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## Review

# The recent advances in constructing designed electrode in lithium metal batteries

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### ABSTRACT

Lithium metal battery, one of the most promising candidates for high-energy-density storage system, has attracted extensive interest due to its extremely high theoretical specific capacity, low gravimetric density and lowest negative redox potential. However, the formation of lithium dendrites, uncontrolled interfacial reactions, and huge volume change during the cycles of charging and discharging lower the Coulombic efficiency and cause harsh safety issues; they are the major hurdles towards the practical applications of lithium metal batteries. This review presents the recent advances in lithium metal battery and focuses on the functional hybrid electrodes, which are constructed to boost the electrochemical performance of metallic lithium and suppress the growth of lithium dendrites. Their general design rules, fabrication strategies, enhanced performances, and potential applications are summarized and analyzed. An outlook of the challenges and the potentials of lithium metal battery is also provided, which facilitates the future development of lithium metal batteries

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## 1. Introduction

With the rapid depletion of fossil fuels and the increasing environmental concerns, such as the global warming and the air pollution, a lot of efforts have been dedicated to develop new green energy, such as wind energy and solar energy [1,2]. However, storage and transportation of energy now become emerging challenges. The recent developments of electric vehicles also demand high-energy-density storage systems [3]. In order to meet the growing requests, large-scale battery systems are required to have high energy density, long life cycle and low cost [4,5]. Though lithium ion battery has achieved tremendous success in last two decades, its low energy density now becomes the key bottleneck to meet the ever-growing demands of new technologies ranging from electric vehicles to grid-scale energy storages [6–9]. Rechargeable lithium metal battery, showing the advantages of extremely high

theoretical specific capacity (3860 mAh/g), low gravimetric density (0.59 g/cm<sup>3</sup>) and lowest negative redox potential (−3.04 V vs. standard hydrogen electrode), has been extensively investigated as the next generation high energy storage system and opens up the opportunities for high-energy un-lithiated cathode materials such as sulphur and oxygen, among others [10].

Lithium metal is considered as the holy grail of energy storage system due to its unique properties [10,11]. The use of lithium metal in battery has been explored for decades [12,13]. The lithium metal can be paired with sulfur cathode for lithium-sulfur batteries with very high energy density [14–17]. When solid electrolyte is introduced between routine oxide cathode, all solid state battery with lithium metal anode is also expected with very high energy density [18,19]. However, the practical application of lithium metal battery is limited by its inhomogeneous lithium deposition and subsequent dendrite growth, which results in unreliable performances and safety issues. Because metallic lithium has a high Fermi energy level, the lithium anode continually consumes liquid electrolytes to form a solid electrolyte interphase (SEI) film on the surface [20,21]. During the charging and discharging cycles, lithium deposits and dissolves at the electrode and its inhomogeneous deposition behavior causes the formation of lithium

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dendrites and dead lithium fractions, resulting in decreased Coulombic efficiencies [22,23]. Ultimately, the growth of lithium dendrites can bridge the interelectrode gap and short the circuit of the battery, causing overheating or even thermal runaway [24,25]. Controlling the lithium deposition and inhibiting its dendritic growth are thus indispensable to capitalize the benefits of lithium metal battery for commercial applications.

Intensive efforts have been made to address the problems of lithium metal batteries. Numerous experiments and theoretical simulations have been carried out to understand the failure mechanism of lithium metal anode and to improve the performance of lithium metal batteries. The nucleation and growth of lithium dendrites are considered to be the main factor, causing the failure of a cell. An analytical framework had been developed to study the early stages of the nucleation and growth of lithium metal during heterogeneous electrodeposition of reaction rate limited systems [26]. Five regimes, *i.e.*, the nucleation suppression regime, the long incubation time regime, the short incubation time regime, the early growth regime, and the late growth regime, were clearly identified to illustrate the complex heterogeneous nucleation behavior. The stability of deposition at the lithium anode had also been investigated, which was determined by five parameters, *i.e.*, the current density ( $i$ ), the surface tension of lithium anode in the electrolytes ( $S$ ), the transference number of lithium ion ( $t_{Li}$ ), the ionic conductivity ( $\sigma$ ) and the shear modulus of the separator ( $G$ ) [12]. To address the problem of lithium dendrites, a polymer electrolyte with a rigid-flexible structure for solid-state lithium metal batteries had been proposed [27]. The interpenetrating network of poly(ether-acrylate) electrolyte formed on the lithium surface suppressed the growth of lithium dendrites during the battery cycling and enhanced the transportation of lithium ion for high-rate operation of the battery. Fluoroethylene carbonate was also used to assist the uniform deposition of lithium [28]. The additive is benefited to obtain a compact and stable LiF-rich SEI film, which is beneficial to achieve a uniform plating of metallic lithium and a significantly high Coulombic efficiency.

