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## 二、专利

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REVIEW ARTICLE

# Multi-electron Reaction Materials for High-Energy-Density Secondary Batteries: Current Status and Prospective

Xinran Wang[1] · Guoqiang Tan[1,2] · Ying Bai[1] · Feng Wu[1] · Chuan Wu[1]

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## Abstract

To address increasing energy supply challenges and allow for the effective utilization of renewable energy sources, transformational and reliable battery chemistry are critically needed to obtain higher energy densities. Here, significant progress has been made in the past few decades in energetic battery systems based on the concept of multi-electron reactions to overcome existing barriers in conventional battery research and application. As a result, a systematic understanding of multi-electron chemistry is essential for the design of novel multi-electron reaction materials and the enhancement of corresponding battery performances. Based on this, this review will briefly present the advancements of multi-electron reaction materials from their evolutionary discovery from lightweight elements to the more recent multi-ion effect. In addition, this review will discuss representative multi-electron reaction chemistry and materials, including ferrates, metal borides, metal oxides, metal fluorides, lithium transition metal oxides, silicon, sulfur and oxygen. Furthermore, insertion-type, alloy-type and conversion-type multi-electron chemistry involving monovalent $Li^+$ and $Na^+$ cations, polyvalent $Mg^{2+}$ and $Al^{3+}$ cations beyond those of alkali metals as well as activated $S^{2-}$ and $O^{2-}$ anions are introduced in the enrichment and development of multi-electron reactions for electrochemical energy storage applications. Finally, this review will present the ongoing challenges and underpinning mechanisms limiting the performance of multi-electron reaction materials and corresponding battery systems.

**Keywords** Multi-electron reaction · Multi-ion effect · Lightweight element · Secondary battery · Energy density

## 1 Introduction

To address the issues of climate change and energy shortages caused by the depletion of fossil fuels and related carbon emissions, significant efforts have been devoted to the development of clean, efficient, cost-effective and reliable energy storage systems that can capitalize on solar, wind or nuclear energy to provide sustainable energy supplies in the future. Due to the intermittent nature and uneven distribution of these clean energy sources however, electrical energy storage systems are needed to address these power variations and allow for the efficient harvesting of energy. To achieve this, electrochemical batteries have shown particular promise, especially in terms of electronic portability, vehicle electrification and large-scale power gird regulation [1]. In this regard, corresponding battery chemistry and materials have been intensively developed to maximize standard criteria such as energy density, lifespan, operational feasibility and safety. Here, a major challenge lies in the development of cost-effective high-energy-density materials that can be used for large-scale applications to allow for deep market penetration [2, 3] and based on this, electrochemical batteries require critical breakthroughs in either battery chemistry or material based on charge transfer reactions to achieve high energy density and more importantly, the full utilization of next-generation renewable power resources [4–6].

Overall, Li-ion batteries (LIBs) are one of the most successful examples of electrochemical energy storage devices and are widely used as the main power source of laptops,

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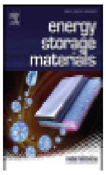

# Chlorinated dual-protective layers as interfacial stabilizer for dendrite-free lithium metal anode

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## ABSTRACT

Lithium metals offer great promises to achieve higher energy density beyond conventional lithium-ion batteries (LIBs) because of its ultrahigh specific capacity (3860 mAh $g^{-1}$) and the lowest reduction potentials (-3.04 V *vs.* standard hydrogen electrode). Unfortunately, the application of lithium metal anode has been long-standingly handicapped by uncontrollable dendrite growth, which induces instable solid electrolyte interface (SEI), performance degradation and thermal runaway. Herein, a compositionally favorable and structurally robust dual-protective layer (DPL) is proposed, where at the bottom, *in-situ* formed LiCl film provides sufficient rigidity (6.5 GPa) and low $Li^+$ diffusion barriers (0.09 eV) against dendrite growth. The poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) gel-electrolyte as the top layer is rationally selected with high flexibility to accommodate volume variation. Due to the synergy of DPL, the instability of interface is ultimately regulated to favor an extremely stabilized SEI with enhanced $Li^+$ diffusion kinetics. Depth profiling of X-ray photoelectron spectroscopy (XPS) revealed a spontaneously-formed gradient SEI hierarchy, a first-of-this-kind structure that enables long-term cycle stability and high rate capability. Cryo-electron microscopy (cryo-EM) provides direct proof on the formation of halide-rich SEI interlayers that strengthen the interfacial stability during cycles. As a consequence, dendrite-proof lithium deposition, critical $Li^+$ flux and fast ion-diffusion kinetics have been synergistically achieved to greatly improve the high-rate cycle stability (10 mA $cm^{-2}$), high Coulombic efficiency (99.5%), and prolonged cycle lifespan (1600 h) for lithium metal batteries (LMBs). The design of DPL from this contribution has opened up opportunities of lithium chlorides in purpose of constructing dendrite-free and $Li^+$ permeable interface, and provided insights for the realization of high energy density LMBs.

## 1. Introduction

Safe and high energy density rechargeable batteries are essentially required to fulfill the overwhelmingly increased demand from a wide range of applications, including electronics portability, vehicles electrification, power-grid intellectualization and renewable energy harvesting [1]. Conventional lithium-ion batteries (LIBs) can no longer satisfy such requirement, which possess limited energy density of 350 Wh $kg^{-1}$ [2]. In order to achieve high energy density, lithium metal batteries (LMBs) is revived owing to the use of lithium metal anode, featuring extremely high capacity (3860 mAh $g^{-1}$), low density (0.53 g $cm^{-3}$) and the lowest reduction potential (-3.04 V *vs.* standard hydrogen electrode) [3]. It not only adapts to high capacity yet lithium-free cathodes, but also contributes to a 4∼5 times increase of energy density than that in LIBs (such as $Li-V_2O_5$≈2118 Wh $kg^{-1}$, Li−S ≈2600 Wh $kg^{-1}$ and $Li-O_2$ ≈3600 Wh $kg^{-1}$) [4]. Because of the uncontrollable dendrite formation, early attempts of LMBs came to a failure, where dendrites pierced the separator to cause short-circuits upon further charging [5]. Since then, the overall level of application is not as effective as desired. Multiple limitations and challenges still exist against the development of LMBs, such as high $Li^+$ diffusion barriers, continuous side reaction, infinite volume changes and the so-called "dead lithium" [6]. These drawbacks destroy the stability of native solid electrolyte interface (SEI) and lead to rapid degradation as well as safety issues. More recent studies have proved that due to the high reactivity, nonaqueous electrolytes are prone to be reduced with lithium, which forms a compositionally inhomogeneous

