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Ether-based electrolytes for sodium ion batteries

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Sodium-ion batteries (SIBs) are considered to be strong candidates for large-scale energy storage with the benefits of cost-effectiveness and sodium abundance. Reliable electrolytes, as ionic conductors that regulate the electrochemical reaction behavior and the nature of the interface and electrode, are indispensable in the development of advanced SIBs with high Coulombic efficiency, stable cycling performance and high rate capability. Conventional carbonate-based electrolytes encounter numerous obstacles for their wide application in SIBs due to the formation of a dissolvable, continuous-thickening solid electrolyte interface (SEI) layer and inferior stability with electrodes. Comparatively, ether-based electrolytes (EBEs) are emerging in the secondary battery field with fascinating properties to improve the performance of batteries, especially SIBs. Their stable solvation structure enables highly reversible solvent-co-intercalation reactions and the formation of a thin and stable SEI. However, although EBEs can provide more stable cycling and rapid sodiation kinetics in electrodes, benefitting from their favorable electrolyte/electrode interactions such as chemical compatibility and good wettability, their special chemistry is still being investigated and puzzling. In this review, we provide a thorough and comprehensive overview on the developmental history, fundamental characteristics, superiorities and mechanisms of EBEs, together with their advances in other battery systems. Notably, the relation among electrolyte science, interfacial chemistry and electrochemical performance is highlighted, which is of great significance for the in-depth understanding of battery chemistry. Finally, future perspectives and potential directions are proposed to navigate the design and optimization of electrolytes and electrolyte/electrode interfaces for advanced batteries.

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1. Introduction

Clean and renewable energy has intensively penetrated the energy market to reduce the dependence on fossil energy and meet the requirements of high energy efficiency and environmental protection. However, among the available clean


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Unraveling Anionic Redox for Sodium Layered Oxide Cathodes: Breakthroughs and Perspectives

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Sodium-ion batteries (SIBs) as the next generation of sustainable energy technologies have received widespread investigations for large-scale energy storage systems (EESs) and smart grids due to the huge natural abundance and low cost of sodium. Although the great efforts are made in exploring layered transition metal oxide cathode for SIBs, their performances have reached the bottleneck for further practical application. Nowadays, anionic redox in layered transition metal oxides has emerged as a new paradigm to increase the energy density of rechargeable batteries. Based on this point, in this review, the development history of anionic redox reaction is attempted to systematically summarize and provide an in-depth discussion on the anionic redox mechanism. Particularly, the major challenges of anionic redox and the corresponding available strategies toward triggering and stabilizing anionic redox are proposed. Subsequently, several types of sodium layered oxide cathodes are classified and comparatively discussed according to Na-rich or Na-deficient materials. A large amount of progressive characterization techniques of anionic oxygen redox is also summarized. Finally, an overview of the existing prospective and the future development directions of sodium layered transition oxide with anionic redox reaction are analyzed and suggested.

have been taken to develop satisfactory electrode materials to achieve high-energy and commercialized SIBs. The appraisal of the associated costs of different components has shown that cathode materials account for the highest cost proportion of 32.4%.^[5,6] Cathodes are critical factors determining the electrochemical performance of SIBs. Therefore, the development of suitable cathode materials is essential for commercial application of SIBs. The investigated cathode materials include layered transition metal oxides,^[7,8] polyanion compounds,^[9–12] Prussian blue analogues^[13,14] and organic salts.^[15] Among them, layered transition metal oxides are the most promising candidates due to their appropriate operational potentials, 2D Na⁺ diffusion channels, and the scalable and simple synthesis. Sodium-based layered materials can be categorised into four main groups of P2-type, P3-type, O2-type, and O3-type on the basis of oxygen stacking ordering and occupation

1. Introduction

To satisfy the ever-increasing requirements of large-scale electrochemical energy storage for electronics, electric vehicles, and smart grid, rechargeable batteries have received considerable attention as high-energy-density storage systems. Among various rechargeable batteries, sodium-ion batteries (SIBs) are regarded as the most promising alternative systems for grid-scale storage applications due to their low cost and large and evenly distributed contents of sodium as well as availability of an Al foil as a current collector of both negative and positive electrodes in them.^[1–4] In the past few years, substantial efforts

sites of Na ions, which was first described by Delmas and co-workers.^[16,17] The letters “P” and “O” indicate the prismatic and octahedral coordination environment of Na ions, respectively, and the numbers 2 and 3 represent the number of transition metal layers in the repeated unit of stacking. **Figure 1a** illustrates the crystal structures. The P-type structure shows a better cycling stability and rate capabilities than the O-type structure due to its integrated structure and relatively lower diffusion barrier. Na ions can directly diffuse between two face-sharing trigonal prismatic sites. By contrast, O-type structures offer a high capacity due to their high initial Na content.

Since the commercialization by Sony Company in 1991, rechargeable lithium-ion batteries (LIBs) have achieved considerable success in various applications of portable electronics and electric vehicles. For SIBs, further achieving the large-scale application is difficult because of a low specific capacity of traditional layered oxide cathode materials, which mainly depends on the charge compensation of cationic redox reaction, such as O3-Na_{0.9}Cu_{0.22}Fe_{0.3}Mn_{0.48}O₂ (100 mAh g⁻¹),^[18] P2-Na_{2/3}Fe_{1/2}Mn_{1/2}O₂ (134 mAh g⁻¹),^[19] O3-NaFeO₂ (120 mAh g⁻¹).^[20] Consequently, the practical performance of layered transition metal oxide materials is quite limited. To promote the practical application of SIBs, their energy density and power density must be urgently improved. Recently, increasing studies have focused on electrochemical performance of layered oxide cathodes on the basis of anionic redox reactions,

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Interfacial-Catalysis-Enabled Layered and Inorganic-Rich SEI on Hard Carbon Anodes in Ester Electrolytes for Sodium-Ion Batteries

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Constructing a homogenous and inorganic-rich solid electrolyte interface (SEI) can efficiently improve the overall sodium-storage performance of hard carbon (HC) anodes. However, the thick and heterogenous SEI derived from conventional ester electrolytes fails to meet the above requirements. Herein, an innovative interfacial catalysis mechanism is proposed to design a favorable SEI in ester electrolytes by reconstructing the surface functionality of HC, of which abundant C=O (carbonyl) bonds are accurately and homogeneously implanted. The C=O (carbonyl) bonds act as active centers that controllably catalyze the preferential reduction of salts and directionally guide SEI growth to form a homogenous, layered, and inorganic-rich SEI. Therefore, excessive solvent decomposition is suppressed, and the interfacial Na⁺ transfer and structural stability of SEI on HC anodes are greatly promoted, contributing to a comprehensive enhancement in sodium-storage performance. The optimal anodes exhibit an outstanding reversible capacity (379.6 mAh g⁻¹), an ultrahigh initial Coulombic efficiency (93.2%), a largely improved rate capability, and an extremely stable cycling performance with a capacity decay rate of 0.0018% for 10 000 cycles at 5 A g⁻¹. This work provides novel insights into smart regulation of interface chemistry to realize high-performance HC anodes for sodium storage.

low-cost and high-performance anode materials is essential.^[3] Hard carbon (HC) anodes are considered to be the most promising candidates due to their low cost and large specific capacity.^[4] However, HC anodes are still limited by low initial Coulombic efficiency (ICE), poor rate capability, and unsatisfactory cycling stability, which are key indicators for commercial SIBs.^[5] Numerous studies have shown that it is far from enough to improve the above-mentioned performances of HC anodes only by optimizing their intrinsic properties, such as heteroatomic doping or microstructure control.^[6,7] Notably, regulating HC/electrolyte interface chemistry through building a satisfactory solid electrolyte interface (SEI) is the core technology to improve performance of HC anodes.^[8,9] That is because the interfacial Na⁺-transfer kinetics and interfacial stability are highly influenced by the physicochemical properties of the SEI,^[10] which can directly determine SIB performance.^[10,11] Unfortunately, it is difficult for HC anodes to form good SEI in commercial ester electrolytes.


1. Introduction

Sodium-ion batteries (SIBs) have been regarded as a sustainable technology for large-scale energy storage and smart electric grid because of abundant resource and cost-effectiveness of Na.^[1,2] The development of preeminent SIBs is greatly dependent on advanced electrode materials, and thereinto, the construction of

As we all know, ester electrolytes have been commercialized due to their low cost, excellent stability, and high compatibility with high-voltage cathodes.^[12] However, ester-derived SEI (ester-SEI) is inhomogeneous with heterogeneous thickness due to serious electrolyte decomposition, which insufficiently protects HC anodes and fails to stabilize the HC/electrolyte interface, leading to undesirable ICE and cycling stability.^[8,13] In addition, the uneven inorganic-organic hybrid structure with dominant organics of ester-SEI further limits the interfacial Na⁺ transfer, resulting in poor rate capability.^[14] In contrast, ether-derived SEI (ether-SEI) is much thinner and more homogeneous, contributing to a better ICE.^[5,15] The inorganic species are dominant and compact in the inner layer of ether-SEI, while a small number of organic components are distributed in the outer layer, showing a layered structure,^[16,17] which is conducive for Na⁺ transfer and enhances the rate performance.^[14,18] The inorganic-rich structure with high mechanical strength can effectively protect HC anodes for stable cycling.^[19] However, due to the high production cost and the failure of matching high-voltage cathodes, the commercialization of ether electrolytes remains challenging.^[16]

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Multilevel Gradient-Ordered Silicon Anode with Unprecedented Sodium Storage

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While cost-effective sodium-ion batteries (SIBs) with crystalline silicon anodes promise high theoretical capacities, they perform poorly because silicon stores sodium ineffectively (capacity $<40 \text{ mAh g}^{-1}$). To address this issue, herein an atomic-order structural-design tactic is adopted for obtaining unique multilevel gradient-ordered silicon (MGO-Si) by simple electrochemical reconstruction. In situ-formed short-range-, medium-range-, and long-range-ordered structures construct a stable MGO-Si, which contributes to favorable Na–Si interaction and fast ion diffusion channels. These characteristics afford a high reversible capacity (352.7 mAh g^{-1} at 50 mA g^{-1}) and stable cycling performance (95.2% capacity retention after 4000 cycles), exhibiting record values among those reported for pure silicon electrodes. Sodium storage of MGO-Si involves an adsorption–intercalation mechanism, and a stepwise construction strategy of gradient-ordered structure further improves the specific capacity (339.5 mAh g^{-1} at 100 mA g^{-1}). Reconstructed Si/C composites show a high reversible capacity of 449.5 mAh g^{-1} , significantly better than most carbonaceous anodes. The universality of this design principle is demonstrated for other inert or low-capacity materials (micro-Si, SiO_2 , SiC, graphite, and TiO_2), boosting their capacities by 1.5–6 times that of pristine materials, thereby providing new solutions to facilitate sodium storage capability for better-performing battery designs.

1. Introduction

Sodium-ion batteries (SIBs), which are cost-effective and environmentally sustainable, are emerging in the grid-scale energy storage market.^[1–5] The remarkable promise of Na-based energy storage has placed significant emphasis on the development of high-performance electrode materials.^[6–8] In terms of anode

materials, while hard carbon is the most promising anode material for industrialization, its capacity is limited and presents a bottleneck for further development. Therefore, providing additional SIB-anode choices urgently requires the development of novel promising materials. Silicon, which has been widely used as an electrode in commercial lithium-ion batteries owing to its ultrahigh capacity and cost-effectiveness, also has a high theoretical capacity (954 mAh g^{-1}) for SIBs.^[9,10] Predictably, the use of Si-based SIBs will create new opportunities for the development of Na-based energy storage. Unfortunately, silicon delivers negligible experimental capacity ($<40 \text{ mAh g}^{-1}$) in SIBs. Hence, Si was considered electrochemically “inactive” for a long time because crystalline Si was regarded as unsuitable for alloying with Na atoms;^[11] this inactive nature of Si is believed to originate from positive binding energy of Na in bulk Si ($+0.6 \text{ eV}$),^[12] low thermodynamic driving force ($\approx 0.1 \text{ eV}$),^[13] and high diffusion barrier (3.12 eV in a Si nanosheet),^[14] which indicate that Na insertion into Si is energetically infeasible under

realistic battery operating conditions. Although some nanoengineering,^[15] carbon-coating,^[16] and porous-structure^[17] strategies promote Na^+ diffusion and storage, limited progress has been reported because such efforts still hardly solve intrinsically unfavorable Na–Si interactions and sluggish Na^+ diffusion in the Si lattice.

