

RECENT ADVANCEMENTS IN QUANTITATIVE MODELING OF COMPOSITE METAL LITHIUM ANODES

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Abstract: Lithium metal has extremely high specific capacity and extremely low redox electrode potential, and is one of the core energy Materials in the field of secondary batteries. However, metallic lithium anodes face challenges such as volume expansion and uneven lithium deposition. Introducing a three-dimensional skeleton into the metallic lithium anode to construct a composite lithium anode is an effective method to alleviate volume expansion and regulate lithium deposition. The composite metal lithium anode has complex composition and structure, and the factors affecting the electrochemical reaction are strongly coupled. With the advancement of physical and chemical models and the large-scale improvement of computing levels, numerical model analysis can effectively study the physical and chemical mechanisms in composite lithium anodes. This article first summarizes the core process mechanisms that occur in composite metal lithium anodes and reviews the development of physical and chemical models. Then the quantitative model of the electrochemical Mass transfer process such as the surface electric field and ion field of the composite lithium anode was introduced, and the progress of the analysis and control strategies of the dynamic evolution mechanism of lithium deposition morphology based on the phase field model or finite element model was reviewed. The structural stability of the composite lithium anode during cycling was analyzed from the perspective of the electrochemical field. These quantitative model works reveal the electrochemical principles of lithium anodes and promote the efficient screening and optimized design of composite lithium anodes.

Keywords: Lithium metal battery; Composite metal lithium anode; Theoretical simulation; Mass transfer process; Morphology evolution

1 INTRODUCTION

USA has integrated carbon peaking and carbon neutrality goals into economic and social development, and is committed to building a clean, low-carbon, safe and efficient energy system, which has promoted the rapid development of the green energy storage industry. Among various energy storage systems, batteries have become a key growth point due to their high energy density, good environmental adaptability and durability, and have become the core of various energy storage technologies. Among various types of anode Materials, metallic lithium has extremely high specific capacity (3860 Mah/g) and extremely low electrode potential (-3.04 V compared to the standard hydrogen electrode potential) [1-3]. Making it a promising energy Material. The core anode system.

In metallic lithium batteries, uneven deposition of metallic lithium will lead to the growth of lithium dendrites, increase in interface side reactions, and aggravate the volume expansion of the negative electrode, thus reducing the charge and discharge efficiency and cycle life of the battery [4-12]. In order to solve these problems, methods such as designing highly stable liquid or solid electrolytes [13-18], adding artificial protective layers [19-22] and constructing three-dimensional composite lithium anodes [23-24] can be used. In particular, combining lithium metal with a three-dimensional skeleton can reduce the local current density of the negative electrode and guide the uniform and reversible deposition of metallic lithium, thus becoming an important solution to the cycle life challenge of metallic lithium batteries [25].

Depending on whether lithium is pre-stored, the composite lithium anode is divided into a skeleton structure without lithium storage and a skeleton structure with pre-stored lithium. Using melt injection method [26-31], roll pressing method [23, 32-34], alloy method [35-36], surface modification method [37], methods such as electroplating method [38-39] and lithium powder mixing method [40] can effectively construct composite lithium anodes. In the obtained composite lithium anode, the three-dimensional skeleton Material has the following functions: ① Alleviating the volume expansion of metallic lithium [41-44], effectively disperse the stress concentration caused by lithium deposition; ② According to the Sand model, host Materials with high specific surface areas can reduce local current density, inhibit lithium dendrite growth, and improve cycle performance [45-47]; ③ The skeleton can regulate the lithium nucleation process and transport, thereby modulating the deposition and stripping behavior of lithium metal. Therefore, the composite metallic lithium structure can effectively regulate the transmission channels of ions and electrons and adjust the distribution of electrochemical reaction sites, thereby improving the performance of lithium metal batteries. This composite structure can provide better mechanical support and electronic conduction, alleviate interface reactions, and improve the stability, cycle performance and safety of lithium metal batteries [32, 40, 48-53].

In the composite lithium anode, the transmission of electrons and ions accompanying the electrochemical reaction process constitutes the electric field and concentration field [54]. The deposition site of lithium can be predicted based on the distribution of electric field and concentration field. Uneven electric fields and concentration fields can lead to uneven nucleation and irregular growth of lithium dendrites. Therefore, the directional deposition of metallic lithium can be induced by regulating the electric field and concentration field [55-57]. Lithium deposition is usually accompanied by native stress, which has an impact on the structure of the composite anode. However, the composition and structure of the composite metal lithium anode are very complex, and there is a strong coupling between the influencing factors involved in the electrochemical reaction. This makes it difficult to accurately obtain the dynamic evolution and stress distribution of the composite metal lithium anode using current experimental research methods, and it is impossible to accurately obtain the dynamic evolution and stress distribution of the composite metal lithium anode. Describe the reaction behavior of lithium metal. With the advancement of physical and chemical models and computational levels, numerical simulations can provide quantitative simulation results [58]. For example, the model can be used to adjust parameters such as the channel structure and modified Material interface in the composite lithium anode skeleton, thereby effectively predicting the charge and discharge behavior of the composite lithium anode.

This article first introduces the core processes in composite metal lithium anodes, including electron transport mechanism, ion transport mechanism and interface reaction mechanism, and reviews the development of physical and chemical models in lithium batteries. Next, we will discuss in detail the influence of ion and electron transport regulation on electrochemical reactions and Mass transfer processes, and discuss the impact of Mass transfer characteristics on the precipitation mechanism and dynamic evolution of metallic lithium, from the perspective of force-electrochemical physical field coupling. This article reviews the structural stability of composite metal lithium anodes from a perspective, and finally puts forward prospects for the development of quantitative models for composite metal lithium anodes to promote scientific understanding and technological progress of high energy density secondary batteries.

2 CORE PROCESS MECHANISM OF COMPOSITE LITHIUM ANODE

The deposition and extraction behavior of lithium in composite lithium anodes are closely related to ion transport, electron transport and interface reaction mechanisms. By establishing a numerical model, the impact of these processes in lithium batteries can be effectively analyzed, providing a basis for the efficient and reasonable design of composite metal lithium anodes. The design provides theoretical guidance and improves the cycle stability of the negative electrode.

2.1 Ion Transport Mechanism

In the electrochemical reaction process of lithium metal batteries, the ion transport process is usually the "speed-determining step". Fast enough ion transport can provide sufficient lithium ions to deposit at the bottom of the current collector, improve the utilization of the pore space at the bottom of the current collector, reduce concentration polarization, ensure the uniformity of the electrochemical reaction process, and thus promote the uniform deposition of lithium metal. . The lithium ion transport process is affected by concentration polarization, electromigration and convection in the battery. The concentration polarization is determined by the concentration gradient and diffusion coefficient of lithium ions. Electromigration is related to the concentration, mobility, and electrostatic potential of lithium ions, so the convection effect in the battery system can usually be ignored. Considering the Mass transfer process of an ideal dilute solution and ignoring the role of solvation, the lithium ion flux N in the ion transport medium can be described by the Nernst-Planck equation (1):

$$N = -D \nabla c - z \mu c \nabla \phi + cu \quad (1)$$

Among them, D is the diffusion coefficient; c is the concentration; z is the chemical valence of lithium ions, $z = 1$; μ is the mobility, u is the convection flux of the electrolyte plasma ion transport medium, $u = 0$; ϕ is the ion transport medium The electrostatic potential in can be solved by Poisson's equation in equation (2). Usually, for the convenience of distinction, the electrostatic potential in the ion transport medium is recorded as ϕ_l , and the electrostatic potential in the electron transport medium is recorded as ϕ_s .

