrite growth, the issues related to lithium dendrites, and the recent advances for technical solutions.

Keywords: Lithium metal anodes, Lithium dendrites, Lithium-ion battery, Lithium-sulfur battery, Lithium-oxygen battery

* Dr. Xiangbo Meng
Email: xbmeng@uark.edu


1. INTRODUCTION

Since the first commercialization in the early 1990s, lithium ion batteries (LIBs) now have been widely applied in portable electronics. The state-of-the-art of LIBs can typically achieve an energy density of 100-220 Wh/kg, which hindered their further applications for smart grids and transporation. A LIB cell typically consists of a metal oxide cathode (such as LiCoO$_2$ or LiFePO$_4$), an anode (such as LiC$_6$ or Li$_x$Ti$_5$O$_{12}$), an electrically insulated polypropylene membrane and an non-aqueous electrolyte (Figure 1 (a)). The graphite anode of LIBs has a low theoretical specific capacity of 372 mAh/g, which makes it impossible to satisfy the increasing demand for high-energy storage. At the same time, LIBs have issues in stability, cost, and safety. In this context, there have been new lithium-based battery technologies under development, such as lithium-sulfur (Li-S) batteries and lithium-oxygen (air) (Li-O$_2$) batteries. Using Li metal and sulfur as the anode and cathode, respectively, Li-S batteries enable a theoretical specific energy of ~2600 Wh/kg, five to ten times higher than that of LIBs (Figure 1 (b)). Based on the reaction of 2Li$^+$ + O$_2$ $\leftrightarrow$ Li$_2$O$_2$ (E$^{\text{th}}$ = 2.96 V), Li-O$_2$ batteries (Figure 1 (c)) are thought to be one of the most attractive energy storage devices and have a specific energy density of 3600 Wh/kg theoretically. Calculated purely on the mass of Li metal, in particular, Li-O$_2$ batteries can even achieve a theoretical specific energy of 12000 Wh/kg, which is comparable to the gasoline energy.

In Li-S and Li-O$_2$ batteries, Li metal are proposed as their anodes, ascribed to the facts that Li metal has a high theoretical capacity of 3860 mAh/g and a low electrochemical potential (i.e., −3.04 V vs standard hydrogen electrode). However, lithium metal batteries (LMBs) have been concluded being impractical for decades, due to several serious issues associated with the utilization of Li metal anodes poor cyclability, low efficiency, and safety risks. For instance, Li metal anodes are prone to grow into dendritic structures to endanger battery cells. In a typical charge process of lithium metal battery cycling, Li$^+$ gains $e^-$ on the Li anode surface and become metallic lithium. Given the complex surface chemical reaction and morphological structure of a Li anode, the reductive electrodeposition of Li (i.e., Li plating) is generally non-uniform and difficult to control, leading to the dendrite-like growth of Li locally. The heterogeneous property of lithium dendrites becomes distinct with electrochemical cycles. It is considered to be one of the sources for battery failures. Large-scale dendrites not only continuously consume available Li and electrolyte but also possibly penetrate the separator and short the battery cell, leading to fire and/or explosion. On the other hand, the irreversible reaction between lithium metal and electrolyte results in the formation of solid interphase electrolyte (SEI) on the metal surface. It is important for SEI to be stable. However, the fragile SEI layer could be broken with large volume expansions of Li anodes during Li plating. This will expose fresh Li to electrolyte and cause a new formation of SEI layers. As a result, a battery cell with a Li anode often exhibits low Coulombic efficiencies (CE) and evident capacity fading. All these make Li metal a big challenge to be used as anodes for commercial LMBs.

In this chapter, we focus on clarifying the problems associating with lithium dendrite formation and growth and various strategies for inhibiting the Li dendritic growth. A large number of studies has been devoted to exploring the dendrite formation mechanism and there are mainly five approaches employed for inhibiting lithium dendrite growth, i.e.,

1. Electrolyte modification. Electrolyte additives can be employed to tune the electrolyte composition and further electrochemically regulate the lithium deposition kinetics, for example, Cs$^+$ additive and LiNO$_3$. 

2. Electrode modification. One of the most promising and effective approaches is to introduce an intercalation material (e.g., graphene or conducting polymer, etc.) or a solid electrolyte interlayer (SEIL) between the Li metal anode and the electrolyte. The SEIL can not only accommodate the volume change of Li plating/stripping but also preclude the direct contact between Li metal and the electrolyte. The electrode modification strategy has several advantages over the electrolyte modification approach, such as the increased cycling stability, the decreased thermal hazards, etc.

3. Cyclic voltammetry. Cyclic voltammetry is a promising strategy to tune the SEI formation and growth. Under the driving force of an external bias, the Li dendrites can be electrochemically regulated, for example, the electrochemical plating of Li film can be reduced or eliminated, or the morphology of Li dendrites can be controlled to dendrite-free. The regulation of Li dendrite is closely related to the concentration and properties of electrolyte additives, the Li metal anode, the applied potential, etc.

4. Electrochemical plating. Electrochemical plating is a straightforward method to tune the SEI formation and growth. Under an external bias, the Li dendrites can be electrochemically regulated to dendrite-free, dendritic, or dendrite-like, depending on the applied potential.

5. Electrochemical plating of Li film. Electrochemical plating is a straightforward method to tune the SEI formation and growth. Under an external bias, the Li dendrites can be electrochemically regulated to dendrite-free, dendritic, or dendrite-like, depending on the applied potential.
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(2) Solid-state electrolyte. Inorganic ceramic electrolytes (e.g., Li_{10}GeP_{2}S_{12} and Li_{3}La_{6}Zr_{2}O_{12}) and polymer electrolytes (e.g., PEO-LiTFSI, PEA-LiTFSI, LAGP-PEO) can be used to physically block the dendrite propagation, provide superior thermal stability. The non-liquid battery systems normally operate under high voltages and temperatures, enabling higher energy densities than the liquid electrolyte system.