In essence, Na-storage chemistry is realized via interactions or electrochemical reactions involving Na^+ and the atoms of the host material. Therefore, the atomic structure and ordering of the host material greatly affect Na–host-material interactions, and consequently, the Na-storage performance. For instance, graphite, a long-range-ordered crystalline carbon material, was also considered inactive toward Na storage due to its small layer spacing and its inability to form stable binary Na–C compounds, such as NaC_6 and NaC_8 .^[18–21] By contrast, hard carbon, a short-range-ordered amorphous carbon material, realizes reversible Na storage through the mechanisms of Na intercalation into small short-range ordered graphitic layers, Na adsorption in defects, and Na filling in nanopores.^[22–24] Additionally, expanded graphite, which is more ordered than hard carbon, delivers a favorable Na-storage capacity because its large layer spacing

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Unlocking the local structure of hard carbon to grasp sodium-ion diffusion behavior for advanced sodium-ion batteries†

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Clarifying the microstructure of hard carbon is essential to reveal its sodium storage mechanism and to develop hard carbon negative electrodes for high-performance sodium ion batteries. Currently, although various sodium storage mechanisms for hard carbon models are proposed, they are still controversial. Besides, the puzzling and abnormal variation of a Na⁺ diffusion coefficient during the discharge process cannot be well explained. Inspired by amorphous alloys, we propose and confirm the dispersion region at the junction between amorphous structures and graphite microcrystals, which is closely related to the structure of graphite microcrystals. The special dispersion region plays a buffer role in the sodium ion diffusion process and provides satisfactory storage capacity. Therefore, the effect of synthesis conditions on the local structure in the dispersion region should be considered when designing hard carbon. In this work, a specific graphite microcrystalline structure of hard carbon is precisely synthesized by screening organic molecules, and the constraint relationship between the parameters of the graphite microcrystalline structure is revealed. Importantly, this work is of great significance for resolving the current controversy about the sodium storage mechanism and making clear the anomalies of sodium ion diffusion in the low-voltage interval (<0.1 V) in hard carbon.

Introduction

Sodium-ion batteries (SIBs) can provide effective support for lithium-ion batteries (LIBs) due to their low cost, long life, and high safety, whose rapid rise can alleviate the pressure brought by lithium resources, matching with the energy security and global sustainable development.^{1–4} Owing to the affordable

Broader context

Sodium-ion batteries (SIBs) have the characteristics of abundant resources, low-cost, environmental friendliness and high safety, so they are regarded as one of the most promising candidates for the next-generation large-scale energy storage systems. Improving the capacity and lifespan of hard carbon (HC), one of the core anode materials of SIBs, is the key to realize the commercialization of SIBs. Unfortunately, the microstructure of HC designed for this purpose has been poorly reported and investigated, which limits the practical applications of SIBs. In this manuscript, we comprehensively and systematically analyze the reasons for the phenomenon that the diffusion coefficient of sodium ions remains stable, then decreases sharply and recovers rapidly during the discharge process. Additionally, the influence of the 'dispersion region' structure on the diffusion coefficient of sodium ions and its sodium storage mechanism is proposed and analyzed. This article can provide guidance for the design and future development of high-performance HC microstructures, and is of great reference significance for analyzing and understanding the electrochemical reaction kinetics of the whole energy storage system.

cost and satisfactory reversible capacity, hard carbons (HCs) as the preferred anode material for SIBs have become the focus of research.^{5,6} HCs are composed of amorphous carbon and graphene nanosheets with obvious turbostratic disorder and curvature.^{7,8} Based on the typical HC models, a series of sodium storage mechanisms, such as intercalation–adsorption,⁹ adsorption–intercalation,^{10–13} adsorption–pore filling,¹⁴ and adsorption–insertion–pore filling,^{15,16} have been successively proposed with the goal of revealing the relationship between the local microstructure and sodium-ion storage behaviors. However, there is a lack of unified understanding of the relationship between the microstructure and the diffusion behavior of sodium in different potential intervals of the HC anode, especially in the low-voltage plateau regions.^{17–19}

Numerous studies have demonstrated that with the increase of discharge depth, the diffusion trend of sodium ions exhibits three stages.^{20–25} As shown in Fig. 1, during the whole discharge process, the sodium ion diffusion coefficient can be divided into

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Engineering homotype heterojunctions in hard carbon to induce stable solid electrolyte interfaces for sodium-ion batteries

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Abstract

Developing effective strategies to improve the initial Coulombic efficiency (ICE) and cycling stability of hard carbon (HC) anodes for sodium-ion batteries is the key to promoting the commercial application of HC. In this paper, homotype heterojunctions are designed on HC to induce the generation of stable solid electrolyte interfaces, which can effectively increase the ICE of HC from 64.7% to 81.1%. The results show that using a simple surface engineering strategy to construct a homotypic amorphous Al₂O₃ layer on the HC could shield the active sites, and further inhibit electrolyte decomposition and side effects occurrence. Particularly, due to the suppression of continuous decomposition of NaPF₆ in ester-based electrolytes, the accumulation of NaF could be reduced, leading to the formation of thinner and denser solid electrolyte interface films and a decrease in the interface resistance. The HC anode can not only improve the ICE but elevate its sodium storage performance based on this homotype heterojunction composed of HC and Al₂O₃. The optimized HC anode exhibits an outstanding reversible capacity of 321.5 mAh g⁻¹ at 50 mA g⁻¹. The cycling stability is also improved effectively, and the capacity retention rate is 86.9% after 2000 cycles at 1 A g⁻¹ while that of the untreated HC is only 52.6%. More importantly, the improved sodium storage behaviors are explained by electrochemical kinetic analysis.



KEYWORDS

hard carbon anodes, homotype heterojunctions, sodium-ion batteries, solid electrolyte interface, surface engineering

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Carbon-based interface engineering and architecture design for high-performance lithium metal anodes

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Abstract

Metallic lithium (Li) is considered the “Holy Grail” anode material for the next-generation of Li batteries with high energy density owing to the extraordinary theoretical specific capacity and the lowest negative electrochemical potential. However, owing to inhomogeneous Li-ion flux, Li anodes undergo uncontrollable Li deposition, leading to limited power output and practical applications. Carbon materials and their composites with controllable structures and properties have received extensive attention to guide the homogeneous growth of Li to achieve high-performance Li anodes. In this review, the correlation between the behavior of Li anode and the properties of carbon materials is proposed. Subsequently, we review emerging strategies for rationally designing high-performance Li anodes with carbon materials, including interface engineering (stabilizing solid electrolyte interphase layer and other functionalized interfacial layer) and architecture design of host carbon (constructing three-dimension structure, preparing hollow structure, introducing lithiophilic sites, optimizing geometric effects, and compositing with Li). Based on the insights, some prospects on critical challenges and possible future research directions in this field are concluded. It is anticipated that further innovative works on the fundamental chemistry and theoretical research of Li anodes are needed.

KEYWORDS

carbon materials, dendrites, hosts, interfacial layers, Li metal anodes

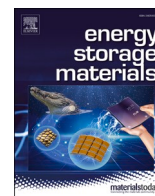
1 | INTRODUCTION

Extensive investigation on the energy storage technologies for sustainable energy sources (solar, tidal, and wind energy) is on the way in pursuit of carbon neutrality. Among the possible candidates, lithium-ion batteries (LIBs) have achieved the best compromise between energy density, service life, efficiency, and cost.^{1–5} However,

LIBs face severe limitations due to their complex chemistry, preventing them from fulfilling the constantly increasing energy density requirements, so the race for new batteries beyond LIBs has already begun. Metallic lithium (Li) exhibits the lowest reduction potential of -3.04 V versus standard hydrogen electrode and a very high theoretical specific capacity of 3860 mAh g^{-1} , enabling a higher energy density than commercial LIBs

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Unveiling the role of multifunctional framework for high-energy P2-Na_{0.8}Li_{0.12}Ni_{0.22}Mn_{0.66}O₂ cathode materials

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ABSTRACT

Enhancing the interfacial stability between cathode active material and liquid/solid electrolyte is a vital step toward the development of high energy density sodium-ion batteries (SIBs). One of the challenges plaguing this field is an economical and feasible method to construct valid protective layers on cathode materials. Herein, an effective strategy based on synergetic effect of multifunctional framework by simultaneous surface NaTi₂(PO₄)₃ (NTP) coating and bulk Ti⁴⁺ doping is designed to improve the performance of P2-Na_{0.8}Li_{0.12}Ni_{0.22}Mn_{0.66}O₂ (NLNM@NTP). The combined analysis of *in-situ* X-ray diffraction (*in-situ* XRD), scanning transmission electron microscopy (STEM) and density functional theory (DFT) calculations demonstrates that the multifunctional framework optimizes the lattice structure, improves the Ni oxidation states and enhances the stability of crystal and interfacial structure. NLNM@NTP cathode displays high average discharge potential and fast diffusion of Na-ions and electrons. As a result, the NLNM@NTP cathode reveals highly Na storage performance in both liquid-state and solid-state SIBs. The excellent capacity retentions after 500 cycles at 5 C in liquid-state batteries and after 100 cycles at 1 C in solid-state batteries are both close to 100%.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been considered as the dominating energy storage technology and gained great success of consumer devices[1–4]. However, there still remains an increasing requirement for more sustainable and cost-effective energy storage system for smart electric grid and large-scale storage. As complementary candidates to LIBs, sodium-ion batteries (SIBs) have been supposed as a prospective candidate for the next-generation battery system due to the abundance of Na element on the earth, wide distribution, and low cost [5–8]. The battery performance and the expenditure are principally dominated by the selected cathode materials. Among various sodium storage cathode materials, including layered oxides[9–11], polyanion compounds[12–14], and prussian blue analogues[15], layered transition metal oxides (Na_xTMO₂, TM: transition metal) have been widely investigated as attractive cathode materials owing to their suitable operating voltages, 2D Na⁺ diffusion paths, abundant resources and simple synthesis[16,17]. Na-based layered transition metal oxide cathode materials can be classified into four groups of P2, O2, P3, and

O3-types in terms of oxygen alignment around the Na-ions and the stacking of the transition metal oxide layers. The letters “P” and “O” represent the prismatic (P) and octahedral (O) coordination environment of Na⁺, respectively. The numbers 2 and 3 indicate the number of TM layers in the repeated unit of stacking[18].

