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Research Status and Development Direction of Anode Materials for Sodium-ion Batteries

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Abstract: With the depletion of lithium resources, people gradually began to look for alternatives to lithium-ion batteries, and then sodium-ion batteries entered the public eye. In the past decade, sodium-ion batteries have developed at a high speed, establishing the beginning of the post-lithium era in the field of energy storage. This technology focuses on improving the performance of cathode and anode as well as electrolyte and optimising the preparation method of sodium-ion batteries. This paper mainly introduces the research status and development direction of anode materials for sodium-ion batteries. Firstly, the main structure of sodium-ion batteries is briefly introduced, and then it focuses on the electrochemical properties of several key anode materials such as carbon-based, titanium-based, organic-type and alloy-type anode materials, as well as the problems they face, and finally it takes the actual production and industrial application as a starting point to look ahead to the direction of the development of anode materials for sodium-ion batteries.

Keywords: Sodium-ion Batteries; Anode Materials; Carbon-based Materials.

1. Introduction

Against the backdrop of the depletion of fossil energy sources, the world's demand for energy tends to be more efficient and green. Renewable energy industries such as wind power and solar power are developing rapidly. Matching this, the development of the energy storage field is also crucial, in which the battery is also an important component. As one of the most successful secondary ion batteries in the field of energy storage, lithium-ion batteries are used in a wide variety of electronic products. Research on lithium-ion batteries can be traced back to the 1970s, and they have been commercially available since the 1990s, which is a milestone in the field of energy storage.

Around 2010, with the depletion of lithium-ion resources led to lithium battery cost increases, limiting its deep development, however, sodium-ion batteries have a rich source of resources, low cost and other advantages, which can bring new solutions for the field of energy storage, promote the wide application of clean energy, research institutes and enterprises gradually focus on the direction of the sodium-ion batteries, and then the global research and development of sodium-ion batteries has made some progress, but there are still some challenges and obstacles. The research and development of sodium-ion battery has made some progress, but there are still some challenges and obstacles. In particular, the lack of high-performance anode materials has largely limited the commercialisation of sodium-ion batteries. Therefore, it is of great significance to understand the current research status of anode materials for sodium-ion batteries and discuss their future development direction to promote the progress of renewable energy and sodium-ion battery technology.

2. Structure

2.1. Positive Pole

The cathode of sodium-ion batteries is usually made of sodium oxide materials such as sodium oxides ($Na_2 O$), sodium transition metal oxides (e.g., sodium-nickel oxides), or sodium sulfides. The cathode material is capable of accepting and releasing sodium ions during the charging and discharging process, enabling the storage and release of charge. The choice of cathode material has an important impact on the performance of sodium-ion batteries, such as capacity and cycle life

2.2. Negative Pole

The anode of a sodium-ion battery is usually made of sodium metal or carbon. Sodium metal is the most common anode material, which is able to embed and release sodium ions for charge storage and release. Carbon materials such as graphite and carbon nanotubes can also be used as anode materials with good conductivity and stability

2.3. Electrolytes

During operation, the electrolyte facilitates sodium ion transfer between the anode and cathode, maintaining electrical separation to avert short circuits. A high-quality electrolyte significantly contributes to both the cycle durability and safety of sodium-ion batteries. Complementing these core components, additional materials like conductive agents and separators are integral to the battery structure. The conductive agent boosts the conductivity of electrode materials, thereby optimizing battery performance. The separator serves as an essential barrier to isolate the electrodes, preventing shorts and safeguarding the battery integrity.