It can be seen that in order to improve the lithium ion transport capacity and avoid dendrite growth due to insufficient lithium ion transport, the most effective method is to improve the lithium ion diffusion coefficient, lithium ion mobility and lithium ion transport medium in the electrolyte, SEI and other ion transport media. ion concentration. Although increasing the electrostatic potential gradient and concentration gradient can also improve lithium ion transport capabilities, it is usually limited by the actual working conditions of the composite metal lithium anode, Making it difficult to achieve effective control. In addition, by regulating the structural parameters of ion transport channels, ion transport behavior can also be effectively regulated.

2.2 Electron Transport Mechanism

In composite metal lithium negative electrodes, the electron transport process usually occurs in the negative electrode current collector, conductive skeleton structure Materials, and deposited metallic lithium. Improving the electron transport capacity helps to increase reaction sites and reduce the electrochemical electrode. change. Electron transport capacity is usually related to the number of reaction sites and specific surface area. During the Mass transfer process, it can be considered that there is a stable electrostatic field in the negative electrode current collector, conductive framework Material, and deposited metallic lithium at all times, and the entire conductive part satisfies the electrical neutrality condition, that is, the net spatial charge density is zero. The distribution of electrostatic potential is Mainly related to the conductive surface topography and potential distribution boundary conditions, and the relative dielectric constant has no effect on the electrostatic potential distribution. The spatial distribution of electrostatic potential ϕ can be described by Poisson's equation formula (2):

$$\nabla \cdot (-\epsilon_r \epsilon_0 \nabla \phi) = \rho \quad (2)$$

Among them, ϵ_r is the relative dielectric constant of electron transport media such as current collectors, conductive framework Materials, and deposited metallic lithium; ϵ_0 is the vacuum dielectric constant; ρ is the net charge density in space, $\rho = 0$.

In order to improve the electron transport capacity and electron transport surface structure, by increasing the porosity of the skeleton, improving the conductivity of the Material, and increasing the conductive specific surface area, the reaction active sites can be greatly increased and the electrochemical reaction polarization can be reduced. In addition, designing the structural size parameters of the conductive structure can also regulate the reaction sites and enhance the electron transport capability.

2.3 Interface Reaction Mechanism

An in-depth understanding of the interface reaction mechanism will help to achieve controllable growth of lithium dendrites by regulating the interface reaction. In composite metallic lithium anodes, the deposition and growth behavior of metallic lithium is inseparable from the electrochemical reaction rate. A higher overpotential is conducive to increasing the nucleation density and reducing the nucleation size. A larger exchange current density is helpful to promote the reaction. to promote uniform deposition of lithium metal. Ignoring the influence of SEI, the above lithium metal deposition behavior can be described by the Butler-Volmer equation (3):

$$j = j_0 (\exp \alpha \frac{an F}{RT} \eta - \exp -\alpha \frac{cnF}{RT} \eta) \quad (3)$$

Among them, j_0 is the exchange current density; α_a and α_c are the charge transfer coefficients in the negative and positive electrode directions respectively, satisfying $\alpha_a + \alpha_c = 1$; n is the electron transfer number in the electrode reaction, and during the lithium metal deposition process, $n = 1$; F , R , and T are Faraday's constant, ideal gas constant, and temperature respectively; η is the total overpotential during the electrochemical reaction, that is, the difference between the interface voltage and the equilibrium potential. The interface voltage is the interface electrode ϕ_s (electron transport medium), the voltage on both sides of the electrolyte ϕ_l (ion transport medium); the equilibrium potential E_{eq} is the equilibrium potential of the electrochemical reaction at this point, which is related to the activity of the redox reaction product. The total overpotential η and the equilibrium potential E_{eq} are given by the formula (4), formula (5) description

$$\eta = \phi_s - \phi_l - E_{eq} \quad (4)$$

$$E_{eq} = E_{eq,0} - \frac{RT}{nF} \ln \left(\frac{c_R}{c_0} \right) \quad (5)$$

Among them, $E_{eq,0}$ is the equilibrium potential, and c_R and c_0 are the products of the activities of the oxidation reaction product (Li^+) and the reduction reaction product (Li_0) of the reversible electrochemical reaction, respectively.

In order to effectively increase the interface reaction rate and regulate the stable deposition of lithium metal, the exchange current density and overpotential of the system can be increased. The former is related to Mass transfer processes such as ion transport and electron transport, and can be adjusted and optimized for the reaction surface to regulate and optimize electrochemical activity, deposition sites, etc.; overpotential can be increased by increasing the voltage at the reaction interface, lithium ion concentration, etc. method implementation. By designing the geometric structure of the skeleton, metallic lithium deposition can be stabilized and dendrite growth suppressed.

The Mass transfer process regulated by ion transport and electron transport can affect interfacial reactions. In the actual process, the deposition behavior of metallic lithium in the composite metallic lithium anode is very complex. Its morphological evolution not only involves the electrochemical process, but is also inseparable from the force field. For example, the accumulation of internal stress due to dendrite growth causes the solid electrolyte interface The rupture of the membrane (SEI), or the excessive stress gradient caused by the difference in mechanical parameters between different phases in the alloy negative electrode causes structural failure, etc. Therefore, in order to solve the complex multi-factor coupling problem in composite metal lithium anodes, it is extremely important to introduce multi-physics coupling in combination with practical work, and it is also very challenging.

2.4 Model Development History

Due to the complex composition and structure of the composite metal lithium anode, and the strong coupling of influencing factors on electrochemical reactions, it is difficult to independently explore electrochemical mechanisms such as ion transport and electron transport by controlling a single variable experimentally. With the continuous development of quantitative physical and chemical models, numerical analysis models have gradually transitioned from static Mass transfer process calculations to dynamic simulation calculations, and have developed from a single electrochemical field to a force-electrochemical field, a therMal-electrochemical field, etc. Physical field coupling and the use of numerical analysis models can perform quantitative analysis that is difficult to achieve experimentally, thereby providing an effective basis for the design of composite metal lithium anodes.

The initial static model Mainly uses MatheMatical models to calculate the nucleation process and dendrite growth mechanism, and establish numerical relationships in the electrochemical deposition process. The dynamic model Mainly simulates the dynamic process in the electrochemical deposition process. The finite element method can study the interface reaction process under the coupling of multiple physical fields at a Macro level. It is usually used to solve the distribution of heat, force, current, concentration, etc. inside the battery. Monte Carlo and phase field methods Mainly solve the problem of phase interface movement. The phase field method considers factors such as surface energy in the calculation of dendrite growth, and can track the phase change reaction interface in real time during the precipitation and removal of metallic lithium.

