Overview of the Recent Progress of Suppressing the Dendritic Growth on Lithium Metal Anode for Rechargeable Batteries

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Abstract. The lithium metal has been considered as a competitive material for anode on the high-energy storage battery because of its various advantages, such as high capacity, low density, and the lowest electrochemical potential. However, the uncontrolled dendritic growth on the anode surface could cause the short circuit, even explosion of the battery. Therefore, strategies about how to effectively inhibit the formation of dendrites is of great importance. This paper will first give a brief introduction on the growth of dendrites. The attention is then focused on the recent advancements to suppress the dendrite growth of lithium metal, such as the optimization of electrolyte, application of artificial solid electrolyte interphase (SEI), and the modification of lithium anode. The future research directions will be presented at the end.

Keywords: Anode, Dendrite growth, Additives, Artificial SEI.

1. Introduction
In the past decades, the increasing demand for energy has led people to start investigating the efficient energy storage system. Lithium-ion batteries (LIBs) have many excellent features, such as high energy density, and therefore this type of battery has gradually become the dominant power source for portable electronics. [1] Nowadays, the most widely used anode for LIBs is graphite, which only has a theoretical specific capacity of 372 mAh g⁻¹. [2] Hence, an anode material with a high theoretical capacity has become a focus in order to satisfy the growing demand for high-energy density batteries, and that enables people to work on lithium again. Lithium metal has a very high theoretical specific capacity of 3860 mAh g⁻¹ and the lowest electrochemical potential of -3.04 V (vs. the standard hydrogen electrode). [3] These features are the essential components for an outstanding anode material. However, lithium metal still faces some challenges, one of which is the dendrites growth. This could directly lead to the short circuit or explosion. In order to achieve the commercialization of lithium-ion batteries, the prevention of dendrite growth on anode is the key problem. In this essay, we will review the process of the growth of lithium-ion batteries briefly, and then move on to the advanced solutions introduced in recent years.

2. Dendritic growth
Dendrites, needle-like structures which grow on the anode, could lead to short circuit and a great consumption of lithium-ions in the battery. Because of the lowest electrochemical potential of lithium, nearly all the electrolytes could react with it, forming a large solid electrolyte interphase (SEI) layer encasing the anode. (The formation of that layer consumes the active Li-ions in the electrolyte, as a result of which, reducing the coulombic efficiency (CE) in the battery. [4]) During the battery operation,
lithium-ions are reduced at the anode, but uneven charge distribution will cause local excess lithium deposition. The huge volume change caused by the lithium protrusions causes the rupture of the fragile SEI layer. [5] The tips of the exposed fresh lithium underneath would attract lithium-ions to migrate from the electrolyte, forming lithium whiskers. In addition, the large specific surface area of the dendrites would continuously expose the fresh lithium and further elongate themselves. [6] This phenomenon significantly reduces the coulombic efficiency and shortens the batteries’ lifespan. Besides, these lithium dendrites also induce a series of safety hazards. The uncontrolled dendrites could penetrate through the separator and contact the cathode at the other end, resulting in short circuit or, more seriously, leading to the explosion of the battery. During stripping, the roots of dendrites break and then introduce the isolated Li to the electrolyte. These ‘dead’ Li would be deposited at the surface of the electrode, and a thick SEI layer would be formed after several cycling processes. Hence, the combined effect of the accumulated ‘dead’ Li and the thick SEI layer at the electrode would directly impede the ion transportation and also bring about an increase in the internal resistance of the battery.[7]

3. Suppression strategies for anode dendrites
With a deep understanding of the origin of dendrite growth, it is vital for the lithium-ions to distribute evenly on the anode surface in order to improve the cycling performance of LIBs. In the past decades, a wide range of strategies used to inhibit the growth of dendrites have been introduced. In this part, we will review the recent development of those strategies designed for suppressing the uncontrolled dendrite growth.

