The Research About Anode Material for Sodium-Ion Batteries

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Abstract. Sodium-ion batteries are replacing lithium-ion batteries due to their lower cost and more abundant resources. The sodium-ion battery anode, including carbon-based materials, alloy materials, and organic materials, plays a key role in improving battery performance but also faces problems such as poor conductivity, which limits sodium storage capacity attenuation and irreversible volume expansion. To solve these problems, researchers have proposed a variety of solutions, such as chemical activation, element doping, micro-nanostructure design, composite material preparation, surface coating application, and buffer medium introduction. This article summarizes these strategies and points out the direction of future research, including the development of innovative anode materials with better conductivity and sodium storage capacity, and improved manufacturing processes. Further research and development of sodium-ion batteries anode is expected to make important contributions to the new energy field.

Keywords: Sodium-ion battery, Anode material, Modification.

1. Introduction

In the 21th century, the energy crisis and the pollution of environment have become the key issues in the development of civilization. To reduce the reliance on the fossil fuels, it is imperative to promote the innovation of new environmental protection and renewable energy sources. Lithium-ion battery plays an important role in new energy devices as its advantages such as high voltage, high energy density and long cycle life [1]. However, owing to the limited reserves of lithium element and high costs, the application of lithium-ion battery still faces certain limitations. As a result, sodium-ion batteries as an alternative technology have attracted wide attention due to their abundant sodium resource reserves, high energy density and superior environmental adaptability [2]. The anode material of sodium-ion battery, mainly including carbon, alloy and organic compounds, has a crucial influence on its performance. For example, the anode material degrades and transforms into a hydrated phase when the anode is exposed to air [3]. This article summarized the disadvantages of several anodes and the corresponding modification strategies. Carbon, alloy materials and organic compounds can serve as anode materials for sodium-ion batteries, but they all face different challenges. The main problems of carbon-based materials are low electrical conductivity and limited sodium storage capacity, which can be improved by chemical activation to increase porosity, doping elements, and recombining composite carbon. Although the alloy anode material has a high theoretical capacity, the volume expansion problem may lead to the decline of cyclic stability, which can be solved by designing micro-nano structure, composite with other materials, surface coating and the introduction of buffer media. Organic materials need to improve their conductivity and simplify strict synthesis methods. These improvements help to improve the overall performance and application prospects of sodium-ion batteries.

2. Research progress of anode materials

2.1. Carbon-based materials

Carbon-based materials encompass hard carbon, soft carbon, nanotubes, and graphene. However, the primary focus of research lies on hard carbon and soft carbon due to their exceptional properties. Hard carbon derives its name from its rigid nature and microporous/mesopore structure, which enables it to maintain its shape in diverse environments. Typically, hard carbon is obtained by high temperature pyrolysis of natural biomass, such as lignin or cellulose [4]. Soft carbon is another outstanding anode material characterized by a semi-graphite structure with relatively few defects and disorder, which is usually obtained through high temperature pyrolysis of compounds containing aromatic rings (such as plastics and benzene) [4,5]. Recent research has indicated that anthracite is used as the precursor to prepare soft carbon with higher yield only by simple grinding and carbonization treatment, which is a cost-effective production [5,6].

However, conventional hard carbon is constrained by its low electrode conductivity and poor sodium storage capacity. By increasing the porosity through chemical activation (e.g. KOH or H3PO4), the microstructure and the volume expansion issue during sodium ion insertion are optimized to some extent, thereby improving sodium storage performance and cycle life [6,7]. Soft carbon exhibits good conductivity and an ordered structure, but the specific capacity is lower than hard carbon. Doping elements such as nitrogen and phosphorus can significantly enhance its electrochemical capacity [8,9].

Some researchers are trying to combine soft carbon and hard carbon organically to make a new type of composite material that has the advantages of both. For example, Xie et al. used filter paper and asphalt as raw materials, and by controlling the temperature and the ratio of soft carbon to hard carbon, they successfully prepared composites with better properties than pure hard carbon materials or pure soft carbon materials prepared under the same conditions [10]. Liu et al. prepared soft and hard carbon composites doped with nitrogen and oxygen by oxidizing acid treatment and catalytic graphitization, which had good electrochemical properties [11]. The proper introduction of soft carbon and heteroatoms can improve the first-cycle Coulombic efficiency and increase the reversible capacity [11]. However, excessive introduction of these substances can cause negative effect on sodium storage [11]. Three preparation methods of soft and hard carbon composites, heat treatment, physical mixing and sol-gel, are discussed in this paper. These methods have their own characteristics and are suitable for different production requirements and material properties.