In 1983, Professor Hills' research group at the University of Strathclyde, UK, applied the theoretical model calculation method to calculate the nucleation process of electrochemical deposition. This work is based on the ion transport equation under the action of concentration diffusion and electromigration in the electrolyte, combined with two-dimensional nucleation growth kinetics, to establish the relationship between nucleation process parameters such as nucleation number density and electrochemical deposition reaction overpotential. numerical relationship. In 1990, Professor Chazalviel's research group at Ecole Polytechnique in Paris, France, proposed the space charge theory to explain the nucleation process of lithium dendrites. In 2003, Professor Newman of the University of California, Berkeley, discovered that lithium metal tends to be preferentially deposited at the tips of metallic lithium dendrites. Around 2013, the Akolkar team of Case Western Reserve University also analyzed the growth mechanism of lithium dendrites through MatheMatical model calculations.

After the above theoretical calculation research based on the static model, in order to quantitatively calculate the phase changes during the deposition and extraction process of metallic lithium, and further analyze the dynamic relationship between the interface electrochemistry and physical fields such as force field and therMal field, dynamic simulation calculations were carried out. Research has also been gradually proposed and developed continuously. Various methods including deformed geometry, level set, finite element method, Monte Carlo method, phase field method, etc. gradually come into view.

In lithium battery simulation calculation problems based on the finite element method, the quasi-two-dimensional (P2D) model has certain universality and is widely used in the research of lithium batteries. The P2D model can accurately analyze the distribution state and dynamic process of charge and lithium ions in the battery, so that it can further simulate and analyze the charging and discharging process to achieve higher calculation accuracy. In 2004, Monroe et al. conducted a series of pioneering model theoretical studies to explore the growth and deforMation of lithium protrusions in PEO, laYing a good foundation for force-electrochemical research in polymer systems. It modified the Bulter-Volmer formula describing the interface reaction according to formula (5), thereby proposing the influence of mechanical stress on interface dynamics. In 2009, Professor Dunn's research group at the University of Colorado Denver used the finite element method to study the interaction between ion transport and mechanics in the porous electrode of lithium batteries, and analyzed the surface dynamics and electrochemical-mechanical phenomena of individual particles in the porous electrode. In 2016, Professor Lee's research group at Hanbat National University in South Korea used the finite element method to design a template for the lithium dendrite deposition morphology, and used stamping technology to modify the surface of the current collector according to the design to inhibit dendrite growth during the lithium deposition process. However, the finite element method has limitations and cannot solve phase interface movement problems such as the generation and detachment process of lithium dendrites.

Monte Carlo and phase field methods can solve the problem of phase interface movement. The former simulates the micron-level deforMation process by randomly stacking tens of tHousands of large particles. However, due to the excessive size and insufficient number of particles, the accuracy of the dendrite morphology calculated by this method is not high. In 2014, Professor Hoffmann's research group at the California Institute of Technology simulated the growth process of lithium dendrites under DC conditions and pulse current conditions based on the Monte Carlo method, and proposed that under pulse current, due to the existence of pulse intermittent periods, lithium ions can grow more efficiently. Diffusion and supplementation to the roots of dendrites allows more lithium ions to be deposited at the bottom, easing the forMation of dendrites.

Phase field methods can track continuous phase changes at multiple scales. In order to track the phase change reaction interface in real time during the precipitation and removal of metallic lithium, phase field theory has been applied to the calculation of related electrochemical phase change processes in lithium-ion batteries, lithium metal batteries, etc. Researcher Guyer's research group at the National Institute of Standards and Technology was the first to combine phase field theory with electrochemical reaction thermodynamics and kinetics, and proposed the earliest one-dimensional

electrochemical phase field theory. Afterwards, the research group of Professor Shibuta from the University of Tokyo in Japan combined the Cahn-Hilliard equation of phase field theory with the Butler-Volmer equation of electrochemical reaction kinetics to realize the phase field theory simulation of the two-dimensional electrochemical deposition process of copper electroplating. In 2015, in order to realize the phase field simulation of the growth of metallic lithium dendrites, Professor Chen Longqing's research group at Pennsylvania State University in the United States proposed a lithium metallic dendrite model based on the Allen-Cahn equation of phase field theory and the Butler-Volmer equation of nonlinear electrochemical reaction kinetics. Crystallographic phase field theory was the first to realize the phase field theoretical simulation calculation of metallic lithium dendrites, and completed the prediction and comparison of the morphology of lithium dendrites grown under nucleation sites of different sizes. In 2019, Professor Qi's research group at Michigan State University in the United States collaborated with Professor Chen Longqing's research group to extend the phase field theory of metallic lithium anode to the solid electrolyte system, and simulated the nucleation and growth of metallic lithium dendrites in the solid electrolyte grain boundaries. In the same year, in order to further explore the deposition behavior of lithium in composite metal lithium anodes, the key factors affecting the deposition and removal rate of metallic lithium in composite metal lithium anodes were proposed [58], and the electron transport and ion transport in composite metal lithium anodes were clarified. The regulation effect of transport on dendrite growth and the mechanism of uniform deposition of metallic lithium inside the pores were summarized. In 2022, the research group of Professor Huang Jiaqi of Beijing Institute of Technology proposed a phase field model of the constant current charge-discharge precipitation and desorption process. By regulating the lithium metal in the skeleton structure, at the deposition site, the lithium deposition under different diffusion coefficients, lithium ion concentrations and activity gradients was explored. In 2019, Professor Garcia's research group from Purdue University combined the electrochemical phase field theory with the stress model to simulate the growth of metallic lithium dendrites under stress electrochemical conditions, and summarized the key points in the metallic lithium dendrite growth model. Main mechanism.

With the continuous deepening of the research on the internal mechanism of lithium metal batteries, the physical and chemical quantitative models have gradually been improved, from the initial static models such as exploring the two-dimensional nucleation mechanism to the current dynamic multi-physical field coupling and regulation of lithium deposition behavior in specific materials. Generally speaking, theoretical simulations gradually adapt to the actual working environment of batteries during development, in order to solve the actual working problems of batteries, and they play an indispensable role in the research process.

3 MODEL DESIGN OF LITHIUM COMPOSITE ANODE

Compared with metallic lithium anodes, the electrochemical reactions occurring inside composite metallic lithium anodes are complex and difficult to control. In order to deeply understand the impact of different ion and electron transport in the composite metal lithium anode on the interface reaction process, we will study the mass transfer model of the composite metal lithium anode, the morphological evolution model of lithium dendrites during the precipitation and removal process, and the addition of a force field. The multi-physics model is used as the starting point to introduce and summarize the related work of composite metal lithium anodes in regulating the electrochemical reaction process, the evolution of lithium precipitation and desorption morphology, and the stress evolution under force-electrochemical field coupling, and proposes corresponding design plans and suggestions.