(3) Artificial solid electrolyte interphase. A stable and compact solid electrolyte interphase is effective to inhibit the lithium dendrite and therefore improve the cycling performance of lithium anode. An ideal SEI protection layer should be electrochemically and chemically stable, robust enough to suppress lithium dendrite penetration, and can accommodate the volume expansion during Li deposition/dissolution. Atomic layer deposition (ALD) was an effective strategy based on self-limiting chemical reactions to prepare artificial SEI, which can finely control the thickness of coating layer at atomic-scale and inhibit the lithium dendrite growth to maintain a smooth lithium surface.

(4) Separator modification. The separator should be mechanically flexible, highly ionic, heat conductive and heat stable. Because the separator has significant effects on Li\(^+\) diffusion in electrolyte and on the lithium dendrite growth, separator modifications via surface coating have been considered as an effective method to improve Li metal safety.

(5) Li metal framework design. Inhomogeneous lithium ion distribution leads to nonuniform lithium nucleation, which then induces inhomogeneous lithium deposition and dendrite growth. Lithium dendrites can be suppressed if Li\(^+\) distribute uniformly on the anode surface. Rational 3D Li electrode frameworks have demonstrated to enable the stable operation of Li plating/stripping and stabilize the lithium metal anode.

Following this introductory section, in this chapter we present the SEI formation mechanisms and models in the section 2. Then, we pay a special attention on lithium dendritic growth in the section 3. In the section 4, we summarize the main strategies invested for inhibiting lithium dendrites. In the end, we conclude this chapter in the section 5.

2. SOLID ELECTROLYTE INTERPHASE

2.1. SEI formation mechanism

A typical electrolyte system in lithium batteries consists of an organic electrolyte (e.g., ethylene carbonate (EC), dimethyl carbonate (DMC), ethylmethyl carbonate (EMC), 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), and so on) (Figure 2 (a)) and a Li salt (e.g., LiPF\(_6\), LiClO\(_4\), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), bis(trifluoromethanesulfonyl)imide (LiTFSI), and so on)\(^{28-30}\). Since these organic solvents commonly have a reduction potential lower than 1.0 V vs. Li\(^+/Li\) and lithium metal is highly reactive, a bare Li metal can easily react with one of these electrolytes at a current, resulting in the formation of SEI. SEI has been regarded as an electrically insulating but ionically conductive film, first discovered by Dey in 1970s\(^{35}\) and later named by Peled\(^{36}\) as “solid electrolyte interphase” in 1979.

To date, there have been several mechanisms proposed for the SEI formation on lithium metal anode:

(1) The Peled model\(^{36,37}\). This model explains the SEI formation via a surface reaction and the established SEI layer exhibits an integral structure besides some Schottky defects for Li\(^+\) migration.
(2) The mosaic model. This model indicates that the SEI is not homogeneous. Compared with the Peled’s model, the mosaic model illustrates that there are several different electrolyte compositions decomposed on negatively charged anode surface simultaneously and that the mixture of multiphase products deposits on the anode. Therefore, the SEI layer presents a mosaic structure for Li⁺ migration.

(3) The Coulombic interaction mechanism. After surface reaction, the decomposition products are lined up with positively charged Li⁺ and partially positively charged carbons. This double electric layer enables the attachment of the decomposition products to the existing film. Based on the Coulombic interaction mechanism, the SEI layer is more stable than those from the other two models afore-discussed, ascribed to the effect of the ion pairs.

Among all the SEI models, the most famous and acceptable one to date is the Peled model, in which the SEI layer is 15-25 nm in thickness. The SEI layer serves as a passivation layer separating the electrode from electrolyte and has the property of solid state electrolyte.

2.2. Surface chemistry

Surface chemistry for the SEI formation is very complex (Figure 2 (b), (c)) 41-47. The SEI layer in thickness direction presents a dual-layer structure. The inorganic layer close to the Li metal surface contains Li2O 38, Li2S/Li2S2 39, LiOH, LiF 50-52, and Li2CO3 53, while the outer organic layer consists of ROLi, ROClLi, ROCO₂Li, and RCOO₂Li (R = alkyl groups). The inorganic components (e.g. Li2CO3) of SEI is very important for high capacity retention, since losing the components may induce new SEI formation where they dissolved 54,55.

2.3. Mechanical property

The huge volume change of lithium metal anodes during Li plating/stripping significantly affects the stability of their SEI film. It is favorable for SEI to have good mechanical property in order to suppress the lithium dendrite growth. It has been reported that Li dendrites could be inhibited partially if a SEI film could have a high shear modulus of ~10⁹ Pa, a value comparable to that of Li anode 56. However, the practical SEI layers generally have a low shear modulus.

Atomic force microscopy (AFM) has been used for detecting the topographic and mechanical property of SEI layers over anodes. Li et al 57 characterized the artificial Li3PO4 film on a lithium metal anode using AFM and found that the artificial film showed a Young’s modulus within the range 10-11GPa, which can effectively inhibit the lithium dendrite growth. Wan et al 58 measured the force curve (Figure 2 (d)) to characterize the mechanical property of the SEI layer composed of Li2S/Li2O in a Li/NCM (i.e., LiNi1−x−yCoₓMnᵧO2) full cell, and they revealed that the SEI layer had a smooth surface and a Young’s modulus of ~2.0 GPa, which is higher than that of the traditional ROCO₂Li2 species (0.31 GPa), but still far below the intrinsic values of Li2S/Li2O (82.6/169.0 GPa). This may be attributed to the incorporation of some organic species into the Li2S/Li2O-rich SEI layer, such as ROLi and RCOO₂Li.

2.4. Theoretical calculations

A number of studies has been devoted to the mechanism of SEI in the past four decades. In this respect, simulations are an important tool enabling insightful views into the evolutions of SEI in a battery cell.

Using density functional theory (DFT), Takenaka et al 59 investigated the SEI stability in EC-based and PC-based electrolytes, respectively. They found that the SEI generated on graphite surface in EC electrolyte was dense enough to prevent the electrolyte from excess
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reduction. While the SEI formed on graphite surface in the PC electrolyte was less dense and could not protect the electrolyte effectively. Thus, any difference in electrolyte structures at microscopic scale could significantly affect the formation of SEI (Figure 3). Using DFT and G09 Gaussian package, Yushin et al. disclosed that, the electrochemical reduction of the electrolyte (LiFSI in DOL:DME (1:1, v/v)) generated a protective coating on both the cathode and anode surfaces in Li-S battery, which was activated and initiated by the FSI (i.e., -F) anion radicals. In addition, such a reduction resulted in the formation of SEI layer with LiF.