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Review

# Lithium metal batteries for high energy density: Fundamental electrochemistry and challenges

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ABSTRACT

The dependence on portable devices and electrical vehicles has triggered the awareness on the energy storage systems with ever-growing energy density. Lithium metal batteries (LMBs) has revived and attracted considerable attention due to its high volumetric (2046 mAh $cm^{-3}$), gravimetric specific capacity (3862 mAh $g^{-1}$) and the lowest reduction potential (−3.04 V vs. SHE.). However, during the electrochemical process of lithium anode, the growth of lithium dendrite constitutes the biggest stumbling block on the road to LMBs application. The undesirable dendrite not only limit the Coulombic efficiency (CE) of LMBs, but also cause thermal runaway and other safety issues due to short-circuits. Understanding the mechanisms of lithium nucleation and dendrite growth provides insights to solve these problems. Herein, we summarize the electrochemical models that inherently describe the lithium nucleation and dendrite growth, such as the thermodynamic, electrodeposition kinetics, internal stress, and interface transmission models. Essential parameters of temperature, current density, internal stress and interfacial $Li^+$ flux are focused. To improve the LMBs performance, state-of-the-art optimization procedures have been developed and systematically illustrated with the intrinsic regulation principles for better lithium anode stability, including electrolyte optimization, artificial interface layers, three-dimensional hosts, external field, *etc.* Towards practical applications of LMBs, the current development of pouch cell LMBs have been further introduced with different assembly systems and fading mechanism. However, challenges and obstacles still exist for the development of LMBs, such as in-depth understanding and in-situ observation of dendrite growth, the surface protection under extreme condition and the self-healing of solid electrolyte interface.

Mingda Gao received his bachelor's degree from China University of Geosciences (Beijing). He is currently a graduate student in the School of Materials Science and Engineering at Beijing Institute of Technology. His current researches focused on advanced lithium metal battery.

Li Xu received her Ph.D. from the University of Science and Technology Beijing. She is currently a senior scientist in the Department of New Electrical Materials at Global Energy Interconnection Research Institute Co., Ltd. She is mainly engaged in the research and development of new energy materials for power systems, corrosion and protection. She has hosted or participated in the National 863 Project, the National Natural Science Foundation of China, the Beijing Municipal Science and Technology Commission, and the State Grid Corporation of Science and Technology.

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# Vanadium Organometallics as an Interfacial Stabilizer for $Ca_xV_2O_5$/Vanadyl Acetylacetonate Hybrid Nanocomposite with Enhanced Energy Density and Power Rate for Full Lithium-Ion Batteries

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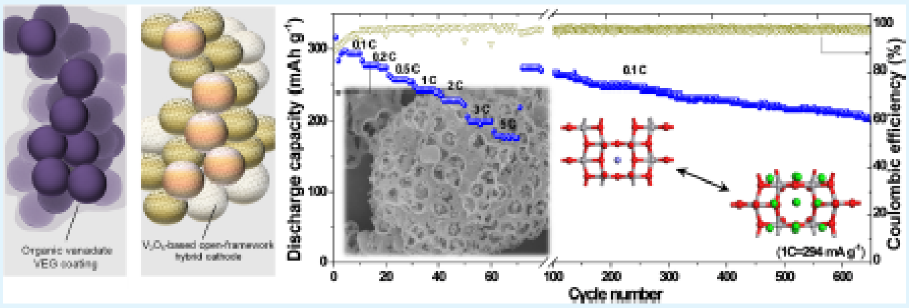
*Supporting Information*



**ABSTRACT:** Vanadium pentoxide ($V_2O_5$) offers high capacity and energy density as a cathode candidate for lithium-ion batteries (LIBs). Unfortunately, its practical utilization is intrinsically handicapped by the low conductivity, poor electrode kinetics, and lattice instability. In this study, the synergistical optimization protocol has been proposed in the conjunction of interstitial Ca incorporation and organic vanadate surface protection. It is revealed that regulating Ca occupation in the body phase at a relatively low concentration can effectively expand the layer distance of $\alpha$-$V_2O_5$, which facilitates the intercalation access for Li-ion insertion. On the other hand, organometallics are first applied as the protective layer to stabilize the electrode interface during cycling. The optimized coating layer, vanadium oxy-acetylacetonate (VO(acac)$_2$), plays an important role to generate a more inorganic component (LiF) within the solid electrolyte interface, contributing to the protection of the Ca-incorporated $V_2O_5$ electrode. As a result, the optimized $Ca_{0.05}V_2O_5$/VO(acac)$_2$ hybrid electrode exhibits much improved capacity utilization, rate capability, and cycling stability, delivering capacity as high as 297 mAh g$^{-1}$ for full LIBs. The first-principle computations reveal the lattice change caused by the Ca incorporation, further confirming the lattice advantage of $Ca_{0.05}V_2O_5$/VO(acac)$_2$ with respect to Li-ion intercalation.

