Mechanism of Lithium Dendrites Formation and Suppression Strategies in Li Metal Batteries

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Abstract. This paper describes and summarizes the modifying progress established on Li metal anode in recent years. With the increasing demand for high-capacity batteries, Li-ion batteries, one of the most commercialized batteries, can no longer meet the demand. Thus, the high-energy-density lithium metal battery using lithium metal as anode is widely researched due to the lowest electrochemical potential (-3.04 V) of lithium and ultimate theoretical capacity (3860 mAh/g). However, the Li dendrites formation becomes the main obstacle for the commercialization as it will trigger thermal runaway and short circuit. In this paper, the growth process of Li dendrites was discussed, and various modifying solutions based on electrolytes, Li alloy and current collectors to suppress Li dendrites were summarized.

Keywords: Li metal anode, Li dendrites, Li metal battery, SEI.

1. Introduction

It is undeniable that Li-ion batteries have made a significant contribution to the development of human society since 1991 SONY company produced the world's first commercial Li-ion battery[1,2]. Due to its relatively long-lasting cycling ability, high energy density and high output voltage, Li-ion batteries have been widely investigated. However, with the development of electrical products and electric vehicles, traditional Li-ion batteries with graphite anode can no longer meet the great demand due to the low theoretical specific capacity (372 mAh/g). An alternative must be considered. Lithium metal has an ultimate high capacity of 3860 mAh/g with a low density of 0.59 g/cm3 and the lowest negative electrochemical potential of -3.04 V [3]. Thus, it seems that Li-metal batteries can replace Li-ion batteries in any aspect. Unfortunately, rechargeable Li-metal battery has not been commercially generated as the growth of Li dendrites during cycling becomes its most dangerous shortage, which leads to short circuits and thermal runaway that threaten customers' safety directly[4–6]. Recently, scientists have been trying to resolve the formation of dendritic Li formed during cycling. In this article, three practical and valid approaches based on modifying electrolytes, Li metal and current collectors have been introduced here and discussed, which broaden the horizon of methods of modifying Li-metal batteries.

2. The formation of lithium dendrite

Dendrite deposition on the Li-metal anode becomes the primary obstacle towards commercial Li-metal batteries. Li dendrites will penetrate the solid electrolyte interphases (SEI) generated spontaneously during the discharge process, preventing further contact between the electrolyte and anode. Dendrite deposition usually occurs on high current electroplating of metals like Li, Zn, Ni. In short, Li ions gain electrons at the anode during the recharging process and plates on the anode. This process triggers
volume expansion, which fracture the SEI film and create high curvature protrusions with a considerably higher electric field at their tips[7]. What is more, instead of one dimensional diffusion observed in flat surfaces, the hemispherical tips of protrusions empower three-dimensional Li-ion diffusion which leads to rapider Li deposition on the tips[8]. Furthermore, these tips will attract more Li-ions during the recharging process while the valley attracts considerably fewer Li-ions comparatively[7]. This leads to the formation of Li dendrites which shoot out through the cracks[5]. Later on, Li dendrites are more likely to be oxidized to Li-ions during the discharge process and detached from the Li surface. These dendrites are no longer in contact with the anode and thus cannot be oxidized to ion forms anymore. Even worse, SEI will form on these isolated Li to deactivate them. These isolated Li with coated SEI is called 'dead' Li[9]. After several plating/stripping cycles will lead to accumulated dead Li floating above the thick SEI and making the anode electrode porous.

3. Electrolyte modification.

The deposition behaviours of lithium metal are closely related to the SEI film, and the electrolyte composition mainly determines the properties of the SEI film. Therefore, some researchers have improved the properties of the SEI film by optimizing the electrolyte, thereby inhibiting the formation of lithium dendrites. Electrolyte additives have been extensively studied as an economical and efficient method. Researchers introduced metal cations M⁺, such as Cs⁺ and Rb⁺ to the electrolyte system.⁷ During the charging process, both Li⁺ and Cs⁺ are adsorbed on the surface of the Li anode under an applied voltage which is considerably higher than the reduction potential but lower than Li reduction potential of Cs⁺. Thus, Cs⁺ will accumulate in the surface of the tips to form a positive charge shielding field to prevent further lithium deposition instead of electroplating on the tip. The shielding field will force further Li ions to deposit on the adjacent sections of the anode until a flat and smooth deposition layer is generated. This mechanism can resolve the Li dendrites problem and re-establish a smoother Li anode layer, eliminating the lithium dendrites formation. Experimental data showed that during long term cycling test, LiPF₆ cell with 0.05M CsPF₆ additives performed a Coulombic efficiency (CE) of 99.86% while that of LiPF₆ without additives was only 76.5%.

Besides, the choice of electrolytes also leads to different cycling efficiency and the ability to suppress the Li dendrites. Conventional liquid electrolytes cannot prevent the growth of Li dendrites during the recharging process because of poor mechanical properties. Thus, solid electrolytes with good mechanical properties are used to replace traditional liquid electrolytes.

