

The growth mechanism and strategies of dendrite in lithium metal anode

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Abstract. Lithium metal batteries offer an incredibly high potential energy density when compared to the present large-scale commercial lithium-ion batteries. In recent years, with the development of technology, the energy density of lithium-ion batteries has rapidly reached its theoretical energy density. People are gradually pursuing higher energy density batteries. The negative electrode of batteries, made of lithium metal, has the lowest reduction potential and the highest theoretical specific capacity, which has great research value and a number of possible uses for the creation of secondary batteries with large capacities. However, actual uses may present safety risks. Lithium dendrites, which can result in short circuits, fires, or explosions, and decreased battery efficiency are caused by the ease with which Li^+ can deposit unevenly on the anode's uneven surface. As a result, this study focuses on the development process of lithium dendrite and analyzes three elements of electrolyte regulation: artificial SEI layer, solid electrolyte, and strategies to restrict the growth of lithium dendrite.

Keywords: Lithium battery, Lithium dendrite, SEI, electrolyte.

1. Introduction

Utilizing cutting-edge energy storage technologies with high energy density and prolonged life is essential given the proliferation of mobile electronics and new-energy vehicles. Lithium metal batteries are increasingly widely used in daily life as a result of their advantages of high levels of safety and prolonged cycle life. The main anode material in traditional lithium-ion batteries, graphite, has a relatively low theoretical specific capacity, which prevents future improvements in energy density. On the contrary, lithium metal anodes have the advantages of high energy density, high voltage, excellent electrochemical characteristics, good cycling performance, and low internal resistance, which have great potential.

However, the lithium metal anode is frequently accompanied by phenomena like lithium dendrite growth, electrolyte side reactions, and significant volume changes throughout the cycle. These phenomena can result in serious issues like short-circuits, explosions, shortened lives, and capacity attenuation. In this study, four different lithium dendrite development mechanisms are outlined. Three different electrolyte regulation solution strategies—electrolyte additive, high-concentration electrolyte system, synthetic SEI film, and solid-state electrolyte—are then examined.

It is necessary to research ways to reduce the development of lithium dendrite, optimize the construction of SEI layer, and other issues in order to successfully improve the performance of the batteries and ultimately promote their commercial large-scale usage.

2. The growth mechanism of lithium dendrite

The public first became aware of lithium dendrite in the 1960s. Before putting up numerous theories for the lithium dendrite's nucleation and growth, several researchers spent years detailing the fundamental process. However, there is no one model that has universal support, and there are inconsistencies among the models. The growing process of lithium dendrite is explained in this work using four basic theories [1]. Figure 1 depicts the lithium dendrites' growing process [2].

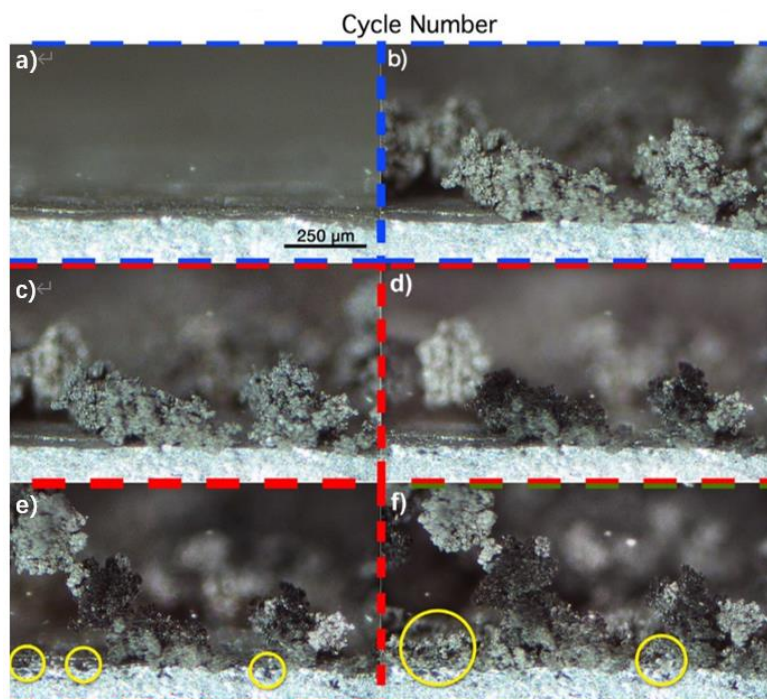


Figure 1. Lithium dendrite growth process [2].

2.1. Charge-induced growth

Li^+ separates from the cathode and enters the electrolyte during the battery cycle. It enters the anode surface through the diaphragm, mixes with the electrons in the external circuit, and then deposits on the metal surface. Lithium will be deposited unevenly, creating a protrusion that will eventually become a lithium nucleus. It will build up a lot of electrons at the tip, creating a strong local electric field that draws in additional Li^+ deposits and leads to the development of lithium dendrite.