**KEYWORDS:** *vanadium pentoxide, metal incorporation, organic vanadate, cathode material, lithium-ion batteries*

## ■ INTRODUCTION

Owing to the ever-worsening fuel depletion and environmental deterioration, electrochemical energy storage has triggered extensive concern in recent years. In this regard, lithium-ion batteries (LIBs) are emerging as one of the most promising candidates because of their large energy density, high rate capability, and relative long-term operational lifespan. However, the performance of LIBs is expected to be further upgraded to fulfill rapid development of electrical vehicles, household portable devices, and smart electrical power grids.[1−4] As a result, a great deal of attention has been paid to those insulating but high capacity electrode candidates. Practically, the performance of these insulating candidates is generally limited by the intrinsically low conductivity, poor electrochemical reversibility, severe material dissolution and so forth.[5−9] It is still challenging to adopt these materials into current LIBs setup while achieving sufficient cycle stability, rate capability, and operational lifespan.[10−12]

Layered vanadium pentoxide ($\alpha$-$V_2O_5$) has been intensively investigated as intercalation-type Li-host materials for LIBs due to its high theoretical capacity, high energy density, earth abundance, and cost effectiveness.[13−17] Its multiple oxidation states (III−V) and unique layered structures allow for multielectron and Li-ion transfer during the lithiation/delithiation process, offering even higher capacity than most of transition-metal oxides, such as Li(Ni$_{0.33}$Co$_{0.33}$Mn$_{0.33}$)O$_2$.[18]

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# Hyperaccumulation Route to Ca-Rich Hard Carbon Materials with Cation Self-Incorporation and Interlayer Spacing Optimization for High-Performance Sodium-Ion Batteries

Kaihua Yu, Huichun Zhao, Xinran Wang,* Minghao Zhang, Ruiqi Dong, Ying Li, Ying Bai,* Huajie Xu, and Chuan Wu*

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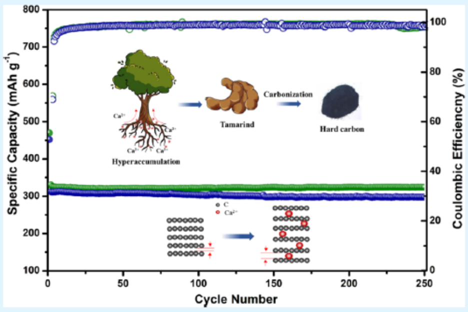

**ABSTRACT:** The hard carbon (HC) has been emerging as one of the most promising anode materials for sodium-ion batteries (SIBs). Incorporation of cations into the HC lattice proved to be effective to regulate their *d*-interlayer spacing with a modified SIB performance. However, the complexity and high cost of current synthetic processes limited its large-scale application in SIBs. Through the natural hyperaccumulation process, a cost-effective and scale-up-driven procedure to produce Ca-ion self-incorporated HC materials was proposed by applying tamarind fruits as the precursor with the enrichment of Ca ions. In virtue of one-step pyrolysis, the self-incorporated and well-distributed Ca ions in tamarind fruits had successfully served as the buffer layer to expand the *d*-interlayer spacing of HC materials. Furthermore, the natural porosity hierarchy could be largely preserved by the optimization of calcination temperature. As a result, the Ca-rich HC material had exhibited the optimized cycling performance (326.7 mA h g$^{-1}$ at 50 mA g$^{-1}$ and capacity retention rate of 89.40% after 250 cycles) with a high initial Coulombic efficiency of 70.39%. This work provided insight into applying the hyperaccumulation effect of biomass precursors to produce doped HC materials with ion self-incorporation and the optimized *d*-interlayer spacing, navigating its large-scale application for high-performance SIBs.

**KEYWORDS:** *sodium-ion batteries, hard carbon, anode, tamarind, hyperaccumulation*

## 1. INTRODUCTION

Although the renewable energy has been in active exploration in recent years, its utilization remains a challenge due to the intermittent conveying and the uneven distribution.[1−3] As a result, several of advanced energy conversion and storage devices have been continuously developed to address the challenge. In this regard, lithium-ion batteries (LIBs) have become the most promising and attractive choice for portable electric devices and storage devices. However, the insufficient Li resources can hardly cover the ever-growing demand of LIBs in particular with the demanded large-scale storage devices in future.[2−4] Alternatively, sodium-ion batteries (SIBs) are recently attracting the tremendous attention on the large-scale energy storage on account of their abundance of Na, low-cost, environmental-friendliness, and the similarity between Li and Na. Therefore, it is essential to develop the corresponding electrode materials of low cost and renewability, while fulfilling the large-scale applicable requirements arising from the boom of electrical vehicles and stationary energy systems.[3−6]

According to the literature, a great deal of materials have been studied as anode candidates, including carbon materials,[7−9] sulfides,[10−12] metal oxides,[13−15] alloys,[16−18] and so forth. To date, the hard carbon (HC) material is still identified as the most promising and industry-accessible anode because of its large *d*-interlayer spacing for Na ion insertion, low average potential of sodiation/desodiation, and the most cost-effectiveness, which is the top priority for the industrialization of SIBs.[19] Owing to the advantages of being low-cost, renewable, and environmentally friendly, the biomass has showed great promises as precursors to produce HC materials, while minimizing the wastes caused by the current handling of incineration or landfill.[20] Accordingly, many recent researches have reported the biomass-derived HC materials with the

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# Insight to defects regulation on sugarcane waste-derived hard carbon anode for sodium-ion batteries

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ABSTRACT

A great deal of attention has been paid on developing plant-derived hard carbon (HC) materials as anodes for sodium-ion batteries (SIBs). So far, the regulation of HC has been handicapped by the well-known ambiguity of Na$^+$ storage mechanism, which fails to differentiate the Na$^+$ adsorption and Na$^+$ insertion, and their relationship with the size of *d*-interlayer spacing and structural porosity. Herein, bagasse-derived HC materials have been synthesized through a combination of pyrolysis treatment and microwave activation. The combined protocol has enabled to synergistically control the *d*-interlayer spacing and porosity. Specifically, the microwave activation has created slit pores into HC and these pores allow for an enhanced Na$^+$ adsorption with an increased sloping capacity, establishing a strong correlation between the porosity and sloping capacity. Meanwhile, the pyrolysis treatment promotes the graphitization and it contributes to an intensified Na$^+$ insertion with an increased plateau capacity, proving that the plateau capacity is largely contributed by the Na$^+$ insertion between interlayers. Therefore, the structural regulation of bagasse-derived HC has provided a proof on positively explaining the Na$^+$ storage with HC materials. The structural changes in the pore size distribution, specific surface area, *d*-interlayer spacing, and the electrochemical properties have been comprehensively characterized, all supporting our understanding of Na$^+$ storage mechanism. As a result, the HC sample with an optimized *d*-interlayer spacing and porosity has delivered an improved reversible capacity of 323.6 mAh g$^{-1}$ at 50 mA g$^{-1}$. This work provides an understanding of Na$^+$ storage mechanism and insights on enhancing the sloping/plateau capacity by rationally regulating the graphitization and porosity of HC materials for advanced SIBs.