Solid electrolytes fall into two classes, inorganic ceramics electrolytes(Sulfides[10], Oxides[11], Nitrvides[12]) and solid polymer electrolytes (SPEs). Polymer electrolytes have been widely applied due to their low cost, low density and excellent processability. A recent study has shown ultra-strong composite polymer electrolytes (CPE) to be adequate to suppress the Li dendrites growth by introducing a stiff mesoporous SiO2 aerogel as the backbone for polymer electrolytes[5]. Compared with pure polymer electrolytes, the CPE with the strong interconnected SiO2 aerogel backbone have a higher elastics modulus, which could mechanically suppress the growth of Li dendrites. Moreover, the SiO2-aerogel composite electrolytes maintained their mechanical strength at elevated temperatures, while pure polymer was significantly reduced. In addition, the ultra-fine silica with a high specific surface area is uniformly distributed, which increases the interaction between the polymer and lithium ions, thereby promoting the decomposition of lithium salts and improving the migration number of lithium ions in the electrolyte. The dissociation ratio of LiTFSI increased from 84.7% to 94.4%[5]. The cell with CPE shows a specific capacity of 100 mAh/g, which was almost twice that without SiO2 aerogel (57 mAh/g). The symmetric cells without CPE have more significant voltage fluctuation (100 mV) and less cycling life for approximately 100 times, while the cells using CPE shows a more stable voltage plateau (70 mV) and longer cycle life without a short circuit.
4. Li metal anode Modification

![Figure 1](three-dimensional-model.jpg)

**Figure 1.** three dimensional model of fabricating CF with Ag and Li (A) and scanning EM images(B). Since the lithium metal is a host-less electrode, the considerable volume change will damage the SEI film during the cycle. For this reason, researchers tried to create some hosts with a three-dimensional structure to accommodate lithium metal and alleviate the problems caused by the volume effect. The regulation of Li+ deposition and induction of dendrites-free morphology can be achieved by applying structured composited anode layer. By doing this, high capacity and long lifecycle lithium metal anode can be achieved. Recently, coralloid carbon fiber (CF)-based composited anode has been investigated and shows a good effect for dendrites suppression[13]. Conductive CF is highly electrical conductive and porous for metallic Li storage which leads to be ideal matrix for Li metal anode[14,15]. Ag was used to decorate the CF due to its lithiophilicity. After coating CF with Ag layer, molten Li was used to infuse with CF/Ag framework to generate Li-occupied CF based Li metal anode (CF/Ag-Li) (Figure 1A). No ‘dead’ Li was detected in the CF/Ag-Li anode during the plating/stripping process. During the charging/discharging process, the thickness of CF/Ag-Li remains constant, implying that almost no volume change during recycling.

The CF/Ag-Li shows good cycling ability for more than 200 cycles with lower hysteresis of 60 mV. More definite surface area and interconnected transfer channels are obtained in the structured anode during the stripping process.

Thus, during repeated cycles, lower hysteresis is achieved and therefore outstanding stability in long standing cycling.

During the first cycle, CF/Ag-Li/LFP holds a high specific capacity of 137 mAh/g and then slowly decays to 86 mAh/g at 50th cycle, while that of Li foil/LFP starts with 110 mAh/g and quickly decays to about 20 mAh/g after 500th cycles.

Furthermore, solid-state electrolytes (SSEs) are outstanding due to their non-flammability and mechanical strength to prevent dendritic Li formation[16,17]. Throughout many researches studied[18,19], cubic garnet phase SSEs are more desirable due to their superb chemical stability, and high ionic conductivities. Nevertheless, the disfavored interfacial contact between garnet SSEs and Li foil result in high resistance. By fabricating metal alloy, the compatibility between garnet SSEs and Li metal alloy will increase, which improve interfacial contact between them. Researchers mixed Li metal with Sn and adjusted the content of Sn to improve the wettability of lithium on substrates[20]. The garnet SSE and Li alloy results in spectacular electrochemical performance due to its tight and continuous contact between them. The interfacial resistance between SSE and Li-Sn is calculated to around 7 Ω/cm², a much smaller number than most of the values reported previously. The symmetrical cells using Li-Sn alloy and garnet pellets showed a stable and safe cycling performance for 100 h. While cycling, the working electrode and counter electrode both keep good contact with solid garnet electrolyte. In
contrast, the cells using pure Li foil is short-circuited quickly in less than 15 mins, implying the deficient stability of the original Li-garnet interface. Except to Sn, other doped metal, such as Zn,[21] Ca,[22] and Mg[23] also showed the ability to control the Li dendrites growth without affecting the electrochemical properties of pure Li metal.