Given the fact that theoretical calculations were based on many hypotheses, they might not exactly show the real conditions of for the SEI formation on lithium metal. To this end, a series of analytical techniques should be applied jointly for gaining a more comprehensive understanding on the SEI formation, such as Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Roman spectroscopy, Auger electron spectroscopy (AES), nuclear magnetic resonance (NMR), Electrochemical Impedance Spectroscopy (EIS), transmission electron microscopy (TEM), scanning probe microscopy (SPY), scanning electron microscopy (SEM) and AFM.

3. LITHIUM DENDRITES

3.1. Formation mechanisms and growth patterns

The growth of Li dendrites is regarded being induced by inhomogeneous Li\(^+\) deposition on the anode surface and is a severe problem in LMBs. It will lower the Coulombic efficiency, reduce the cycling performance of batteries, influence the structure of interface of Li/electrolyte, and hinder the practical applications of LMBs.

Henry J. S. first proposed a diffusing model “Sand’s time” (\(\tau_s\)) in 1901 to measure the initiation time of dendrite growth empirically near the SEI (Equation 1).

\[
\tau_s = \pi D \left( \frac{C_0 \epsilon S_c}{2} \right)^2 \left( \frac{\mu_a + \mu_c}{\mu_a} \right)^2
\]

where \(\mu_a\) and \(\mu_c\) stand for anionic and cationic mobilities, \(\epsilon\) represents electronic charge, \(J\) is initial concentio of Li salt, \(D\) is the diffusion coefficient, \(D = (\mu_a D_a + \mu_c D_c)/(\mu_a + \mu_c)\), where \(D_c\) and \(D_a\) are cationic and anionic diffusion coefficients. Large immigration rate of Li\(^+\) (\(D\) and \(\mu_c\)) and small current density (\(J\)) result in large “Sand’s time” (\(\tau_s\)), indicating that the battery has a long cycling life before Li dendrite growth.

Based on studies of Li/Li symmetric cells, there are different Li dendrite growth observed at different conditions. Three different morphological Li dendrites have been reported, i.e., needle-like, mossy-like and fractal-like, depending on experimental conditions. At low current densities (at \(< 0.5 \text{ mA/cm}^2\) in LiPF\(_6\) DMC/EC 1:1), the needle-like dendrites formed and evolved with increased cell potentials, highly related to the electrolyte components, current density, substrate, and other factors. It was reported that needle-like dendrites grew in both diameter and length simultaneously and this kind of dendrites is prone to cause short circuits of LMBs. In comparison, the mossy-like dendrites occur at higher current densities, associated with a decreased cell potential due to the increased surface area of Li dendrites. In this case, a high ionic flux resulted in more fractures of the SEI layer and more exposure of Li to the electrolyte. During the growth of the mossy dendrites, Li preferentially deposited on many conductive sites along the surfaces of the dendrites, leading to many aggregations. In contrast,
the fractal-like dendrites generated at the interfaces of Li/electrolyte, where the Li ion concentration approached to zero and the potential unstably fluctuated all the times. This kind of fractal-like dendrites is more likely to penetrate the separator of the cell, thereby leading to short-circuiting and even serious safety issues.

Removal of Li was easy from low-impedance sites and this will generate a pit, i.e., a SEI fracture. With continuous removal of Li from the pits till the polarity changes, mossy dendrites formed. Electronically detached and physically porous Li (dead Li) could be generated, as active Li was unable to be removed completely from dendrites inside. This would worsen the mass transport across the whole interphase. For example, it has been reported that the Li/NCA cell failed due to dead Li accumulation on the surface of Li anode. The mossy dendrites formation in the initial Li deposition process was ascribed to inhomogeneous nucleation and growth. In a subsequent process, Li was removed from the pre-existing mossy dendrites first, since these surfaces represent lower-impedance pathway than the bulk Li. There would be inactive structures (e.g., “dead Li”) produced, leading to low Coulombic efficiency and the Li inventory depletion. In a following Li dissolution process, Li was preferentially stripped from the bulk which creates surface pits as a result. And Li tended to nucleate as new mossy dendrites on the pits other than on the inactive dead Li once the polarity changed. Eventually, a “compact interphase” layer consisted of dead Li between the bulk Li surface and electrolyte formed (Figure 4 (a)).

Normally, the inhomogeneities of all the three dendrites in the first several cycles will lead to serious problems of the cell. Understanding the mechanisms of the three dendrites is favorable to explain the morphological evolution in cycling process and determining the failure causes of a battery, such as short-circuiting, electrolyte decomposition and excessive overpotential.

3.2. Issues related to Li dendrites

The high chemical reactivity of lithium metal leads to the corrosion of Li in the electrolyte. The Li dendrites will generate several fatal issues (Figure 4 (b), (c)).

(1) Large volume change. Compared with the volume change of intercalated anodes (graphite (10%), silicon (400%)), the Li anode exhibits huge volume change due to its hostless property. During Li plating, the dendrites growth renders the volume change harsher because of the deposition of porous Li. The huge volume expansion will lead to the fractures of the fragile SEI, allowing the dendrites growth in the cracks. While during Li stripping, volume contraction further ruptures the SEI, resulting in dead Li.

(2) Dead Li evolved from dendrites. The interaction between Li metal and electrolyte gives rise to Li dendrites, which were wrapped by the reactions of SEI films and blocked ion transport. The Li stripping from the roots or kinks of the dendrites will produce electrochemically inert dead Li, as a result, the Coulombic efficiency decreased and capacity faded.

(3) More serious parasitic reactions. Dendrites growth significantly increases the surface area of Li and renders parasitic reactions between the electrolyte and Li metal. The side reactions not only continuously consume the electrolyte and Li metal irreversibly, but also greatly reduce the Coulombic efficiency.

(4) Large polarization. Because of the porous structure, the Li anode with dendrites will lead to increased diffusion pathway and high resistance of Li$^+$ and e$, in this regard, enabling an increased polarization.
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(5) Short circuit of cell. Li dendrites can penetrate the separator, reach the cathode and cause the cell short circuit, more serious, safety issues such as the electrolyte combustion and cell explosion will happen. This also hinders applications of Li metal anode.