3.1. Addition of additives
Additives, which are able to be the constituents of the SEI film on the anode, have been investigated to block dendrite growth and thus improve the electrochemical performance of the battery. On the basis of induction charging model, lithium dendrites will preferentially grow on protrusions with higher charge density. Therefore, researchers introduced metal cations M⁺ (Cs⁺, Rb⁺) into the electrolyte: When the reduction potential of metal cations is smaller than the lithium cations, M⁺ would accumulate at the surface of the protrusions and form an electrostatic shield, hence, inhibiting the uneven distribution of lithium and the continuous growth of dendrites (figure 1). According to the experiment conducted by Li’s team, [9] the average coulombic efficiency could be maintained at near 99% of 200 cycles with the addition of additives. The results clearly showed promising performance of LIBs and effective suppression of dendritic growth. It is also worth noting that the control of the concentration of cations is very important. According to the Nernst equation, a high concentration of metal cation solution would result in a higher reduction potential of M⁺. If the concentration is much lower compared to lithium cation solution, the inhibition of the growth of whiskers would be effective. [7] Besides metal cation additives, inorganic salts (AlI₃, MgI₂, SnI₂ [10], Acidic gas (CO₂, SO₂) [11], ethers (Et₂O) [12] and ionic liquids ([C₅mPyr][FSI]) [13] could also adsorb on the surface of anode and form protective layers, maintaining the high cycling performance of LIBs.

3.2. The use of solid and gel electrolytes
The solid polymer electrolyte is generally composed of lithium salt and a polymer. With experimental investigation, the modulus of most of the solid polymers could reach hundreds of gigapascals. [7] That could be sufficient to prevent the penetration of lithium whiskers. However, this new solution still faces some challenges: (1) low ionic conductivity compared to liquid electrolytes, and (2) large interface contact resistance between solid electrolyte and electrode. Two solutions are suggested for boosting the conductivity of ions. The first one is to use polyethylene oxide with lithium salt (PEOₓ-LiX), which is confirmed to be able to increase the ion conductivity higher than 10⁻⁵ S cm⁻¹. [14] The reason for that could originate from the conductivity of ions of the oxygen-assisted part in PEO, which allows the mobile motion of lithium cations. The second solution is the application of block copolymers. Poly (styrene-block-ethylene oxide) copolymer (SEO) is one of the examples. When the relative molecular mass of this copolymer increases, the salt would be more frequently localized at the middle of the lamella
of the poly (ethylene oxide). [15] As a result, the ion conductivity is observed to reach $2 \times 10^{-3}$ S cm$^{-1}$ at certain conditions. [16] In order to solve the problem induced by the large interface contact resistance, a copolymer with a liquid-like behavior could be applied to the battery. It ensures a good contact between electrolyte and the electrode, hence eliminating the concern of great interfacial resistance drawn by the poor surface adhesion. [17]

![Figure 1](image-url)

**Figure 1.** a) Lithium-ions are attracted to the anode and lead to the dendritic growth. b) A schematic illustration about the well–functioning additives, such as Cs$^+$ and Rb$^+$. These ions are capable to form an electrostatic field in advance and repel lithium-ions, thus preventing the formation of dendrites. [8]

The gel polymer electrolyte is made of highly conductive material, which is swollen by lithium salt solution. The ionic conductivity is relatively satisfactory compared to solid electrolyte. Taking a pentaerythritol tetraacrylate (PETEA)-based gel polymer electrolyte as an example, it could reach a conductivity of $1.13 \times 10^{-2}$ S cm$^{-1}$, [18] which is 2 times greater than the conductivity of solid polymer electrolyte. However, gel electrolyte shows a less stable mechanical strength, but this problem could be solved by the combination of crosslinked hairy nanoparticles and gel polymer electrolyte. This nanocomposite exhibits an outstanding performance in blocking the whiskers growth while maintaining a stable cycling performance. [19]

In addition to optimizing the electrolyte to improve the properties of in-situ SEI film on the surface of lithium metal, it is another effective way to prepare ex-situ artificial SEI film on the surface of lithium metal before the battery is used.

