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Research Status and Prospects of Sodium-Ion Batteries

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ABSTRACT
With the rapid development of clean energy, electrochemical energy storage technology has become a critical support. Sodium-ion batteries (SIBs) have shown great potential in the energy storage field due to their abundant resources and low cost. This paper comprehensively reviews the progress in the performance of sodium-ion batteries, delving into electrode materials, electrolytes, and overall battery performance. It analyzes the existing problems in current research and provides an outlook on future development directions.

KEYWORDS
Sodium-ion batteries; Electrode materials; Electrolyte; Battery performance

1 Introduction

To reduce dependence on lithium resources, it is essential to develop high-performance sodium-ion batteries. Lithium resources are unevenly distributed globally, and China faces a scarcity of lithium. In contrast, sodium is several times more abundant than lithium and is evenly distributed. Developing high-performance sodium-ion batteries can reduce reliance on external lithium resources, ensuring the security of critical energy raw materials in China. In large-scale energy storage scenarios such as grid storage and renewable energy integration, the cost, safety, and cycle life of batteries are of paramount importance. Improving the performance of sodium-ion batteries can better meet these demands, allowing them to occupy a significant position in the large-scale energy storage market due to their cost advantages and good safety performance. This will promote the integration of renewable energy and the stable operation of the power grid. China has a certain technological foundation and industrial advantages in the field of sodium-ion batteries.

2 Working Principle of Sodium-Ion Batteries

2.1 Role of Cathode and Anode

During charging, the cathode undergoes an oxidation reaction, and sodium ions de-intercalate from the cathode material lattice, entering the electrolyte. Simultaneously, electrons flow through the external circuit from the cathode to the anode to maintain charge balance. At the anode, sodium ions migrate through the electrolyte and separator under the influence of electric field and concentration gradients, embedding into the anode material lattice. The discharge process is the reverse of charging, with the anode undergoing oxidation and the cathode undergoing reduction, generating current to power the load.

2.2 Role of Separator

The separator is a crucial component in sodium-ion batteries, allowing sodium ions to pass through while preventing direct contact between electrons and the active materials of the cathode and anode, thereby preventing internal short circuits and ensuring safe operation.

2.3 Role of Electrolyte

The electrolyte facilitates the conduction of sodium ions in sodium-ion batteries. Common electrolytes are divided into liquid and solid electrolytes.

3 Electrode Materials for Sodium-Ion Batteries

3.1 Cathode Materials

3.1.1 Transition Metal Oxides

Transition metal oxides are one of the earliest and most widely studied cathode materials for sodium-ion batteries.

Doping with different valence metals significantly affects their performance. Low-valence ion doping enhances stability and increases average voltage, while high-valence ion doping inhibits O/P phase transitions and accelerates diffusion rates. Density functional theory (DFT) studies on volume change, interlayer spacing, sodium de-intercalation, migration barriers, and lattice oxygen activity provide theoretical guidance for developing high-performance cathode materials. Various transition metal oxide systems differ in reversible capacity, voltage, and structural stability. Research on preparation methods, structural stability, and electrochemical performance is crucial for optimizing these materials [1-3].

3.1.2 Polyanionic Materials

Polyanionic materials offer structural stability and good safety performance. Their anionic groups (e.g., SO_4^{2-}, PO_4^{3-}) are connected to the central atom through strong covalent bonds, providing high structural stability. However, these materials often suffer from low electronic conductivity and ion diffusion rates, limiting their rate performance. Nanostructuring, surface coating, and element doping can improve their electrochemical performance. For example, carbon coating on $Na_3V_2(PO_4)_3$ enhances electronic conductivity, improving rate performance and cycle stability [1-3].

3.1.3 Prussian Blue Analogues

Prussian blue analogues have an open framework structure that facilitates rapid sodium ion diffusion and intercalation/de-intercalation. However, the presence of crystalline water and vacancy defects in their structure affects the initial Coulombic efficiency and cycle stability. Optimizing synthesis processes to reduce crystalline water and vacancy defects, along with surface modification and element doping, can improve their performance. For example, co-precipitation methods to prepare K-Na-Fe-Mn Prussian blue analogues, by controlling potassium-sodium ratios and iron-manganese content, improve capacity and cycle performance [1-3].