(6) Heat and gas generation. In LIB, heat is generated in two processes: Li\(^+\) move from cathode to anode during charging and from anode to cathode during discharging. In most cases, LIBs use cobalt oxide, which is easy to undergo “thermal runaway”. When heated up, this material begins self-heated and generate gas such as CO\(_2\) and O\(_2\), leading to fire and explosion.

4. APPROACHES FOR INHIBITING LITHIUM DENDRITE GROWTH

4.1. Electrolyte modifications

4.1.1 Liquid nonaqueous electrolytes

Carbonates (PC, EC, DMC, DEC) and ethers (DOL, DME, TGDME) are widely used as electrolytes in LIBs. However, carbonate-based electrolytes are not advantageous in suppressing Li dendrites and improving cell life. Previous studies have noticed that carbonated-based electrolytes decomposed in both LiO\(_2\) and Li-S batteries, due to the nucleophilic reaction with reduced oxygen species or polysulfides \(^{71,72}\). In comparison, ether-based electrolytes are relatively compatible with LiO\(_2\) and Li-S batteries, contributing to low voltage hysteresis and high Coulombic efficiency \(^{73}\).

4.1.2 Electrolyte additives

Functional additives have been applied in LBM to stabilize the Li/electrolyte interface, modify the physico-chemical properties of SEI, and prevent the Li corrosion. Typical additives (including gaseous molecules (CO\(_2\)) \(^{74,75}\), fluorinated compounds (HF) \(^{76,77}\), 2-methykfuran \(^{78}\), vinylene carbonate (VC) \(^{79}\), metal ions (Na\(^+\), Mg\(^{2+}\)) \(^{80,81}\) and organic aromatic compounds \(^{82}\)) are used for stabilizing the interface between an anode and electrolyte, reducing interface impedance, improving Coulombic efficiency, and mitigating Li dendrite growth \(^{19,83}\).

Small amounts of HF and H\(_2\)O in carbonate-based electrolyte are favorable to generate LiF/Li\(_2\)O bilayer on the surface of Li anode, leading to uniform and smooth Li deposition, therby improving Coulombic efficiency \(^{84}\). CO\(_2\) can react with Li to produce a Li\(_2\)CO\(_3\) layer enabling to stabilize the Li/electrolyte interface. VC can stabilize the interface of Li/electrolyte by ring-opening polymerization at Li surface to give rise to a SEI layer. Similarly, 2-methykfuran has the same mechanism as VC to generate a SEI layer for reducing interfacial impedance and increasing Coulombic efficiency. Fluroethylene carbonate (FC) \(^{83}\) interacted with Li to produce a uniform LiF-rich surface film, thus preventing the Li dendrite formation and increasing Coulombic efficiency. Inert additives (such as toluene) enable to reduce the cell impedance via accumulating dead Li that are isolated from Li anode to form a film \(^{85}\).

Based on the self-healing electrostatic shield mechanism, adding Rb\(^+\) and Cs\(^+\) in carbonate electrolyte can help realize dendrite-free Li deposition (Figure 5 (a)) \(^{86}\). During Li deposition, metal cation additives (M\(^+\)) absorbed on the Li surface. The non-uniform Li cations absorbed on the Li surface spontaneously from the positively charged shield, this shield repels more incoming Li\(^+\) and reduces Li dendrites growth (Figure 5 (b)) \(^{16}\).
Masahiro et al. used magnesium bis(trifluoromethanesulfonyl)amide (Mg(TFSA)$_2$) as the additive to suppress Li dendrites growth. They prepared the electrolytes, $x$Mg(TFSA)$_2$+(1-x)M LiTFSA ($x=0, 0.1, 0.5$) in triethylene glycol dimethyl ether (G3), and found that the application of Mg(TFSA)$_2$-free electrolyte led to Li dendrites regardless of the potential applied. There had no metallic Mg formation and no improvements in Li deposition morphology detected with a 1.9 Mg(TFSA)$_2$:LiTFSA electrolyte. However, the electrochemically alloyed Li-Mg (i.e., Li$_{0.9}$Mg$_{0.1}$) (Figure 5 (c)) formed via the intermediate phase of Li$_{0.14}$Mg$_{0.86}$ when the Mg salt concentration increased to 0.5 M. More importantly, the deposited Li under different applied potentials showed a relatively smooth and dendrite-free morphology.

Novel functional additives such as LiNO$_3$ was one of the most widely used additive in Li-S battery. LiNO$_3$ can passivate Li surface to suppress the interaction between polysulfide and Li metal, thereby mitigating the shuttle effect of lithium sulfide. The synergistic effect of LiNO$_3$ and lithium polysulfide is detected and a layer of Li$_2$S/Li$_2$S$_2$ on the top of the SEI formed, accommodating stable cycling at high current density. Unfortunately, the protective film formed by LiNO$_3$, consisting of inorganic species like Li$_2$O$_3$ and organic species such as ROLi and ROCO$_2$Li constructed by the strong oxidation of LiNO$_3$, is not stable. In addition, the inorganic layer exhibited low mechanical stability and would break into fragments.

### 4.1.3 High concentration salts

LiPF$_6$, LiTFSI, LiFSI, and LiSO$_3$CF$_3$ are the most popular Li salts used in LIBs and LMBs. Previous studies have revealed that electrolytes with a high Li salt concentration (e.g., > 3 M) showed some properties like ionic liquids and had less free solvent molecules. Yamada et al. reported that 4.5 M LiFSI in acrylonitrile (AN) enabled a high ionic conductivity of $10^{-2}$ S/cm at 30 °C. Suo et al. developed a new electrolyte with a 7 M Li salt for Li-S batteries, which could suppress Li dendrites effectively and mitigated the dissolution of lithium polysulfide, ascribed to incomplete solvated Li ions. Zhang et al. applied 4 M LiFSI in DME and found that this electrolyte system resulted in superior performance of the Li metal anode such as high Coulombic efficiency at high current density.

