

The Analysis of the Sodium-ion Battery and Its Development

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Abstract: In recent years, as the demand for energy storage systems has continued to grow, sodium-ion batteries have become a promising alternative to traditional lithium-ion batteries. This paper mainly introduces the research of sodium-ion batteries. The advantages of sodium-ion batteries are abundant sodium resources, low cost and excellent electrochemical performance potential. In this paper, the working principle and structure of the sodium-ion battery are introduced, including the key materials such as cathode, anode and electrolyte, and the latest progress of the sodium-ion battery is described. At the same time, this paper also compares the sodium-ion battery and a traditional lithium-ion battery, revealing the potential of sodium-ion battery. In addition, the challenges and prospects of sodium-ion batteries are also discussed. Despite some limitations, sodium-ion batteries have great potential for large-scale energy storage and low-power applications. With further research and optimization, sodium-ion batteries are expected to play an important role in the future energy landscape.

Keywords: Rechargeable battery, sodium ion battery, anode and cathode materials, lithium-ion batteries, energy density.

1. Introduction

In the context of the global pursuit of sustainable development, the importance of energy storage technology has become increasingly prominent. With the wide application of renewable energy sources such as solar and wind energy, efficient and reliable energy storage systems have become a key link to achieve stable energy supply. Among the many energy storage technologies, battery technology has attracted much attention for its flexibility, mobility and efficiency. The main battery technology in the market is rechargeable batteries.

Rechargeable batteries, also known as secondary batteries, can be charged by an external power source, converting electrical energy into chemical energy for storage, and converting chemical energy into electrical energy output when needed. The main types of rechargeable batteries are lithium-ion batteries, nickel-metal hydride batteries and lead-acid batteries. Lithium-ion batteries have the advantages of high energy density, lightweight, low self-discharge rate, and are widely used in mobile phones, laptops and electric vehicles, etc. The working principle is that lithium ions are embedded and removed between positive and negative electrodes. Nickel-metal hydride batteries are relatively environmentally friendly, with high capacity, good charge-discharge performance and small memory effect. They are charged and discharged by the transfer of hydrogen between the negative metal hydride electrode and the positive nickel hydroxide electrode [1]. Lead-acid battery technology is

mature, low price, high reliability, common in automotive starting power supply and UPS and other fields, the use of lead and lead dioxide in sulfuric acid electrolyte REDOX reaction work. Performance characteristics of rechargeable batteries include energy density, which determines how much storage a battery can hold, which is critical for mobile devices and electric vehicles, and lithium-ion batteries generally have a higher energy density.

In recent years, sodium-ion batteries have emerged as a promising alternative to traditional rechargeable batteries. Sodium-ion batteries have several advantages. First, sodium is abundant in nature, making sodium-ion batteries more cost-effective due to the breadth of raw materials. Secondly, they have good electrochemical properties. While their energy density is currently slightly lower than lithium-ion batteries, ongoing research and development efforts are focused on improving this aspect. The sodium-ion battery also has good rate performance and cycle stability [1]. In addition, they are considered more environmentally friendly because sodium is extracted and processed with less energy consumption and less environmental impact than some other battery chemicals. With the further development of technology, sodium-ion batteries are expected to be applied in various fields such as large-scale energy storage, electric bicycles, and low-power electronics.

This paper emphasizes several key parameters of sodium-ion batteries (interlayer distance, energy density), and attempts to optimize the selection of cathode and anode materials. Among the methods to increase the energy density, Prussian blue structured metal cyanides are chosen as the cathode in this article to achieve a higher energy density. In another study, metal oxides are expected to be excellent intercalation hosts to anode, greatly increasing sodium storage capacity. These studies demonstrate the potential of sodium-ion batteries and lay the foundation for future research.

2. Basic information of Sodium-ion battery

2.1. Operation mode and sodium storage mechanism

The working principle of the battery involves the process of embedding sodium ions between the positive and negative electrodes to realize the process of charging and discharging. During charging, the Na^+ detaches from the positive electrode and is embedded in the negative electrode through the electrolyte, while the electrons flow through the external circuit to the negative electrode to maintain the charge balance between the positive and negative electrodes. In the discharge process, the process is reversed, Na^+ from the negative electrode, through the electrolyte embedded in the positive electrode.

Sodium-ion batteries have three ways to store energy: 1. Intercalation reaction: Sodium ions intercalate between layers of the negative material, like the working principle of lithium-ion batteries. 2. Alloying reaction: the negative electrode material is alloyed with sodium to form a sodium alloy, thus achieving energy storage. 3. Conversion reaction: The negative material is chemically converted to embed sodium ions in the lattice and store energy.