P2-type Mn-based layered oxides have attracted much attention as cathode materials for SIBs, owing to their open prismatic channel and direct Na⁺ diffusion paths[18–20]. Nevertheless, it should be noted that P2-phase Mn-based materials usually exhibit significant volumetric variations and lattice distortions upon Na⁺ extraction/insertion, leading to deteriorative crystal structure and rapid capacity decay[21]. Furthermore, the attenuation of electrochemical performances is also caused by unstable interfaces[22]. The detrimental side reactions between cathode materials and electrolyte tend to destroy the integrity of cathode/electrolyte interface (CEI), causing the exfoliation of active material, impeding the diffusion of Na-ions and electrons. In response to these problems, many approaches have been provided to enhance the structural and interfacial stability of the electrode. For example, element substituting is an effect strategy to inhibit phase transformation and

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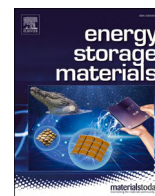
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Pursuing high voltage and long lifespan for low-cost Al-based rechargeable batteries: Dual-ion design and prospects

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ABSTRACT

Aluminum (Al) is the most abundant metal element in Earth's crust. Al-based rechargeable batteries have aroused booming attention by virtue of high theoretical capacity and low cost, while detrimental shortages such as lower voltage and inferior lifespan limit their practical application. Regarded as a promising opportunity to tackle this issue, Al-based rechargeable batteries are redesigned for dual-ion configuration with the aid of anion-inserting cathode, which is called Al-based dual-ion batteries (ADIBs). In this review, in-depth insights into ADIBs are comprehensively established, including basic merits, fundamental mechanisms and underlying challenges. Moreover, diverse strategies for advanced cathode, electrolyte and Al metal anode in ADIBs are also outlined. Afterwards, the pivotal perspective towards future development of ADIBs are discussed in detail.

1. Introduction

To achieve sustainable development of modern society, it is essential to overcome the environmental and energy problems caused by the uncontrolled combustion of fossil fuels. Renewable energies such as solar, wind and tide can provide solutions to these issues, turning into the main driving force for the development of energy storage technology. In recent years, as a new large-scale energy storage technology, lithium-ion batteries (LIBs) have rapidly occupied the market of portable consumer electronics, electric vehicles and stationary energy storage devices because of their advantages of high energy density and long cycle life. However, with the increasing demand for large-scale energy storage, the supply of lithium will face a potentially huge challenge due to the limited reserves of lithium in the Earth's crust. In addition, the application of cobalt in cathode materials is also troubled by the problem of metal resources [1]. Therefore, it is necessary to develop alternative battery technologies employing more abundant elements [2,3]. To this end, researchers have developed multiple next-generation secondary batteries, such as monovalent sodium/potassium ion batteries, divalent magnesium/calcium/zinc ion batteries, and trivalent aluminum ion batteries (AIBs) [4–13].

Aluminum (Al) was discovered by a German chemist, Andreas Marggraf, in 1750s for the first time, possessing the electron configura-

tion of $1s^2 2s^2 2p^6 3s^2 3p^1$, and it crystallize in the space group $Fm\bar{3}m$. Within crystalline structure, the free movement of three valence electrons seems unaffected by the existence of metal ions, producing a high electrical conductivity of $3.8 \times 10^7 \text{ S m}^{-1}$, a value that reaches about 65% of copper. It endows aluminum with great application potential in the field of batteries [14]. Pure Al can be prepared from minerals or scrap recycling process. For example, 1 kg of Al can be produced from 4 kg of bauxite mineral. Compared with lithium, the concentration of Al in raw materials is more than two orders of magnitude higher than that of lithium. Additionally, the building-up of Al recycling infrastructure dramatically decrease the energy consumption, which contributes to 35% of the Al supply. Benefiting from abundant reserves in Earth's crust, mature industry and recycling infrastructure, the Al metal is priced at just 1.9 USD kg^{-1} , about one tenth of lithium metal. Furthermore, the Resource Risk Index (RRI) was put forward by the Cologne Institute for Economic Research, aiming for the assessment of natural resource supply risks. There are 45 elements divided into three classes of criticality with: critical, less critical and not critical. As one of the raw materials for LIBs cathode, Co is considered critical, while Al are slightly less critical than Li [15]. In addition, unlike Li and Na, Al appears to be highly stable upon exposure to air and water, which avoids manufacture inconvenience. Therefore, Al possesses great potential to be used in rechargeable batteries, with the aid of its low cost and good availability, paving the

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Advances in free-standing electrodes for sodium ion batteries

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Sodium-ion batteries (SIBs) have recently reemerged as a promising technology in the fields of large-scale energy storage systems and low-speed electric vehicles, owing to the abundance and even distribution of sodium resources. Moreover, the similarity in working principles between SIBs and lithium-ion batteries (LIBs) further accelerates their development. However, the development of SIBs still faces challenges, such as the limited availability of electrode materials that demonstrate both satisfactory cycling stability and high-rate performance. Typically, common electrodes utilize specific binders to integrate the active materials with conductive additives. Unfortunately, frequently used binders are often dielectric and mechanically unstable, leading to a decrease in specific capacity and poor cycling stability. In addition, strongly electronegative groups within binders can irreversibly capture Na⁺ ions, resulting in an increase in irreversible capacity. Therefore, the use of binder-free, free-standing electrodes is crucial for the development of high-performance SIBs due to their enhanced electronic conductivity and reversible electrochemical reactions. This review provides a comprehensive overview of the recent advancements in free-standing electrodes for SIBs and flexible SIBs. It examines the challenges specific to free-standing electrodes and flexible SIBs and proposes effective strategies to overcome these obstacles. By addressing these challenges, this review aims to stimulate significant progress in the development of flexible energy storage devices, fostering their extensive utilization across diverse applications.

Keywords: Free-standing electrodes; Limitations; Optimizations; Practical applications; Sodium-ion batteries

Introduction

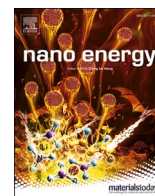
Since the successful commercialization of lithium-ion batteries by Sony in 1991, these batteries have found extensive applications across various domains of our daily lives [1]. However, the increasing demand for lithium resources has led to a significant rise in the cost of LIBs. To address the growing need for

energy storage and power systems, researchers have been exploring various rechargeable battery systems [2–5]. SIBs have gained substantial attention among these alternatives due to their similar physical properties to lithium and the abundance of sodium resources [6–13]. However, the larger ionic radius of sodium ions (Na⁺) compared to lithium ions (Li⁺) generally results in slower dynamics and shorter cycle lifespans [14,15]. To overcome these challenges, extensive research efforts have been dedicated to exploring strategies such as chemical composition modifications [16,17], surface modifications [18,19], structural adjustments

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Impurity-vibrational entropy enables quasi-zero-strain layered oxide cathodes for high-voltage sodium-ion batteries

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ABSTRACT

Layered transition metal oxides based on cationic/anionic redox have gained much attention for high-energy-density sodium ion batteries (SIBs). However, irreversible oxygen activity and unstable crystal structure lead to fast capacity fading and undesired rate performance, limiting its large-scale commercial application. Based on the solid-state physics theory, here we demonstrate that the electrochemical capability in P2-type $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ cathode can be significantly improved when impurity-vibrational entropy is increased by simultaneously constructing surface ZrO_2 coating and Zr^{4+} doping (P2-NaNM@Zr). *In-situ* and *ex-situ* X-ray diffraction (XRD) verifies that quasi-zero-strain P2-NaNM@Zr cathode maintains P2 phase structure during the charging/discharging process, achieving an ultra-low volume change (1.18%) upon Na^+ entire extraction at a high cut-off voltage of 4.5 V. Besides, according to First-principles calculations, we first investigate that the oxygen vacancy formation energy of P2-NaNM@Zr (−2.11 eV) is higher than that of sample P2-NaNM (−2.61 eV), strongly indicating stable and reversible anionic redox reaction. As a result, P2-NaNM@Zr material reveals highly Na storage performance, retaining 86% capacity retention after 1000 cycles at the rate of 5 C within the voltage range of 2.5 – 4.0 V, delivering reversible capacity of 132 mA h g^{-1} after 50 cycles within 2.0 – 4.5 V.

1. Introduction

Considered the low cost and high abundance of sodium, sodium ion batteries (SIBs) have drawn considerable attention as a promising technology for large-scale energy storage [1–5]. An estimation of the relative costs of SIBs shows that the cathode materials are the highest proportion (32.4%) [6–8]. Therefore, development of cathode materials with high density energy and stable electrochemical performance is a crucial factor to accelerate commercial application of SIBs. Among various sodium storage cathodes, layered oxides have aroused much interest over recent years owing to their variety of compositions, high specific capacity, environmental benignity, high ionic conductivity and feasible synthesis [9]. Generally, the sodium-based layered oxide materials based on the occupation sites of sodium ions and oxygen stacking ordering could be classified into four main groups: P2-type, P3-type, O2-type and O3-type. The letters “P” and “O” suggest prismatic and

octahedral coordination environment of Na ions respectively, and the numbers “2” and “3” represent the number of transition metal layers in each repeated unit [10]. It is widely accepted that P2-structure sodium intercalated oxides show superior electrochemical behaviours than the O3-featured ones due to their wide prismatic paths within TMO_2 slabs and direct Na-ion diffusion.

P2-type $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ material as a layered sodium manganese oxide has been extensively studied for SIBs due to the high discharge capacity of 173 mAh g^{-1} based on cationic and anionic redox, high operating voltage (i.e., ~3.8 V), reversibly extract all of sodium ions and ambient atmosphere [11]. However, severe capacity fade and undesirable rate performance especially at the voltage of 2.0 – 4.5 V limit its high energy density. One of the main reasons is that P2-type $\text{Na}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ usually undergoes undesired P2-O2 phase transformation and large volume change during the charging process, which leads to exfoliated materials and impedes the electrons/ions transfer [12].

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Metal Selenides Anode Materials for Sodium Ion Batteries: Synthesis, Modification, and Application

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The powerful and rapid development of lithium-ion batteries (LIBs) in secondary batteries field makes lithium resources in short supply, leading to rising battery costs. Under the circumstances, sodium-ion batteries (SIBs) with low cost, inexhaustible sodium reserves, and analogous work principle to LIBs, have evolved as one of the most anticipated candidates for large-scale energy storage devices. Thereinto, the applicable electrode is a core element for the smooth development of SIBs. Among various anode materials, metal selenides (MSe_x) with relatively high theoretical capacity and unique structures have aroused extensive interest. Regrettably, MSe_x suffers from large volume expansion and unwished side reactions, which result in poor electrochemistry performance. Thus, strategies such as carbon modification, structural design, voltage control as well as electrolyte and binder optimization are adopted to alleviate these issues. In this review, the synthesis methods and main reaction mechanisms of MSe_x are systematically summarized. Meanwhile, the major challenges of MSe_x and the corresponding available strategies are proposed. Furthermore, the recent research progress on layered and nonlayered MSe_x for application in SIBs is presented and discussed in detail. Finally, the future development focuses of MSe_x in the field of rechargeable ion batteries are highlighted.