3.1 Mass Transfer Model

The mass transfer process in composite metal lithium anodes is mainly controlled by designing mass transfer channels and modifying the interface. The design of mass transfer channels can control ion and electron transport from the perspective of channel size, pore arrangement, and curvature. The design of modified interfaces mainly reduces the nucleation barrier by adding lithiophilic sites, and designs different conductivities. Skeleton surface implementation. These designs can evenly distribute the internal electric field, reduce concentration polarization caused by insufficient lithium ion transport capacity, increase the conductive specific surface area, reduce local current density, and reduce electrochemical polarization caused by excessive electron transport resistance. polarization.

3.1.1 Ion channel design

The mass transfer process in composite metal lithium anodes includes ion transport and electron transport. In order to improve the ion transport capacity, the channel structure design of the framework material or current collector can homogenize the lithium ion flux, stabilize the deposition of metallic lithium, and inhibit the growth of dendrites. Professor Cui Yi's research group at Stanford University designed a vertical nanochannel with a high aspect ratio and simulated the lithium ion flux through the finite element method, proving that compared with untreated electrode materials, the modification of the vertical nanochannel electrode can make lithium ions migrate along a specific path, limit the free transmission of lithium ions, avoid excessive local concentration and uneven distribution of lithium ions, and achieve uniform nucleation of lithium in the horizontal direction. Professor Yang Shubin's research group at Beihang University combined the finite element method and also proposed a vertical array to control the electric field

and lithium ion flux. This array induces metallic lithium to uniformly plate/delithium in the horizontal electric field direction, achieving high Stable cycle under surface capacity (50 Mah/cm²), and improved the high rate capability (20 Ma/cm²) and cycle life (2000 h) of the battery. This design of regulating lithium ion transport in vertical channels provides a new method to improve the Mass transfer capacity of lithium ions and stabilize lithium metal deposition. Based on the above work, further gradient pore structure design of vertical channels can be Accelerate the lithium deposition rate and Make the lithium deposition smoother. Combined with finite element method analysis, in a lithium-carbon composite anode with one-dimensional porous carbon as a skeleton with a gradient pore structure, since the pore size and porosity inside the channel gradually decrease from top to bottom, this structure can accelerate the lithium ion transmission rate. Reduce the lithium ion concentration gradient in the composite negative electrode and avoid surface clogging caused by lithium ions concentrating on the upper part of the skeleton.

3.1.2 Electronic channel design

Improving electron transport capabilities can be achieved by designing channel parameters for the current collector, increasing the conductive specific surface area to reduce local current density and achieve uniform electron transport. The team of researcher Guo YuGuo from the Institute of Chemistry, Chinese Academy of Sciences [56] reported a porous copper current collector with vertically arranged microchannels. The current density distribution in different structural channels is simulated through the finite element method (Figure 1), detailed description

The current density distribution under different pore sizes, depths and distributions was determined, lithium ion transport was predicted by regulating electron transport, and the lithium deposition morphology was confirmed experimentally. This model can also be applied to host structures with other morphologies. Electrochemical experiments show that compared to the 80% capacity retention rate corresponding to planar copper current collectors, batteries using porous copper current collectors with a specific structure show a high capacity retention of 90% after 100 cycles, reflecting the method's ability to control Rationality in electronic transportation and huge advantages in long-life battery design.

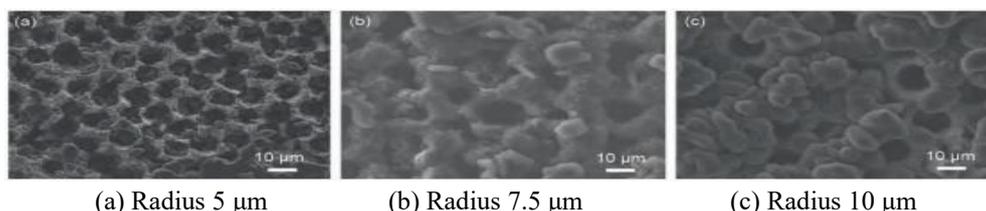


Figure 1 Lithium deposition morphology on porous copper current collectors with different pore sizes when the deposition capacity is 0.3 Mah/cm²

In addition, in addition to the consistent design of different sizes for all channels, the size of a single channel can also be adjusted in the vertical direction to control electron transport. Professor Lee's research group at Seoul National University increased the porosity at the bottom of the copper current collector to increase the conductive specific surface area. This work used the finite element method to simulate and calculate the current density in three different gradient pore size skeleton structures, proving that the higher the bottom porosity, the lower the local current density, the more uniform electron distribution, and the more uniform lithium metal deposition.

In terms of increasing the conductive specific surface area, a rich electronic reaction interface can also be obtained by regulating the electric field distribution. The team of researcher Li Xianfeng from the Dalian Institute of Physical Chemistry, Chinese Academy of Sciences prepared a composite lithium anode with an upright coiled structure. This process adjusts the electric field distribution. After being oriented horizontally, a rich internal reaction interface can be obtained. This work combines the finite element method to analyze the two-dimensional current density distribution of upright lithium, and proves that the local current density is the largest at the Maximum curvature, which is consistent with the "lightning rod theory". After coiling, the larger conductive surface area effectively reduces the local current density. , alleviate the growth of lithium dendrites. The full battery composed of the composite negative electrode and Li₄Ti₅O₁₂ positive electrode can achieve more than 2000 cycles at 5 C, with a reversible capacity of 129 Mah/g and a Coulombic efficiency of 100%. Similarly, polyimide (PI)-coated copper current collector (E-Cu) also increases the conductive surface area by regulating the electric field distribution, reducing the risk of lithium dendrites puncturing the electrolyte.

In order to deposit metallic lithium at a designated location, in-depth exploration of the distribution of local current density under different surface morphologies can help predict the interface evolution process of lithium. Lee's team at Hanbat National University in South Korea used stamping technology to modify the surface of metallic lithium, and studied the relationship between this unique surface design and current density through finite element simulation, giving the results when the current density is concentrated at the tip of the inverted pyramid pattern. , the optiMal size of the surface pattern, the optimized structure significantly inhibits the growth of dendrites.