One example is hard carbon (HC). By studying the steady state of sodium in hard carbon, scientists explained the mechanism of sodium storage by theoretical calculation. And the new method uses conventional methods to carbonize sucrose. The existence of steady-state quasi-metallic sodium was directly verified by the different chemical reaction characteristics of metallic sodium and ionic sodium immersed in protic solvent [2].

2.2. Interlayer distance

In addition, a very important parameter of sodium-ion batteries is the interlayer distance. Since sodium (ion radius is $1.16 \text{ \AA}$) is larger than lithium (ion radius is $0.90 \text{ \AA}$), there is a large amount of intercalation and deintercalation in sodium-ion batteries. Obstacles in conventional graphite anodes. The interlayer distance of traditional graphite is about 0.34 nm , which cannot accommodate sodium

ion parameters. If one wants to insert sodium into graphite layers, the interlayer distance should be increased to at least 0.37nm [3]. Therefore, in the design of sodium-ion batteries, the layer spacing will be a key parameter.

3. Selection of anode and cathode materials

Negative electrode materials can be divided into intercalation, alloying and conversion according to the electrochemical reaction mechanism. Carbon materials and titanium-based oxides developed based on intercalation reaction mechanisms were applied to SIB anode materials. Although these electrode materials exhibit good long-term cycling performance, their specific capacity is still limited due to their inherently low theoretical capacity. Alloy-based anode materials, such as tin, antimony and red phosphorus, can provide higher specific capacities by forming sodium-rich compounds. However, these materials undergo significant volume changes during cycling, leading to problems with electrode pulverization and capacity decay. In recent years, due to their high theoretical capacity and low cost, metal oxides, sulfides, selenides, phosphates, nitrides and fluoride conversion anode materials have also received attention [4]. Therefore, the development and design of advanced SIBs conversion anode materials is likely to become mainstream in the future.

When researching cathodes for sodium-ion batteries (SIBs), research mainly focuses on three major categories of compounds. According to Pu's study, the first category is sodium transition metal oxides, these materials have high reversible capacity and high operating voltage [5]. Nonetheless, most of them still suffer from irreversible phase transitions, air instability, and insufficient battery performance. The second category is Prussian blue analogues, which exhibit good operating voltage, cycling stability, and rate capability. However, the main obstacles to their practical application are the control of lattice defects, thermal instability, and low tap density. Finally, polyanionic compounds are another category of cathode materials that have attracted much attention due to their good structural stability, high safety, and small cycle volume change.

4. Comparison with lithium-ion batteries and problems

Lithium-ion batteries (LIB) are the trendsetter in rechargeable batteries, dominating the portable electronics and electric vehicle markets, but the market for grid-scale batteries is immature. Therefore, SIB has attracted much attention as one of the most promising energy storage and conversion devices for grid-level energy storage systems. Although SIBs exhibit lower specific capacity and operating potential than LIBs and therefore exhibit poorer energy density, in fact, power density rather than energy density is usually a more important parameter for SIBs in energy storage systems. Grid-level batteries are required to provide short-term emergency backup power and provide active power when the grid frequency is below a certain lower threshold and charge when the frequency is above a certain upper threshold, thus facilitating frequency regulation [5]. In this case, the power capabilities of SIBs are crucial for their successful application in power storage systems. At the same time, sodium resources are very abundant. Although it cannot directly significantly reduce battery costs, in the context of lithium shortage and related price increases, the application of sodium can bring huge cost advantages. One of the most well-known advantages of SIB is the use of aluminum as the anode current collector, as aluminum is more cost-effective and lighter than copper. Aluminum resists excessive battery discharge, while copper is susceptible to oxidation, which can lead to serious battery problems, including thermal runaway [6]. In addition, SIBs can be stored and transported in a fully discharged state, significantly reducing safety issues and thus costs.

It is worth noting that there are still many problems with sodium-ion batteries. Although sodium-ion batteries and lithium-ion batteries are mechanically similar, many electrode materials are not as good at storing sodium as they are at storing lithium, and currently cannot meet the needs of practical

applications. As the radius increases, the destructive power of sodium ions on the electrode material structure increases during the insertion and extraction processes. Therefore, electrode materials with a more stable structure are needed. The structure should also contain larger channels to promote sodium ions' transmission [7]. Therefore, electrode materials still need to be further optimized.

5. Solutions to increasing energy density

According to Zhao, various materials composed of layered metal oxides, Prussian blue structured metal cyanides, have been evaluated as cathodes for sodium-ion batteries that can achieve high energy densities[8]. In this work, $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$ was proposed and synthesized. Interestingly, $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$ exhibits a three-step redox reaction at 3.7, 4.2 and 4.5 V vs Na/Na, corresponding to the redox pairs of $\text{Mn}^{2+}/\text{Mn}^{3+}$, $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Cr}^{3+}/\text{Cr}^{4+}$, respectively. The open and stable NASICON structure ensures excellent cycle stability, with a capacity retention rate of 85% after 500 cycles at 100 mA g⁻¹ in the 2.5–4.3 V range and a capacity retention rate of 73.3 in the 2.5–4.6 V range.

