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Design, perspectives, and challenges of modification strategies for alkali metal anodes

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Abstract. The alkali metal anode has emerged as a focal point of research due to its extremely low oxidation-reduction potential and high theoretical specific capacity. However, challenges such as unstable solid electrolyte interphase (SEI), infinite volume expansion, and uncontrollable dendrite growth result in low coulombic efficiency and irreversible losses during the deposition and stripping processes. To address these issues, various effective strategies have been proposed to protect the alkali metal anode and achieve dendrite-free growth. In this review, we summarize recent advancements in enhancement strategies for alkali metal anodes, including the construction of three-dimensional current collectors and interface engineering. Specifically, we delve into the development of carbon-based current collectors with various dimensions and structures and the application of interface engineering techniques to tackle the challenges of unstable SEI, volume changes, and dendrite growth. Furthermore, we explore advanced characterization techniques that provide deeper insights into the reaction mechanisms and behavior of these enhancement strategies. Finally, we discuss the current limitations and future research directions in protecting alkali metal anodes, aiming to provide valuable insights into the study of dendrite growth and the development of effective protection strategies for alkali metal anodes.

Keywords: alkali metal anode, 3D current collector construction, interface engineering.

Figure 1. Summary of the challenges of alkali metal anodes and the strategies for modifying alkali metal anodes

1. Introduction

The exploitation and utilization of fossil fuels make us face the exhaustion of resources and various environmental problems, which seriously limits the sustainable development of human society. Therefore, developing clean and efficient green energy is imperative. Among them, lithium-ion batteries stand out among a plethora of traditional rechargeable batteries due to their advantages such as no memory effect, high specific energy, and long lifespan, achieving rapid development and commercialization.[1] The energy storage mechanism of lithium-ion batteries involves the insertion and extraction of ions in their material, and after more than 30 years of development, the specific capacity of graphite anodes has approached its theoretical capacity (372 mAh·g-1), but that's still not enough to meet market demand.[2] Therefore, it is urgent to develop battery materials with higher energy density to accelerate the development of modern energy storage technology.

Compared to lithium-ion batteries, lithium metal batteries have the lowest anode potential (compared to the standard hydrogen electrode at -3.04 V) and an exceptionally high theoretical specific capacity (3860 mAh·g-1,about 10 times of the graphite anode), which is called the "Holy Grail electrode" by many people, and its application in Li-S and Li-O2 batteries has great potential.[3] Nevertheless, the amount of lithium in the Earth's crust is only 17ppm, and the lithium battery consumer market is growing rapidly, which may make lithium resources scarcity.[4] Sodium and potassium, as alkali metal elements in the same group as lithium, have become research hotspots due to their high abundance in the earth's crust and low extraction cost, even though their anode potential and theoretical specific capacity are inferior to lithium.[5] Therefore, the alkali metal anode as a candidate for new energy storage materials is of great significance to the sustainable development of the entire battery industry.

Although alkali metal batteries possess lower anode potentials and higher theoretical specific capacities, they still face numerous challenges, such as unstable solid electrolyte interface (SEI), infinite volume expansion of alkali metals, and uncontrollable dendrite growth, leading to low coulombic efficiency during deposition and stripping processes. In recent years, researchers have extensively explored these issues, including the construction of current collectors and interface engineering. This review summarizes the latest advancements in strategies to enhance alkali metal anodes, with a particular focus on the construction of carbon-based current collectors in various dimensions and the application of interface engineering techniques to address the challenges of SEI instability, volume changes, and dendrite growth. Additionally, we discuss advanced characterization techniques that provide deeper insights into the reaction mechanisms and behaviors of these enhancement strategies. Finally, we outline the current limitations and future research directions in protecting alkali metal anodes, aiming to offer valuable insights into the study of dendrite growth and the development of effective protection strategies for alkali metal anodes.

2. The main challenges faced by alkali metal anode

2.1. Unstable SEI and infinite volume expansion

The chemical properties of alkali metals are very reactive. When they are used as the anode material in batteries, they can have side reactions with the electrolyte, and forming a solid electrolyte interface (SEI).[6] However, the imbalance of ion flux in the electrolyte causes uneven deposition of alkali metal ions on the anode surface, leading to the unevenness of the SEI membrane. In addition, with the increase of deposition amount, the volume of alkali metal anode expands infinitely, causing the SEI membrane to rupture.[7] Therefore, the uneven and incomplete SEI during the cycling process is the main factor leading to irreversible capacity loss in metal batteries.

2.2. Uncontrollable dendrite growth

The alkali metal anode reacts with the electrolyte to form an uneven SEI film, which provides nucleation sites for dendrite formation and forms protrusions with certain mechanical stress during subsequent growth, called dendrites. Meanwhile, the newly exposed fresh metal reacts with the electrolyte to form a new SEI film. With the increase of ion deposition amount, irregular protrusions break through the SEI film, and dendrites start to grow (as shown in **Fig. 2**, taking lithium as an example).