1. Introduction


The vigorous development of smart grid, new-energy automobile industry, and consumer electronics devices has put forward higher requirements for rechargeable batteries.^[1] Lithium-ion batteries (LIBs) have attracted extensive research interest worldwide since they have been first commercialized in 1991.^[2] By virtue of their high energy density, robust security, and long cycle lifespan, LIBs vigorously expand into newly emerging application fields.^[3] However, the less and uneven distribution of lithium resources makes it challenging to sustainably satisfy

demands for large-scale energy storage systems.^[4] To mitigate the situation, developing an alternative rechargeable battery system has attracted broad attention. Among many candidates, sodium-ion batteries (SIBs) stand out with abundant sources, appropriate redox potential, and low cost, and have been considered as the better substitutions for LIBs and the key technology with great potential for large-scale energy storage.^[4c–7] As shown in Figure 1a, SIBs work in an analogous principle to LIBs, which are also “rocking chair” batteries.^[8] Therefore, the significant progress have made in LIBs could strongly support the development of SIBs. Besides, cheaper, lighter, and more abundant aluminum (Al) foil can be used as the current collector for SIBs, while copper (Cu) is the only choice for LIBs, meaning that SIBs have lower cost and greater commercial potential. Although there are many attractive advantages, SIBs also face many formidable challenges. The ionic radius (1.02 Å for Na^+ , 0.76 Å for Li^+) and molar mass (22.99 g mol⁻¹ for Na,

6.94 g mol⁻¹ for Li) of Na are larger than those of Li, which is not conducive to Na^+ diffusion kinetics and structural stability of electrode materials during sodiation/desodiation processes (Figure 1b).^[9] Unfortunately, it means that most of the conventional electrode materials for LIBs cannot be committed to SIBs. Thus, the critical technology for the development of SIBs lies in the exploitation of electrode materials with satisfactory electrochemical performances.^[5c,10,11]

The investigations of SIBs cathode materials have achieved encouraging progresses, including layered materials,^[5b,12] polyanionic compounds,^[9,13] and Prussian blue analogs.^[14] However, the development of anode materials with low electrochemical reaction platform, relatively high reversible capacity, and stable structure is still insufficient. Until now, common anode materials for SIBs include carbonaceous materials,^[1–19] titanium materials,^[10e,20] alloy materials,^[21] metal oxides/sulfides/selenides,^[13,22] and organic materials,^[23] etc. In terms of reaction mechanisms, these materials can be assigned to three main types: intercalation-, conversion- and alloying-type anodes.^[23] Specifically, carbonaceous materials and Ti-based materials are the most widely studied intercalation-type anode materials for SIBs.^[24] Graphite with stable electrochemical performance has developed into the most common commercial anode material for LIBs. However, theoretical calculations

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RESEARCH ARTICLE

Construct NiSe/NiO Heterostructures on NiSe Anode to Induce Fast Kinetics for Sodium-Ion Batteries

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It is of great significance to design and innovate electrode materials with unique structures to effectively optimize the electrochemical properties of the secondary battery. Herein, inspired by neuron networks, an ingenious synthesis is proposed to fabricate NiSe with multidimensional micro-nano structures, followed by in situ construction of NiSe/NiO heterostructures via a temporary calcination. The major structure of bulk NiSe synthesized by the solvothermal method is 3-dimensional micron cluster spherical particles interwoven by uniform one-dimensional nanofibers. Such structures possess the synergistic advantages of nano and micro materials. After a temporary calcination in air, NiSe/NiO heterostructures should be formed in the bulk NiSe, which provides a built-in electric field to enhance diffusion kinetics of sodium ions. This special neural-like network and heterojunction structures ensure the excellent structural stability combined with rapid kinetics of the electrode, releasing 310.9 mAh g⁻¹ reversible capacity after 2,000 cycles at 10 A g⁻¹. Furthermore, the electrochemical storage and ion transport mechanisms are elaborated by electrochemical analysis and theoretical calculation in more detail.

Introduction

With the rapid development of electric vehicles and large-scale electricity grids, high-performance and low-cost energy storage devices have become particularly substantial [1]. Lithium-ion batteries (LIBs) are currently the most widely commercialized battery systems [2]. However, limited by scarce lithium resources, high raw material costs, and frequent safety issues, the large-scale energy storage industry is supposed to develop a lower-cost technology to replace LIBs [3]. Sodium-ion batteries (SIBs) are considered to be an ideal choice in the field of large-scale energy storage due to their abundant resources and cheaper price [4,5]. Nevertheless, compared with Li⁺, the larger size of Na⁺ impairs reversibility and cycling performance, leading to tardy reaction kinetics of SIBs [6,7]. Therefore, it is undoubtedly of great significance to seek high-performance sodium storage electrode materials, and further modify them to improve the sodium ion diffusion in the materials.

Recently, transition metal chalcogenides (TMCs) have been successfully used as anode materials for SIBs [8]. Among them, metal sulfides (MS_x) exhibit excellent electrochemical performances [9], while relatively few studies have been focused on metal selenide (MSe_x). It is found that MSe_x perform better than MS_x in several fields due to their narrower band gaps and better electronic conductivity [10]. However, owing to the basically similar reaction mechanism with MS_x in the battery, Se of the MSe_x electrode inevitably dissolves in the electrolyte during the

reaction, resulting in the destruction of the material structure and the loss of active substances [6]. In addition, the sodium storage mechanism of the MSe_x is the conversion reaction, which causes a serious volume expansion of the electrode in the electrochemical cycle process, leading to the electrode breakage and substantial capacity decline [11]. To address these deficiencies, particle size changing [6], shape/interlayer spacing regulation [12], and fabrication of carbon material composites [13] have become commonly adopted approaches and the desirable effects of these measures have been realized. Wang et al. [14] prepared 3-dimensional porous carbon-coated FeSe₂ particles by the template-free calcination method, which delivered excellent cycling stability and a superior rate capability of 455 mAh g⁻¹ after 100 cycles at a current density of 0.1 A g⁻¹ due to the significantly shortened electron/ion transmission path by the 3-dimensional carbon skeleton. Chen et al. [15] embedded MoSe₂ nanosheets on the surface of Fe₇Se₈@C with a core-shell structure to prepare the Fe₇Se₈@C@MoSe₂ composite. MoSe₂ as a buffer layer can effectively alleviate the volume expansion of selenide during the cycle, so as to obtain a stable cycle performance. At the current density of 1 A g⁻¹, the capacity retention rate after 600 cycles is 87.1%.

It can be seen that the researches on MSe_x mainly focus on coating modification through conductive carbon. In fact, designing the particles with multidimensional micro-nano structures also exhibit the markedly improved stability of the electrode [16]. Firstly, nanoscale electrodes effectively shorten the diffusion path

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Metal Chalcogenides with Heterostructures for High-Performance Rechargeable Batteries

Yu Li, Feng Wu, Ji Qian, Minghao Zhang, Yanxian Yuan, Ying Bai,* and Chuan Wu*

Heterostructures exhibit intriguing and significant properties for functional material applications, such as photosensing devices, semiconductor materials, and supercapacitors. Rechargeable batteries as typical energy-storage devices have drawn widespread attention in the past several decades, on account of high energy density, being low-cost, and ecofriendly. Preparing superior active materials is the critical technology to ameliorate the electrochemical performance of batteries. In recent years, the concept of constructing heterostructures for the application of electrode materials has been considered as a promising design approach. Among all the electrode materials, metal chalcogenides (MCs) have presented excellent properties due to their high theoretical capacity based on multielectron reaction. Herein, the progress on MCs with heterostructures is summarized in terms of various material species and their specific application for several typical battery systems. Finally, possible challenges and comprehensive perspectives are given to provide an instructive direction for the thoughtful design strategies of heterostructures and the development of MCs for next-generations rechargeable batteries.

series of issues caused by the ever-growing demands for higher electrochemical performance and longer cycle life. As discussed, batteries' performances mainly depend on the active materials including cathodes and anodes.^[2] Researchers have made tremendous efforts to fabricate excellent active materials through various synthesis methods and ingenious processing technologies, like coating conductive materials,^[3] doping heteroatoms,^[4] designing specific morphologies (nanostructures,^[5] hollow structures,^[6] core-shell structures,^[7] hierarchical structures,^[8] etc.), etc. Therefore, constructing heterostructures composed of two or more different components has been recently emerged and widely studied, due to the fact that they may amalgamate the advantages of single components and even endow new functions to further improve their properties.^[9]

To further elevate the energy density of rechargeable battery systems, considerable

1. Introduction

The high-speed development of economy and the enhanced awareness of environmental protection are providing huge opportunities and challenges for the electrochemical energy storage (EES) field. Especially, rechargeable batteries as typical energy-storage devices have attracted much attentions in the past few decades, due to their superiorities like high energy density, being low-cost, and ecofriendly.^[1] Nevertheless, they must face a


attention has been paid to exploring active materials based on the chemistry of multielectron reactions, which are expected to provide a higher theoretical capacity. Among these multielectron reaction materials, metal chalcogenides (MCs) have become research hotspots and show great prospects for application due to their layer-dependent bandgap, which can offer excellent electronic and mechanical performance.^[10] MCs can be defined as a generalized abbreviation of MCs, where M is a metal atom (Fe, Co, W, Mo, Sn, and so on) and C is a chalcogen atom (S, Se, and Te). They usually have an open structure with a weak interlayer Van der Waals force and may contribute to fast intercalation/deintercalation for ions (Li^+ , Na^+).^[11] In addition, the electrochemical reaction mechanisms of MCs are mainly based on the conversion reaction or alloying reaction, which can achieve higher reversible capacity and make them more outstanding compared with other electrode active materials. However, the electrochemical performances of MC electrodes for batteries are still severely restricted by many problems, like their intrinsic electronic conductivity, extensive aggregation, and unstable bulk structure (terrible volume expansion) during the charge/discharge process.

In recent years, constructing MCs with heterostructures, namely, hybridization of MCs with other analogous functional materials, is becoming an interesting strategy to synthesize a new-type composite, which can solve the aforementioned limitations. Several published review articles mainly focused on the synthesis and application for various MCs. Until now, research

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Surficial modification enabling planar Al growth toward dendrite-free metal anodes for rechargeable aluminum batteries

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Al metal possesses ultrahigh theoretical volumetric capacity of 8,040 mAh cm⁻³, and gravimetric capacity of 2,980 mAh g⁻¹, and thus is highly attractive for electrochemical energy storage. However, it suffers from several issues, such as the dendrite formation, during Al stripping–deposition cycling, which has been verified to account for the short circuit and limited cyclic performance. Herein, we use a facile and applicable method to *in-situ* reconstruct the Al anode surface with F–Al–O chemical bonds, which could preferentially induce the planar growth of Al along the interface plane, thus leading to the dendrite-free morphology evolution during the cycling. Benefiting from F–Al–O chemical bonds on the surface of Al anodes, long lifespan of symmetric cells can be realized even under 1 mA cm⁻² and 1 mAh cm⁻². Coupling the F–Al anode with graphite-based cathodes, high-voltage dual-ion Al metal batteries can be achieved with long-term cycle stability up to 1,200 cycles (at 0.5 mA cm⁻²), surpassing the counterparts using pristine Al metal anode. Furthermore, the effectiveness of this surficial modification strategy is also elucidated with the aid of theoretical calculation. This work provides novel insights on low-cost and facile strategies against the Al dendrite growth in aluminum batteries.

rechargeable aluminum batteries, Al metal anode, Al dendrite, dual-ion batteries, surficial modification

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1 Introduction

Increasing research attention has been focused on next-generation rechargeable batteries to overcome the limitation of metal resources (*e.g.*, lithium, cobalt and nickel) used in lithium-ion batteries (LIBs) [1–3]. Multivalent metal batteries have been considered as potential alternatives, which is ascribed to their good metal availability, high theoretical capacity, low flammability and cost [4–7]. Serving as one of the most promising candidates among multivalent metal batteries, rechargeable aluminum batteries (RABs) are en-

dowed with various advantages including abundant Al source and high theoretical capacities [8–11]. With regard to Al metal anodes, ultrahigh theoretical volumetric capacity up to 8,048 mAh cm⁻³ and a competitive theoretical gravimetric capacity of 2,981 mAh g⁻¹ can be achieved [12–14]. Owing to the passivation effect of oxide layers on the Al metal surface, the stable Al stripping/plating is impeded in typical aqueous electrolytes [15–17]. Fortunately, ionic liquid electrolytes (*e.g.*, AlCl₃–1-ethyl-3-methylimidazolium chloride (EMIC)) ensure the reversible electrochemical deposition of Al metal at anodes, which further promotes the investigation on RABs [18–21]. Many efforts have been devoted to pursuing high-performance cathode materials for the improvement of energy density and cyclic lifespan in RABs [22–26].