## 1. Introduction

The ever-increasing demand of energy has triggered a massive amount of environmental issues due to the extensive use of traditional fossil energy. In response to these environmental issues and energy crisis, renewable energies have brought transformative changes and a sustainable solution to solve these problem, such as solar energy and wind power. In order to effectively use these renewable energy, techniques for energy storage have been raised up worldwide with great scientific interests and fast market penetration. Due to the high energy density, lithium-ion batteries (LIBs) have capitalized on the current choices of energy storage devices and engaged to support the development of vehicle electrification and device portability [1–3]. Unfortunately, there are great pressures and wide concerns about the shortage of lithium resources in future due to its limited reserves and uneven distribution, which may constitute one of the biggest stumbling blocks for the further development of LIBs. As a result, it has triggered the exploration of alternative energy storage systems in particular with respect to abundant and cost-effective charge carriers. In this regard, sodium-ion batteries (SIBs) have underscored as the most promising candidate and been in active exploration now owing to the similar physical and chemical properties with Li$^+$ [4,5] and the high crustal content (~2.3%). Its abundance and cost-effectiveness have further promoted the application on cost-sensitive energy storage, such as the smart electrical power grid and scale-up energy storage for renewable energy.

In order to attain sufficiently high SIBs performance, variety of anode materials have been continuously reported with characteristics of high capacity, good cycle stability, and low sodiation/desodiation potential, including alloys [6,7] sulfides [8,9] metal oxides

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ACS APPLIED MATERIALS & INTERFACES

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Research Article

# Rational Tuning of a $Li_4SiO_4$-Based Hybrid Interface with Unique Stepwise Prelithiation for Dendrite-Proof and High-Rate Lithium Anodes

Yanxia Yuan, Feng Wu, Yiran Liu, Xinran Wang,* Ke Zhang, Lumin Zheng, Zhaohua Wang, Ying Bai,* and Chuan Wu*

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**ABSTRACT:** Lithium metal batteries (LMBs) are among the most promising candidates for high energy-density batteries. However, dendrite growth constitutes the biggest stumbling block to its development. Herein, $Li_4SiO_4$-dominating organic−inorganic hybrid layers are rationally designed by $SiO_2$ surface modification and the stepwise prelithiation process. $SiO_2$ nanoparticles construct a zigzagged porous structure, where a solid electrolyte interface (SEI) has grown and penetrated to form a conformal and compact hybrid surface. Such a first-of-this-kind structure enables enhanced Li dendrite prohibition and surface stability. The interfacial chemistry reveals a two-step prelithiation process that transfers $SiO_2$ into well-defined $Li_4SiO_4$, the components of which exhibits the lowest diffusion barrier (0.12 eV atom$^{-1}$) among other highlighted SEI species, such as LiF (0.175 eV atom$^{-1}$) for the current artificial layer. Therefore, the decorated Li allows for an improved high-rate full-cell performance ($LiFePO_4$/modified Li) with a much higher capacity of 65.7 mAh g$^{-1}$ at 5C (1C = 170 mAh g$^{-1}$) than its counterpart with bare Li (∼3 mAh g$^{-1}$). Such a protocol provides insights into the surface architecture and SEI component optimization through prelithiation in the target of stable, dendrite-proof, homogenized $Li^+$ solid-state migration and high electrochemical performance for LMBs.

**KEYWORDS:** *silica, metallic Li, anode, cycle stability, dendrite*

## 1. INTRODUCTION

Engaging to support the demanding development of vehicle electrification, electronic portability and smart grid regulation, significant interests have been triggered into materials of higher energy density beyond lithium-ion batteries (LIBs).[1,2] Metallic lithium (Li) is one of the most promising anode candidates because of the highest theoretical specific capacity (3860 mAh g$^{-1}$) and the lowest electrochemical potential (−3.04 V vs standard hydrogen electrode).[3,4] Furthermore, the use of a Li anode offers indispensable opportunities to apply Li-free yet high capacity cathodes, such as sulfur[5] and metal fluorides,[6] breaking through limits of the energy density achieved in the well-established intercalation-based LIBs.[7] In this regard, however, the use of metallic Li has been challenged by the unstable surface chemistry. Due to the inhomogeneous $Li^+$ flux, the formation of Li dendrites is the biggest obstacle that induces the short circuits and causes the thermal runaway.[8,9] The origin of Li dendrites associate with the fragile and poor quality of the protogenic solid electrolyte interface (SEI), which fails to passivate and protect the electrode surface.[8,10] This results in the cracks of the SEI, leading to the decomposition of electrolytes, the formation of "dead Li", and the increase of surface resistance.[11] The surface instability has been further deteriorated by the inhomogeneous composition, which causes different ionic conductivities, nonuniform Li deposition, and excessive side reactions to destroy the cycling stability.[3]

Previous studies have proved the importance of interfacial engineering and composition optimization in addressing the above challenges.[2,8,12] An ideal SEI should be electrochemically stable during cycling, fulfilling the desired characteristics as follows: (1) high mechanical strength against Li dendrites; (2) chemical and electrochemical stability to prevent the continuous SEI growth; (3) sufficient ionic conductivity and electron-blocking for homogeneous and fast $Li^+$ flux; (4) sufficient elasticity to buffer the volume expansion.[13,14] Accordingly, a great variety of strategies have been proposed, including the use of electrolyte additives,[15−17] salt-concentrated electrolyte,[18,19] notable three-dimensional (3D)-Li

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Review article

# Charactering and optimizing cathode electrolytes interface for advanced rechargeable batteries: Promises and challenges

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## Abstract

With the advancement of secondary batteries, interfacial properties of electrode materials have been recognized as essential factors to their electrochemical performance. However, the majority of investigations are devoted into advanced electrode materials synthesis, while there is insufficient attention paid to regulate their interfaces. In this regard, the solid electrolyte interphase (SEI) at anode part has been studied for 40 years, already achieving remarkable outcomes on improving the stability of anode candidates. Unfortunately, the study on the cathode electrolyte interfaces (CEI) remains in infancy, which constitutes a potential restriction to the capacity contribution, stability and safety of cathodes. In fact, the native CEI generally possesses unfavorable characteristics against structural and compositional stability that requires demanding optimization strategies. Meanwhile, an in−depth understanding of the CEI is of great significance to guide the optimization principles in terms of composition, structure, growth mechanism, and electrochemical properties. In this literature, recent progress and advances of the CEI characterization methods and optimization protocols are summarized, and meanwhile the mutually−reinforced mechanisms between detection and modification are explained. The criteria and the potential development of the CEI characterization are proposed with insights of novel optimization directions.