Nowadays, the main approaches to suppress the growth of lithium dendrites could be categorized into the following four aspects. (1) Developing functional electrolytes or adding additives in the electrolytes to form a compact and stable SEI layer at the surface of the lithium anode [29–36]. Metallic lithium is thermodynamically active and will react with the electrolyte to form a SEI layer on the surface, which protects lithium from the electrolyte and assists the uniform deposition of lithium. However, most SEI layers are fragile and they break easily during the plating and stripping process of lithium. Their breaking sites are generally the nucleation and growth sites of lithium dendrites. Developing a compact and stable SEI layer using functional electrolytes or additives are promising to suppress the growth of lithium dendrites. However, the electrochemical/chemical reaction in the battery is very complicated and the SEI layer, which consists of complex reduction products of the electrolyte and degradation products of the lithium salt, is not fully understood yet. (2) Introducing a solid state electrolyte [37–43]. Solid state electrolytes could suppress the unfavorable side reactions with lithium metal and have a high mechanical modulus to hinder the growth of lithium dendrites. However, the low ionic conductivity and the large interfacial impedance between the solid state electrolyte and the electrode need to be improved substantially. (3) Using a mechanically strong separator to physically prevent the penetration of lithium dendrites [44–48]. Though it could prevent the lithium dendrites short-circuit the cell, the separator can not suppress the formation of lithium dendrites and dead lithium fractions during the cycling, which will persistently decrease the Coulombic efficiency. (4) Constructing a functional hybrid electrode [49–53], such as modifying the current collector with

some nanostructure, which lowers the local current density and homogenizes the distribution of the lithium ion flux, prelithiating the 3D host matrix with molten lithium, which alleviates the huge volume change of lithium metal during cycling and improves the nucleation behavior of lithium, and adding a protective layer, which assists the deposition of lithium and suppresses the growth of lithium dendrites. Recent studies of lithium metal batteries in this area have shown promising results and it has become the most rigorous area.

In this review, we focus on the design of lithium electrode and its recent advancements, which suppress the growth of lithium dendrites and improve the performance of the rechargeable batteries. To suppress the growth of lithium dendrites, the general design rules of the system require a uniform lithium ion flux, a low current density, a homogeneous nucleation process and a stable SEI layer. Improvements of the battery performance have been achieved through the delicate design of lithium electrode and here they are summarized into three groups: i) optimizing the 3D porous nanostructure of current collector, ii) constructing rational host for lithium metal and prelithiating the 3D host matrix through the molten lithium infusion, iii) protecting the surface of lithium metal by functional layers. An outlook of the challenges and the potentials of lithium metal battery is also provided, which will facilitate the future development of lithium metal battery.

## 2. Advanced current collector

### 2.1. Planar current collector versus 3D porous current collector

The current collector, a key component of the electrode, significantly influences the initial nucleation and subsequent growth of lithium metal deposits. In a battery with planar current collector, if the surface is perfectly smooth, a uniform electric field over the entire electrode surface is expected, which drives a uniform lithium ion flux to the anode and thus a homogeneous deposition of lithium metal. However, the planar current collector is generally not perfect. Both the strength of electric field lines and preferential transportation of lithium ions to the rough regions on the surface render spatially inhomogeneous plating of lithium metal, which is the original formation of lithium nuclei. Once the nuclei are large enough, it will grow faster than others and form a protuberance on the flat surface. More charge will accumulate at the tip of the lithium protuberance, the high charge density in turn results in a stronger electric field near the tip and thus a larger lithium ion flux, which further speeds up the growth of lithium dendrites. Different from conventional planar electrode, lithium metal electrode with rationally designed structure is able to homogenize the electric field and the lithium ion flux over a large area. Therefore, advanced electrodes with various 3D frameworks have been developed to improve the deposition behavior of lithium metal and suppress the growth of lithium dendrites, which have significantly benefited the developments of lithium metal battery.

To ensure a relatively even deposition of lithium metal under a relatively uniform electric field and resist the growth of lithium dendrites, a submicron 3D skeleton on the copper current collector was introduced to improve the deposition behavior of metallic lithium [54]. Numerous protuberant tips are designed on the submicron fibers, which serve as the charge centers to obtain a globally uniform electric field. Therefore, metallic lithium prefers to nucleate and grow on the copper skeleton, eventually filling the 3D framework and forming a relatively stable and flat lithium surface (Figs. 1a and b). The lithium metal batteries using these electrodes can run for 600 h without any short-circuit. A simple dealloying process was also used to produce a 3D interconnected framework in the copper current collector (Figs. 1c and d) [55]. The lithium metal battery with such a 3D porous current collector

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