Three stepwise oxidation peaks located at 3.75, 4.25 and 4.4 V vs Na/Na are clearly shown in Figure 1, indicating the continuous oxidation reactions of $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$, $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ and $\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$. Therefore, the three reduction peaks located at 4.3, 4.0, and 3.4 V were assigned to the insertion of sodium ions and the phase transition from $\text{NaMnCr}(\text{PO}_4)_3$ to $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$. The highly overlapping CV curves illustrate the good reversibility of the sodium ion extraction/insertion process.

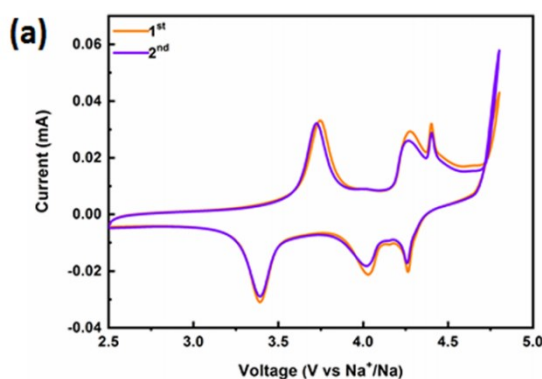


Figure 1: Elevating Energy Density for Sodium-Ion Batteries through Multielectron Reactions [8]

In another study, P2-type $\text{Na}_{0.55}[\text{Ni}_{0.1}\text{Fe}_{0.1}\text{Mn}_{0.8}]\text{O}_2$ was proposed as an effective intercalation host for high energy density sodium-ion batteries (SIB). We optimized the structure of the manganese-based P2-type Na_xMeO_2 cathode by partially replacing Ni^{2+} and Fe^{3+} in the transition metal layer. Through a simple electrochemical method, partial replacement of Ni and Fe in the Mn site significantly improves the reversibility of the sodium intercalation and deintercalation process [9].

In the study of Gu, they successfully prepared $\text{Na}_3\text{V}_{1.9}(\text{Ca}, \text{Mg}, \text{Al}, \text{Cr}, \text{Mn})_{0.1}(\text{PO}_4)_2\text{F}_3$ (referred to as HE-NVPF) carbon-free high-entropy phosphoric acid through in-situ partial substitution of V atoms. Salt positive electrode [10]. The favorable high-entropy effect in HE-NVPF promotes the realization of a significant increase in the average voltage plateau (from 3.67 to 3.81 V), greatly improving the sodium storage capacity and energy density. It has excellent cycling stability compared to pristine NVPF (p-NVPF, i.e., non-high-entropy NVPF) and other fluorophosphate counterparts.

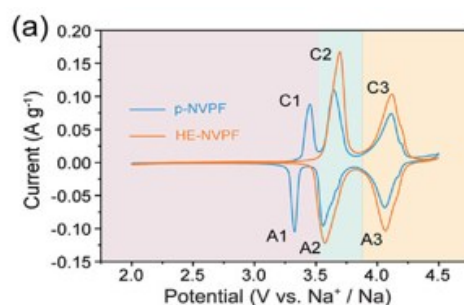


Figure 2: An Advanced High - Entropy Fluorophosphate Cathode for Sodium - Ion Batteries with Increased Working Voltage and Energy Density [10]

Cyclic voltammetry (CV) curves were used to evaluate the impact of high entropy effects on the electrochemical behavior of NVPF materials. In Figure 2, the CV curve of the as-prepared p-NVPF cathode shows three pairs of redox peaks, labeled A1/C1, A2/C2, and A3/C3. However, in the CV curve of the HE-NVPF cathode, the A1/C1 peak in the low voltage region (<3.5 V) is absent, consistent with subsequent studies.

Finally, Chen's team proposed another sodium superion conductor (NASICON) structure: $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. Most NASICON-type electrodes rarely undergo complex phase change reactions during sodium storage, resulting in satisfactory cycling stability, which is an important factor for large-scale EES [11]. Among them, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ can be regarded as a universal representative material because it has a relatively high operating voltage (about 3.4 V) and a theoretical capacity of 117 mAh g^{-1} , and despite its relatively low conductivity, excellent rate performance.

6. Conclusion

In conclusion, sodium-ion batteries are a very promising energy storage technology. Thanks to the abundance of sodium resources, the cost of sodium-ion batteries is more effective. At the same time, the energy density of sodium ions also has room for improvement. The selection of a cathode material and an intercalated anode material are introduced in this paper, but the optimization of the whole reaction mechanism is not fully studied. Like the choice of electrolytes. This article is still a good illustration of the potential of sodium-ion batteries and is likely to be studied more fully in the future.

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