3.1.3 Interface modification design

Interface modification refers to adding lithiophilic sites or constructing lithiophilic-lithiophobic interfaces in framework Materials to reduce the nucleation overpotential and achieve uniform nucleation, as well as designing composite Materials with conductivity gradients such as conductive-dielectric Materials to regulate electron transport. . The introduction of lithiophilic sites can reduce the nucleation barrier, thereby reducing the nucleation overpotential and reducing the polarization during the nucleation stage; the high conductivity surface increases the nucleation sites and increases the active sites for electrochemical reactions. Both methods reduce the overall activation overpotential required to drive the same reaction current, resulting in lower polarization during the deposition phase and therefore lower local current density, affecting interfacial reactions through the Butler-Volmer equation. During the deposition process in composite metal lithium anodes, although composite lithium anodes with higher specific surface areas can effectively uniformly distribute ions and reduce local current density, the poor lithiophilicity of the composite skeleton will lead to increased polarization, especially in Under higher current density and deposition capacity, lithium metal tends to be deposited on the top, which greatly reduces the energy density of lithium metal batteries. Doping with highly lithiophilic metal elements (gold, silver, zinc, Magnesium, etc.), lithiophilic functional groups (pyridine nitrogen, pyrrole nitrogen, etc.) or nanoparticles (nitrogen-doped graphene, ZnO, etc.) is beneficial. The uniform nucleation and deposition of lithium in the skeleton increases the utilization of internal pores. On this basis, in order to understand the mechanism of lithiophilicity, the research group calculated and verified the lithiophilic chemistry of heteroatoms through first principles, revealing the doping site from the perspective of electronegativity, local dipole and charge transfer. The reason for the lithiophilicity of the dots proves that there is a strong interaction between the doping sites with high binding energy and high charge density and lithium atoms. Among them, O doping and O/B co-doping have the strongest lithiophilicity, which helps Based on the uniform nucleation of lithium, this work reveals that the essence of lithiophilicity is lithium bond chemistry and provides mechanistic guidance for the design of lithium metal anode skeletons for safe secondary batteries. Composite skeletons are also important candidates in the field of composite metal lithium anodes. For example, a self-supporting TiC/C core/shell nanowire array is used as the skeleton to be composited with lithium metal. The strong lithiophilicity of the lithiophilic TiC/C skeleton can provide a fast transfer path for electrons, and due to the Al on the substrate It can form an alloy with Li, and the strong interaction between the two enhances the adsorption of Li^+ . The finite element method was used to simulate and analyze the electric field distribution after nucleation of the bare lithium anode and the composite anode. The electric field distribution of the former has a tip effect, while the latter is more uniform. The composite anode was cycled 200 times at a current density of 3.0 Ma/cm^2 . The polarization is less than 85 mV, and the Coulombic efficiency is still as high as 98.5% after 100 cycles at 1.0 Ma/cm^2 , showing excellent electrochemical performance. Similarly, in terms of doping with lithiophilic metal elements, ZHou Yongning's team at Fudan University designed a molybdenum mesh/lithium metal film (MLF) composite electrode. Compared with other positions, the current of the lithiophilic Mo site is higher. The density is relatively high, enabling control of the lithium deposition position; the phase field method was used to simulate the lithium concentration distribution in the LiIn alloy (Figure 2), and the defect formation energy of lithium atoms in the LiIn alloy was calculated based on first principles analysis. , quantified the kinetic evolution of lithium in solid-state batteries and the transition from alloying reaction to metal deposition, which helps to understand the lithium atom migration behavior in alloy anodes from a mechanistic perspective.

In addition to doping metal lithiophilic sites on the interface and using the strong interaction between metals to regulate the interface reaction, nanoparticles with strong lithiophilicity can also achieve the same effect. The research group of Professor Li Baohua of Tsinghua University [57] proposed a three-dimensional porous copper fiber skeleton doped with CuO/Cu₂O nanoparticles, using finite element method simulation analysis. Compared with the untreated skeleton, the modified skeleton surface electric field distribution and lithium The ion flux is more uniform and the lithium deposition is smoother. The composite electrode can be deeply cycled 53 times at a high capacity of 15 Mah/cm^2 , with an average Coulombic efficiency of 98.97%. Amorphous ZnO is also highly lithiophilic and can reduce the nucleation overpotential, thus facilitating the uniform nucleation of lithium. Finite element analysis shows that compared with ordinary carbon skeletons, the internal electric field of ZnO-doped carbon fiber skeletons with a more even distribution of lithium ion flux. The team of Professor Peng DongLiang of Xiamen University designed a lithiophilic-lithiophobic-lithiophilic double-gradient framework structure. Zn and ZnO with strong lithiophilic properties can provide a large number of nucleation sites and are deposited on the Cu-Ag substrate and ZnO. The lithium between -PAN-ZnO tightly combines the dual gradient structure to achieve bottom-up deposition and inhibit the growth of lithium dendrites.

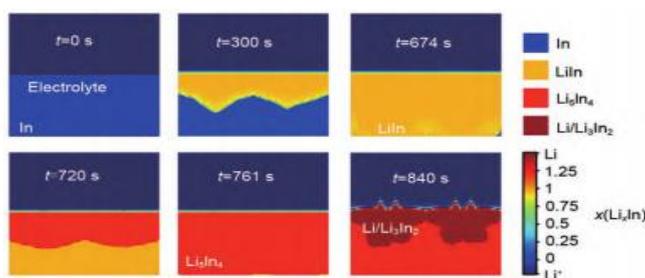


Figure 2 Lithium concentration distribution and phase change simulation of Li_xIn alloy during lithiation when the current density is 5 Ma/cm^2

Interface modification can also regulate electron transport and affect interfacial reactions by designing the conductivity difference on the surface of composite Materials. Yang Cheng's team prepared a conductive-dielectric skeleton composite with lithium metal. The conductive-dielectric layer on the surface of the skeleton is periodically distributed, ultimately showing ideal "bottom-up" lithium deposition. Using the finite element method to simulate the electric field distribution during the deposition process, it was found that when lithium dendrites are formed at the bottom and gradually grow to contact the conductive layer, the entire conductive layer will become an equipotential body, inhibiting the further growth of the dendrites and showing itself "Self-correction" feature. The results show that the Maximum capacity of the host Material that can accommodate lithium metal is 15 Mah/cm^2 , and the space utilization rate is about 83.7%. This composite lithium anode exhibits low charge-discharge overpotential and long cycle life at a current density of up to 5 Ma/cm^2 and an extremely high cycle capacity of 15 Mah/cm^2 .

In addition to the periodic arrangement of conductivity and dielectric on the skeleton surface, top-down conductance gradient design of vertical channels can also directionally induce lithium deposition. Lee's team at the Ulsan Institute of Science and Technology in South Korea [53] prepared a conductivity gradient skeleton structure composed of copper nanowires and nanocellulose. The finite element method was used to simulate the lithium ion concentration distribution under the influence of electron transport, which can prove that the conductivity gradient skeleton structure The ion transport in the lithium ion exhibits a gradient distribution. Comparing different ion transport gradients with the corresponding lithium deposition morphology and electrochemical performance can provide the most appropriate design solution.

The above is to regulate the ion and electron transport and thereby control the interface reaction by regulating the lithiophilic sites and conductivity on the interface. At present, it is difficult to quantitatively describe the impact of ion transport and electron transport on interfacial reactions through a single experimental design. In order to overcome this problem, exploring the interface reaction mechanism through theoretical simulation is helpful for the physical property design and development of framework Materials. Dimensional design provides a reference to accelerate the development of composite metal lithium anodes.