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Sulfur Encapsulation and Sulfur Doping Synergistically Enhance Sodium Ion Storage in Microporous Carbon Anodes

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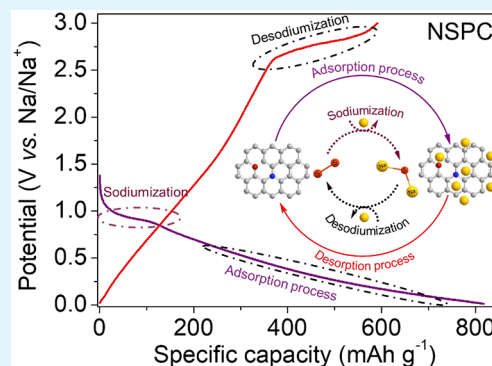
Article Recommendations



Supporting Information

ABSTRACT: MOF-based materials are a class of efficient precursors for the preparation of heteroatom-doped porous carbon materials that have been widely applied as anode materials for Na-ion batteries. Thereinto, sulfur is often introduced to increase defects and act as an active species to directly react with sodium ions. Although the sulfur introduction and high surface area can synergistically improve capacity and rate capability, the initial Coulombic efficiency (ICE) and electrical conductivity of carbon material are inevitably reduced. Therefore, balancing sodium storage capacity and ICE is still the bottleneck faced by adsorbent carbon materials. Here, sulfur-encapsulated microporous carbon material with nitrogen, sulfur dual-doping (NSPC) is synthesized by postprocessing, achieving the reduced specific surface area by encapsulating sulfur in micropores, and the increased active sites by edge sulfur doping. The synergy between encapsulation and sulfur doping effectively balances specific capacity, rate capability, and ICE. The NSPC material exhibits capacities of 591.5 and 244.2 mAh g⁻¹ at 0.5 and 10 A g⁻¹, respectively, and the ICE is as high as 72.3%. Moreover, the effect of nitrogen and sulfur on the improvement of electron/ion diffusion kinetics is resonantly demonstrated by density functional theory calculations. This synergistic preparation method may reveal a feasible thought for fabricating excellent-performance adsorption-type carbon materials for Na-ion batteries.

KEYWORDS: sodium ion batteries, microporous carbon anodes, sulfur encapsulation, sulfur doping, synergistically enhance, pseudocapacitive



INTRODUCTION

Over the past few years, sodium-ion batteries (SIBs) have received increasing attention in large-scale energy storage fields due to their advantages of abundant resources, high energy density, lower price, and environmental friendliness.^{1–5} Sodium ions have a larger ionic radius than lithium ions, and the graphite used for lithium batteries is difficult to apply in sodium batteries. Therefore, it is necessary to fabricate suitable electrodes with large interlayer spacing to intercalate and accommodate Na⁺. Benefitting from low cost, an appropriate working voltage platform, and high Coulombic efficiency, hard carbon materials have become the most popular anode materials.^{6–10} Unfortunately, hard carbon materials tend to have poor rate performance due to their inability to adequately accommodate Na⁺ with a large radius, making them fail to match the needs of fast charging/discharging in large-scale energy storage.^{11–14}

Current research has already proved that carbon materials with pseudocapacitive properties can store Na⁺ through the reversible adsorption process of Faraday capacitance.^{15–17} Rapid sodium storage of materials can be realized by pseudocapacitive characteristics, leading to materials with excellent rate performance that would meet the market of

fast charging and discharging.^{18–21} Notably, doping heteroatoms into carbon materials can not only effectively enhance the pseudocapacitance of the materials but also adjust the surface wettability and electronic conductivity, thereby promoting charge transfer and improving the interaction between electrodes and electrolytes. Up to now, various heteroatom-doped carbon-based anode materials have been extensively studied and applied in SIBs.^{22–24} The commonly used heteroatoms in carbon materials are nitrogen,²⁵ sulfur,^{21,26} oxygen,²⁷ phosphorus,^{28–30} and other elements.³¹ Since the covalent radius is similar to that of carbon, nitrogen can be doped to create more defects in carbon materials and increase electronic conductivity. Oxygen doping can effectively enhance the reversible adsorption and desorption of Na⁺ to increase the pseudocapacitance of carbon material.^{15,18,32} As for sulfur doping, it not only participates in the electrochemical

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Dual-Functionalized Ca Enables High Sodiation Kinetics for Hard Carbon in Sodium-Ion Batteries

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Supporting Information

ABSTRACT: Hard carbons (HCs), while a leading candidate for sodium-ion battery (SIB) anode materials, face challenges in their unfavorable sodiation kinetics since the intricate microstructure of HCs complicates the Na⁺ diffusion channel. Herein, a *Hovenia dulcis*-derived HC realizes a markedly enhanced high-rate performance in virtue of dual-functionalized Ca. The interlayer doped Ca²⁺ effectively enlarges the interlayer spacing, while the in situ-formed CaSe templates induce the formation of hierarchical pore structures and intrinsic defects, significantly providing fast Na⁺ diffusion channels and abundant active sites and thus enhancing the sodium storage kinetics. Achieved by the synergistic effect of regulation of intrinsic microcrystalline and pore structures, the optimized HC shows remarkable performance enhancements, including a high reversible capacity of 350.3 mA h g⁻¹ after 50 cycles at 50 mA g⁻¹, a high-capacity retention rate of 95.3% after 1000 cycles, and excellent rate performance (108.4 mA h g⁻¹ at 2 A g⁻¹). This work sheds light on valuable insight into the structural adjustment of high-rate HCs, facilitating the widespread utilization of SIBs.

KEYWORDS: sodium-ion batteries, hard carbon anodes, interlayer spacing regulation, pore engineering, sodiation kinetics



INTRODUCTION

Secondary batteries have earned great consideration to meet the escalating demand for energy storage technologies. Among these secondary batteries, lithium-ion batteries (LIBs) have gained prominence due to their remarkable energy density and cycle life. However, the constrained supply of lithium resources leads to its high cost, which hinders the widespread use of LIBs in large-scale energy storage systems (LSESS).^{1–3} Conversely, sodium-ion batteries (SIBs) serve as a promising alternative battery system to be applied in LSESS because of their abundant raw material reserves as well as low price.^{4,5} Unfortunately, suffering from the larger ionic radius of Na⁺ and weak interaction between Na⁺ and graphitic layers, traditional commercial graphite anodes fail to store Na⁺ reversibly in ester-based electrolytes.^{6–8} To enhance the reliability and broaden the applications, it is imperative to focus on the development of anode materials that combine cost-efficiency and high capacity for SIBs. Currently, carbon materials,^{9,10} metal oxides/sulfides,^{11–13} and alloying materials¹⁴ are developed as viable anode materials for SIBs. Among them, hard carbons (HCs) have gained significant attention as promising candidates for anode materials in SIBs due to abundant resources.¹⁵ More importantly, HCs are composed of typical nongraphitizable structures with randomly packed carbon layers, which possess large interlayer spacing to store Na⁺, contributing to the high reversible sodium storage capacity in HCs. However, the complicated microstructure of

HCs inevitably leads to the hindered Na⁺ diffusion channel, resulting in unsatisfying sodiation kinetics and an inferior rate performance.

To date, regulating the graphitic microcrystalline structure and pore structure is an effective approach to ameliorating the sodium storage kinetics of HCs. Tuning microcrystalline parameters, such as the length (L_a), thickness (L_c), and (002) interlayer spacing (d_{002}) of graphitic layers, can effectively facilitate Na⁺ transfer and increase the Na⁺ storage capacity, particularly in the low-voltage region.^{16–18} Optimizing carbonization temperature, introducing heteroatoms (e.g., N, S, and P)^{19–22} and metal ions (e.g., Ca²⁺, K⁺, and Mn²⁺)^{23,24} have been investigated to regulate the lattice spacing and graphitization level in HCs. Specifically, it is crucial to obtain a suitable d_{002} since large interlayer spacing causes low intercalation capacity, while a small one hinders Na⁺ insertion. Our group used K⁺-enriched biomass precursor to modulate the interlayer spacing of HCs to 0.40 nm, benefiting an impressive capacity of 314 mA h g⁻¹.²⁵ More recently, HCs with atomic Zn-doping in which zinc acetate

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Article

Constructing Robust Solid Electrolyte Interface via ZrO₂ Coating Layer for Hard Carbon Anode in Sodium-Ion Batteries

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Abstract: Hard carbon (HC) has attracted extensive attention due to its rich material source, environmental non-toxicity, superior sodium storage capacity, and lower sodium storage potential, and is considered most likely to be a commercial anode material for sodium-ion batteries (SIBs). Nevertheless, the limited initial Coulombic efficiency (ICE) of HC is the main bottleneck hindering its practical application. To alleviate this issue, herein, a ZrO₂ coating was skillfully constructed by using a facile liquid phase coating method. The ZrO₂ coating can act as a physical barrier to prevent direct contact between the HC surface and the electrolyte, thus effectively reducing irreversible sodium adsorption and inhibiting the continuous decomposition of the electrolyte. Meanwhile, this fresh interface can contribute to the generation of a thinner solid electrolyte interface (SEI) with high ionic conductivity. As a result, the ICE of the ZrO₂-coated HC electrode can be optimized up to 79.2% (64.4% for pristine HC). Furthermore, the ZrO₂-coated HC electrode delivers outstanding cyclic stability so that the capacity retention rate can reach 82.6% after 2000 cycles at 1 A g⁻¹ (55.8% for pristine HC). This work provides a flexible and versatile surface modification method to improve the electrochemical property of HC, and hopefully accelerate the practical application of HC anodes for SIBs.



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Keywords: sodium-ion battery; hard carbon anode; ZrO₂ coating; solid electrolyte interface

1. Introduction

Developing green and low-carbon renewable resources is an important strategy to achieve sustainable development. Increasing attention has been paid to the exploitation and utilization of clean renewable energy, such as solar energy, water energy, and wind energy. However, the output of these renewable resources is intermittent and particularly vulnerable to the effects of time, space, and seasonal climate changes, which can severely limit the stable operation of the electrical grids. To date, constructing various large-scale energy storage systems is an effective tactic to ameliorate this issue. Electrochemical energy storage, which mainly includes secondary battery technology, has attracted extensive attention due to its superiorities of flexibility and convenience, easy maintenance, high energy density, and reliable conversion efficiency [1]. Therefore, lithium-ion batteries (LIBs) have been widely applied to various portable electronic devices since their commercialization [2]. Especially in recent years, with the rapid development of the electric vehicle industry, the demand for LIBs has increased sharply. Nevertheless, the limited abundance in the earth's crust and uneven geographical distribution of lithium resources result in the increasing cost of LIBs year by year, hindering their further application in the field of energy storage [3]. In contrast, sodium-ion batteries (SIBs) have inexhaustible sodium resources and low cost, and their electrochemical reaction mechanisms are similar to those of LIBs [4,5]. Based on this, developing SIBs as an imperative alternative to LIBs has a positive significance for large-scale energy storage systems [6–10].

The high-performance anode materials are essential for the large-scale commercialization of SIBs. Although the graphite anode has been successfully commercialized in LIBs, its

Manipulating the corrosion homogeneity of aluminum anode toward long-life rechargeable aluminum battery

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Abstract

Aluminum metal batteries are considered to be promising secondary batteries due to their high theoretical specific capacity. However, metallic aluminum suffers from corrosion, pulverization, and crushing problems in nonaqueous electrolytes. Constructing a solid-electrolyte interphase layer on the anode electrode has been confirmed to be the key to improving the cycling performance of rechargeable batteries. Herein, we demonstrate an Al metal anode with a physical protective layer achieved by a simple blade coating method. This modified Al metal anode demonstrates ultra-low voltage hysteresis (~ 25 mV at 0.1 mA cm^{-2} and ~ 30 mV at 1 mA cm^{-2}), and superior stability (630 h at 0.1 mA cm^{-2} and 580 h at 1 mA cm^{-2}). When coupling this anode with flake graphite cathode, the assembled full cells exhibit superior cycling stability (92 mAh g^{-1} maintained after 740 cycles at 0.1 A g^{-1}). The current work presents a promising approach to stabilize Al metal anodes for next-generation rechargeable aluminum batteries.

