A Review of Research on Potential Solutions for Dendrite Growth in Solid State Cells

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Abstract. The formation of lithium dendrites can lead to irreversible capacity loss and pose safety risks in lithium batteries. One proposed model suggests that when the current density is too high, a depletion layer of lithium ions forms near the anode, promoting dendrite growth. Lithium dendrites may puncture the membrane of the battery and reach the positive electrode, causing the battery to short circuit, causing the battery to overheat and possibly explode. This growth can result in short circuits in conventional lithium batteries. Several strategies can be employed to inhibit the growth of lithium dendrites. These include coating the lithium metal surface with durable layers or alloy compounds, micro-modulating the solid-state electrolyte to reduce dendrite nucleation, and managing nano-cracks in the electrolyte. These approaches have shown promising results in enhancing the stability and cycling performance of lithium metal anodes. However, technological constraints still limit the widespread implementation of these strategies, and more advanced characterization techniques are needed to better understand and address the issue of dendrite growth in solid-state batteries.

1 Introduction

In light of the global trend toward decarbonization, efficient and environmentally friendly energy storage technologies have become a central focus of research [1]. Among these, lithium batteries hold a prominent position. Despite their potential to achieve high energy densities, existing lithium-ion batteries do not meet the increasing demands for performance in the future energy market. For instance, electric vehicles are expected to travel approximately 500 kilometers on a single charge, yet most current models equipped with lithium-ion batteries can only manage about 200 to 300 kilometers per charge. This limitation is largely due to the capacity constraints of commercial lithium-ion batteries, which typically offer around 250 Wh/kg and 770 Wh/L [2].

To address future energy needs, the development of solid-state batteries—known for their higher energy density, superior cycling performance, and enhanced safety—has become essential. Solid-state batteries are considered an ideal solution because of their exceptional performance [3]. However, in practical applications, solid-state electrolytes still face challenges, particularly with the issue of short circuits caused by the growth of lithium

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dendrites. For example, the grain boundaries in ceramic solid-state electrolytes often provide a pathway for these dendrites to grow, which can ultimately lead to battery failure [4].

The purpose of this paper is to review recent research advancements and the challenges faced by various solid-state electrolytes in addressing the issue of lithium dendrite growth, which can lead to short circuits. Additionally, it aims to refine strategies for mitigating this problem. This work is essential for enhancing the safety and stability of solid-state electrolytes, thereby supporting the commercialization of solid-state batteries and facilitating updates and improvements in the energy market.

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2 Lithium dendrite formation mechanism

The formation of lithium dendrites is primarily explained by the physical model proposed by Chazalviel. As shown in Figure 1, the deposition of lithium dendrites on the surface of the lithium anode occurs in two main phases. When the current density is below a critical value, the ion concentration near the lithium anode is similar to that of the electrolyte. In this scenario, the growth of lithium dendrites is hindered. However, when the current density exceeds this critical value, lithium ions near the anode are rapidly consumed, creating a depletion layer of lithium ions. This results in a localized space charge that encourages the reduction of lithium atoms and promotes the formation of dendrites [5].

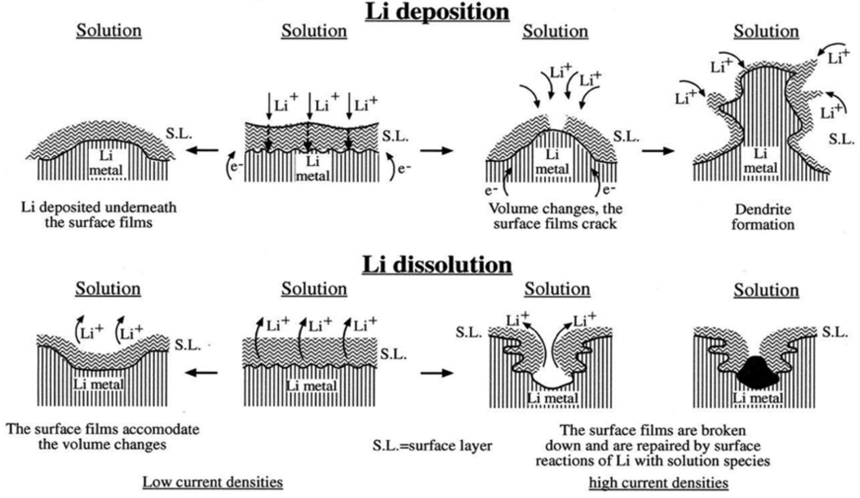

Fig. 1. the deposition mechanism of lithium dendrites on the lithium anode [6].