5. Current collector modification

In addition to the modification of lithium metal itself to solve lithium dendrites, the improvement of the current collector is another method to boost the recyclability of the lithium metal anode. Desirable current collectors should be able to minimize local current density and provide mechanical support to accommodate large volume change of the anode during the "hostless" Li deposition and stripping. In 2019, a team fabricated robust lithium anodes by combining three dimensional current collectors with optimized surface and skeleton characteristics[24]. Metal foams wrapped with N-doped porous carbon nanosheets (NPCN) were used as three dimensional current collectors, which could accommodate high amounts of Li and guide uniform Li growth. On the one side, the three dimensional structure could reduce local current density and alleviate the enormous volume change of lithium in charge/discharge processes. On the other side, the N-doped carbon nanosheets could provide many deposition sites and reduce nucleation overpotential. Thus, by integrating the benefits of both carbon and metal, the modifying three dimensional porous collectors are tunable to maximize the areal capacities and stability of the Li anodes qualified for high-sulfur-loading cathodes. Experimental results indicates that even at ultrahigh Li plating areal capacity of 10 mAh/cm², a smooth Li surface could still be maintained. When NPCN loading reaches 0.3 mg/cm², a current density of 1 mA/cm² and areal capacity of 1 mAh/cm², Cu-NPCN shows a stable CE of 99.0% for 400 cycles. Even at high areal capacity of 50 mAh/cm² Cu-NPCN still maintained CE of 99.2% after 1000 h of recycling at 1 mA/cm². Except using NPCN to decorate, a novel three dimensional electrode based on atomic layer deposition (ALD)-coated hollow carbon spheres (HCS) was developed to act as a mechanically sturdy frame to confine electrochemical lithium plating, which holds a CE of 99% for 500 cycles. Similarly, another facile strategy fabricating three dimensional porous/Li metal composite anode was developed by mechanical embedding copper mesh in Li metal, which also shows a relatively high coulombic efficiency of 93.8% in 100 cycles[25].

![Figure 2](image)

**Figure 2.** three dimensional diagrams of Li deposition on bare Cu (a) and with h-BN layer (b). Due to the lack of confinement, Li ions will deposit on bare Cu uncontrollably and thus form Li dendrites. The SEI layer formed spontaneously will ratify the growth of lithium dendrites. (a) The subnanometer defects in h-BN film can confine the shape and serve as channels for Li ions.

Besides, another promising interfacial nanomaterial approach was used for surface modification of Cu collectors and shown to be adequate to suppress Li dendrites[24]. If bare Cu was used during Li
deposition, large Li dendrites will form due to the lack of confinement (Figure 2a). The researchers coated Cu collectors with h-BN or graphene by chemical vapor deposition (CVD) [26]. For the h-BN/Cu electrodes, Li⁺ pass through the defect position of the h-BN layer and well deposit on the current collector (Figure 2b). Due to the chemical inertness and compactness of the h-BN, the protective layer can well protect the current collector and prevent it from reacting with the electrolyte. By doing so, this electrode consumes much less electrolytes due to the reduced surface area of the h-BN/Cu electrodes compared with bare Cu electrode which is a much larger one.

A complex film covering is generated by combining h-BN and genuine SEI and acts as a complex film to cover deposited lithium. With its good mechanical strength and ionic conductivity, this complex film can stabilize the surface of lithium strongly. Results showed that over the anode surface, no Li dendrites was found, implying a successful suppression of Li dendrites which is attributed to the high Young's modulus (1.0 Tpa) [27] of h-BN layers.

Even at a high areal capacity, the CE of h-BN/Cu electrode reams is soaring at 95–97%, which is more stable than the bare Cu that decrease from 92 to 80%. By reducing the reaction between lithium metal and electrolytes, an improvement of CE is presented, which indicates that SEI layer composited with h-BN is more enduring than before.

6. Conclusion
To summarize, with the increasing demand of high-capacity batteries, the possibility of Li metal battery replace lithium-ion battery have been widely discussed. Multiple modifying approaches based on electrolytes additives, Li alloy and current collectors have been summarized in this paper. By modifying traditional organic electrolytes with functional additives, improving the physical and chemical properties of SEI film to protect the lithium anode. Also, solid electrolytes such as CPE possesses a stiff and robust structure to enhance mechanical strength while providing good conductivity, which could suppress lithium dendrites formation. Furthermore, Lithium metal modification, such as surface coating, Li-Sn alloy, carbon fiber (CF)-based composited anode, can improve the properties and performance of lithium anode to a certain extent. With respect to current collector, a three-dimensional structure can reduce the local current density and alleviate the volume effect, which could be a good solution.

Currently, most research are in the theory verification progress, and various process problems block the ways for the commercialization of Li metal anode batteries. It may not be possible to resolve the Li dendrites problems through one perspective. Careful considerations through multiple perspectives from electrolytes, Li anode surface and current collectors may be able to make LMB be viable. On the one hand, in the context of the rapid progress of contemporary theory, characterization and material science, the research of lithium metal anodes has extensively developed. As the core material of high specific energy batteries, lithium metal anode has received extensive attention from scientists and engineers all over the world. On the other hand, the approaches, basic principles, and protection strategy of lithium metals remain at the beginning. Thus, it’s encouraged that for more research efforts and investment need to go into this field to achieve the commercial success of high-energy density lithium metal batteries earlier.

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