The phase field theory was used to conduct a quantitative analysis of the mechanism of lithium metal deposition in the three-dimensional framework. It was found that there is a two-stage mechanism for controlling the deposition of metallic lithium by specific surface area. Two factors affecting lithium metal deposition were proposed: limited electron exchange provided by limited surface area. rate; the finite ion transport rate of a finite ion transport channel. Combining these two points, the electrochemical deposition resistance is proposed to reflect the difficulty of lithium deposition. This work explores the deposition behavior of lithium metal from the perspective of regulating ion transport and electron transport, and provides a reference for skeleton design in actual work. In addition, the electrochemical phase field theory is used to regulate the interface reaction by increasing the electrolyte concentration, ion diffusion coefficient and electrochemical activity gradient modification of the structure surface, thereby alleviating the problem of concentrated deposition of lithium metal on the top of the framework.

The Lee team of Daegu Gyeongbuk Institute of Science and Technology proposed an interface activity gradient strategy. This work combined with finite element method analysis showed that by reducing the interfacial activity in the top region of the Ag-Cu framework (top passivation), it increased the interfacial activity in the bottom region (bottom activation), which can inhibit the reduction of lithium ions at the top, allow lithium ions to migrate to the bottom of the framework, and promote the interface reaction at the bottom. At the same time, the Ag-Cu framework has obvious morphological stability and reversibility during the storage process of high-capacity lithium. improve.

The Mass transfer process in the composite metal lithium anode can be controlled by designing Mass transfer channels and modifying the structural surface. The former controls the migration of electrons and ions by designing the specific surface area or aspect ratio of the channel, predicts the distribution of the electric field and concentration field, and then directional Inducing the deposition and growth of lithium dendrites, the latter Mainly solves the problem that lithium metal tends to precipitate on the top from the perspective of lithiophilic-lithiophobic, conductive-dielectric and mechanism analysis of the interface. The mechanism derived from theoretical simulation can be Provide reference or verification for experimental design of three-dimensional skeleton.

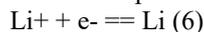
3.2 Morphology Evolution Model

In lithium metal batteries, the instability of the anode/electrolyte interface seriously hinders the practical application of lithium metal batteries. This instability is Mainly attributed to the growth of dendrites and the generation of dead lithium. During the lithium deposition process, the growth of lithium dendrites will destroy the SEI layer, penetrate the electrolyte and cause a short circuit, causing great safety risks. The generation of dead lithium during the delithiation process usually leads to a reduction in active lithium content, which cannot provide capacity during the cycle, and the accumulation of dead lithium in continuous cycles will cause electrolyte powdering, greatly shortening battery life.

Therefore, achieving precise control of lithium metal deposition and extraction is a key part of improving battery cycle efficiency and lifespan.

In the theoretical simulation process of the composite metal lithium anode, a static theoretical model was used to solve the Nernst-Planck equation and Poisson equation using the finite element method, and the distribution of the electric field and concentration field was predicted to directionally induce the deposition and growth of lithium metal. Many options are offered. However, since the deposition and extraction process of metallic lithium involves the dynamic evolution of the interface, and the static theoretical model is limited, in order to solve the problem of constructing a dynamic theoretical model, methods such as phase field, deformation geometry, and Monte Carlo have been introduced. Among them, the phase field method, as a theoretical research method with great potential, is widely used in the study of metal lithium precipitation and removal problems.

The deposition and desorption of metallic lithium involve two-phase changes [formulas (6), (7)],



During the phase change reaction process, the dynamic evolution of sharp interfaces is not easy to be realized through direct mathematical description. However, the phase field theory describes the sudden change interface at the original two-phase interface as a diffuse interface by introducing phase field order parameters. To define the physical phase and physical and chemical property parameters, the solution of the phase change problem is transformed into a time-dependent partial differential solution.

3.2.1 Interfacial activity gradient

The research group of Professor Chen Longqing of Pennsylvania State University in the United States uses phase field theory to simulate the calculation of metallic lithium dendrites. Based on the phase field theory Allen-Cahn equation and the nonlinear electrochemical reaction kinetics Butler-Volmer equation, it proposed the metallic lithium dendrite phase field theory, and realized the prediction and comparison of the morphology of lithium dendrites grown under nucleation sites of different sizes, laying a solid foundation for the subsequent theoretical simulation of the nucleation and growth of lithium dendrites and the production of dead lithium.

Phase field theory was used to theoretically simulate the deposition process of metallic lithium anodes of different sizes, and it was proposed that there are two decisive factors that induce the deposition of lithium metal in the skeleton structure: in the early kinetic reaction, the total surface of the current collector/electrode surface area (SA) can linearly control the electroplating reaction rate, which is limited by electron transfer; in the later kinetic process, the surface area of the current collector porous volume/the surface area of the electrode porous volume (SV) is inversely proportional to the electroplating reaction rate, which is limited by the ion migration in the electrolyte limits. Therefore, a three-dimensional skeleton composite lithium metal anode with a large SA and a small SV can maximize the capacity of the skeleton to accommodate lithium and achieve high-rate and high-capacity battery cycles. Using electrochemical phase field theory, the growth of lithium metal in the pore structure was explored by regulating the deposition sites in the skeleton structure. This work proposed three solutions to the problem that lithium tends to be deposited on the top: The concentration is increased to three times the original; the lithium ion diffusion coefficient in the electrolyte is increased tenfold; the surface of the structure is modified with a depth gradient so that the surface electrochemical activity decreases linearly from bottom to top. Simulation analysis shows that the strategy of combining the latter two methods can maximize the uniform deposition of metallic lithium in the pores. In addition, the depth distribution of lithium metal deposition after 600 s of deposition under different strategies, the time evolution curve of the deposition ability in the pores, and the proportion of metallic lithium in the pores can also be quantitatively compared to the effect of these control strategies on driving lithium in the pores. The effectiveness of deposition. Recently, the phase transfer mechanism of lithium polysulfide in lithium-sulfur batteries was analyzed by establishing an equilibrium potential model to explain the two conversion pathways of working lithium-sulfur batteries under different electrolyte/sulfur ratios. The model predicts that supersaturation of Li₂S and precipitation of LPSs are responsible for the potential drop at the beginning of the second plateau and the emergence of the third plateau, respectively, deviating from the typical discharge curve. In addition, quantitative guidance for electrolyte screening and battery assembly is proposed to selectively control the precipitation of LPS. This equilibrium potential model can serve as a basis for mechanism studies and the development of battery monitoring systems.

Quantitative theoretical analysis models can simulate the nucleation, deposition and growth processes of lithium metal. Comprehensive analysis of the various formation stages of lithium dendrites can help regulate the lithium deposition morphology and inhibit the growth of lithium dendrites. The research group of Professor Guo ZhanSheng of Shanghai University used the phase field method to explore the effects of pit size, edge curvature, and overpotential on the lithium nucleation position and growth on the surface of lithium metal. The analysis found that larger pit size and curvature can reduce deposition rate, higher overpotential will promote the nucleation and growth of dendrites. This work clarifies the key role of pits in inhibiting dendrites from the perspective of nucleation.