Chazalviel explains that the lithium-ion deposition process is crucially situated beneath the solid electrolyte interface of the battery [7]. Here, the reduced lithium atoms are subjected to internal stresses and interfacial surface tension and move along the grain boundaries, leading to increasing internal stresses at the lithium anode. This condition significantly increases the internal stress at the lithium anode. When this stress surpasses a critical threshold, lithium atoms exit the pores and form lithium dendrites. As these dendrites expand and reach a certain size, they become detached from the root, resulting in dead lithium. This phenomenon leads to irreversible capacity loss, emphasizing the need for improved battery management strategies [8].

The growth of lithium dendrites is an irreversible process. In conventional lithium batteries, if lithium dendrites penetrate the separator, they can cause the battery to short-circuit. In contrast, solid-state batteries are less susceptible to puncture by lithium dendrites due to the dense nature of their electrolyte. However, their operation depends on lithium penetration and ion transport, which can lead to the formation of lithium dendrites within the electrolyte, potentially resulting in short circuits.

The location and growth patterns of lithium dendrites are significantly influenced by the quality of the electrolyte material. These factors are closely related to the morphology of the crystal boundaries and defects in the electrolyte[6]. Ceramic electrolytes are generally more likely to promote the growth of lithium dendrites compared to polymer electrolytes, primarily due to the presence of nano-cracks.

3 Modification strategies

Recent studies indicate that lithium dendrite growth can be inhibited through various methods, including the coating of anode lithium metal surfaces, micro-modulation of solid-state electrolytes, and control of nano-cracks.

3.1 The coating of anode lithium metal surfaces

The short-circuit principle highlights a critical issue: the diffusion of lithium atoms along grain boundaries beneath the solid electrolyte interface (SEI) is constrained, resulting in stress and dendrite formation at the anode. By employing a robust SEI layer with exceptional insulating properties, we can effectively curb the growth of lithium dendrites while preventing direct contact between the anode and the electrolyte. Research efforts have increasingly concentrated on both organic and inorganic coatings, alongside promising polymer and alloy compound coatings that have produced impressive results.

Chang et al. have made significant advancements by creating an artificial SEI using planar polycyclic aromatic hydrocarbons on lithium metal electrodes through an innovative in-situ formation technique. Their product, the dihydroxy violet anthracene (DHV) layer, acts as a powerful protective shield, enhancing the stability of the SEI. Remarkably, the DHV layer has been shown to enhance the Coulombic efficiency of the lithium metal anode significantly, achieving outstanding cycling stability of over 1,000 hours at a rate of 4 mAh cm^{-2}. Furthermore, lithium-metal anodes shielded with the DHV layer demonstrated an impressive Coulombic efficiency of 99.8% and sustained excellent long-term cycling stability after 300 cycles in $LiFePO_4$/Li batteries. This innovation marks a pivotal step forward in battery technology [9].

Inorganic coatings play a significant role in this field. Liu et al. employed an innovative technique where they alternately sprayed negatively charged graphene oxide and positively charged polylysine solutions onto a copper substrate using spray coating. They then utilized microwave plasma chemical vapor deposition (CVD) to grow a nanodiamond film on this copper substrate, creating a high-strength protective layer. This layer boasts a modulus of elasticity exceeding 200 GPa, effectively preventing the propagation of lithium dendrites. Moreover, it demonstrates exceptional stability during cycling tests.

A key aspect of Liu's innovation is the two-layer design. By repeating the processes of seed-layer spraying and CVD, they were able to grow a second layer of nanodiamond thin film. This approach significantly enhances the defect tolerance of the interface [10].

In 2017, Liu proposed the use of dynamically crosslinked polymers, such as Play-Doh, as an interfacial layer for lithium metal anodes. This polymer exhibits viscoelastic characteristics, providing it with a unique “solid-liquid” hybrid property [11].

As shown in Figure 2, (a) illustrates the structural formula of the material, while (b) and (c) display comparison graphs for the scenarios without and with the coating, respectively. The results indicate that the crosslinked polymer coating effectively prevents the growth of lithium dendrites. This efficiency arises from the material's ability to reversibly transition between "liquid" and "solid" properties based on the lithium growth rate. Consequently, it maintains good contact even as the volume and morphology of the lithium metal change. This innovation provides a new perspective on stable operation and uniform deposition/stripping of lithium metal anodes.

In addition, alloying the lithium metal surface by magnetron sputtering at a specific temperature provides higher conductivity efficiency by lower resistance of the alloy compounds compared to other coating materials.