3.1.4 Organic Molecules and Polymers

Organic molecules and polymers as cathode materials are environmentally friendly and offer design flexibility. However, they often suffer from poor conductivity and low electrode potential. Composites with conductive materials such as carbon nanotubes and graphene can enhance conductivity and battery performance [4].

3.2 Anode Materials

3.2.1 Hard Carbon

Hard carbon, with its wide availability and high electrochemical performance, is a research hotspot and one of the best choices for sodium-ion battery anode materials. It has low redox potential, stable structure, large interlayer spacing, and relatively low cost. However, hard carbon anodes face challenges such as low initial Coulombic efficiency, poor long-term cycle stability, and rate performance.

Research shows that carbonization temperature, pre-oxidation processes, pore structure, and heteroatom doping significantly affect hard carbon performance. Increasing carbonization temperature improves graphitization, enhancing sodium storage performance. Pre-oxidation introduces oxygen-containing functional groups, improving hydrophilicity and initial Coulombic efficiency. Optimizing pore structure increases micro- and mesopore proportions, facilitating sodium ion storage and diffusion. Heteroatom doping (e.g., N, P, S) alters the electronic structure, improving conductivity and sodium storage sites. Biomass, due to its low cost and renewability, is a promising precursor for hard carbon anode materials.

Different biomass precursors yield hard carbons with varying structures and properties. Hydrothermal carbonization, activation, and template methods are common preparation techniques. Pyrolysis conditions, including temperature, heating rate, and holding time, also significantly impact the structure and performance of biomass-derived hard carbons [5-6].

3.2.2 Carbon-Based Composites

Carbon-based composites overcome the limitations of single carbon materials. For example, 3D porous carbon (3DPC) prepared using NaCl as a template and freeze-drying technology, when composited with $FeSe_2$, yields $FeSe_2$/3DPC composites with superior electrochemical performance. Other examples include sulfur-doped pitch-based hierarchical porous carbon materials and phosphorus-doped pitch-based multi-layer reduced graphene oxide composites. Element doping and compositing introduce new active sites, enhancing conductivity and structural stability, thereby improving sodium storage performance [7-8].

3.2.3 Alloys and Metal Oxides

Alloy anode materials (e.g., Sn, Sb) have high theoretical specific capacity but suffer from significant volume changes during charge/discharge, leading to material pulverization and electrode structure damage. Composites with carbon materials or nanostructuring can mitigate volume changes and improve cycle stability. Metal oxides (e.g., TiO_2, Fe_2O_3) are also studied for sodium-ion battery anodes, offering similar advantages and challenges. Nanostructuring, surface modification, and compositing with conductive materials can enhance their electrochemical performance. For example, TiO_2 nanotube arrays with oxygen defects exhibit improved electronic conductivity and ion diffusion rates, showing high rate performance in lithium batteries [9-10].

3.3 Electrolytes for Sodium-Ion Batteries

Electrolytes play a crucial role in connecting the cathode and anode materials in sodium-ion batteries. Organic electrolytes are widely used due to their low viscosity, high dielectric constant, and good compatibility with common electrode materials. However, organic electrolytes face challenges such as low oxidation potential, limited cycle performance, and flammability. Research on new solvent systems, such as fluorinated organic solvents, offers higher oxidation potential and thermal stability, potentially improving electrolyte performance. Different sodium salts (e. g., $NaClO_4$, $NaPF_6$, $NaBF_4$) affect dissociation, ionic conductivity, and solvent interactions, influencing battery performance. Additives, such as film-forming, flame-retardant, and overcharge protection additives, can improve the properties of the electrode/electrolyte interface, enhancing initial Coulombic efficiency, cycle stability, and safety [11-14].