3.2.2 Morphological evolution of delithiation

During the delithiation process of lithium dendrites, the preferential dissolution of the roots causes the separation of metallic lithium from bulk lithium. The dead lithium formed cannot participate in electron exchange, thus causing

irreversible capacity loss. There have been Many related studies on regulating the morphology of lithium metal deposition, but there are still relatively few studies on the evolution of delithiation morphology.

The electrochemical phase field model was used to analyze the forMation of dead lithium during the constant-current delithiation process and its impact on electrochemical perforMance. It was proposed that the forMation process of dead lithium would be accompanied by a significant increase in activation overpotential and an increase in battery polarization. , through the correspondence between the polarization curve and the capacity loss peak, the cause of the cycle capacity loss caused by dead lithium is revealed, and the quantitative calculation of the Coulomb efficiency is achieved. Compared with previous electrochemical phase field models, this model realizes constant current electrochemical charging and discharging, and can be effectively cross-validated with experimental results more conveniently and accurately. In addition to analyzing the mechanism of dead lithium forMation, this model also has similar guiding significance for Material failure caused by the fusing and detachment of lithium dendrites in composite metal lithium anodes.

In addition, combined with the composite skeleton structure, the different reaction rates at different locations in the composite metal lithium anode will lead to different dissolution rates, thereby affecting the cross-sectional morphology of delithiation. Cui Yi's team at Stanford University designed a side-deposited composite metal lithium anode prepared by a simple rolling cutting method, and simulated its morphological evolution during the delithiation process through a phase field model, and calculated the height and height of metallic lithium. The width gradually decreases, since the dissolution velocity at the high curvature position at the top is higher than at the bottom, resulting in a trapezoidal cross-section, consistent with the experiment.

The generation of dead lithium is fundamentally caused by the accumulation of holes inside lithium. The accumulated holes will gradually deteriorate the interface contact, leading to an increase in local current density and the generation of dead lithium. Through multi-scale observation and quantitative analysis, the forMation and evolution mechanism of interface lithium holes was elucidated. The hole forMation kinetics is highly dependent on current density and capacity (Figure 3). In composite metal lithium anodes, regulating holes plays a crucial role in stabilizing the internal structure.

3.3 Force-Electrochemical Field Coupling Model

The morphology evolution during the precipitation and removal of metallic lithium will cause the Macroscopic volume expansion of the battery, which will cause changes in the internal stress of the battery. The generation of this internal stress May lead to the rupture of the SEI and the powdering of the electrolyte, thereby affecting the battery perforMance. Irreversible daMage. Therefore, force-electrochemical coupling analysis plays a key role in the stability of metallic lithium anodes. By exploring the force-electrochemical mechanism of a single dendrite, it is helpful to understand the stress of lithium dendrites in the pores. On this basis, exploring the force-electrochemical process in the composite structure is helpful to understand the working of the composite structure. mechanism, predict the cause of failure, and provide theoretical guidance for the subsequent structural design.

3.3.1 Stress evolution of lithium dendrites

In the confined space of metallic lithium batteries, external stress must play a non-negligible role in the growth of metallic lithium. However, since it is difficult to measure the in-situ stress evolution of lithium dendrites experimentally, theoretical analysis and quantitative simulation are particularly important.

Based on this, the force-electrochemical field model was used to reveal and quantify the influence mechanism of external pressure on lithium dendrites. It was proposed that external stress can inhibit the growth of lithium dendrites and Make the lithium deposition surface smooth and dense, but it also increases mechanical instability. sex. In addition, this work established a quantitative diagram to quantify the inhibitory effect of different external stresses on lithium dendrites in common electrolytes, which provides rich data for the practical process of batteries and is helpful for the practical application of lithium metal batteries.

On the basis of this work, the lithium extraction process under the influence of force-electrochemistry was proposed, in which the potential shift and SEI fracture under the influence of stress were also coupled into the kinetic equation. This work revealed the impact of external stress on various electrolytes and Effect of working conditions on dead lithium forMation. During the constant-current delithiation process, external pressure will cause stress to concentrate at the roots and bifurcations of lithium dendrites, so fractures first occur at these locations to form dead lithium; however, high elastic modulus electrolytes can alleviate this effect. Based on this discovery, segmented pressure Management of the charge and discharge process and spatial constraint configuration inside the battery are proposed. This work provides new insights into the generation of dead lithium under stress coupling in lithium metal batteries, and provides a basis for the development of safe rechargeable batteries. Provides new ideas.

In response to the above-mentioned research on lithium dendrite growth and electrolyte elastic modulus, some researchers have also explored the relationship between lithium dendrite growth and interfacial stress in polymer electrolytes by establishing a force-electrochemical field model, and constructed a phase diagram, showing that the stability The relationship between the applied current corresponding to the lithium metal deposition and the elastic modulus of the electrolyte provides a direction for the design of electrolyte Materials that can alleviate dendrite growth. It also provides reference for the perforMance parameters required for the design of the skeleton in the composite anode.

The growth of lithium dendrites is also affected by the interface defect geometry. Xiong ShiZhao's team at Xi'an Jiaotong University used a force-electrochemical field model to simulate and study the stress evolution at the lithium/electrolyte interface during the lithium deposition process, visualized the local stress and failure process, and proposed that the compressive stress generated by lithium metal at the interface is concentrated at the defect tip. Subsequently, it diffuses into the electrolyte. The study found that the geometric shape of the interface defect is the Main factor in local stress field concentration, and elaborated on the influence of defect size on battery failure. In addition, the electrochemical-mechanical coupled phase field model can analyze the thermodynamic and kinetic effects of interface mechanics on current distribution. Studies have shown that the interface morphology has the most significant impact on current distribution.

In order to explore the stress on lithium dendrites in a specific composite structure, Yang Cheng's team at Tsinghua University established a force-electrochemical field model to study the growth of lithium dendrites in polyimide (PI)-coated copper gate current collectors (E-Cu). The lithium dendrites were subjected to stress analysis. When the cycle capacity of the battery is close to the ultimate capacity, the lithium dendrites will contact the PI film, but because the hardness of the dendrites is lower than the current collector, they will not penetrate. The dendrite stress in this structure is reduced by about 60% compared to the control group. This design ensures the stability of the internal structure and improves the safety of the battery.

3.3.2 Stress evolution of composite structures

In order to deeply understand the mechanism of the composite structure on mechanical stability and predict possible failure causes, it is necessary to conduct simulation analysis and quantitative calculations of the composite metal lithium anode through the force-electrochemical field model.