3. Main Materials for Negative Electrode

3.1. Carbon-based

Currently, the most desirable carbon anode materials are amorphous carbon with a large degree of disorder, which can be divided into two categories: soft carbon and hard carbon. Soft carbon is an amorphous carbon material that can be graphitised above 2800o C. Soft carbon is usually derived from the carbonisation of aromatic substances such as bitumen, anthracite, or plastics with low oxygen content. The sodium storage mechanism in soft carbon anodes is primarily caused by the adsorption of Na+ on the carbon layer's edge, surface, and microcrystals. The sodium storage mechanism in soft carbon anodes is primarily caused by the adsorption of Na+ on the carbon layer's edge, surface, and microcrystals. As a result, the charge and discharge curves frequently exhibit a general sloping curve without a clear low-voltage plateau. This reduces the likelihood of side reactions and dendritic crystal formation, which leads to improved multiplicity performance and longer cycle life. Hard carbon is generally derived from the pyrolysis of biomass (e.g. plant waste, cellulose, lignin, etc.) and lacks aromatic compounds. The disordered structure of hard carbon provides ample space for the insertion of Na+, resulting in a higher specific capacity. Hard carbon has many advantages, such as higher capacity, low voltage platform, abundant carbon source, lower cost, and simple preparation process, so hard carbon is one of the most promising anode materials among carbon-based anode materials [1].

3.2. Iron-based

Iron has been widely studied as an anode material for sodium-ion batteries due to its advantages of abundant resources and low cost [2]. Latest research indicates that iron-based electrode materials' ability to store energy through multi-electron reactions endows them with a significant reversible specific capacity. This, coupled with their numerous benefits like being abundant in resources, cost-effective, and eco-friendly, positions them as potential choices for developing advanced lithium/sodium ion batteries. However, iron-based electrode materials have problems such as large volume change when embedded in lithium/sodium, low conductivity of itself, and easy agglomeration. For this reason, researchers have proposed the following solutions: Li [3] further selenide and phosphide treatments on top of his prepared Fe O34 @CNFs-40 composites to finally obtain Fe7 Se8 @CNFs-40 and FeP4 @CNFs-40 composites. The viability of this all-purpose approach for the synthesis of anode materials for sodium-ion batteries is confirmed by the composites' good electrochemical performance when employed as a binder-free anode. Qin [4] produced two iron-based nanomaterials by phosphatising or sulphurising the precursors to maximise the optimisation of the material properties. Wang [2] et al. developed FerSs-FeP@NC featuring a heterojunction framework through a singular carbonation/phosphatisation/sulphurisation process, and utilizing the FePS-3 complex as an anode for sodium-ion batteries. This heterojunctional structure, rich in defects, offers numerous active sites, leading to significant capacitive input at elevated currents.

3.3. Alloys

3.3.1. Antimony

Antimony (Sb) is a folded layered structure [5] with high density and high conductivity (2.5 × 104 S/cm); and the interlayer spacing is capable of accommodating a large number of sodium ions, which allows for the formation of a variety of alloys [6]. Antimony and sodium ions exhibit a special two-stage alloying/de-alloying mechanism, with intermediates exhibiting superior mechanical properties and weaker interatomic interactions, mitigating mechanical fracture while improving structural stability [7]. Antimony as an anode material undergoes volume expansion (~390%) back during cycling, and the cracking of the SEI causes the antimony-sodium alloy to produce a large number of fresh surfaces, which continually consume the electrolyte and also lead to the continuous thickening of the SEI, rapidly depleting the active sodium. Moreover, the pulverisation of the active material as well as the detachment from the electrodes will also lead to cell failure. In order to improve the service life of antimony negative electrodes, structural nanosizing and composite with porous conductive media are commonly used methods.

Antimony is usually used as a lumpy material, which suffers from poor electrolyte wettability, low efficiency during cycling and susceptibility to pulverisation. These problems can be alleviated by reducing the size of the bulk antimony. In addition, antimony is able to exist in two-dimensional (e.g., nanosheets), one-dimensional (e.g., nanorods, nanowires), and zero-dimensional (e.g., nanoparticles, nanorods, quantum dots) structures, and the low-dimensional structure has a higher specific surface area to build directional channels, which enhances the sodium ion/electron transport capacity.