*Keywords:* Cathode electrolyte interface; Secondary battery; Characterization methods; In *situ*/*operando*; Synchrotron radiation

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## 1. Introduction

With electrification and portability of devices such as electric vehicles, smart electric power grid, and intelligent electronic devices, there is an overwhelmingly increased demand of rechargeable batteries with high energy density, long cycle life, and operational safety. Using a positive electrode with high−voltage and high−capacity has become an effective approach to satisfy this demand. However, the recent commercial cathodes face challenges in terms of structural and phase transition instability, transition metals (TM) dissolution, oxygen gas ($O_2$) releasing, and the continuous decomposition of the electrolyte at the interface. These critical shortcomings have caused insufficient cycle stability, fast capacity degradation, and undesired thermal runaway in practical, severely restricting the state−of−the−art performance and development of rechargeable batteries.

The electrode/electrolyte interfaces have provided passivating yet ion−permeable layers for secondary batteries. Due to its formation, the separation of electrodes from electrolytes is

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Review

# Multivalent metal–sulfur batteries for green and cost-effective energy storage: Current status and challenges

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ABSTRACT

Multivalent metal–sulfur (M-S, where M = Mg, Al, Ca, Zn, Fe, etc.) batteries offer unique opportunities to achieve high specific capacity, elemental abundancy and cost-effectiveness beyond lithium-ion batteries (LIBs). However, the slow diffusion of multivalent-metal ions and the shuttle of soluble polysulfide result in impoverished reversible capacity and limited cycle performance of M–S (Mg–S, Al–S, Ca–S, Zn–S, Fe–S, etc.) batteries. It is a necessity to optimize the electrochemical performance, while deepening the understanding of the unique electrochemical reaction mechanism, such as the intrinsic multi-electron reaction process, polysulfides dissolution and the instability of metal anodes. To solve these problems, we have summarized the state-of-the-art progress of current M–S batteries, and sorted out the existing challenges for different multivalent M–S batteries according to sulfur cathode, electrolytes, metallic anode and current collectors/separators, respectively. In this literature, we have surveyed and exemplified the strategies developed for better M–S batteries to strengthen the application of green, cost-effective and high energy density M–S batteries.

## 1. Introduction

Since the first Industrial Revolution, there is an overwhelming increase in the need for energy. Renewable energy resources, such as biological and geothermal energy, compensate for the deficiencies and shortage of conventional fossil fuels, which have potentially fulfilled the social sustainable development. Nowadays, these renewable energies have already become practically available and achieved promising environmental benign. However, due to the fluctuation of natural resources, their intermittent power supply has blocked the large-scale utilization and the stability of electrical grid. Such unique problem has triggered wide attention to the adaptable rechargeable batteries for energy storage [1–3]. On this matter, lithium-ion batteries (LIBs), such as $LiCoO_2$/graphite or $Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O_2$/graphite, have dominated the current choice of rechargeable batteries owing to the acceptable energy density and lifespan [4,5]. Nevertheless, large-scale use of LIBs has been potentially restrained by the low contents of lithium, cobalt, and other rare metals, the reserves of which may not be sufficient to support the rapid demands of LIBs manufacturing. Meanwhile, the energy density of current LIBs, which is the most essential parameter for rechargeable batteries, has already approached to the upper limit (~300 Wh $kg^{-1}$). New electrodes and systems based on abundant and cost-effective elements are urgently required to break through these obstacles [6,7]. For a certain electrode material, the theoretical specific capacity can be determined by Eq. (1) as follows [8,9]:

$$\text{Capacity}\ (C) = nF/3.6M, \qquad (1)$$

where $C$, $F$, $n$, and $M$ represent the theoretical capacity of the electrode material, the Faraday constant, the total electron transferred, and the molar mass of the electrode material, respectively. According to Eq. (1), reducing $M$ or increasing $n$ are both effective ways to improve energy density. In order to maximally fulfill the criteria, in this regard, sulfur is highlighted because of relatively low molar weight [10–13], two-electron transfer [14], and high crustal content [15,16]. It can provide a theoretical specific capacity as high as 1672 mAh $g^{-1}$ [17] with respect to $Li^+$, triggering wide interests to its alloying-type electrode reaction [18–21]. For example, the lithium–sulfur (Li–S) battery has become the most widely-explored M–S battery systems with continuous outcomes and performance upgradation. However, the current status of Li–S battery

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# $PY_{13}FSI$-Infiltrated SBA-15 as Nonflammable and High Ion-Conductive Ionogel Electrolytes for Quasi-Solid-State Sodium-Ion Batteries

Yongsheng Gao, Guanghai Chen, Xinran Wang,* Haoyi Yang, Zhaohua Wang, Weiran Lin, Huajie Xu, Ying Bai, and Chuan Wu*

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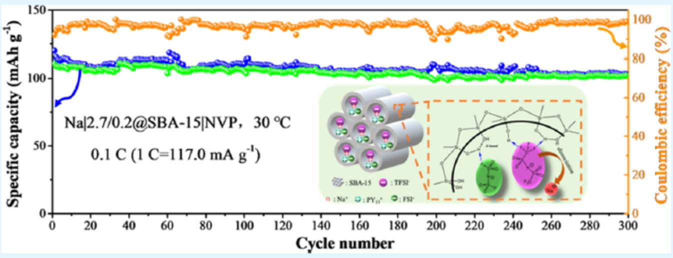