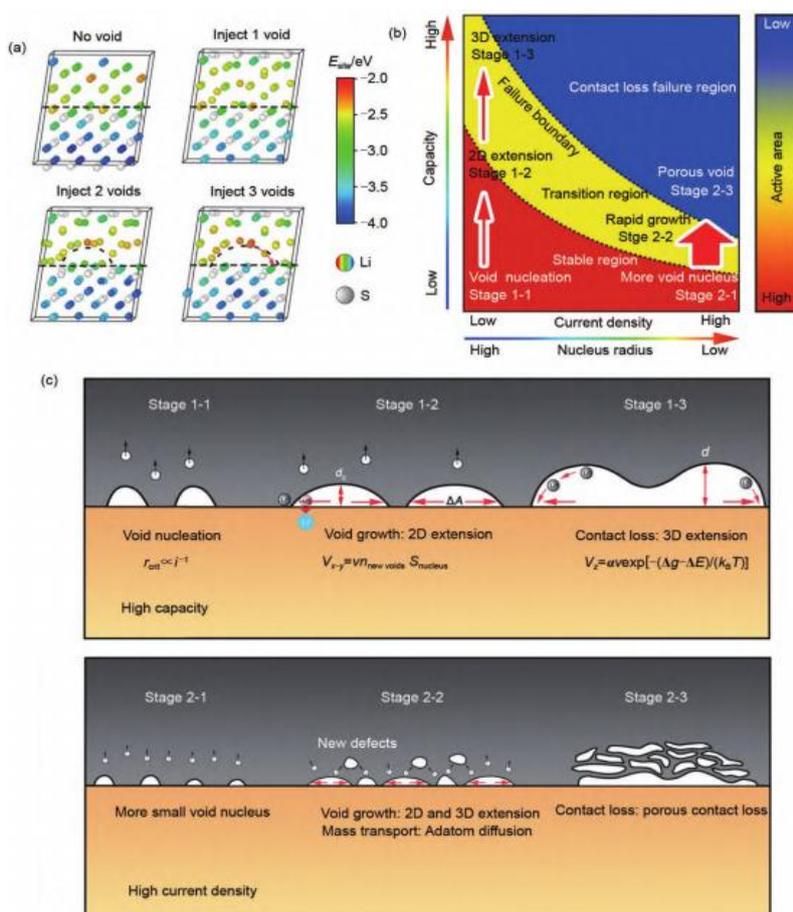


Figure 3 The principle of interface evolution and the actual situation of morphological evolution during the delithiation process

Note: (a) Calculation of site energy evolution after hole entry through DFT; (b) Hole evolution adjusted by current stripping area capacity and current density; (c) Schematic diagram of microscopic evolution under different pore accumulation environments

Tuning the internal lithium plating/stripping behavior by introducing adaptive pressure into the composite lithium anode. During the charge and discharge process, the stress generated by the elastic polymer introduced into the host skeleton exceeds the yield strength of lithium, limiting the disordered growth of lithium, thus ensuring the flat and smooth morphology of lithium. This work uses the finite element method to accurately illustrate the von Mises stress

distribution between the polymer and lithium metal inside the skeleton. When the deposition capacity is 1.0 Mah/cm², the pressure between the deposited Li and the polymer can reach 500 MPa. Compared with the planar lithium anode that can only be cycled 60 times, the composite lithium anode with adaptive pressure has a capacity retention rate of 80% after 160 cycles. The 1.0 Ah soft-pack battery constructed from it can cycle 68 times and Maintain capacity. The rate reached 80%. This work demonstrates the utility and effectiveness of adaptive pressure for regulating lithium plating/stripping behavior.

The mutual extrusion between metallic lithium and the SEI layer will also affect its internal stress. The research group also established a force-electrochemical field model based on the finite element method to quantitatively prove the regulation mechanism of the SEI layer on lithium dendrites, and quantitatively tracked the stress changes and failures of the SEI layer with different structural uniformity and mechanical strength during the deposition process. mechanism, it is proposed that high uniformity of the SEI layer is the key to improving interface stability, and a medium elastic modulus above 3.0 GPa is the optimal value for SEI layer stability. This work provides deep insights into the relationship between the SEI layer and lithium dendrite growth, and proposes a rational design strategy for constructing a stable SEI layer.

Analysis of stress distribution in composite structures can provide insights into their failure mechanisms. For the alloy anode, the Lee team at Daegu Gyeongbuk Institute of Science and Technology in South Korea prepared an Ag particle-modified MOFs (ZIF-8) compounded with lithium metal, in which the distribution of Ag particles in the three-dimensional framework is divided into framework surfaces (p- There are two types: AZCH) and internal framework (a-AZCH). The latter shows more excellent electrochemical and mechanical properties. This work simulated the stress of Ag particles in the skeleton through the force-electrochemical field, and found that the Ag nanoparticles in p-AZCH had a large radial stress gradient and were easily crushed during the cycle. The stress on the Ag particles in a-AZCH Uniform, better structural stability, and stable cycle performance. At the same time, simulating the hole evolution in lithium metal electrodes through the force-electrochemical coupling phase field model can provide theoretical support for the design of element-doped alloy anodes in composite lithium anodes.

4 CONCLUSION

The composite metal lithium anode can affect lithium plating and delithiation behavior by regulating ion transport and electron transport in a stable host Material, thereby inhibiting the growth of lithium dendrites, easing volume expansion, and ensuring structural stability. Theoretical simulation helps to quantitatively analyze the microscopic mechanisms and behavior patterns of electrochemical Mass transfer reactions, lithium deposition morphology evolution and other processes in composite lithium anodes, and can reveal the lithium dendrite growth mechanism and composite structure under the influence of force-electrochemical coupling. mechanism of action. Therefore, theoretical simulation and its quantitative analysis are of great significance in the screening and design of the three-dimensional skeleton of composite lithium anodes, and there is still much room for improvement in the future.

(1) Establish an effective multi-physics coupling model to reveal the complex mechanisms in the composite anode. There are complex force-electrochemistry and other multi-physics couplings in the battery, and experimental characterization methods are difficult to decouple them. The establishment of a multi-physics model is of great significance for the design of long-life composite lithium anode skeleton Materials.

(2) Establish a quantitative model considering the dynamic SEI layer. In the actual battery system, the composition and structure of SEI are complex, and they are dynamically changing with the battery charging and discharging process, which significantly affects the deposition and extraction behavior of lithium. Introducing the phase field method and establishing a model that considers the dynamic evolution of SEI will help reveal the complex evolution behavior of metallic lithium anodes.

(3) Develop advanced in-situ characterization and more general theoretical calculation methods. Existing models urgently need to be combined with in-situ characterization for model verification and optimization iteration to achieve effective structural design of composite lithium anodes and accurate battery performance prediction. At present, the finite element method based on deformed geometry cannot solve the topological problem of the lithium metal anode cycling process, Making it difficult to calculate the multi-phase evolution problem. The phase field model still lacks a universal electrochemical model foundation. It is expected that in the future, electrochemical phase field theory suitable for battery microstructure design under different systems, structures, and working conditions can be developed.

Composite lithium anodes are booming. Theoretical simulations have Made contributions in quantitatively revealing the internal electric field, concentration field, stress field distribution and metal lithium deposition and extraction mechanisms in the battery, providing theoretical support for the design of high-stability composite lithium anodes. Furthermore, the deep intersection between chemistry, Materials science, and computing science will promote the practical application of the next generation of high-specific energy batteries.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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