By compositing antimony with matrix materials such as carbon, it has the effect of inhibiting swelling, reducing material pulverisation and increasing electrical conductivity. Gu et al [7] Utilizing an oxidation-coating-reduction technique, hollow core-shell rod-like antimony-carbon composites were created, densely dispersing antimony monoatoms within the carbon layer. The reversible specific capacity of the material exceeded 620 mAh/g at 0.1 C, and the first-loop coulombic efficiency reached 84.9%.Liu et al [8] embedded Sb2O3 in a carbon nanotube framework by one-step solvent-thermal method, and then thermally reduced it to obtain loofah-like Sb@CNTs@C, which was able to maintain its capacity of 221 and 206 mAh/g for 1,000 cycles at the current densities of 0.2 and 1 A/g, respectively. 221 and 206 mAh/g, respectively.

3.3.2. Bismuth

Bismuth (Bi) has a structure similar to that of antimony, with a layer spacing of 3.94 Å and a conductivity of about 7.75×103 S/cm; the "sodium-friendly" property ensures rapid migration and uniform distribution of sodium ions. Bismuth also suffers from severe volume expansion and elastic softening during the sodiation process, which leads to a decrease in the mechanical properties [9]. Wang et al.

In [10], Initially, employing a bismuth and graphene nanocomposite as an anode in sodium-ion batteries led to achieving reversible capacities of 561 mAh/g and 358 mAh/g at voltages of 2.0~0.01 V and 0.9~0.3 V, respectively. Simultaneously, non-in situ XRD analysis showed that bismuth conserves sodium through an intercalation method rather than alloying with sodium ions, with its broader layers being more beneficial for accommodating sodium ions. Similarly, bismuth's issue mirrors that of antimony, stemming from volume increase during sodiation, and creating a composite structure to mitigate this expansion is a frequent remedy, potentially enhancing the electron/ion transport ability.

Based on the top-down (up-down) assembly technique, bismuth can be composited with other matrices based on electrostatic interactions, hydrogen bonding and so on. Composite of bismuth with carbon and other matrices can effectively solve the problems of particle crushing and SEI rupture caused by the volume expansion of bismuth during charging and discharging processes. Chen et al [11] prepared bismuth intercalated graphite by using the intercalation-conversion reaction of binary graphite intercalation compounds, which achieves the fast charging of 300 C and the full charging/full discharging can be accomplished in 12 s. Chen et al [12] used bismuth intercalated graphite in a vacuum and evaporation process. Cheng et al [13] designed and synthesized a flexible film composed of one-dimensional ultrafine bismuth nanowires and two-dimensional reduced graphene oxide heterostructures with the help of a simple vacuum filtration technique, which provides a general strategy for the preparation of alloy-based flexible anode materials.

Based on the bottom-up synthesis technique, composites with different morphologies and sizes can be prepared by domain-limited reduction and cladding-carbonisation. The construction of core-shell structures is one of the most common strategies for the preparation of composites, and core-shell structures with uniform carbon encapsulation can be obtained by carbonisation of organic cladding and in situ reduction of bismuth-containing precursors. Zhang et al [14] used lignin gel encapsulation to encapsulate bismuth nanorods in lignin-derived carbon shells, and ether-based electrolyte to form SEIs enriched with inorganic components. During long cycling processes, the carbon skeleton facilitates the transformation of bismuth into a three-dimensional porous structure, which promotes electron transport and shortens the ion diffusion pathway. Yan et al [15] The carbon layer shell effectively compensates for volume changes, thereby safeguarding against bismuth disintegration. This attribute allows the material to undergo swift charging and discharging, achieving a current density of 100 A/g within a mere 6.4 seconds, while still maintaining a substantial capacity of 178 mAh/g. Xue et al [16] utilised Rayleigh instability to encapsulate bismuth in nitrogen-doped carbon nanotubes, achieving a high-power density of 1190 W/kg.

4. Conclusion and Outlook

Although sodium-ion batteries have many benefits, including quick charging and discharging times and a vast development space in the field of large-scale energy storage, their development is hindered by the absence of reasonably acceptable anode materials. This study examines the advancements made in the field of anode materials research for sodium-ion batteries, weighing the benefits and drawbacks of different materials as well as the strategies used by researchers to build upon their findings. It is anticipated that as long as researchers keep up their current efforts, the study of anode materials for sodium-ion batteries will advance and lead to the commercial application of these batteries' high specific energy, long lifespan, and high safety.

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