### 4.2. Solid-state electrolytes

Liquid electrolytes are widely used in rechargeable batteries, due to their high ionic conductivity. As discussed above, they also pose many issues in practical applications, such as leakage, poor electrochemical stability, and flammability. To this end, solid inorganic or polymer electrolytes are potential solutions, because these solid electrolytes may have high modulus to efficiently suppress Li dendrites, high Li$^+$ conductivity at room temperature, better electrochemical stability, and low interfacial resistance and excellent adhesion to electrodes.

The widely used inorganic electrolytes to date include nitrides, sulfides, oxides and phosphates (e.g., Li phosphorous nitride (LiPON), Li$_3$N, Li$_{1+x}$La$_{3}$Zr$_{2}$O$_{12}$, Li$_{1+x}$La$_{3}$Ge$_{2}$O$_{12}$, Li$_{14}$Zn(GeO$_3$)$_4$, xLi$_2$O-(1-x)GeP$_2$S$_12$, xLi$_2$S-(1-x)P$_2$S$_5$). Generally, inorganic ceramics have good ionic conductivity and mechanical properties. For example, Li$_{10}$GeP$_2$S$_{12}$ could even enable a higher ionic conductivity (~12 mS/cm) than some liquid electrolytes. These solid electrolytes also exhibit high elastic modulus ranging from tens to hundreds of GPa, which are sufficient to inhibit Li dendrites growth. However, these solid electrolytes may also suffer technical issues in applications. For example, solid sulfide electrolytes exhibited narrow electrochemical stability windows, and may not be stable in contacting Li metal anode directly.
Solid electrolytes are often poor in air-stability. For example, Li et al.\textsuperscript{115} reported that Li$_3$La$_5$Zr$_2$O$_7$-based Li-rich garnets could react with CO$_2$ to form Li$_2$CO$_3$ on the garnet surface, causing a higher interfacial resistance for Li$^+$ transport.

Solid polymer electrolytes (SPE) are mainly based on copolymers, cross-linked polymers, or polymer/nanoparticle composites, having an ionic conductivity 2-5 orders of magnitude lower than that of liquid ones and a mediocre elastic modulus (< 0.1 GPa). Compared to solid inorganic electrolytes, polymer electrolytes have a stronger adhesion to electrodes. For instance, Khurana et al.\textsuperscript{116} reported a cross-linked polyethylene/poly(ethylene oxide) SPE composed of semicrystalline polyethylene (PE) and poly(ethylene oxide) (PEO) (Figure 6 (a)). By changing the ratio of poly(ethylene glycol) (PEG) to PE-PEO, Khurana et al.\textsuperscript{116} found that the 39 wt% PEG enabled a high ionic conductivity of 2.0×10$^{-4}$ S/cm at 25 °C and showed excellent resistance to dendrite growth (Figure 6 (b)). Meanwhile, galvanostatic cycling tests were conducted to demonstrate the dendrite-resisting effect of the PE-PEO SPEs. The results indicated that the cross-linked SPEs (1790 C/cm$^2$) probed the lifetime of the Li metal cells to a higher value than that of PEO (105 C/cm$^2$) under 0.26 mA/cm$^2$ and 90 °C, implying the excellent resistance of PE-PEO SPEs to Li dendrites growth. This is due to the nanoporous network of the polymer, which facilitated the Li$^+$ migration and suppressed the dendrites proliferation. In another work, Pan et al.\textsuperscript{117} fabricated a cross-linked oligomeric silsequioxane-poly(ethylene glycol) (POSS-PEG) hybrid polymer electrolyte to suppress Li dendrites, which not only afforded sufficient strength but also enabled the ion conductivity by solvating the Li ions.

Inorganic/polymer hybrid electrolytes also have been developed in order to achieve a more desirable performance, in terms of ionic conductivity, anode surface contact, and mechanical stability.\textsuperscript{5,118,119} Traditional strategy is to combine polymer with Li salt or other insulating oxides, such as SiO$_2$, Al$_2$O$_3$, TiO$_2$, ZrO$_2$. Choudhury et al.\textsuperscript{122} have integrated a crosslinked SiO$_2$ nanoparticle into a gel polymer electrolyte with improved mechanical strength and ionic conductivity. Kim et al.\textsuperscript{121} fabricated a composite polymer electrolyte (CPE) by using ultraviolet cured ethoxylated trimethylolpropane tricrylate (ETPTA) as the mechanical framework and Al$_2$O$_3$ nanoparticles as functional filler (Figure 6 (c)), and the mechanical bending test results demonstrated that the CPE could preserve its dimensional stability for 32 cycles, while the GPE, the control sample fabricated by using the same components as those used for CPE except for Al$_2$O$_3$ nanoparticles, only lasted for 11 bending cycles, indicating a significant improvement in the mechanical bendability. CPE was also effective in suppressing Li dendrite during charge-discharge cycling. The cell assembled with CPE has achieved a high discharge capacity retention of 96.2% after 50 cycles, comparable to that of the cell assembled with GPE (95.9%)\textsuperscript{123}. Zhao et al.\textsuperscript{124} dispersed garnet-type Al-doped Li$_{x}$La$_{0.73}$La$_{0.27}$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ (LLZTO) ceramic particles in a polyer-Li salt matrix to fabricate a PEO-LiTFSI-LLZTO (PLL) solid electrolyte, which realized a high ionic conductivity of 1.12×10$^{-4}$ S/cm at 25 °C and also a wide electrochemical window of 5.5V. The PLL electrolyte is freestanding, mechanically flexible and also helps maintain a smooth surface with few protuberances. Fu et al.\textsuperscript{125} prepared a 3D garnet-type Li$_{0.4}$La$_{0.6}$Zr$_{2}$Al$_{0.2}$O$_{12}$ (LLZO) nanofiber networks to improve the ionic conductivity of a dry polymer electrolyte. Compared with isolated nanoparticles, nanofibers could afford higher ionic conductivity. The garnet nanofibers afforded a fire-retardant property, demonstrating the good mechanical support to the polymer. Additionally, the garnet-nanofiber-based electrolyte exhibited a high ionic conductivity of 2.5×10$^{-4}$ S/cm at 25 °C. Liu et al.\textsuperscript{126}
used ceramic nanowires of Li$_{0.33}$La$_{0.557}$TiO$_3$ as Li-ion conductive fillers in the composite electrolyte (Figure 6 (d)), and the prepared electrolyte with 15wt. % Li$_{0.33}$La$_{0.557}$TiO$_3$ had a high ionic conductivity of $2.4\times10^{-4}$ S/cm at 25 °C. Wang et al.\textsuperscript{27} designed a Li$_{1.5}$Al$_2$Ge$_1.5$(PO$_4$)$_3$-poly(ethylene oxide) (LAGP-PEO) composite solid electrolyte and modified the lithium metal anode using PEO (lithium bis(trifluoromethane)sulfonimide)) [PEO (LiTFSI)] for the all-solid-state lithium batteries (Figure 6 (e)). They found that, among all PEO (LiTFSI) membranes with various PEO molecular weights such as 6000, 100000, 500000 and 900000, the PEO-500000(LiTFSI) film on lithium anode showed the highest elongation at break (185%) while its tensile strength was 0.81 MPa. This film also protected Li from reacting with LAGP. LAGP-PEO (LiTFSI) composite solid electrolyte and the PEO (LiTFSI) modified Li anode can effectively suppress Li dendrites growth.