KEYWORDS

Al metal anode, corrosion mechanism, graphite surface modification, rechargeable aluminum battery, stable long-cycle performance

1 | INTRODUCTION

The rapid development of renewable energy technology and electric vehicles has put forward higher requirements for energy storage systems. In particular, rechargeable batteries provide an efficient way to fulfill the growing need for energy conversion and storage.^[1–5] Hence, secondary batteries should be characterized by high energy density, safety, long cycle life, low cost, and environmental friendliness. Among them, Al-based energy storage systems could satisfy the abovementioned criteria due to their low cost, high gravimetric capacity

(2980 mAh g^{-1}) and high volumetric capacity (8040 mAh cm^{-3}).^[6] During the past few years, the research mainly focuses on cathode materials of rechargeable aluminum batteries (RABs) such as transition metal oxides,^[7,8] transition metal sulfide,^[9,10] carbon-based materials,^[11,12] and polymer materials.^[13–15] Compared with the heavily studied cathode materials, the high-stability anode electrode has not been studied deeply enough.

Currently, most researchers choose Al foil as the anode electrode for RABs due to its advantages of light weight, low cost, and good plasticity. However, in the system of ionic liquid electrolytes, Al foil will react with

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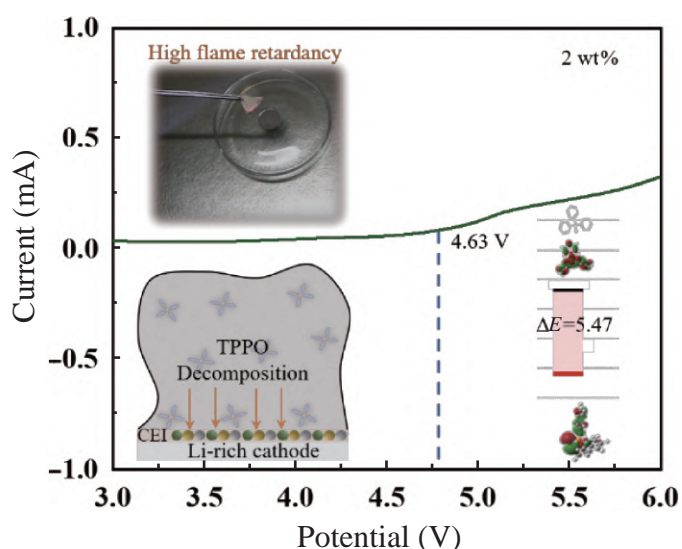
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Research Article

Enhanced safety of sulfone-based electrolytes for lithium-ion batteries: broadening electrochemical window and enhancing thermal stability

Qiaojun Li, Wenya Wu, Yu Li , Haixia Ren, Chuan Wu , and Ying Bai 

Graphical Abstract



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By introducing 2 wt% triphenylphosphine oxide (TPPO) as a film-forming agent into a sulfone-based electrolyte containing 1 mol L^{-1} of lithium difluoro (oxalate) borate, the electrochemical window of the lithium-ion battery electrolyte can be increased to 4.63 V. Moreover, this addition considerably enhances the thermal stability of the electrolyte.

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Review

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Constructing three-dimensional architectures to design advanced anodes materials for sodium-ion batteries: from nanoscale to microscale

Yu-Feng Sun¹, Yu Li^{1,2,*}, Yu-Teng Gong¹, Zhi-Xu Qiu¹, Ji Qian¹, Ying Bai¹, Zi-Lu Wang¹, Ri-Peng Zhang¹, Chuan Wu^{1,2,*}

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Abstract

Sodium-ion batteries (SIBs) are emerging as a possible substitute for lithium-ion batteries (LIBs) in low-cost and large-scale electrochemical energy storage systems owing to the lack of lithium resources. The properties of SIBs are correlated to the electrode materials, while the performance of electrode materials is significantly affected by the morphologies. In recent years, several kinds of anode materials involving carbon-based anodes, titanium-based anodes, conversion anodes, alloy-based anodes, and organic anodes have been systematically researched to develop high-performance SIBs. Nanostructures have huge specific surface areas and short ion diffusion pathways. However, the excessive solid electrolyte interface film and worse thermodynamic stability hinder the application of nanomaterials in SIBs. Thus, the strategies for constructing three-dimensional (3D) architectures have been developed to compensate for the flaws of nanomaterials. This review summarizes recent achievements in 3D architectures, including hollow structures, core-shell structures, yolk-shell structures, porous structures, and self-assembled nano/micro-structures, and discusses the relationship between the 3D architectures and sodium storage properties. Notably, the intention of constructing 3D architectures is to improve materials performance by integrating the benefits of various structures and components. The development of 3D architecture construction strategies will be essential to future SIB applications.

Keywords: Sodium-ion batteries, anode materials, three-dimensional architectures, nanostructure, microstructure



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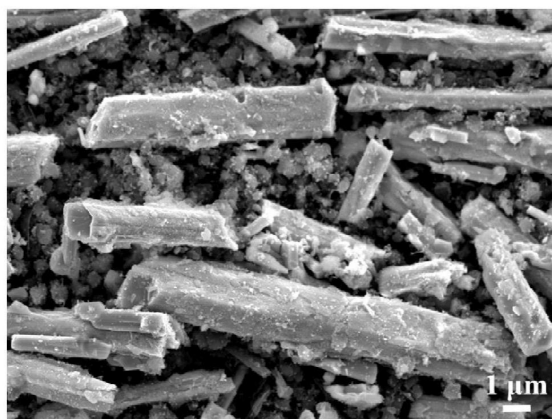
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(54) 发明名称

一种钠离子电池金属硒化物负极材料及其制备方法和应用

(57) 摘要

本发明公开一种钠离子电池金属硒化物负极材料及其制备方法和应用,将金属硒化物、分散剂、金属盐以及咪唑类有机物混合于甲醇溶液中,在金属硒化物表面原位生成均匀的金属有机骨架包覆层;将所得前驱体在保护气氛下进行热处理后即得电极材料。本发明的方法不需要引入额外的硒源,经一步热处理就可以得到具有两种不同类型金属硒化物的复合材料。该复合材料借助两种不同金属硒化物间适度的晶格失配,诱导产生大量硒空位。硒空位的引入可以解决本体金属硒化物固有的低电子电导问题,改善离子/电子传输动力学,提高材料的电化学性能。本发明提供的制备方法操作简单,可拓展应用于多种负极材料的制备,具有广泛的应用前景。





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(54) 发明名称

钠离子电池多维度异质结构负极材料

(57) 摘要

钠离子电池多维度异质结构负极材料,其制备方法包括:将硒粉与金属镍盐混合溶于柠檬酸的乙醇溶液中,之后逐滴添加水合肼溶液并搅拌均匀,将混合溶液进行溶剂热反应;离心洗涤溶剂热反应产物,得到本体金属硒化物材料;将干燥后的金属硒化物置于马弗炉中进行煅烧一段时间,迅速退火至室温,即得到具有多维度的NiSe/NiO异质结构复合材料。本发明通过煅烧具有多维分级结构的本体金属硒化物即可原位构筑异质结和金属氧化物保护层,制备的多维度异质结构复合材料作为钠离子电池负极材料表现出极佳的倍率性能和循环性能。

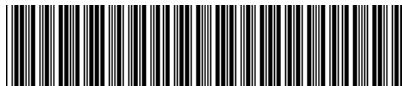


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申请人: 北京理工大学

发明人: 李雨,吴川,白莹,李欢宇,吴锋

发明创造名称: 一种水系锌离子电池电解液用添加剂、电解液及水系锌离子电池

经核实,国家知识产权局确认收到文件如下:

权利要求书 1份2页,权利要求项数: 10项

说明书 1份13页

说明书附图 1份2页

说明书摘要 1份1页

发明专利请求书 1份5页

实质审查请求书 文件份数: 1份

申请方案卷号: PCN1231693

提示:

1. 申请人收到专利申请受理通知书之后,认为其记载的内容与申请人所提交的相应内容不一致时,可以向国家知识产权局请求更正。

2. 申请人收到专利申请受理通知书之后,再向国家知识产权局办理各种手续时,均应当准确、清晰地写明申请号。

审查员: 单嘉卉

联系电话: 010-62356655

审查部门: 初审及流程管理部



200101
2022.10

纸件申请,回函请寄: 100088 北京市海淀区蓟门桥西土城路6号 国家知识产权局专利局受理处收
电子申请,应当通过专利业务办理系统以电子文件形式提交相关文件。除另有规定外,以纸件等其他形式提交的文件视为未提交。



100081

北京市海淀区西三环北路甲2号中关村国防科技园5号楼19层1910
室 北京理工大学专利中心
张洁(15601312525)

发文日:

2023年12月22日



申请号: 202311784006.8

发文序号: 2023122202356860

专利申请受理通知书

根据专利法第28条及其实施细则第38条、第39条的规定,申请人提出的专利申请已由国家知识产权局受理。现将确定的申请号、申请日等信息通知如下:

申请号: 2023117840068

申请日: 2023年12月22日

申请人: 北京理工大学

发明人: 李雨,白莹,吴川,张日朋,吴锋

发明创造名称: 一种钠离子电池用高电压快充电解液、制备方法及钠离子电池

经核实,国家知识产权局确认收到文件如下:

权利要求书 1份2页,权利要求项数: 10项

说明书 1份10页

说明书附图 1份1页

说明书摘要 1份1页

发明专利请求书 1份5页

实质审查请求书 文件份数: 1份

申请方案卷号: PCN1231694

提示:

1.申请人收到专利申请受理通知书之后,认为其记载的内容与申请人所提交的相应内容不一致时,可以向国家知识产权局请求更正。

2.申请人收到专利申请受理通知书之后,再向国家知识产权局办理各种手续时,均应当准确、清晰地写明申请号。

审查员: 自动受理

联系电话: 010-62356655

审查部门: 初审及流程管理部





投稿邮箱: xueshu@bitpress.com.cn

咨询电话: (010) 68911947 68911085

绿色二次电池先进技术丛书

吴锋

中国工程院院士, 国际欧亚科学院院士, 亚太材料科学院院士, 北京理工大学杰出教授、材料学院首席教授。获国家技术发明二等奖, 国家科技进步二等奖各 1 项, 获何梁何利



科学与技术进步奖, 国际电池材料学会科研成果奖、国际电化学学会电池技术成就奖、国际车用锂电池协会终身成就奖、中国储能杰出贡献奖。

- 轻元素多电子二次电池新体系
- **新型二次电池体系与材料**
- 金属锂电池
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- 电池资源再生

项目负责人: 丛 森
丛书总策划: 李纳蒙
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执行编辑: 宋 肖
封面设计: 李 颖



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吴川 李雨 吴锋 著



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丛书主编 吴 锋

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吴川 李雨 吴锋 著

NEW SECONDARY
BATTERIES & MATERIALS

北京理工大学出版社
BEIJING UNIVERSITY OF AERONAUTICS AND ASTRONAUTICS PRESS

吴川

北京理工大学教授。长期从事先进能源材料研究工作, 主要关注能量储存与转换体系及其关键材料。入选国家科技创新领军人才、英国皇家化学会会士、教育部新世纪优秀人才支持计划、北京市科技新星、北京市优秀人才资助计划。



李雨

北京理工大学材料学院副研究员。主要从事高性能二次电池电极材料的设计与优化。入选中国博士后创新人才支持计划(“博新计划”), 曾获中国发明协会发明创新二等奖、中国颗粒学会优秀博士学位论文奖、中国博士后创新人才支持计划优秀创新成果奖。