2.2. Surface-nucleation growth

The literature has demonstrated that lithium's surface energy and diffusion coefficient have a significant influence on the development of lithium dendrites. Lithium foil is often produced with an uneven primary layer and surface flaws, with the elevated region receiving preferential Li^+ deposition. Since undeposited Li^+ may travel less laterally at this point, if the diffusion coefficient of lithium on the surface is low, many one-dimensional lithium dendrites will develop in these elevated regions.

2.3. SEI film diffusion control

When the mechanical stability of the SEI film is inadequate, the stress brought on by lithium deposition on the SEI film may cause the film to rupture, which then causes dendritic growth to occur at the crack site. These fissures not only expose the internal fresh lithium to the electrolyte due to the increase in local Li^+ flow, which worsens the development of lithium dendrite, but also produce a "hotspot" for the electrochemical chemistry of lithium deposition.

2.4. Deposition-dissolution factors

The electrode's surface will get strained as a result of the lithium's ongoing deposition and growth, which boosts the area's Li^+ conductivity and quickens lithium deposition. As a result, the deposition of lithium may be uneven, causing the SEI film to become stressed and eventually rupturing. The lithium dendrites then proceed to grow like whiskers. The lithium falls from the head to produce "dead lithium" and granular lithium because it is simple to break from the neck and dissolve quickly during the discharge process.

3. Solution strategy

The problem of lithium dendrite is one of the major barriers to the widespread adoption of lithium metal anode, as was earlier mentioned. Based on the four development stages indicated above, this paper focuses on recent investigations of lithium dendrite from three angles, including electrolyte control, synthetic SEI film, and solid electrolyte.

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3.1.1. Electrolyte additive

In general, the majority of methods rely on the electrolyte's assistance in the cycle's production of the SEI layer to improve anode performance. To prevent the occurrence of lithium dendrites in the battery, Peng et al. employed N-fluoropyridine (ArF^+) bis (trifluoromethane) sulfonamide as an electrolyte additive [3]. Zhao et al. effectively prevented the growth of lithium dendrite and increased battery life by adding $\text{Cu}(\text{NO}_3)_2$ to the carbonate electrolyte [4]. Lei et al. used molecular ATU as an electrolyte additive to produce a stable SEI layer with high lithium-ion conductivity and little internal resistance [5].

The stability of the SEI layer is also clearly improved by the addition of trace quantities of tris(2,2,2-trifluoroethyl) borate, fluoroethylene carbonate, and other inorganic and organic components [2]. Even if the exact methods of different types of additives vary, they all essentially try to change the SEI film's composition and structure in order to improve Li^+ deposition behavior, which may be thought of as one of the ways to manage the SEI film.

3.1.2. High-concentration electrolyte system

According to study done by Yamada et al., the concentration of free solvent molecules will drop and the interaction between anions, cations, and solvents will be strengthened when the salt concentration rises. An electrolyte with a three-dimensional structure is produced when the threshold is exceeded (typically $>3\text{-}5\text{ M}$, depending on the salt solvent combination), and is known as a "high concentration electrolyte" [6]. Additionally, several investigations revealed that in the high-concentration electrolyte system, side reactions are reduced while the concentration of free-state solvent molecules is reduced and the coordination number of salt-solvent rises. Additionally, the high concentration system reduces gradient variations in the electrolyte concentration, resulting in more uniform Li^+ deposition, which helps to prevent the formation of lithium dendrite. The high-concentration electrolyte system, however, suffers from issues such excessive viscosity, poor wettability, low conductivity, and high cost. The direction of the local high concentration electrolyte, i.e., lowering the concentration of electrolyte by diluent, is therefore the subject of current study. This type of technology can prevent lithium and electrolyte from recombining spontaneously, allowing the battery to maintain high electrochemical stability.

3.2. Artificial SEI film

High mechanical strength and strong Li^+ conductivity is necessary for the optimum SEI layer in order to reduce electrode volume change and prevent lithium dendrite formation. Because the original SEI film's components and structure are intricate and its production mechanism is poorly understood, researchers have focused on an approach called artificial SEI film that is easier to regulate. The synthetic inorganic SEI coating, which is now made up of nitride, fluoride, sulfides, and oxides, has

begun to take shape. The development of artificial organic and organic-inorganic SEI films will be the main topic of this essay.

Researchers have been paying close attention to the artificial organic SEI layer recently due to its great strength, pressure resistance, and strong adherence to lithium metal anode [3]. As a layer of defense for the lithium metal anode, Liu et al. created a robust lithium-rich organic film (TLOF) using MLD utilizing LiOtBu and HQ precursors. This significantly increases the cycle life and stability of lithium plating/stripping. Additionally, it has strong volume change resistance, which may successfully stop the formation of lithium dendrite. HU et al. prepared a sturdy SEI film, which uses polyvinyl alcohol as the outermost structure and fluorine containing boron nitride as the inner layer. The specific structure of SEI thin film is shown in Figure 2. It exhibits strong resistance to lithium dendrite development as a consequence, and steady cycling performance for more than 1200 hours [7].