2.1.1. Heat treatment

Heat treatment is a technique for converting carbon-containing precursors into soft and hard carbon composites by a high-temperature pyrolysis or carbonization process. The advantage of this method is that the process is simple and flexible control, as well as the structure and properties of the carbon anode can be controlled. Li et al. successfully prepared amorphous carbon materials with high sodium storage capacity by heat-treating asphalt and phenolic resins at high temperatures of 1200 to 1600 ℃ [12]. In addition, He et al. used kerosene asphalt as a carbon source, sublimed sulfur as a sulfur source, and prepared sulfur-doped asphalt-based carbon materials by the two-step heat treatment method. By precisely controlling sulfur content and carbonization temperature, they successfully obtained high-performance materials with layer spacing of 0.368 nm. Under the current density of 100 mA/g, the reversible specific capacity in the first charge-discharge cycle is up to 482.8 mAh/g [13]. However, the heat treatment method also has some limitations, such as high temperature may lead to the loss of some carbon materials, reduce the preparation efficiency and material utilization, and may cause unpredictable chemical reactions or phase changes, affecting the stability of material properties.

2.1.2. Physical mixing method

Soft carbon and hard carbon materials are mixed by mechanical mixing or solvent treatment to form a composite structure, thereby improving the electrical conductivity and stability of the material. The soft and hard carbon composites obtained by Wang et al. through ball milling and the high

temperature sintering show moderate specific surface area and order degree, and their electrochemical properties are better than that of single soft carbon and hard carbon materials [14]. Based on bitumen-based soft carbon prepared by pre-oxidation and low temperature carbonization, Jiang et al. mixed soft carbon with peanut powder, rice husk powder and cellulose as the precursor in different ratios by ball milling, and found that when the mass ratio of bitumen to cellulose was 7:3, the material showed the best sodium storage performance, and at the current density of 20mA/g, the material showed the best sodium storage performance. The first-cycle charging capacity reached 331.9mAh/g, and the initial Coulomb efficiency reached 74.26%. The remaining reversible specific capacity of the battery is 175 mAh/g after 250 cycles of charge and discharge under the current density of 50mA/g [15]. Although the physical mixing method is simple in operation and low cost, it may face the problem of poor mixing uniformity, especially in the preparation of large-scale or complex structural composite materials, it is difficult to achieve completely uniform mixing, so it is more suitable for small-scale production.

2.1.3. Sol-gel method

Sol-gel method is a more refined preparation method, which forms a sol by dissolving a soft and hard carbon precursor in a solvent, and then forms a gel through the gelation process, and finally gets a soft and hard carbon composite through heat treatment. Xue et al. successfully prepared a high performance soft and hard carbon composite porous material by first mixing dimethylimidazole with cobalt nitrate in ethanol solution and vinyl alcohol to produce gel [16]. The biggest advantage of the sol-gel method is that it can achieve a high uniform distribution in particle size and strong controllability of the material, which is particularly important for the preparation of composite materials with specific structures. However, the cost of this method is high, and the preparation term is long, so the application in large-scale production is limited.

2.2. Alloy anode materials

The choice of anode material significantly impacts the performance of sodium-ion batteries. Alloy materials, such as tin-based, silicon-based, and titanium materials, offer higher theoretical specific capacity compared to traditional carbon-based materials. However, the anode material may suffer from inactivation and reduced cyclic performance due to significant volume changes caused by multi-electron transfer reactions in alloying processes. To address this issue, researchers have proposed several solutions [17]:

1. Designing micro-nano structures to control sodium ion diffusion range and reduce mechanical strain on embedded materials.
2. Creating composites with other materials to enhance stability and electrochemical performance.
3. Applying surface coatings on the negative electrode material to improve cycle stability and durability.
4. Introducing buffer media to adjust the interaction between the electrode and electrolyte.

A research team of Beijing Institute of Technology's School of Materials has developed a multistage gradient ordered silicon (MGO-Si) anode material through electrochemical reconstruction of silicon materials, overcoming silicon's “inertia” in sodium-ion batteries and achieving breakthroughs in silicon sodium storage performance [18]. Antimony (Sb) is one of the most extensively studied alloy anode materials for SIBs due to its high theoretical specific capacity of 660 mAh/g. However, the volume expansion of the anode materials can reach about 390% during sodium insertion or extraction. Tin (Sn)-based electrode materials are considered as the potential candidates for SIBs owing to their low reaction potential, high theoretical specific capacity of 847 mAh/g by forming Na15Sn4, wide availability, and environmental friendliness. However, it may experience a volume expansion of up to 420% due to the phase transition. Silicon (Si) can form an NaSi alloy with sodium, and its theoretical specific capacity can reach 960 mAh/g. It should be emphasized that the overall volume expansion is only 114%, which is lower than that observed in other alloy materials. Nanoscale crystalline silicon can be alloyed with sodium, where amorphous silicon will be formed after initial cycling and then become the primary reaction phase in subsequent cycles. However,

micron-scale crystalline silicon cannot undergo this process, which proposes that crystalline silicon is electrochemically inactive towards elemental sodium while amorphous silicon exhibits greater reactivity than its crystalline counterpart [19].

2.3. Organic materials

Organic anode materials offer distinct advantages including flexible structural properties, cost-effectiveness derived from abundant raw material sources, minimal environmental impact and relatively gentle synthesis conditions. Furthermore, certain types of anode components exhibit reversible capacitance characteristics. Organic anode materials primarily fall into three categories: small organic molecules, polymers and organic composite.