4.3. Artificial SEIs

SEI layers work as a protecting layer for lithium metal anodes and prevent parasitic reactions between Li metal and an organic electrolyte. The SEI layers are prone to crack during dendrite growth. In this regard, three strategies have been suggested for constructing artificial SEI with improved properties, including chemical pretreatment, physical pretreatment, and electrochemical pretreatment.

Using chemical pretreatment, Li et al.\textsuperscript{57} immersed Li metal in polyphosphoric acid (PPA) and then there was an artificial Li$_3$PO$_4$ layer generated on the Li metal surface. The Li$_3$PO$_4$ (50 nm) was uniform and smooth morphologically, and had a high modulus of 10–11GPa. These characteristics of the artificial Li$_3$PO$_4$ are beneficial for inhibiting Li dendrite growth. In another work, Liu et al.\textsuperscript{127} designed an artificial SEI layer consisting of Cu$_3$N nanoparticles connected by a styrene-butadiene rubber (Cu$_3$N+SBR). Contacting with Li, the Cu$_3$N nanoparticles were passivated with the formation of a Li$_3$N layer. The Li$_3$N layer showed a high mechanical strength of 0.81GPa and a high ionic conductivity at the order of $10^{-3}$–$10^{-4}$ S/cm at room temperature. Li et al.\textsuperscript{128} produced a Li polyacrylic acid (LiPAA) SEI layer, and the fabricated SEI layer was flexible to accommodate the volume change during Li plating/stripping for 700h and effectively restrain Li metal from dendrite growth.

Analogous to chemical pretreatment, physical treatment has also been used for Li-surface passivation. It has been reported that a layer of 5 or 14 nm Al$_2$O$_3$ coating via atomic layer deposition (ALD)\textsuperscript{129} was capable of protecting the lithium metal from degradation in atmosphere. The 14-nm ALD-Al$_2$O$_3$ coated Li metal demonstrated a superior chemical stability to the bare Li metal anode against long-chain Li polysulfides. In addition, the coated Li metal anode enabled a high initial discharge capacity of 1200 mAh/g and maintained a Coulombic efficiency of > 95% after 100 cycles. Using symmetric cells, another work revealed that 2-3 nm thick Al$_2$O$_3$-coated Li electrodes\textsuperscript{130} could have a much longer cycling lifetime than the bare Li electrodes. The 20-cycle coated electrodes had been confirmed being with a much smaller impedance at different cycling stages, varying the effects of the ALD coatings in mitigating unwanted side interactions between the lithium metal anode and the organic electrolyte. It has been observed that, after 100 electrochemical cycles, the 20-cycle ALD-coated Li electrode showed a uniform, smooth, and dense morphology. The ALD-Al$_2$O$_3$ coatings on Li metal\textsuperscript{131} are conducive to pertain a uniform morphology against Li dendrite formation. This has been further verified by observing the evolutions of surface roughness, $0.15 \pm 0.18$ nm/h of the ALD-coated Li metal vs. $2.01 \pm 0.26$ nm/h of the bare Li metal. In addition, the Li-S cell using the
ALD-coated Li anode is relatively more stable, for there was no noticeable H₂ release detected. In addition, the ALD Al₂O₃ coatings were found to improve the wettability of Li anodes in both carbonate and ether electrolytes. A model (Figure 7 (a)) has been proposed to illustrate the effects of the conformal Al₂O₃ coating in improving wettability, thus leading to a more uniform Li deposition over the surface. Kozen et al. deposited a hybrid artificial SEI on Li metal directly with a combined method of self-healing electrochemical polymerization (EP) and ALD (Figure 7 (b)). This hybrid SEI layer could suppress Li dendrites at 2 mA/cm² after 100 plating/stripping cycles. Zheng et al. proposed a monolayer composed of interconnected hollow carbon nanospheres (Figure 7 (c)) by using flash-evaporation strategy. This thin amorphous carbon layer had a high modulus about 200 GPa, which is sufficient to inhibit Li dendrites. Additionally, during Li plating/stripping, the carbon layer loosely attached to the current collector moved up and down to eliminate the volume change. And the nanosphere protected anode exhibited high Coulombic efficiency about 99% for over 150 cycles at 1 mAh/cm².

Electrochemical pretretment, such as FEC, also was used to form an artificial SEI film on Li metal anodes.