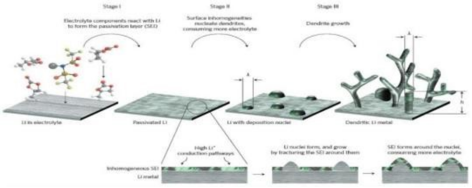

Figure 2. Three stages of lithium dendrite formation.[8]

The growth of dendrites can be explained from two major perspectives: thermodynamics and kinetics. The thermodynamic model emphasizes the influence of energy and temperature on dendrite growth. Research has shown that low adsorption energy and surface energy, as well as high diffusion barriers, promote dendrite formation,[9] while dendrite nucleation occurs less frequently under high temperature conditions.[10] The kinetic model covers more factors, including current density and stress.[11] In 1990, Chazalviel et al.[12]proposed the space charge model to explain that the large electric field generated due to the decrease in Li+ concentration is the driving force for dendrite growth. Sand et al.[13] defined the "Sand time" — the moment when Li+ concentration reaches zero, indicating the start of dendrite growth, and this time is inversely proportional to the square of the current density. Therefore, reducing the current density can effectively alleviate dendrite growth. In 1998, Yamaki J. et al.[14] proposed the stress release model, demonstrating that dendrite formation is the result of stress release. Subsequent studies have shown that when the stress increases from 2.0 MPa to 14.0 MPa, the structure of lithium dendrites tends to be smooth and dense.[15]

3. Strategies for stabilizing alkali metal anode

To address the challenges faced by alkali metal anodes, researchers have adopted various strategies to enhance its stability: (1) Constructing a three-dimensional current collector framework, especially using carbon-based skeletons and alloy skeletons to effectively alleviate the problem of volume expansion;[16] (2) Interface engineering, such as artificial SEI.[17]

3.1. Advanced skeletons in alkali metal anodes

Researchers have conducted in-depth studies on carbon-based current collectors. For example, Li et al.[18] implanted NiO into puffed millet (PM) using a typical pore-forming reaction, which not only enhanced the nucleation site effect but also provided a strong base for stabilizing the alkali metal anode. This method significantly reduces the nucleation overpotential of K and suppresses dendrite growth (as shown in **Fig. 3a**).Carbon-based materials with high specific surface area promote uniform metal deposition by reducing local current density.[19]Based on these advantages, carbon-based materials are considered as excellent candidate materials for alkali metal anode current collectors. According to spatial dimensions and structure, they can be classified into zero-dimensional, one-dimensional, two-dimensional, and three-dimensional carbon-based flowable materials.

3.1.1. Carbon based skeletons

0D Carbon Particles/Spheres. Carbon materials are considered ideal substrates for lithium metal anodes due to their superior mechanical properties and conductivity. However, the lithiophobe nature of the original carbon surface leads to high potential and uneven deposition.[20] Doping carbon-based materials with heteroatoms can enhance their lithiophilicity. Ye et al.[21] prepared nitrogen-doped hollow porous carbon spheres (N-HPCSs) through a simple and low-cost method. Researchers confirmed through in-situ transmission electron microscopy (TEM) and scanning electron microscopy (SEM) that when multiple N-HPCSs are connected (as shown in **Fig. 3b**), lithium exhibits high reversibility and repeatability during filling and stripping processes. Zhang and his team [22] in-situ synthetized carbon nanospheres with S-doped, high surface area and ordered mesoporous channels as a lithium metal anode skeleton. This structure achieves a coulombic efficiency as high as 97.5% within 220 cycles, providing uniform nucleation sites and regulating local current density to achieve dendrite-free growth (as shown in **Fig. 3c**). In addition, metal nanoparticles or metal oxides can be introduced, which have good bonding ability with lithium metal, thereby enhancing the lithiophilicity of the carbon-based materials.[23] For example, Wang et al.[24] prepared nano Cu through simple heat treatment and embedded it into porous carbon (Cu @ Carbon), where the CuCx at the Cu interface provided lithium nucleation and growth sites, ensuring uniform deposition of the metal anode (as shown in **Fig. 3d**). This technique effectively addresses the issue of unstable coulombic efficiency of a single Cu foil electrode.