绿色二次电池先进技术丛书

丛书主编 吴 锋

新型二次电池 体系与材料

吴川 李雨 吴锋 著

新型二次电池体系与材料

吴川

李雨

吴锋

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证 明

兹有北京理工大学白莹、李雨等编著之《钠离子电池关键材料》，出版合同已签署，稿件符合“齐、清、定”收稿要求，已正式收稿，即将出版。

特此证明。

北京理工大学出版社有限责任公司

2023年3月10日





项目批准号	22279009
申请代码	B0908
归口管理部门	
依托单位代码	10008108A0053-0094



222790091002348

国家自然科学基金 资助项目计划书 (预算制项目)

资助类别：面上项目

亚类说明：

附注说明：

项目名称：高钠层状正极材料的多格点缺陷构建及表界面结构高熵化

直接费用：54万元 执行年限：2023.01-2026.12

负责人：李雨

通讯地址：北京市海淀区中关村南大街5号北京理工大学五号教学楼902

邮政编码： 电 话：15652998356

电子邮件：liyu0820@bit.edu.cn

依托单位：北京理工大学

联系人：刘文清 电 话：010-68913590

填表日期：2022年09月16日

国家自然科学基金委员会制



项目组主要成员

编号	姓名	出生年月	性别	职称	学位	单位名称	电话	证件号码	项目分工	每年工作时间(月)			
1	李雨	1988.08	女	副研究员	博士	北京理工大学	15652998356	320305198808200427	项目负责人	12			
2	赵然	1989.02	女	无	博士	北京理工大学	15201436701	220104198902073320	表征技术	8			
3	赵志坤	1992.11	男	无	博士	北京理工大学	010-68918770	410825199211207537	材料合成技术	8			
总人数		高级		中级		初级		博士后		博士生		硕士生	
7		1						2		3		1	



项目批准号	22005033
申请代码	B050803
归口管理部门	
依托单位代码	10008108A0053-0094



国家自然科学基金委员会 资助项目计划书

资助类别：青年科学基金项目

亚类说明：

附注说明：

项目名称：分级结构金属硒化物中本体硒缺陷的构筑与调控及其复合材料储钠机制的研究

直接费用：24万元 执行年限：2021.01-2023.12

负责人：李雨

通讯地址：北京市海淀区中关村南大街5号北京理工大学五号教学楼902

邮政编码： 电 话：010-68912528

电子邮件：liyu0820@126.com

依托单位：北京理工大学

联系人：包成刚 电 话：010-68912490/3590

填表日期： 2020年09月25日

国家自然科学基金委员会制



项目组主要成员

编号	姓名	出生年月	性别	职称	学位	单位名称	电话	证件号码	项目分工	每年工作时间(月)			
1	李雨	1988.08	女	博士后	博士	北京理工大学	010-68912528	320305198808200427	项目负责人	10			
总人数		高级		中级		初级		博士后		博士生		硕士生	

中国工程科技发展战略福建研究院 战略研究与咨询项目 任务书

(项目总体部分)

项目名称：福建省储能电池产业发展研究

项目类型：重大

重点

项目负责人：吴锋

项目联系部门：中国工程科技发展战略福建研究院

项目研究助理：李雨 联系电话：15652998356

电子信箱：liyu0820@bit.edu.cn

项目财务助理：赵然 联系电话：15201436701

电子信箱：ransp9122@163.com

研究周期：2021年12月1日——2022年11月30日

中国工程科技发展战略福建研究院制

6	李雨	副研究员	北京理工大学	240	课题第二负责人
7	王欣然	副研究员	北京理工大学	180	研究成员
8	高洪才	教授	北京理工大学	120	研究成员
9	白莹	教授	北京理工大学	120	研究成员
10	谭国强	教授	北京理工大学	90	研究成员
11	李宁	研究员	北京理工大学	90	研究成员
12	谢嫚	副教授	北京理工大学	90	研究成员
13	赵然	博士后	北京理工大学	240	研究成员
14	李莹	博士生	北京理工大学	180	研究成员
15	刘明权	博士生	北京理工大学	180	研究成员
16	冯鑫	博士生	北京理工大学	180	研究成员
17	李巧君	博士生	北京理工大学	180	研究成员
18	王亚辉	博士生	北京理工大学	180	研究成员
19	郑路敏	博士生	北京理工大学	180	研究成员
20	龙博	博士生	北京理工大学	180	研究成员
21	张安祺	博士生	北京理工大学	180	研究成员
22	李树强	博士生	北京理工大学	180	研究成员
23	郭瑞琪	博士生	北京理工大学	180	研究成员
24	巩玉腾	硕士生	北京理工大学	120	研究助理
25	杨菁菁	硕士生	北京理工大学	120	研究助理
26	胡志凡	硕士生	北京理工大学	120	研究助理

课题主要工作人员名单

成员类型	姓名	单位	职务职称	手机号码
研究助理	李雨	北京理工大学	副研究员	15652998356
财务助理	赵然	北京理工大学	博士后	15201436701

2. 课题一任务书签署各方

委托方（拨款单位）

钟志华

单位名称：

单位负责人：

财务负责人：

单位开户行：

单位账号：



年 月 日

承 担 方

课题依托单位：北京理工大学

依托单位负责人（签字）：张军

依托单位财务负责人（签字）：潘晓丽

依托单位开户行：中国工商银行北京紫竹院支行

依托单位账号：0200007609014435495

（单位财务信息方章）

张军
潘晓丽



年 月 日

北京理工大学
0200007609014435495
中国工商银行北京紫竹院支行

管 理 方

单位名称：

单位负责人：



本科生课程教学情况统计表

授课教师：李雨

填表时间：2023-09-25

序号	学期	课程名称	学时数	学生数
1	2	能源材料与器件 综合实验	48	73
2	1	环境材料	16	28
3	1	国际视野下的新 能源材料与器件	2	26
4	1	能源与环境材料 学科进展	2	26
合计			68	153

统计时间区间为：2018.1-至今

经办人：
(签名)



本科教学管理部门 (章)
负责人 (签名)



材料

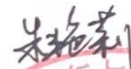
研究生课程教学情况统计表

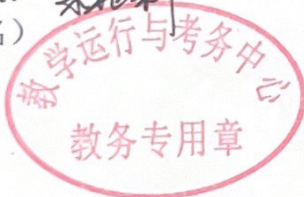
授课教师： 李雨

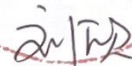
填表时间： 2023-09-25


序号	学期	课程名称	学时数	学生数
1	2	储能二次电池材料与技术	64	8
合计			64	8

统计时间区间为：2018.1-至今

经办人： 
(签名)



研究生教学管理部门(章)
负责人(签名): 





LI-ION BATTERY

CERTIFICATE OF RECOGNITION

We highly appreciate the contribution of

Yu Li

for giving an invited lecture at
2023(17th) International Forum on
Li Battery Technology & Industrial Development
Shenzhen, China
Nov.24-26, 2023

A handwritten signature in black ink, appearing to read 'Liquan Chen'.

Liquan Chen, Professor
Originator of the Forum

A handwritten signature in black ink, appearing to read 'Feng Wu'.

Feng Wu, Professor
President of the Forum

第二届全国钠电池产业高峰论坛

吐故“钠”新，博采众长



扫码报名

邀请函

尊敬的李雨副研究员：您好！

由DT新材料主办，宁波德泰中研信息科技有限公司承办的2023“（第二届）全国钠电池产业高峰论坛”定于2023年05月10-12日在宁波香格里拉酒店召开。您及贵课题组在钠离子电池领域具有出色的研究成果和产业成果转化。组委会诚挚邀请您出席大会并在大会论坛请您分享报告（报告时长25min），为钠离子电池产业和优秀企业的发展提纲挈领，指点迷津。

2021年以来，钠离子电池逐步被市场认可，传统企业和新发企业不断持续参与竞争，产业链各环节竞争愈发剧烈。当前阶段先出产量的企业更具优势，但未来，由于钠离子电池的核心竞争力为低成本，上下游垂直整合能力更强、产品性价比更高的企业更易胜出。然钠离子电池正极三种技术路线之争极具挑战；负极硬碳制造成本与前驱体缺陷有待勘破；产业配套工艺需建立。

大会预期规模600人，组委会将竭诚支持协助相关会务事宜，（会务联系人：盛圆圆，17706484632，casey@polydt.com）。相信在您的鼎力支持和参与下，大会的前瞻性和专业性定将提升并取得圆满成功。

特此致函，顺颂春祺！非常感谢！

另外，会议期间交通住宿费用需自行承担，会期统一餐饮。感谢您及贵单位的积极参与与支持！

论坛主席：夏永姚，复旦大学教授

张立生
宁波德泰中研信息科技有限公司总经理

附件：大会日程安排



荣誉证书

李雨 教授

感谢您应邀于 2023 年 10 月 9 日在 浙江 省

温州 市举办的第 四 届中国新材料产业发展大会

钠离子电池论坛 分会做的题为:

钠离子电池正负极材料的界面修饰 的报告。

特发此证!

分会主席签字:

刘本智

中国新材料产业发展大会

组委会

2023 年 10 月 11 日



第六分论坛：青年科学家（三）

时间：4月16日（周日），上午				
地点：1F 8号会议室				
时间	报告题目	报告人	单位	编号
主持人：余 创、张凤鸣				
8:30-8:50	高比能锂-硫二次电池新体系及关键材料的同步构筑	谭国强	北京理工大学	K6-07
8:50-9:05	金属镁负极-电解液界面研究	李桂村	青岛科技大学	16-39
9:05-9:20	硬碳材料本征结构应力调控及其储钠/钾性能研究	史晓东	海南大学	16-40
9:20-9:35	高比能氧化物正极材料研究与应用	王 军	南方科技大学	16-41
9:35-9:50	高性能钠离子电池 P2 型层状氧化物正极材料	李 雨	北京理工大学	16-42
9:50-10:05	高性能超级电容器电极材料的构筑策略	赵 健	青岛科技大学	16-43
10:05-10:20	维材料结构调控及新型储能电池研究	杨金霖	海南大学	16-44
10:20-10:30	茶歇			
主持人：谭国强、范 兴				
10:30-10:50	基于硫化物电解质的宽温区全固态电池构筑	余 创	华中科技大学	K6-08
10:50-11:05	供价有机框架光催化产氢催化剂的设计与调控	张凤鸣	哈尔滨理工大学	16-45
11:05-11:20	碱性锌基液流电池高性能离子传导膜结构与性能研究	胡 静	浙江大学	16-46
11:20-11:35	高指数晶面 Pt 基纳米晶的可控合成及其电催化性能	范爱鑫	廊坊师范学院	16-47
11:35-11:45	APbX3 钙钛矿光催化无氧氧化芳香醇耦合产氢研究	陈陶然	福建师范大学	06-08
11:45-11:55	过渡金属修饰多层石墨烯储氢性能的第一性原理研究	蒋 祺	陕西理工大学	06-09
11:55-12:05	分级多孔二维 TiO2 纳米片负载钙钛矿 CsPbBr3 的制备及光催化氧化甲苯机制	伊佳雨	福建师范大学	06-10
12:05-12:15	M-N4-Gr_Mxene heterojunction structures as ORR_OER catalysts_ Machine Learning and Density Functional Theory insights	卢 森	陕西理工大学	06-11
12:15-13:30	午餐（铂苑厅、西餐厅）			

首届世界材料大会 中国材料大会2022-2023

国际新材料科研仪器与设备展览会 全国新材料人才招聘会

2023年7月7-10日
广东·深圳国际会展中心

深圳

主办单位：中国材料研究学会

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查询

筛选：

专题分论坛

日期

会场

筛选条件：FB02-钠离子电池青年论坛

FB02-钠离子电池青年论坛

时间：2023年07月08日

地点：17号馆：17D-18 (1层)