Small organic molecules comprising of various carbon are based on compounds such as polyaromatic substances and carbon nanotubes known for their high electrical conductivity utilized predominantly within sodium-ion battery systems. Quinone compounds exhibit the following characteristics: (1) They are capable of reversible oxidation-reduction reactions, allowing for the insertion and extraction of sodium ions; (2) These compounds possess a high theoretical specific capacity and demonstrate excellent reversibility. Representative examples include p-benzoquinone and naphthoquinone. The reaction mechanism involves the storage of sodium ions through oxidation-reduction reactions between quinone-hydroquinone pairs. Carboxylic acid compounds are cost-effective and environmentally friendly. They form ionic bonds with sodium ions via the carboxyl functional group. Representative examples encompass isophthalic acid and fumaric acid. Their reaction mechanism entails the formation of sodium salt through deprotonation, facilitating reversible binding to sodium ions. Nitrogen-containing organic compounds display the following characteristics. Interaction with sodium ions occurs through the lone pair of electrons on nitrogen atoms in these compounds. Some may exhibit high electron density, thereby enhancing electrode conductivity. Representative examples include polypyrrole and polyaniline. The reaction mechanism involves reversible interaction with sodium ions at nitrogen atom sites. Thioether/thioketone compounds showcase exceptional conductivity among small organic molecules, interacting with sodium ions via their sulfur atoms to deliver strong electrochemical performance. Representative examples comprise disulfides and thioether compounds. Their reaction mechanism revolves around storing sodium ions through reversible oxidation-reduction reactions at sulfur atom sites.

Free radical polymers feature stable free radical groups that undergo reversible reactions with sodium ions during electrochemical processes. The representative compound is TEMPO (2,2,6,6-tetramethylpiperidinyl oxyl). The reaction involves electron transfer within free radical groups to facilitate oxidation-reduction reactions for storing and releasing sodium ions. The conjugated carboxylates represent a significant portion within this category exemplified by the design of phenylpyridine dicarboxylate (Na-CPP) demonstrating notable reversible capacity [20], while experimentation with magnesium terephthalate showcased commendable electrochemical activity alongside exceptional amplification performance coupled with robust cycle stability [21]. Conductive polymers possess the following characteristics: they exhibit excellent electrical conductivity in electrochemical reactions and facilitate the transmission of electrons and ions through π-conjugated systems. These materials typically demonstrate high conductivity and exceptional cycling stability. Commonly encountered conductive polymers include polypyrrole (PPy), which interacts with sodium ions, demonstrating notable sodium storage performance; polyaniline (PANI) exhibits superior conductivity and facilitates the adsorption and release of sodium ions through protonated sites; while polythiophene (PTh) effectively adsorbs sodium ions through the electron cloud within its thiophene ring structure. Quinone-based polymers feature reversible quinone-hydroxyquinone oxidation-reduction sites that enable the storage and release of sodium ions via oxidation-reduction reactions. They are characterized by their high theoretical capacity and robust cycling stability. Representative quinone-based polymers such as polyparaphenylene (PPQ) possess multiple reversible reaction sites capable of interacting with sodium ions, whereas poly-naphthoquinone provides additional charge storage sites through its naphthalene ring structure. Polyketone compounds contain reversible

carbonyl (-C=O) sites that can engage in oxidation-reduction reactions with sodium ions during charging and discharging processes. These materials typically exhibit excellent thermal stability and mechanical strength. Representative polyacetylene features multiple carbonyl sites that store sodium ions via oxidation-reduction reactions at the carbonyl oxygen.

Organic composite compositions involve combinations of natural organics together with inorganic nano-materials (e.g., oxides, sulfides etc.), aiming at enhancing battery efficiency & longevity through structural optimization. research on nitrogen-doped porous hard carbons (NDPC)as well as polydopamine coated nitrogen-containing carbon-bismuth composites (NCB/C@PDA) demonstrated significant impacts on electro- chemical properties owing to specific structures developed [22].

3. Conclusion

The research progress of anode materials for sodium-ion batteries, including carbon-based materials, alloy materials and organic materials, was summarized in this paper. Through in-depth analysis, we discovered some key patterns: Although carbon-based materials are favored for their abundant resources and low cost, their electrical conductivity and sodium storage capacity are limited. This paper highlights that the properties of hard carbon materials can be significantly improved through chemical activation and element doping. In addition, the effectiveness of synthesis strategies such as micro-nano structure design, composite material preparation, surface coating application and buffer medium introduction in improving the cycle stability of alloy anode materials is also emphasized. Organic anode materials show potential due to their structural diversity and cost-effectiveness, but their conductivity and synthesis conditions still need to be further optimized.

The work in this paper not only points the way for the future development of anode materials for sodium-ion batteries by developing innovative anode materials with better conductivity and sodium storage capabilities, improving manufacturing processes, and exploring electrolytes that are more compatible with diverse anode materials, but also highlights the importance of using renewable resources in the production of anode materials to enhance the sustainability of batteries. These findings and recommendations are important for promoting sustainable progress in the field of new energy and make a substantial contribution to energy conservation, emission reduction and environmental management. Looking ahead, we expect that the continued exploration of anode materials for sodium-ion batteries will bring breakthroughs in the field of energy storage and further promote the development and application of clean energy technologies.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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