3.4 Separator Materials

3.4.1 Polyolefin Separators

Polyolefin separators, primarily made of polyethylene (PE) and polypropylene (PP), are mature and widely used in lithium-ion batteries. Due to the similar working principles of sodium-ion and lithium-ion batteries, polyolefin separators are also used in sodium-ion batteries. They offer low cost, good mechanical properties, and strong chemical stability. However, they have poor wettability in common sodium-ion battery electrolytes (e. g., esters, ethers), limiting ionic conductivity and charge/discharge performance. They also have poor thermal stability, which can lead to melting and safety risks under overcharge, rapid charge/discharge, or high-temperature conditions [15-16].

3.4.2 Cellulose-Based Separators

Cellulose-based separators, made from abundant natural polymers, offer good adsorption, porosity, environmental friendliness, and low cost. However, they are still in the laboratory research stage, and challenges remain in optimizing preparation processes and improving performance for commercial production [15][17].

4 Strategies to Improve Performance

4.1 Cathode Materials

Element Doping: Doping with elements such as Mg and Ti in layered oxides can optimize crystal structure, enhance sodium ion diffusion, and improve electronic conductivity, boosting rate performance and cycle stability.

Surface Modification: Coating with materials like Al_2O_3 or $LiNbO_3$ can suppress side reactions between the electrode and electrolyte, improving structural stability and extending cycle life.

4.2 Anode Materials

Optimizing Preparation Processes: Precise control of pyrolysis temperature and time can improve the microstructure of hard carbon, increasing interlayer spacing and sodium ion storage sites, enhancing specific capacity and initial Coulombic efficiency.

Compositing: Combining different anode materials, such as alloy materials with carbon, can mitigate volume expansion during charge/discharge, improving cycle stability.

4.3 Electrolytes

Developing New Electrolytes: Research on new solid electrolytes, such as NASICON and LISICON types, can enhance ionic conductivity, chemical stability, and thermal stability, improving overall battery performance and safety.

Optimizing Electrolyte Formulations: Adjusting lithium salt concentration, solvent composition, and additives in liquid electrolytes can form stable solid electrolyte interface (SEI) films, improving cycle performance and low-temperature performance.

5 Challenges

5.1 Performance

The larger ionic radius of sodium compared to lithium leads to structural collapse in electrode materials, limiting energy density.

Sodium ion intercalation and de-intercalation are more complex, resulting in higher resistance and polarization, with charge/discharge efficiency typically around 80%-90%, compared to over 95% for lithium batteries.

5.2 Cost

The declining price of lithium carbonate reduces the cost advantage of sodium-ion batteries.

The sodium-ion battery industry chain is still in its early stages, with high costs for anode materials like hard carbon.

5.3 Industry Chain

The lack of mature supply chains for key materials such as cathode, anode, and electrolytes affects cost control, quality, and production efficiency.

Production equipment is mostly adapted from lithium-ion battery lines, lacking standardized equipment designed specifically for sodium-ion batteries, limiting production efficiency and product consistency.

There is a lack of dedicated chargers, controllers, and battery management systems (BMS) tailored for sodium-ion batteries.

5.4 Market

The diversity of cathode, anode, and electrolyte combinations in mass-produced products leads to a "hundred schools of thought" scenario, with no dominant technical solution emerging.

Limited consumer awareness of sodium-ion battery performance, advantages, and applications poses challenges for market promotion and acceptance.

6 Conclusion and Outlook

In terms of material innovation, developing new cathode materials can improve the energy density of sodium-ion batteries. Using 3D printing to create porous carbon anode materials can enhance unit area capacity and energy density. Developing new solid electrolytes with ionic conductivity above 10^{-3} S/cm can further improve performance. In battery performance enhancement, optimizing electrode structure and assembly processes can increase charge/discharge rates and cycle life. Using porous electrodes can improve rate performance, while improved packaging and electrolyte formulations can extend cycle life. Solid electrolytes and optimized structures can reduce thermal runaway risks. In application expansion, sodium-ion batteries are being piloted in small-scale energy storage stations, and the development system for sodium-ion batteries is continuously improving.

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