Although other artificial SEI coatings have been successful in suppressing lithium dendrite, their extensive commercial application is constrained by the difficult and rigorous conditions required for their fabrication. The main focus of future study will be on creating SEI films that are more affordable, practical, and efficient as the creation process of SEI film is elucidated.

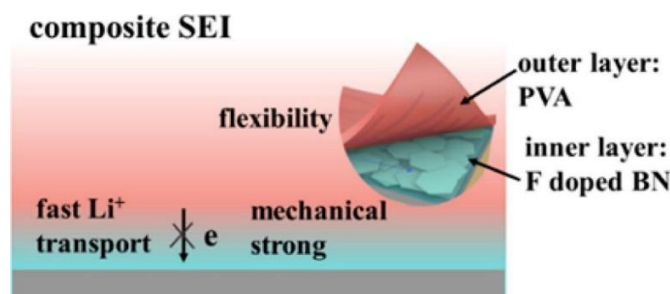


Figure 2. The structure of the SEI [7].

3.3. Solid-state electrolyte

At present, the electrolytes used in lithium-ion battery are mostly liquid electrolytes, but they have hidden dangers such as unstable and liquid leakage. The solid electrolyte can not only solve these problems, but also has good mechanical properties and pyknotic structure, which can fully inhibit the growth of lithium dendrite.

According to reports, two types of electrolytes that have been thoroughly and in-depthly explored up to this point are inorganic solid electrolyte and organic polymer solid electrolyte. Polyethylene oxide (PEO), polyethylene glycol (PEG), polymethyl methacrylate (PMMA), and other materials have all been the subject of extensive investigation [8]. The most typical of them is polyethylene oxide (PEO) [9]. Although they are extremely safe, like other polymer solid electrolytes, their modulus and ionic conductivity are insufficient (far lower than the ionic conductivity of the liquid electrolyte), limiting their potential applications.

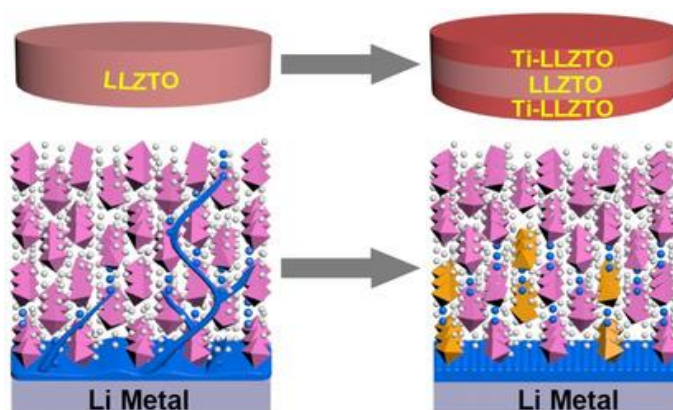


Figure 3. Electrolyte Structure and Inhibition of Lithium Dendrites [10].

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)-based garnet material and its doped variants are primarily explored for inorganic solid electrolytes. In order to lessen the defects/pores at the interface, Zhu et al. created a titanium-doped $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (Ti-LLZTO) double-layer ceramic electrolyte, it increases the reduction of interface resistance, homogenizes the ion/electron flow at the interface, and inhibits dendrite development [10]. Figure 3 shows the structure of the electrolyte and its schematic diagram for suppressing lithium dendrites.

Overall, despite solid electrolyte's promising research potential, there are still many issues to be resolved before it can be used in mature applications, including low stability, reactions with lithium or air, expensive preparation costs, limited ionic conductivity, and others.

4. Summary

As people's demand for energy storage systems continues to grow, the current lithium-ion battery, which uses graphite as the anode, is becoming unable to meet the expanding demand for power consumption. The lithium metal anode has the largest theoretical specific capacity and the lowest reduction potential, which can considerably increase the energy density of the battery. However, the development of lithium dendrite significantly restricts the practical usage of lithium metal anode. This article discusses various experimental solution strategies that have recently emerged from three aspects of electrolyte regulation, artificial SEI film, and solid electrolyte. These strategies are based on the construction of SEI film with both strength and performance, promoting the uniform flow of ions, and improving the ionic conductivity. This clearly demonstrates prospective application possibilities and impacts, as can be observed.

The development of electrolytes, SEI films, and matrix frameworks with stable electrochemical performance and low cost is also crucial; however, most of the current research schemes are demanding and expensive, with some methods having hidden dangers such as unstable material properties and doubtful long-term service performance. Therefore, further exploration of the relevant performance of lithium metal batteries has important practical significance.

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