### 3.3. The artificial SEI layer formed from nanoparticles

Cui et al. [20] used a mixture of Cu$_3$N nanoparticles and styrene-butadiene rubber (SBR) to construct an artificial SEI layer on the anode surface. When the battery is being charged, the lithium-ions in the electrolyte could react with Cu$_3$N and form Li$_3$N without changing the homogeneity of the surface. Li$_3$N is an excellent Li$^+$ conductor ($10^{-3}$-10$^{-4}$ S cm$^{-1}$), which can effectively promote the migration of Li$^+$ on the electrode surface, thereby forming a uniform Li$^+$ flux (figure 2). Based on the experimental results, the coulombic efficiency had reached an approximate average value of 97.4%, and a constant ohmic value of SEI was maintained for more than 100 cycles. It is clearly indicated that the good mechanical stability and flexibility of artificial SEI layer formed from Cu$_3$N nanoparticles greatly ensures the lithium
transport number and electrochemical performance of LIBs. There is also another similar example of recent technology for constructing the artificial SEI, which is the employment of interconnected hollow carbon nanospheres. By evaporating and drying, a hollow carbon nanosphere was coated with the surface of anode. Due to the nanosphere’s small thickness and great Young’s modulus (~200GPa), it could sufficiently block the growth of dendrites without increasing the internal impedance of the battery. As the charging/discharging process of lithium-ions is going on, the hollow nanosphere could adjust its flexibility because of the weak bonds to the metal, hence the formation of cracks could be prevented. As the experimental figures presented, the overall coulombic efficiency reached around 99% after 150 cycles, and this high performance could still be remained for any further cycling. [22] Besides the application of Cu₃N and hollow carbon nanospheres, Li₃PS₄, [23] Al₂O₃, [24] BN and graphene [25] also showed a promising cycling coulombic efficiency while suppressing the dendritic growth on the anode effectively.

Figure 2. Schematic illustration of the Li plating/stripping behavior of bare Li (upper figure) and the artificial SEI protected Li (lower figure) [20]

3.4. Polymer film—one of the alternatives for natural SEI.
Y.S constructed the artificial SEI film by depositing organic film "Polyurea" with many polar groups, such as N=O and C=O, on the anode electrode. The nitrogen containing groups have the ability to regulate the lithium-ions flux so that they could accumulate evenly on the anode surface, hence prolonging the lifespan of the battery. In addition, thanks to the double bond in those polar groups, “Polyurea” could change their shape flexibly, thus effectively preventing the fracture of the film. As the result, the lifespan of LIBs using modified anodes was proved to be 3 times longer than the LIBs with a bare lithium anode under same conditions. [26] There is also another highly conductive polymer film proposed recently, which is composed of a high ionic conductivity polymer (HICP), polyvinylidene fluoride (PVDF) and 18-Crown-6. With the function of oxygen atoms on 18-Crown-6, the Li-ions could possess high affinity to that, consequently, distributing evenly on the surface. With the application of HICP on the Li surface, the coulombic efficiency of LIBs could retain ~97.38% after 200 cycles. [27] Apart from the two polymer films we talked above, the hybrid crosslinking polymer film, such as Lithium polysulfidophosphate/poly (2-chloroethyl acrylate), [28] could also significantly boost coulombic efficiency (~98.7%) and provide sufficient support for inhibiting the dendritic growth on the anode.

Two different approaches (the application of electrolyte and artificial SEI film) are discussed above to promote the stable Li-metal deposition at the anode. In this part, the application of modified Li anode on LIBs will be elaborated in detail.