**ABSTRACT:** Exploring electrolytes of high safety is essential to pave the practical route for sodium-ion batteries (SIBs) toward their important applications in large-scale energy storage and power supplies. In this regard, ionogel electrolytes (IEs) have been highlighted owing to their high ionic conductivity, prominent electrochemical and thermal stability, and, more crucially, high interfacial wettability. However, present studies lack an understanding of the interaction of IEs, which determines the ion desolvation and migration. In this article, IEs comprising an SBA-15 host, an ionic liquid, sodium salt, and poly(vinylidene fluoride)−hexafluoro propylene (PVDF−HFP) have been proposed by mechanical ball milling and roller pressing. The component ratio has been optimized based on the balance between ionic conductivity and self-supporting capability of IEs. The optimal IEs showed sufficiently high ionic conductivity ($2.48 \times 10^{-3}$ S cm$^{-1}$ at 30 °C), wide electrochemical window (up to 4.8 V vs $Na^+/Na$), and high $Na^+$ transference number (0.37). Due to the presence of SBA-15 and an ionic liquid, the IEs exhibited much improved thermal resistance than that of the conventional organic liquid electrolytes (OLEs). Furthermore, Fourier transform infrared (FT-IR) spectroscopy revealed the hydrogen bonding interaction between silanols and the dissolved salts, not only anchoring anions for immobilization but also promoting the dissociation of sodium salts. After being matched with the $Na_3V_2(PO_4)_3$ (NVP) cathode and metallic Na anode, the SIBs presented a specific discharge capacity of up to 110.7 mA h g$^{-1}$ initially at room temperature with 92% capacity retention after 300 cycles. The improved safety and electrochemical performance provided insights into rationally regulating IEs and their interactions with the prospect of strengthening their practical applications in SIBs.

**KEYWORDS:** *sodium-ion batteries, ionogel electrolytes, SBA-15, ionic conductivity, hydrogen bonding*

## 1. INTRODUCTION

Lithium-ion batteries (LIBs) have achieved significant development from laboratories to industries due to their remarkable energy storage performance and versatile application in portable electronics and electrical vehicles.[1,2] However, the limited resources of lithium and its high price are becoming one of the issues that restrain their large-scale utilization, such as the electrical power grid for renewable energy harvesting in the future. Alternatively, the abundant resources of sodium worldwide have triggered considerable attention toward the sodium-ion batteries (SIBs) as cost-effective candidates for scalable electrochemical energy storage.[3−5] To date, many limitations on SIBs still exist regarding the safety, which arises from the use of organic liquid electrolytes (OLEs), for instance, ethylene carbonate (EC), diethyl carbonate (DEC), and propylene carbonate (PC).[6−9] These organic solvents are proposed to be flammable, leakage-prone, and toxic, constituting the main reasons for the thermal runaway.[10]

Protective procedures have been continuously developed to strengthen their operational safety, for example, the opti-

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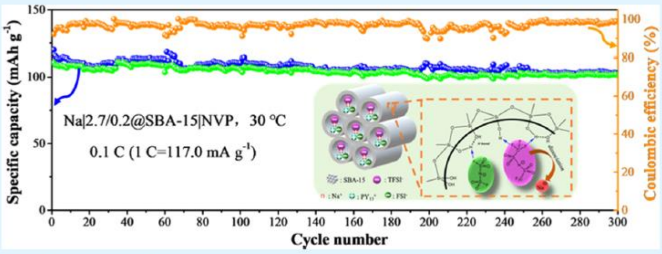

**ABSTRACT:** Exploring electrolytes of high safety is essential to pave the practical route for sodium-ion batteries (SIBs) toward their important applications in large-scale energy storage and power supplies. In this regard, ionogel electrolytes (IEs) have been highlighted owing to their high ionic conductivity, prominent electrochemical and thermal stability, and, more crucially, high interfacial wettability. However, present studies lack an understanding of the interaction of IEs, which determines the ion desolvation and migration. In this article, IEs comprising an SBA-15 host, an ionic liquid, sodium salt, and poly(vinylidene fluoride)−hexafluoro propylene (PVDF−HFP) have been proposed by mechanical ball milling and roller pressing. The component ratio has been optimized based on the balance between ionic conductivity and self-supporting capability of IEs. The optimal IEs showed sufficiently high ionic conductivity ($2.48 \times 10^{-3}$ S cm$^{-1}$ at 30 °C), wide electrochemical window (up to 4.8 V vs $Na^+/Na$), and high $Na^+$ transference number (0.37). Due to the presence of SBA-15 and an ionic liquid, the IEs exhibited much improved thermal resistance than that of the conventional organic liquid electrolytes (OLEs). Furthermore, Fourier transform infrared (FT-IR) spectroscopy revealed the hydrogen bonding interaction between silanols and the dissolved salts, not only anchoring anions for immobilization but also promoting the dissociation of sodium salts. After being matched with the $Na_3V_2(PO_4)_3$ (NVP) cathode and metallic Na anode, the SIBs presented a specific discharge capacity of up to 110.7 mA h g$^{-1}$ initially at room temperature with 92% capacity retention after 300 cycles. The improved safety and electrochemical performance provided insights into rationally regulating IEs and their interactions with the prospect of strengthening their practical applications in SIBs.