4.4. Separator modifications

The penetration of Li dendrites through the separator can lead to the cell failure. Separator modifications were another strategy for improving battery safety. Liu et al. invented a novel silica nanoparticle modified separator with a trilayer structure, in which sandwiched SiO₂ was located between two inert separators. Liu et al. demonstrated that the prepared separator could extend the cell life up to 135 h, five times higher than the separator without SiO₂. Na et al. prepared a hybrid-composite-coated separator, Al₂O₃/LPMA64 (poly(phenyl-co-methacryloxypropyl)silsesquioxane) coated separator (Figure 8 (a)), and confirmed that the fabricated separator could perform with only < 5% thermal shrinkage and a high ionic conductivity of 0.82 mS/cm. With the hybrid composite separator, the LMB cell of Li/LiFePO₄ could sustain a high discharge capacity of 158 mAh/g at low C-rates, close to the theoretical value of 170 mAh/g of the LiFePO₄ cathode. This can be attributed to good mechanical property (Figure 8 (b)), high ionic conductivity, and improved thermal stability of the fabricated separator. Lee et al. designed a Janus-faced separator by coating ultrathin copper thin film (CuTF) on one side of the polyethylene (PE) separator using magnetron DC sputtering. The PE/CuTF separator worked as an additional electrical conducting agent for high Li utilization and a current collector for backside plating. The PE/CuTF separator played a critical role in suppressing the “dead” Li and passivation layer growth. The LMB with LCO cathode and PE/CuTF Janus separator realized an improved capacity over 300 cycles.

4.5. Electrode framework

The huge volume change of Li anode during Li plating/stripping is a big challenge of LMBs. In efforts to tackle this challenge, 3D structured electrodes have been developed. Zheng et al. added glass fibers (GFs) with many polar functional groups on the Cu electrode surface for realizing a uniform and even distribution of Li⁺. The GFs have higher binding energy with Li than that of Cu with Li, which could adsorb a considerable amount of Li⁺ to compensate the electrostatic interactions between Li⁺ and protuberances of Cu foil or Li dendrites. Chang et al. also reported that the application of Kimwipe paper helped enable uniform Li distribution,
suppress Li dendrites, and maintain a smooth surface of the Li anode. Zhang et al.\textsuperscript{141} applied nitrogen doped graphene as the Li plating matrix to tune the Li nucleation and inhibit the growth of Li dendrites. Lithiophilic functional groups, such as pyridinic and pyrrolic nitrogen, contributed to a uniform Li nucleation. The modified Li metal anode maintained a smooth surface during cycling and had a high Coulombic efficiency of 98% for ~200 cycles. Lin et al.\textsuperscript{142} fabricated layered reduced graphite oxide using lithiophilic graphene oxide (GO) as a porous matrix for Li metal (Figure 9). They found that the resultant Li-rGO had a unique lithiophilicity and could reduce the volume change of Li to <20%. When coupled with lithium cobalt oxide (LCO) cathode, the Li-rGO anode not only were free of dendrites, but also remained a capacity of 60 mAh/g at 10 C. Lin et al.\textsuperscript{142} believed that lithiophilic matrix helped guide Li distribution uniformly on Li anode surface via chemical binding thus achieving a dendrite-free Li anode.

3D conductive matrixes could outperform their 2D Cu foil current collectors in inhibiting Li dendrites, owing to their surface area and the effective reduction in local current density. Cheng et al.\textsuperscript{143} developed a Li$_r$B$_{6}$ framework as the conductive matrix for Li deposition. It was found that the fabricated Li$_r$B$_{6}$ nanostructured anode could successfully retard the Li dendrite growth. Assembled into a Li-S battery cell, the anode extended the cell lifetime to 2000 cycles with a high Coulombic efficiency (91-92%). Guo et al.\textsuperscript{144} revealed that 3D Cu foam with a median pore diameter (by volume) of 2.1 μm was also effective to suppress Li dendrite growth and accommodate uniform Li deposition. Zhang et al.\textsuperscript{145} deposited Al$_2$O$_3$ on carbon nanotubes sponge using ALD, the ALD Al$_2$O$_3$-coated CNTS not only afforded a homogenous Li$^+$ nucleation and distribution to achieve high electrical conductivity, but also enabled faster Li$^+$ diffusion to prevent Li dendritic formation. The thin ALD-Al$_2$O$_3$ layer was found to work as an indispensable artificial SEI to stabilize the interlayer of Li$^+$/electrolyte. Plating Li at a fixed current density of 1.0 mA/cm$^2$ and increasing the deposition from 2 to 10 mA/cm$^2$, the average diameter of Li$_r$/ALD-CNTS increased homogeneously from 52.0 to 60.2 nm, suggesting the importance of the ALD-CNTS current collector in mitigating Li dendrite formation. Additionally, the Li$_r$/ALD-CNTS current collector exhibited high CE values of 90.3% after 10 cycles and 92.4% after 80 cycles, which demonstrated the ALD-CNTS current collector is effective in improving the cycling stability of Li-S battery. Chi et al.\textsuperscript{146} explored a Li-Ni composite electrode using metallic nickel foam as a host for pre-storing Li, the conductive property of the interconnected 3D Ni foam enabled a fast ion/electron transfer during Li plating/stripping. The Li-Ni composite electrode exhibited stable voltage profiles (200 mV at 5.0 mA/cm$^2$) for more than 100 cycles in a symmetric cell.

5. CONCLUSIONS

Given its high capacity, Li metal is an ideal anode for rechargeable lithium batteries (e.g., Li-S and Li-O$_2$ batteries). However, the high reactivity of Li to liquid electrolytes and its dendrite growth pose many big challenges to battery’s safety, efficiency, and lifetime. In addressing these issues, recently there have been a large number of efforts invested. In this Chapter, we give a comprehensive review on the SEI formation and Li dendritic growth over Li metal anodes, paying an emphasis on their mechanism and technical solutions (e.g., electrolyte modifications, solid state electrolyte, artificial SEI, separator modifications, and electrode designs). Although all the efforts invested to date have achieved many outcomes in understanding, there are still lots of work to do for ultimately commercializing Li metal anodes in lithium batteries.
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Figure caption:

Figure 1. Schematic representations of (a) Li-ion. Reprinted (adapted) with permission from ref. 10. Copyright (2014) American Chemical Society. (b) Li-S 13. Reprinted (adapted) with permission from ref. 13. Copyright (2015) American Chemical Society. (c) Li-O₂ cells 18. Reprinted (adapted) with permission from ref. 18. Copyright (2012) American Chemical Society.