1D Carbon Fibers/Nanotubes. Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are typical representative one-dimensional carbon materials. For example, nitrogen and oxygen dual heteroatom-functionalized CNTs exhibit outstanding performance in sodium metal storage, with a Coulombic efficiency of up to 99.9%, and a significantly reduced nucleation overpotential to 5 mV (as shown in **Fig. 3e**).[25] Another one-dimensional carbon material, CNFs, is a high-performance fiber compared to CNTs, possessing both the intrinsic properties of carbon materials and the soft processability of textile fibers.[26] Due to this characteristic, CNFs can be prepared by electrospinning.[27] Zhuang and his research team[28]developed gradient SnO2-modified carbon nanofiber (SnO2-CNFs) skeletons, which demonstrated excellent electrochemical reversibility and stability to guide the uniform stripping/deposition behavior of Sodium metal.

2D Carbon Sheets/Graphene. 2D carbon materials are widely used as stable anodes for alkali metal batteries due to their high specific surface area, rich surface chemical properties, and high mechanical strength. Common 2D carbon materials include graphene and carbon nanosheets.[29] Because of the low melting points of metallic lithium and sodium (180.5℃ and 97.8℃, respectively), lithium and sodium can be heated to a molten state and then injected into reduced graphene oxide (rGO) to prepare composite materials. Cui et al.[30] and Wang et al.[31] 4respectively prepared Li-rGO composite films and Na-rGO composite materials using a thermal injection method. With the protection of rGO layers, the formation of dendrites and changes in the anode volume during the deposition/stripping cycle can be suppressed. However, the low charge carrier density of pristine graphene severely limits its further technical development. Studies have shown that heteroatom doping can improve the electrochemical performance of graphene. Cui and his team[32] based on first-principles calculations, self-assembled N-doped graphene through three key steps(as shown in **Fig. 3f**), achieving high-density N doping.

3D Carbon Framework/Skeleton. Due to its high specific surface area and excellent lithium affinity, the three-dimensional carbon framework/skeleton is considered a key technology for alleviating dendritic growth and improving Coulombic efficiency. Cui et al.[33] study lithium nucleation and growth on planar copper electrodes, which demonstrated that the initial size of lithium nuclei is closely related to the current density, supporting the previous view that the growth rate of lithium nuclei is inversely proportional to the current density. The high specific surface area of the three-dimensional framework provides abundant lithiophilic sites, facilitating the uniform deposition of alkali metal ion on the anode.[34] Yang et al.[35] reported a three-dimensional porous current collector CNT sponge, which significantly reduces the nucleation overpotential compared to Cu foil and enables dendrite-free lithium plating at capacities below 10.0 mAh cm-2 as shown in **Fig. 3g** However, these frameworks still face challenges of poor wettability.Hu and his team[36] successfully improved the wettability by applying a SnO2 coating on a three-dimensional carbon fiber (3D-CF) framework as shown in **Fig. 3h**. The modified Li-CF | LFP and bare Li | LFP full cells exhibit a capacity retention of 90% and an efficiency of 99.7% after 500 cycles. The use of three-dimensional current collectors can indeed effectively prolong the life of alkali metal batteries, but it inevitably reduces the capacity of the alkali metal anode.

3.1.2. Other skeletons

MXene, as a new type of two-dimensional electrode material, demonstrates excellent performance in the application of alkali metal anodes. Its outstanding conductivity and rapid charge response have attracted much attention in this field. [37] In particular, Ti3C2 MXene.[38] By introducing metal ions into Ti3C2, the "pillar effect" is achieved, which not only increases the interlayer spacing of MXene but also helps in the uniform deposition of alkali metals, greatly improving the cyclic stability and performance of alkali metal anode. Luo et al.[39] inserted Sn+ into Ti3C2 MXene (as shown in **Fig. 3i**), enabling stable cycling of sodium metal anodes for up to 500 cycles under high current density of 10 mA cm –2 and high areal capacity of 5 mAh cm-2.In addition, 3D fluorine-doped graphene can serve as a self-supporting structure. Li et al.[40] implanted it into a porous network, achieving dendrite-free growth through interface and structural synergy control. The average Coulombic efficiency reached 99% over 300 cycles, providing a reference for constructing high-performance metal batteries.

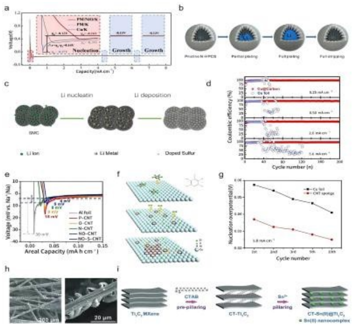

Figure 3. a) Overpotentials deposited by K on PM, PM/NiO, and Cu.[18] b) Schematic diagram of lithium electroplating and stripping process in N-HPCS.[21] c) Schematic diagram of nucleation and deposition process of lithium in SMC.[22] d) Coulombic efficiency of single Cu foil and Cu @ Carbon electrode at different current densities.[24] e) The change in potential of CNTs with different material properties.[25] f) Schematic diagram of self-assembly synthesis process of N-doped graphene.[32] g) Comparison of nucleation overpotential between a single Cu foil and CNT sponge electrode.[35] h) Uniform SnO2 layer on carbon skeleton fibers after coating with solution method.[36] i) Preparation diagram of CT-Sn(II) @ Ti3C2.[39]