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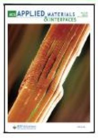

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# High-Capacity Interstitial Mn-Incorporated $Mn_xFe_{3-x}O_4$/Graphene Nanocomposite for Sodium-Ion Battery Anodes

Haixia Ren,[†] Ying Bai,[*,†] Xinran Wang,[*,†] Qiao Ni,[†] Zhaohua Wang,[†] Yu Li,[†] Guanghai Chen,[†] Feng Wu,[†,‡] Huajie Xu,[§] and Chuan Wu[*,†,‡]

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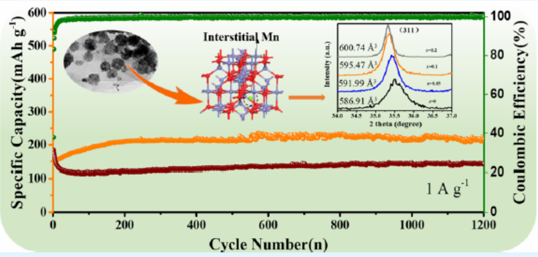
Supporting Information

**ABSTRACT:** Sodium-ion batteries (SIBs) have attracted wide attention because of their prospects for grid-scale electrical regulation and cost effectiveness of sodium. In this regard, iron oxides ($FeO_x$) are considered as one of the most promising anode candidates due to their high theoretical capacity and low cost. Unfortunately, the utilization of $FeO_x$ anodes suffers from sluggish reaction kinetics and significant lattice variation, causing insufficient rate performance and fast capacity degradation during the sodiation/desodiation process. In this study, Mn ions are incorporated through interstitial sites into a $Fe_3O_4$ lattice to form the Mn-incorporated $Fe_3O_4$/graphene (M-$Fe_3O_4$/G) composites through a facile hydrothermal method. Confirmed by XRD Rietveld refinement and the first-principles calculation, Mn occupation into the body structure can effectively condense the electron density around the Fermi level and thus contributes to the increased electrical conductivity and improved electrochemical properties. Accordingly, the $M_{0.1}Fe_{2.9}O_4$/G composite demonstrates a high reversible capacity of 439.8 mA h $g^{-1}$ at a current density of 100 mA $g^{-1}$ over 200 cycles. Even at a high current density of 1 A $g^{-1}$, the M-$Fe_3O_4$/G composites remain stable for over 1200 cycles, delivering a capacity of 210 mA h $g^{-1}$. Coupled with a $Na_3V_2(PO_4)_3$-type cathode, the Mn-incorporated $Fe_3O_4$/G composites demonstrate good suitability in full SIBs (161.2 mA h $g^{-1}$ at the current density of 1 A $g^{-1}$ after 100 cycles). The regulation of Mn ions in the $Fe_3O_4$ lattice provides insights into the optimization of metal oxide anode candidates for their application in SIBs.



**KEYWORDS:** *sodium-ion batteries, interstitial incorporation, iron oxides, graphene, full cell, high capacity*

## 1. INTRODUCTION

Because of the ever-worsening fossil fuel depletion and environmental deterioration, the development and utilization of renewable energy have become urgent, particularly with the rapid demands from electric vehicles and smart electrical grid.[1−3] Nowadays, sodium-ion batteries (SIBs) have alternatively attracted a great deal of attention because of the more abundance and lower cost of sodium than that of lithium.[4−7] In this regard, although graphite anodes have exhibited extraordinary performance to accommodate Li ions in lithium-ion batteries,[8,9] they fail to interactively host Na ions due to the larger ionic radius of sodium (1.02 Å for Na ions) than that of Li ions (0.76 Å). Moreover, guided by quantum-mechanical methods, among the alkali and alkaline earth metals, sodium has a weaker chemical binding to a given substrate, including graphite.[10] As a result, the development of anode candidates has become one of the most urgent issues with respect of SIBs.[11−13] Till now, variety of anode materials have been explored, such as hard carbon,[14−19] metal alloy,[20−23] metal oxides[24,25] and sulfides.[14,26,27] Among them, iron oxide-based materials are considered as one of the most promising materials for SIBs because of their high theoretical capacity (about 924 mA h $g^{-1}$ for $Fe_3O_4$), cost effectiveness, abundance, and environmental friendliness.[28] Different from intercalative ion-insertion anode materials, iron oxides can store Na ions through conversion-type electrode reactions, which allows for full use of the valence states of transition metals and thus breaks through the capacity limitation of conventional intercalation-based anodes. The conversion-type reaction of iron oxides with sodium ions can be expressed as following (eq 1)[29]

$$Fe_3O_4 + 8M^+ + 8e^- \rightarrow 4M_2O + 3Fe \qquad (M = Na,\ Li) \tag{1}$$

Prior study has demonstrated the significant volume expansion of iron oxides with respect of Li-ion storage, causing

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# Application of Metal-Organic Frameworks to the Interface of Lithium Metal Batteries

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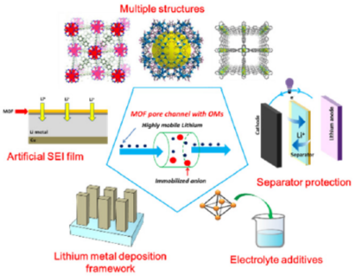
**Abstract:** Lithium metal batteries (LMBs) are representative systems for high-energy-density batteries. The design of LMBs with high capacity and high cycle stability is imperative. However, the development of LMBs is hindered by typical interface-related problems such as lithium dendrite growth, incompatible separator interfaces, and unstable cathode interfaces because of the inhomogeneous ionic flux and composition distribution. The intrinsic instability significantly hinders electron/ion transfer at the interface, causing serious issues such as dendrite growth, volume changes, low coulombic efficiency, dead lithium, interface deterioration, capacity degradation, and loss of safety. Metal–organic frameworks (MOFs) are organic–inorganic hybrid materials with a stable highly porous structure, which can allow for highly efficient gas adsorption, separation and purification, catalysis, etc., in addition to facilitating their application in nanomedicine and other fields. In recent years, MOFs have attracted much attention in the field of LMBs as a possible solution to the typical interface problems abovementioned. The porous structure and open metal sites (OMs) of MOFs provide an excellent interface structure for uniform and high ionic conductivity. As additional bonus, the stable structure provides high mechanical strength with different functional groups and metal sites, resulting in significant versatility of functionality for interface stabilization. MOFs are usually synthesized by hydrothermal/solvothermal, microwave-assisted, electrochemical, and spray-drying methods. The excellent properties of MOFs have prompted researchers to pursue their rational design and modification. Much progress has been made in this direction, and exemplary investigations have been performed to solve the abovementioned interfacial problems encountered with LMBs. Consequently, metallic lithium deposition frameworks, artificial solid electrolyte interface films, electrolyte additives, separator materials, cathode materials for lithium-sulfur batteries, and lithium-air batteries have been developed. However, there is a long way to go before the commercialization of batteries based on MOF materials. In practical, more complex electrochemical reactions occur at the lithium-metal interface, and the operating conditions (temperature, over charging/discharging, external stress, etc.) vary widely. Moreover, MOFs as electrode materials have intrinsic drawbacks, including structural collapse, pore blockage, and low inherent conductivity during the cycles. Based on these interfacial challenges, in LMBs, it introduces the structural characterization and optimization of MOFs and the key chemical components that determines the MOFs of structure (central atom, organic ligand, etc.). Subsequently, we summarized the growth mechanism of lithium dendrites and discussed the applications of MOFs and their derivatives to battery cathodes, separators, anodes, and electrolytes.