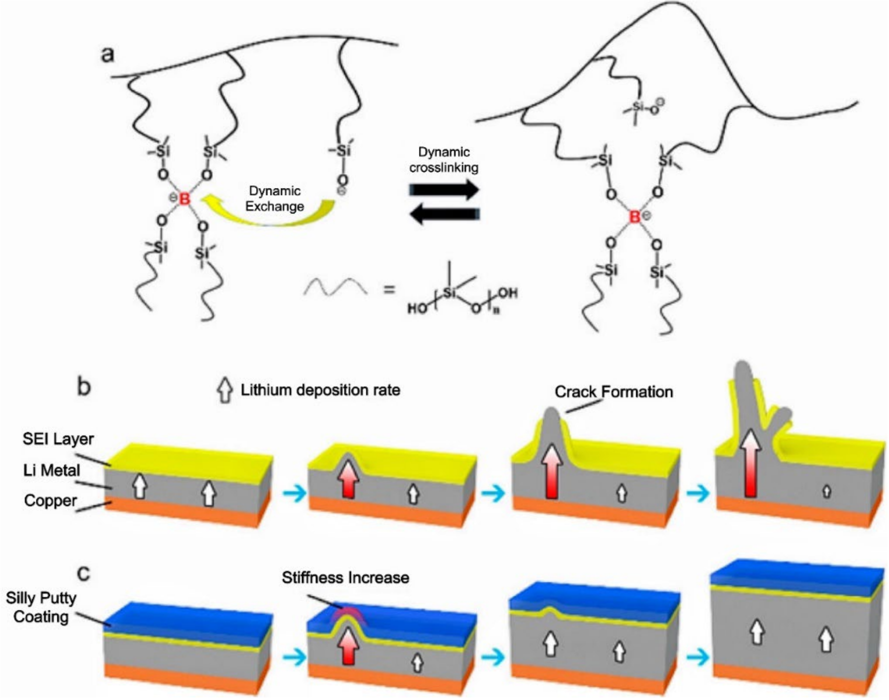

Fig. 2. the design of composite coating SP (plasticine) modified Li anode [11].

3.2 Micro-modulation of solid-state electrolytes

At high current densities, the ion concentration exceeds that of the electrolyte, leading to the formation of a space charge in the dilute electrolyte. This space charge accelerates the nucleation and growth of lithium dendrites. To effectively mitigate this dendrite nucleation process, it is beneficial to use electrolytes with either a zero anion transfer number or a high concentration of supporting electrolyte. Additionally, a single ionic conductor can enhance lithium ion mobility, meaning that lithium ions can move through the electrolyte much more efficiently than other ions, thus reducing ion loss [12].

The performance of the electrolyte can be enhanced by incorporating additives without altering its fundamental properties. For instance, Chae et al. studied a novel electrolyte additive called lithium cyano tris(2,2,2-trifluoroethyl)borate (LCTFEB). Their characterization of lithium metal morphology and the solid-state electrolyte interface used techniques such as field emission scanning electron microscopy (FE-SEM), cryo-transmission electron microscopy (cryo-TEM), and X-ray photoelectron spectroscopy (XPS). The findings demonstrated that the additive could form a solid-electrolyte interphase (SEI) layer on the lithium metal surface, significantly improving the electrochemical performance of both the NCM523/Li battery and the symmetric Li/Li battery [13].

3.3 Control of nano-cracks

Compared to traditional electrolytes, solid electrolytes possess a high shear modulus, which theoretically makes them better at resisting lithium metal penetration. However, a study found that the oxide solid electrolyte LLZO, with a shear modulus of approximately 60 GPa, still experiences intrusion even at a surface-averaged current density significantly lower than 1 mA cm^{-2} [14].

Based on this, Geoff McConohy and his colleagues conducted lithium metal plating experiments on the surface of LLZO using in situ microprobe scanning electron microscopy. They controlled the contact force between the microprobe and the LLZO to observe how lithium penetration initiates and grows. The results showed that increasing the contact force significantly enhanced the likelihood of lithium penetration. This occurs because higher contact forces create new nano-cracks on the electrolyte surface, thereby confirming the positive relationship between nano-crack formation and lithium penetration[15].

To mitigate the risk of lithium metal permeation, it is essential to carefully manage the contact force, as this can help minimize crack formation caused by excessive pressure. Additionally, the study indicated that small compressive strains can effectively guide lithium penetration along the direction of strain, which means that applying external stresses can also be a viable method for influencing crack growth and lithium penetration. Consequently, McConohy suggested using external compressive strains to promote crack closure, thereby increasing the effective fracture toughness of the cracks. This crack closure effect can ultimately reduce the likelihood of lithium metal penetration.

4 Conclusion

Traditional lithium-ion batteries have struggled to meet the increasing demand for new energy solutions, making the practical application of solid-state batteries urgently necessary. A key challenge for the commercialization of solid-state batteries is addressing the growth of lithium dendrites within solid-state electrolytes. Unlike traditional lithium batteries, where lithium dendrite countermeasures focus on different approaches, this paper outlines three methods to mitigate dendrite growth in solid-state electrolytes: the coating of anode lithium metal surfaces, micro-modulation of the electrolyte, and control of nano-cracking.

However, these advancements are still limited by technological constraints. In the future, employing more advanced characterization techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) could provide a clearer understanding of lithium dendrite growth on anodes, thereby enabling more targeted solutions to this issue.

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