Figure 2. (a) Structures of commonly used electrolyte. (b) Illustration of Electrolyte Interphase on lithiated-silicon electrodes 47. Reprinted (adapted) with permission from ref. 47. Copyright (2017) American Chemical Society. (c) Illustration of solid electrolyte interphase on graphite anode. 46. Reprinted (adapted) with permission from ref. 46. Copyright (2017) American Chemical Society. (d) Typical force curves showing mechanical response of Li deposits obtained in the electrolyte with (blue) and without (orange) the DMS additive. Reprinted (adapted) with permission from ref. 58. Copyright (2017) American Chemical Society.

Figure 3. SEI layer formation illustration for different electrolyte systems (a) EC-based electrolyte 59 and (b) PC-based electrolyte 59. Typical snapshots of the aggregation state changes of reaction products (both bulk EC and PC not shown) in the 200th cycle, 400th cycle, 800th cycle, 1600th cycle, and 2000th cycle. Reprinted (adapted) with permission from ref. 59. Copyright (2014) American Chemical Society.

Figure 4. (a) Schematic showing the Li stripping/plating process. Step 1: Li plating causes volume expansion, which cracks the SEI film. Step 2: further plating causes Li dendrites to shoot out through the cracks. Step 3: Li stripping produces isolated Li which becomes part of the 'dead' Li, while volume contraction results in further SEI fracture. Step 4: Continuous cycling causes steps 1-3 to occur repeatedly, and this finally results in accumulated dead Li, thick SEI and porous Li electrode. 16. (b) Correlations among the different challenges in the Li metal anode, originating from high reactivity and infinite relative volume change. Reprinted (adapted) with permission from ref. 16. Copyright (2017) Springer Nature. (c) Scheme of dilemma for Li metal anode in rechargeable batteries. Reprinted (adapted) with permission from ref. 68. Copyright (2017) American Chemical Society.

Figure 5. (a) Schematic of Li deposition and stripping processes when the Cs additive is used. Reprinted (adapted) with permission from ref. 86. Copyright (2014) American Chemical Society. (b) Schematic illustration of the Li deposition process based on the self-healing electrostatic shield mechanism. In the top panel, Li cations (green) are attracted to the negative charge on a protruding point, adding to it and causing further growth. In the presence of metal cation additives (M⁺) with effective reduction potential below that of Li⁺ (lower panel), however, the M⁺ additive (red) can be adsorbed on the Li surface instead to form an electrostatic shield, repelling the incoming Li⁺ and thus slowing the growth of protrusions. 16. Reprinted (adapted) with permission from ref. 16. Copyright (2017) Springer Nature. (c) Schematic illustration of the proposed suppressing effect of Li dendritic growth by addition of Mg-salt. (1) In a commercially available electrolyte, Li deposition occurs inhomogeneously. By repeated deposition-dissolution cycling, the deposition morphology results in dendrites that cause rapid capacity fading and thermal runaway of the batteries. (2) In an electrolyte containing Mg-salt, the Mg-ion preferentially undergoes reduction to form metallic Mg on a substrate due to its higher standard electrode potential. Subsequently, Li deposition proceeds on the Mg and reacts with it to electrochemically form a binary Li-Mg alloy. Reprinted (adapted) with permission from ref. 87. Copyright (2018) Royal Society of Chemistry.

Figure 6. Solid-state polymer electrolytes for Li-metal anodes: (a) Schematic of cross-linked PE–PEO SPE 116. (b) Ionic conductivity of the PE–PEO cross-linked SPEs with different ratios. 116. Reprinted (adapted) with permission from ref. 116. Copyright (2014) American Chemical Society. http://pubs.acs.org/doi/pdf/10.1021/ja502133j (c) A schematic representation illustrating the UV-irradiation-assisted fabrication process and a photograph depicting mechanical bendability of CPE. 123. Reprinted (adapted) with permission from ref. 123.
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Copyright (2013) Royal Society of Chemistry. (d) Schematic of nanowire and nanoparticle fillers in the polymer matrix. Reprinted (adapted) with permission from ref. 126. Copyright (2015) American Chemical Society. (e) All-solid-state Li-PEO (LiTFSI)/LAGP-PEO (LiTFSI)/LiMFP cells. Reprinted (adapted) with permission from ref. 27. Copyright (2017) American Chemical Society.

Figure 7. (a) Schematic of lithium electrodeposition on lithium metal anode via electrolyte: (1) Rough lithium electrodeposition through poorly wetted, bare lithium surface. (2) Uniform and smooth lithium electrodeposition through uniformly wetted, ALD Al₂O₃ coated lithium surface. Reprinted (adapted) with permission from ref. 132. Copyright (2017) Royal Society of Chemistry. (b) SEM images of bare Li metal (top row, (1)) and hybrid-protected Li metal (bottom row, (2)) cycled in 1:1 EC:DEC for 100 cycles with varied current densities. In (1), a dendrite example is circled. Mechanistic schematics of comparison for (3) bare lithium and (4) hybrid elastomer/LiPON protection showing Li metal surface layer evolution after 100 cycles at current densities of 2 mA/cm², above the threshold for Li dendrite formation on unprotected Li metal. Reprinted (adapted) with permission from ref. 133. Copyright (2017) American Chemical Society. (c) Schematics of Li deposition and dissolution on a Cu substrate modified by a hollow carbon nanosphere layer. Reprinted (adapted) with permission from ref. 134. Copyright (2014) Springer Nature.

Figure 8. (a) Schematic depiction of the mechanical suppression preventing lithium dendrite formation with hybrid composite coated separators fabricated in this work. (b) Nanoindentation-derived elastic moduli of pristine PP separator, A2L1 hybrid composite separator, PTFE/Al₂O₃-coated UHMWPE composite separator, and PTFE/Al₂O₃-coated PE-PPPE/Al₂O₃ composite separator. Reprinted (adapted) with permission from (a), (b) ref. 137. Copyright (2016) American Chemical Society.

Figure 9. Fabrication of a layered Li-rGO composite film. Reprinted (adapted) with permission from ref. 142. Copyright (2016) Springer Nature.
Figure 1
Inhibiting lithium dendrite growth for lithium batteries: challenges and strategies

Figure 2
Figure 3
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**Figure 4**
Figure 5
Inhibiting lithium dendrite growth for lithium batteries: challenges and strategies

Figure 6
Figure 7
Inhibiting lithium dendrite growth for lithium batteries: challenges and strategies

Figure 8
Figure 9