13:30 -15:00 | FB02-1 【FB02-钠离子电池青年论坛】

主席：张凯 | 方永进 | 黄永鑫

主持：姚霞银 | 陈重学

编号	时间	类型	题目	讲者	单位
	13:30-13:50	邀请报告	钠离子电池层状正极材料晶格氧活性研究	郭少华	南京大学
	13:50-14:10	邀请报告	钠离子电池高电压磷酸盐类正极材料研究进展	高洪才	北京理工大学
	14:10-14:30	邀请报告	新型高性能高分子基钠离子电池负极材料研	胡方圆	大连理工大学
	14:30-14:45	口头报告	普鲁士蓝基钠离子电池正极的构筑及性能研究	乔芸	上海大学
	14:45-15:00	口头报告	锰基层状氧化物正极材料阴离子氧化还原反应的EPR/NMR研究	李超	华东师范大学

15:00 -15:25 | FB02-2-茶歇 【FB02-钠离子电池青年论坛】

15:25 -17:30 | FB02-3 【FB02-钠离子电池青年论坛】

主席：张凯 | 方永进 | 黄永鑫

编号	时间	类型	题目	讲者	单位
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及其储钠性能

10:00 -10:20 | FB02-11-茶歇 【FB02-钠离子电池青年论坛】

10:20 -11:45 | FB02-12 【FB02-钠离子电池青年论坛】

主席: 黄永鑫 | 方永进 | 张凯

主持: 周亮 | 李文武

编号	时间	类型	题目	讲者	单位
	10:20-10:40	邀请报告	钠离子电池界面结构设计	李雨	北京理工大学
	10:40-11:00	邀请报告	钠离子电池关键材料研究进展	刘琦	北京理工大学材料科学与工程学院
	11:00-11:15	口头报告	锂离子电池本征安全性评价指标体系研究	林春景	重庆理工大学
	11:15-11:30	口头报告	储钠负极材料的微观结构调控设计及电极/电解液界面的储能机制研究	郑程	广东工业大学
	11:30-11:45	口头报告	钠离子在石墨中的共嵌插层反应机制	Zheng-Long Xu	The Hong Kong Polytechnic University

11:45 -12:00 | FB02-13-墙报 【FB02-钠离子电池青年论坛】

编号	时间	类型	题目	讲者	单位
FB02-P001	11:45-11:46	墙报	通过消除非晶格氧化还原提高P2相层状氧化物正极中氧氧化还原的高压稳定性	吴祥	华东师范大学
FB02-P002	11:46-11:47	墙报	MgF2包覆P2型Na0.7Mn0.8Ni0.2O2的制备及电化学性能研究	叶仲强	湘潭大学
FB02-P003	11:47-11:48	墙报	钴镁双掺杂对P3相钠离子锰基正极材料的改性研究	任翹楚	湘潭大学
	11:48-11:49	墙报	Realizing High Capacity and Zero Strain in Layered Oxide Cathodes via Lithium Dual-Site Substitution for Sodium-Ion Batteries	伍忠汉	南开大学化学学院

中国材料大会2022-2023
联系电话: 010-68710443

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技术支持: 400-008-5413  美迪康会务通 京ICP备11011505号-67

日程

时间：2021年6月18日-21日

地点：中国·成都新东方千禧大酒店

(本日程并非最终日程，最终日程将在截稿日期后发布，请以大会通知为准!)

Day1: 6月18日 注册, 展商布展

Day2: 6月19日

6月19日 上午

大会主题报告

时间：6月19日, 08:30-12:30; 地点：待定

主持人:	待定
9:00-9:30	题目: 催化水氧化--从天然到人工光合作用 报告人: 瑞典皇家工学院首席教授, 大连理工大学特聘教授 孙立成院士
9:30-10:00	题目: 待定 报告人: 苏州科技大学材料科学与工程学院院长 李长明院士
10:00-10:30	题目: 以煤炭超临界水气化耦合可再生能源驱动的水和 CO2 还原制燃料技术支撑碳达峰和碳中和目标的实现 报告人: 西安交通大学 郭烈锦院士
10:30-11:00	题目: 车用氢能燃料电池的发展: 现状, 挑战及前景 报告人: 上海大学可持续能源研究院, 理学院院长 张久俊院士
11:00-11:30	题目: Materials for Advanced Energy Chemistry and Engineering: State of the Art and Perspectives 报告人: Dr. Bao Lian Su, Professor, University of Namur, Belgium
11:30-12:00	题目: Energy Conversion and Storage: Novel Materials and Operando Methods 报告人: Dr. Héctor D. Abruña, Professor and Director, Center for Alkaline Based Energy Solutions and Energy Materials Center, Cornell University, USA
12:00-12:30	题目: Hydrogen as a Path to Enhancing the Prospects for Renewable Energy 报告人: Dr. Marc A. Rosen, Professor, University of Ontario Institute of Technology, Canada

15:20-15:35	题 目：聚硫离子转化仿生人工酶的设计与催化机制研究 报告人：温州大学 杨植教授
15:35-15:50	题 目：新型降维钙钛矿材料的结构探索与光电器件应用 报告人：中山大学 杨振宇教授
15:50-16:05	题 目：氮碳光催化材料 报告人：北京理工大学 韩庆副研究员
16:05-16:20	题 目：待定 报告人：华中科技大学 陈炜教授
16:20-16:35	报告位置可申请
16:35-16:50	题 目：水系电化学储能材料与机制 报告人：南京信息工程大学 董升阳教授
16:50-17:05	题 目：可规模化的钠金属负极集流体研究 报告人：哈尔滨工业大学（深圳） 王文辉助理教授

分论坛四：能源与纳米化学及技术

时间：6月20日，13:30-16:55；地点：待定

主席	麦立强教授，武汉理工大学材料科学与工程学院院长 岳秦博士，电子科技大学特聘研究员
13:30-13:50	题 目：待定 报告人：重庆大学 周小元教授
13:50-14:10	题 目：大晶格失配下半导体纳米异质结构合成及新能源应用 报告人：北京理工大学化学与化工学院 张加涛教授
14:10-14:25	题 目：异质结构钠离子电池金属硫族化物负极材料的构建 报告人：北京理工大学 李雨副研究员
14:25-14:40	题 目：异质结构的界面工程提高金属硒化物的储钠性能 报告人：电子科技大学 陈俊松教授
14:40-14:55	题 目：有序金属间化合物电催化 报告人：华中科技大学 王得丽教授
14:55-15:10	题 目：低能耗制氢微纳结构催化剂 报告人：中国科学技术大学 章根强教授
15:10-15:25	茶歇
15:25-15:40	题 目：Atomic Fe Dispersed Mesoporous Nanostructures for an Efficient Oxygen Reduction Reaction 报告人：电子科技大学 岳秦特聘研究员
15:40-15:55	题 目：Nanostructured High-entropy Alloys for Sustainable Energy Applications 报告人：西北工业大学 韩潇副教授
15:55-16:10	题 目：多孔金属化合物纳米材料的构筑及其储能新能研究 报告人：河北农业大学 赵孝先副教授
16:10-16:25	题 目：复合与耦合纳米发电机 报告人：中国科学院北京纳米能源与系统研究所 杨亚研究员
16:25-16:40	报告位置可申请



Retail Expo

第十七届中国零售商大会暨零售商业智能设备及

The 17th China Retailers Convention And Commercial Intelligent Equipment & Retail Goods

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关于发布“2023年度中国商业联合会科学技术奖” 评选结果的公告

来源: 中国商业联合会科技质量工作委员会

发布日期: 2023-12-29 11:03



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各有关单位:

“2023年度中国商业联合会科学技术奖”评审工作已经完成。根据各地商业联合会(行业协会)、相关专业协会、企业集团、科研机构 and 高等院校的推荐,经中国商业联合会组织初评、专家评审、评审委员会审定通过、拟授奖项目公示,决定授予全国商业最高科学技术奖2人,全国商业科技进步奖619项(其中特等奖24项、一等奖142项、二等奖209项、三等奖244项),全国商业科技创新型企业25家,全国商业科技创新人物40人。

特此公告。

附件:

1. 全国商业最高科学技术奖获奖名单
2. 全国商业科技进步奖获奖名单
3. 全国商业科技创新型企业获奖名单
4. 全国商业科技创新人物获奖名单

关于发布“2023年度中国商业联合会科学技术奖”评选结果的公告

各有关单位：

“2023年度中国商业联合会科学技术奖”评审工作已经完成。根据各地商业联合会（行业协会）、相关专业协会、企业集团、科研机构 and 高等院校的推荐，经中国商业联合会组织初评、专家评审、评审委员会审定通过、拟授奖项目公示，决定授予全国商业最高科学技术奖 2 人，全国商业科技进步奖 619 项（其中特等奖 24 项、一等奖 142 项、二等奖 209 项、三等奖 244 项），全国商业科技创新型企业 25 家，全国商业科技创新人物 40 人。

特此公告。

- 附件：
1. 全国商业最高科学技术奖获奖名单
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 4. 全国商业科技创新人物获奖名单

中国商业联合会

2023 年 12 月 29 日

96	面向智能电网低碳储能的电量监测关键技术及应用	西南科技大学、绵阳市维博电子有限责任公司、四川新智绿能测控技术有限公司	王顺利、彭正红、刘冬雷、侯燕、王嘉、朱永杰
97	储能二次电池材料与极片制备技术及应用	北京理工大学、北京理工大学长三角研究院（嘉兴）、贵州容百锂电材料有限公司、国联汽车动力电池研究院有限责任公司、江西汉尧富锂科技有限公司	白莹、吴锋、吴川、胡常青、王建涛、胡伟、李雨、金海波、王欣然、赵然、李莹、冯鑫、郭瑞琪
98	高精度铝卷材退火装备和材料组织性能调控关键技术开发及应用	苏州新光热能科技有限公司、中色科技股份有限公司、中铝材料应用研究院有限公司、中铝资产经营管理有限公司	余广松、黄东男、丁宏波、吴永福、徐相军、张澍、韩正英、徐江云、魏健、李清、李海鹏、国东、何磊、何向问、王云飞
99	高效低碳天然气发动机关键技术及产业化	吉林大学、一汽解放汽车有限公司	王忠恕、窦慧莉、解方喜、李伟峰、马立、韩永强、王丹、许允、李俊、李佳星、李培营、刘阳、郭立新、李鹏、逢晓宇
100	电磁热声无损传感与检测关键技术及应用	湖南大学、江南大学	何赟泽、周德强、杨瑞珍、盛卫锋、耿学锋、李孟川、余赛波
101	多应用场景下大型电池储能系统安全管理与优化运行关键技术	南通大学、沃太能源股份有限公司	华亮、袁宏亮、张新松、林栋、王珺、吴晓新、张新艳、李俊红、游峰、季霆、袁银龙、董嵘、黄杰杰
102	中深层地热高效开采与利用关键技术研究及应用	中石化绿源地热能(陕西)开发有限公司、西南石油大学	李红岩、高小荣、张杰、刘斌、王鹏涛、孙彩霞、张献喻、邹彦荣、曾云、尹文锋、任小庆、赵宇璇、程永刚、李亚亚、卢朝鹏



证书

国科奖社证字第0123号

为表彰发明创业奖创新奖获得者，特颁发此证书。

项目名称：钠离子电池低成本负极材料及其制备技术

奖励等级：二等

完成单位：北京理工大学

北京理工大学长三角研究院（嘉兴）

国联汽车动力电池研究院有限责任公司

完成人：白莹 吴锋 吴川 李雨

王建涛

证书号：2021-CAICX-2-M23



荣誉证书

李雨 老师：

在北京理工大学材料学院 2022 年青年教师
教学基本功大赛中荣获 三 等奖。

特发此证，以资鼓励。

北京理工大学材料学院

二〇二二年八月

荣誉证书

HONORARY CREDENTIAL

李雨同志：

您在“廉洁文化强基固本，崇廉拒腐笃行不怠”党风廉政知识竞赛活动中荣获个人三等奖。

特发此证，以资鼓励。

北京理工大学材料学院党委

二〇二二年七月