3.5. The use of lithium composite Matrix
A nano diamond (ND)-Li matrix could be prepared by embedding the lithium metal to the high-modulus ND matrix. In addition, the surface of nano diamond is coated with lithiophilic ZnO layer to increase the compatibility between ND and lithium, leading to a collector-free Li anode. [29] On the basis of
experimental results, the Young’s modulus of ND-Li composite matrix could reach approximately 30 GPa. [30] which demonstrates a sixfold improvement in the strength of lithium anode. This ultra-high Young’s modulus exhibits an outstanding mechanical confinement behavior during the stripping/depositing process. During cycling, the uneven distribution of lithium-ions could be relieved in the ND-Li matrix, preventing volume changes and leading to a dendrite-free lithium deposition. In the ND-Li/S battery, 607.3 mAh g\(^{-1}\) capacity is maintained after 500 cycles when the cell is working. The ND-Li/LFP battery could retain a high capacity (128.6 mAh g\(^{-1}\)) after 300 cycles and high Coulombic efficiency. [30] Besides ND-Li matrix, lithium-coated polymeric matrix (Li-coated polyimide) [29] and lithium-embedded conductive solid matrix [31] exhibit same intriguing features as well, such as effective restriction for dendritic growth and minimum volume change of the anode.

3.6. Current collector/Li metal composite

Qi Li et al. prepared Cu/Li composite by embedding the mesh like copper sheet with lithium metal. This design lowers the ion flux concentrated at the center because of its large surface area, therefore ensuring the uniform distribution of lithium-ions. [32] In contrast, the conventional composite of Li metal and 2D copper foil would let lithium-ions accumulate unevenly at the anode surface and therefore inducing inhomogeneous lithium deposition, and the large protuberance will directly trigger the continuous growth of dendrites and result in the malfunction of the battery. [33] The coulombic efficiency of the mesh Cu/Li composite ranges from 95.6% to 97.5% during the first 150 cycles. [32] It is obvious that the porous composite ensures an excellent cycling behavior by providing a cage for the lithium-ions and enhances the lifespan of the battery.

3.7. Layered reduced graphene oxide (r-GO) as a stable host for the anode

Cui et al. reported a layered Li–rGO electrode prepared by molten Li infusion into an rGO film with uniform nano gaps. When the graphene oxide (GO) film is partially contacted with the molten lithium, the nano gaps could be formed because of the sudden pressure release within the GO layers. This process successfully removes the surface functional groups, and the capillary force induced by nano gaps could significantly boost the lithiophilicity of r-GO. [34][35] The large surface area possessed by the layered graphene oxide [36] and great mechanical strength (about 300 nN \(\mu\)m\(^{-2}\)) [37] ensures a good Li lithiophilicity and low Li nucleation barrier, [35] which prevents continuous Li consumption and maintains high performance of the battery. During the intercalation of Li-ions, the size of nano gaps of r-GO would only change slightly, therefore restricting the volume change of the anode. The high lithiophilicity of the electrode ensures the even distribution of the lithium on the electrode surface and the mitigation of dendrites formation. With those excellent properties, the layered Li-rGO electrode showed a high capacity of \(~3390\) mAh g\(^{-1}\), low overpotential (\(~80\) mV at 3 mA cm\(^{-2}\)) and a flat voltage profile in a carbonate electrolyte. [35]

4. Conclusion

This review focuses on summarizing the recent progress of preventing the dendrites formation from three different angles which are electrolyte, SEI and lithium anode. The addition of additives, construction of artificial SEI layer from nanoparticles and the introduction of lithium composite matrix could significantly boost the electrochemical performance of LIBs, but all the strategies are still at the experimental level, and remaining questionable when it comes to the production in real life. To summarize, it is impossible to solve the problem induced by dendrites only through one strategy. The formation of dendrites could be tackled efficiently by the combined modification of electrolyte, SEI film and lithium anode. Nowadays, there are huge amounts of discussions about the lithium anode, which requires researchers to put more efforts on the fundamental theory and the design of new materials to improve the performance of LIBs.
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