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Engineering of lithium-metal anodes towards a safe and stable battery

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ABSTRACT

Currently, the state-of-the-art lithium-ion batteries (LIBs) are the most widely used energy storage devices and have brought a great impact on our daily life. However, even many strategies have been reported to improve the energy density, these LIBs still can not meet the rapidly growing demand from the many lately emerged devices. During the pursue of higher energy densities, lithium-metal batteries (LMBs) have been the most promising candidates of the next-generation energy storage devices. Unfortunately, the Li-metal anode usually induces severe safety concerns and inferior cycle performance, because of the dendrite growth, high reactivity, and infinite volume changes of Li metal. As a result, these problems limit the commercial application of LMBs and must be resolved prior to the practical deployment of LMBs. In this review, we will firstly discuss the failure mechanisms of Li-metal anodes and introduce latest characterization technologies to study dendritic Li formation. The advances to improve the safety and performance of Li metal anode through electrolyte modification, interfacial engineering, solid-state electrolyte incorporation, and host materials design will then be comprehensively summarized and discussed. Lastly, we will conclude by summarizing the challenges in the current research on LMBs and highlight the future perspectives as well. Through this review, we hope to present the latest developments of the Li metal anode materials for the readers, and also shed light on the possible solutions for the current issues in order to accelerate both fundamental research and practical deployment of the various LMBs.

1. Introduction

Energy storage, especially with high density and low-cost, is always a hot spot in both research and industry communities. It is the fundamental requirement for the current and future energy strategies, for example, for the utilization of various clean energies (mostly harvested in the form of electricity), for the electrification of the transportation tools, as well as for the development of various smart devices. Lithium-ion batteries (LIBs) are one of the most successfully commercialized rechargeable batteries since the early 1990s, due to their high energy density and superior cycle stability, and have been widely deployed in various applications, including personal electronics and electric vehicles [1].

For the LIBs, graphite is the most commonly used anode material, which can reversibly accommodate and release the Li ions that are extracted from the cathode materials ($LiMO_2$, M = Ni, Co, Mn, *etc.*, $LiFePO_4$, and others) in its layered structure during charge/discharge processes (Fig. 1**a**) [2]. Unfortunately, even though many strategies, including modifying electrode materials and/or electrolytes, have been adopted to further improve the energy density of LIBs, they still can not meet the rapidly growing demands from the current devices, let alone the future ones, because these conventional battery materials are almost approaching their theoretical limitations [2–4]. Consequently, the next-generation energy storage materials/devices are in urgent needs of exploration.

With an extremely high capacity (3860 mAh g^{-1}), low density (0.59 g cm^{-3}), and very negative electrochemical potential (−3.04 V *vs.* the standard hydrogen electrode) [5], Li metal has been considered as an ideal anode material for the future Li-metal batteries (LMBs,

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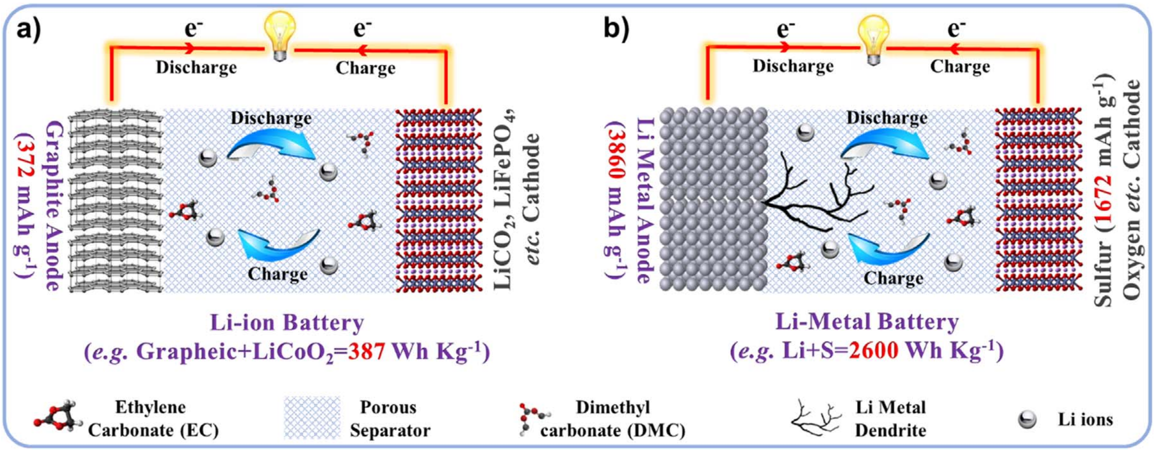


Fig. 1. Operational principles of a) a Li-ion battery and b) a Li-metal battery.