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[†] The authors contributed equally to this work.

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(54) 发明名称

# 含CTAB的金属锂电池电解液

(57) 摘要

一种含CTAB的金属锂电池电解液，其制备方法包括：将二甲醚(DME)和1,3-二氧戊环(DOL)以1:1左右的体积比形成混合溶液；在混合溶液中加入双三氟甲烷磺酰亚胺锂(LiTFSI)和十六烷基三甲基溴化铵(CTAB)，其中LiTFSI在溶液中的浓度为1mol/L左右，CTAB在溶液中的浓度为4-10mmol/L。本发明提供的改性电解液可以有效克服现有金属锂负极材料局部形成锂枝晶从而导致电池短路引发安全问题的缺陷，同时还可使金属锂电池具有较高的库伦效率和循环稳定性。

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工程与材料科学部
2018年8月16日

# 国家自然科学基金资助项目批准通知

王欣然　先生/女士：

根据《国家自然科学基金条例》规定和专家评审意见，国家自然科学基金委员会（以下简称自然科学基金委）决定资助您申请的项目。项目批准号：22075025，项目名称：两亲分子在金属锂界面的自组装调控及锂枝晶自修复机理研究，直接费用：60.00万元，项目起止年月：2021年01月至 2024年 12月，有关项目的评审意见及修改意见附后。

请尽早登录科学基金网络信息系统（https://isisn.nsfc.gov.cn），获取《国家自然科学基金资助项目计划书》（以下简称计划书）并按要求填写。对于有修改意见的项目，请按修改意见及时调整计划书相关内容；如对修改意见有异议，须在电子版计划书报送截止日期前向相关科学处提出。

电子版计划书通过科学基金网络信息系统（https://isisn.nsfc.gov.cn）上传，依托单位审核后提交至自然科学基金委进行审核。审核未通过者，返回修改后再行提交；审核通过者，打印纸质版计划书（一式两份，双面打印），依托单位审核并加盖单位公章，将申请书纸质签字盖章页订在其中一份计划书之后，一并将上述材料报送至自然科学基金委项目材料接收工作组。电子版和纸质版计划书内容应当保证一致。**自然科学基金委将对申请书纸质签字盖章页进行审核，对存在问题的，允许依托单位进行一次修改或补齐。**

向自然科学基金委补交申请书纸质签字盖章页、提交和报送计划书截止时间节点如下：

1. **2020年10月14日16点：**提交电子版计划书的截止时间（视为计划书正式提交时间）；
2. **2020年10月21日16点：**提交电子修改版计划书的截止时间；
3. **2020年10月28日16点：**报送纸质版计划书（其中一份包含申请书纸质签字盖章页）的截止时间。
4. **2020年11月18日16点：**报送修改后的申请书纸质签字盖章页的截止时间。

项目代码 3090041910073

SGTYHT/18-JS-206　科学技术项目合同
合同编号：SGGR0000WLJS1900858

2019209412070

# 科学技术项目合同

合同编号（甲方）：

合同编号（乙方）：

项目名称：一种表面活性剂电化学原位诱导构筑高安全性、长循环锂金属负极材料制备方法

委托方（甲方）：　全球能源互联网研究院有限公司

受托方（乙方）：北京理工大学

签订日期：　　　2019-11-18

签订地点：　北京

# 项 目 简 表

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|---|---|---|---|---|---|---|---|
| 项目名称 | 一种表面活性剂电化学原位诱导构筑高安全性、长循环锂金属负极材料制备方法 | | | | | | |
| 项目负责人 | 姓名 | 王欣然 | 单 位 | 北京理工大学 | | | |
| | 性别 | 男 | 出生<br>1986 年<br>4 月 | 专业 | 化学工艺 | 职 称 | 副研究员 |
| 项目分类 | 技术攻关 | 新技术开发 | 新产品试制 | 技术引进消化吸收 | 应用理论基础研究 | 软科学研究 | 推 广 |
| | | | | | √ | | |
| 项 目 组 人 数 | 10 | 其中 | 高级职称 | 6 | 中级职称 | 1 | |
| | | | 初级职称 | 0 | 研究生 | 3 | |
| 研究开始时间 | 合同签订之日 | 研究成果提交时间 | 2020 年 8 月 | | | | |
| 合 同 总 金 额(万元) | 26.4 | 其中乙方自筹(万元) | 0 | | | | |
| 项目研究成果和最终成果摘要 | [项目内容摘要]<br>锂金属是实现高比能电池的理想负极材料，具有巨大的应用前景。其具有超高的比容量（3860 mAh g$^{-1}$），最低的电化学氧化还原电势（-3.04 V 相对标准电极），被视为锂电池负极材料中的“圣杯”。与金属锂相关的锂-硫电池、锂-氧电池，已突破了现有锂离子电池的能量密度瓶颈，实现单体电池 400 瓦时/公斤的阶段性目标。而超薄金属锂与富锂锰基、高镍三元正极搭配，也有望实现电池比能量的跨越式提高。然而，受制于锂金属沉积过程中的不规则枝晶生长、反复体积膨胀以及锂金属与电解液的不可逆反应，锂金属负极在循环过程中会形成极不稳定的电极-电解液界面，造成电解液干涸、界面钝化膜破裂等不利因素，快速损耗电池容量、增加电池内阻，诱发电池内短路、热失控、燃爆等 | | | | | | |