3.2. Interface engineering techniques

Highly active alkali metals spontaneously undergo side reactions with electrolytes, forming a solid electrolyte interface (SEI) on their surface. This naturally formed SEI is often uneven and incomplete, leading to low Coulombic efficiency and short lifespan.[6] The formation of SEI can be explained by molecular orbital theory: when the energy level of the alkali metal negative electrode material is higher than the lowest unoccupied molecular orbital (LUMO) of the electrolyte (as shown in **Fig. 4a**), electrons will transfer from the anode to the LUMO energy level of the electrolyte, inducing electrolyte decomposition until the passivation of SEI is formed.[41] Interface engineering is one of the effective strategies to alleviate dendrite growth and stabilize SEI, mainly manifested as artificially constructing SEI. Compared to naturally formed SEI, artificially constructed SEI can provide uniform electric field distribution and ion flux, as well as higher mechanical strength, allowing ions to deposit smoothly and achieve dendrite-free growth. [42] Atomic layer deposition (ALD) is a unique technology that can deposit substances on the substrate surface in the form of monolayers, thereby achieving excellent coverage and uniform deposition.[43] Zhao and his research team [44] successfully applied ALD to deposit Al2O3 coating on sodium metal for the first time, which acts as an artificial SEI membrane during cycling processes, reducing the reaction between sodium foil and electrolyte, achieving a thin Al2O3 coating (about 10nm) to protect sodium metal, forming a stable SEI layer, effectively inhibiting dendrite formation, and extending the battery's lifespan.

Compared to inorganic artificial SEI membranes, organic interfaces have stronger mechanical strength. Covalent organic frameworks (COFs) have many advantages, such as high specific surface area, easy chemical modification, and adjustable pore size distribution. COFs also demonstrate outstanding stability and are not easily dissolved in solvents.[45] Zhang et al. [46] successfully constructed sp2 carbon-linked covalent organic frameworks (sp2 c-COF) as the SEI layer(the mechanism process is shown in **Fig. 4b**).This SEI membrane is mainly composed of inorganic and organic materials, which not only reduces interfacial impedance, improves ion migration rate, but also promotes uniform ion deposition, and slows down side reactions between alkaline metal negative electrodes and electrolytes. However, at high current densities, the inorganic components in the SEI may fracture due to volume changes, while the organic components hinder ion diffusion with increasing current density.[47] Moorthy and his research team [48] studied a series of sodium ion conducting alloy-type protective interfaces (Na-In, Na-Bi, Na-Zn, Na-Sn) through self-alloying reactions as artificial SEI layers(as shown in **Fig. 4c**).This SEI layer not only provides a flexible and compact membrane to accommodate volume changes, but also has a low surface energy of the alloy, which is conducive to ion diffusion on the surface. This multifunctional composite interface exhibits excellent cycling stability (as shown in **Fig. 4d**), achieving dendrite-free growth at high capacity and high current densities.

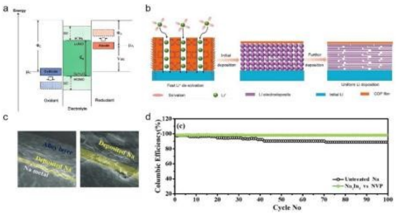

Figure 4. a)Schematic illustration of the formation conditions of SEI in liquid electrolyte.[41] b) Mechanism analysis of surface deposition process of sp2c-COF@Li.[46] c) Cross-sectional SEM images of Na1In1 deposited with 2 mAh cm−2 at 2 mA cm−2 of Na.[48] d) Schematic illustration of the cycling stability of Na1In1 at 1C.[48]

4. Conclusions and perspectives

Alkali metal batteries are one of the most promising candidates in the field of energy storage technology, but their negative electrodes face issues such as unstable SEI, volume changes, and uncontrollable dendrite growth, which severely hinder their commercialization process. Over the decades, researchers have proposed many models to describe dendrite nucleation and growth, and have developed effective strategies to mitigate these problems and extend battery life. This article introduces the main challenges of alkali metal negative electrodes and proposes protective strategies from the perspectives of thermodynamics and kinetics, including constructing three-dimensional current collectors and interface engineering techniques. In addition, this article provides representative case studies, such as the application of three-dimensional current collectors and the modification of negative electrode interfaces, which effectively alleviate dendrite growth, and even achieve dendrite-free growth. Since alkali metals lithium, sodium, and potassium have similar physicochemical properties, the strategies proposed in this article have universal and reference significance for protecting alkali metal (Li, Na, K) negative electSXrodes.

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