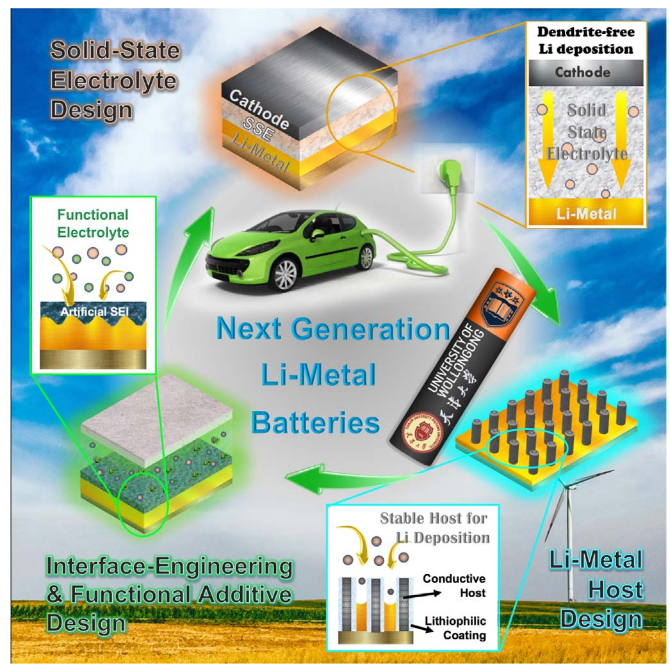
Fig. 1**b**) [6]. By coupling it with the high capacity cathodes, the as-formed Li metal batteries (LMBs) possess exceptionally high energy densities compared to the traditional LIBs (3500 Wh kg^{-1} for Li-O_2 batteries and 2600 Wh kg^{-1} for Li-S batteries) [7–10].

In spite of these advantages, there are still some insurmountable obstacles that have greatly hindered the practical applications of these LMBs since their first emergence in 1970s [11]. Despite the different reaction mechanisms and respective cathode issues in these various LMBs (*i.e.* the sluggish oxygen reduction/evolution in Li-O_2 batteries or the irreversible polysulfide migration of in Li-S batteries), the challenges in the anode section of these battery systems are almost identical, which are closely related with the nature of Li metal and mainly include the dendrite growth, high reactivity, and infinite volume changes of metallic Li anode, which inevitably induces severe safety issues and inferior cycling performance/coulombic efficiency to the batteries [12].

Specifically, the growth of dendritic Li could cause the internal short circuit, generation of heat, or even explosion of battery. Moreover, it can also produce “dead Li” (*i.e.* the electrically detached Li dendrites) [13], which can compromise the coulombic efficiency and shorten the cycle life of LMBs. Meanwhile, Li metal is highly reactive, which will spontaneously react with the electrolytes, leading to uncontrollable solid electrolyte interface (SEI) formation on the surface of Li metal and resulting in the loss of active materials together with the increase of the cell impedance. Moreover, during the striping/plating of Li metal, the theoretically infinite volume change (*i.e.* ideally all the Li metal will be intercalated into the cathode upon fully discharge) would cause structural instability to the batteries, leading to a fast battery failure. Consequently, seeking effective strategies to stabilize the Li surface and bulky structure is essential to ameliorating the overall performance of LMBs for practical applications.

The nucleation and growth mechanism of Li dendrites have been continuously studied during the past 40 years [14]. Various approaches to stabilizing the Li metal surface have been proposed, which focus on protecting the Li surface via coating layers, optimizing the organic electrolytes, modifying the separators, and constructing novel host materials for Li-metal anodes [4,15,16]. Recently, to fundamentally resolve the thermodynamically unstable issue of the Li metal in conventional organic liquid electrolytes [17], new battery configurations with solid-state electrolytes (SSEs) have also been adopted for the LMBs with the expectations to block Li dendrites, extend the cycle life of Li-metal batteries, as well as enhance the safety of the LMBs [18,19].

In this review, we comprehensively summarize and discuss the recent scientific and technological strategies to construct the next generation Li-metal anodes for LMBs with higher energy density and better safety (Scheme 1). Firstly, we will firstly analyze the failure mechanisms of Li metal anodes and the fundamental principles for Li metal surface stabilization, and summarize the latest methodologies to achieve these in-depth understandings, such as cryo-electron microscopy technique. We will then follow up with the recent developments to enhance the safety and cycle performance of LMBs by designing the electrolytes and the associated functional additives. After that, we will focus on the current progress on the solid-state electrolytes and artificial interface engineering to overcome their shortcomings, such as high interfacial impedance and low ionic conductivity. Then, we also include the latest developments of the advanced host materials for Li metals with the purpose of resolving the above-mentioned issues. Finally, we will conclude with the remaining challenges and possible research opportunities to facilitate the practical applications of the Li-metal batteries. By doing so, we hope we can draw a road map of the latest developments of the lithium metal anode materials for the readers, and shed light on the possible solutions for the currently existing issues in order to accelerate both fundamental research and practical deployment of the various LMBs.



Scheme 1. Illustration of the strategies for constructing a safer Li metal anode.

2. The failure mechanisms of Li metal anodes

Over the past few decades, extensive research has been conducted to gain a deep and fundamental understanding on the failure mechan-