Research of Cathode Materials for Sodium-Ion Batteries

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Abstract. Sodium-ion batteries are being extensively studied as a replacement for lithium-ion batteries in some areas. However, there are also some problems with cathode materials at present. Sodium-ion batteries perform worse performance than lithium-ion batteries, which is due to the properties of sodium. For instance, sodium ions possess a greater ionic radius and increased atomic weight compared to lithium ions. This piece presents an overview of the operational principles behind sodium-ion batteries, examining the preparation techniques, structure, and effectiveness of three main cathode materials. Moreover, the current challenges of cathodes and the corresponding solutions for sodium-ion batteries are systematically recognized. This article provides a new perspective or idea for solving the problem of sodium-ion battery cathode.

Keywords: Sodium ion battery, cathode material, modification strategy.

1. Introduction

In recent years, people are facing severe energy and environmental crisis. In different nations, there is a growing trend toward the adoption of new energy vehicles as a substitute for conventional fuel-powered vehicles for transportation purposes. At present, the new energy vehicles powered by lithium-ion batteries dominate the new energy market. However, the raw materials for preparing cathodes of lithium-ion batteries, including lithium, cobalt, nickel and phosphorus, are non-renewable and limited. Moreover, the rapid development of new energy vehicles has led to a shortage of these raw materials and even an insufficient supply, thus raising prices, especially lithium. People are beginning to seek out a different type of battery as a substitute for lithium-ion batteries. Sodium-ion batteries can solve this problem very well [1]. Firstly, they are low cost before sodium element is abundantly stored in the earth, thereby making sodium-ion batteries significantly cheaper than lithium-ion batteries. Moreover, sodium-ion batteries have stronger resistance to high temperatures. So, sodium-ion batteries show better safety than lithium-ion batteries [2]. Consequently, sodium-ion batteries have been attracting increasing interest globally. However, sodium-ion batteries currently face certain challenges. For example, the cathode's sodium ions are larger and heavier than lithium ions, leading to decreased cycle performance and lower energy density capacity [3]. At present, sodium-ion battery cathode materials are primarily classified into three main groups.: Prussian blue analogues, layered transition metal oxides and polyanionic materials, as shown in Figure 1 [4]. This piece presents the cathode materials most frequently utilized in sodium-ion batteries, followed by a discussion of their respective strengths and weaknesses. In conclusion, the future research emphasis will be on cathode materials in sodium-ion batteries.

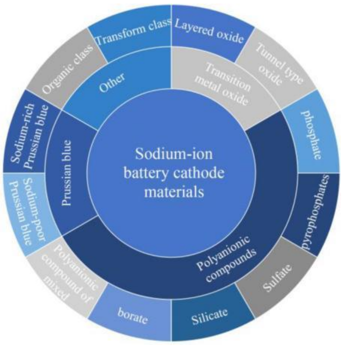

Figure 1. The primary components presently employed in cathodes for sodium ion batteries [3]

2. Sodium-ion battery energy storage mechanism

The principle of operation and configuration design of sodium-ion batteries are quite similar to those of lithium-ion batteries, leading to their shared designation as “rocking chair batteries”. Taking the layered transition metal oxide cathodes as an example, we describe the working principle and composition of sodium-ion batteries, as depicted in Figure 2. Throughout the charging process, sodium ions are extracted from the cathode and then incorporated into the anode following their passage through the electrolyte and membrane. During the discharge stage, sodium ions will be released from the anode and intercalated into the layered transition metal oxide layers [5]. Electrons transfer occur in an external circuit to maintain charge balance at the same time. The continuously directional electron transfer corresponds to the generation of current. The mechanisms of other cathodes are same as the layered transition metal oxide cathodes.

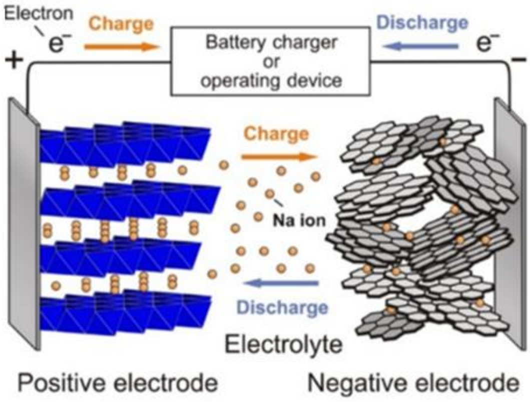

Figure 2. Structural diagram of sodium-ion battery operation [6]. The cathode is a layered metal oxide and the anode is hard carbon

3. Sodium-ion battery cathode materials

3.1. Prussian blue analogues

The Prussian blue analogues are a material with a cubic crystal structure, and this type of cathode material can be denoted by $A_{2-x}M[M'(CN)_6]_{1-y}\square_y \cdot nH_2O$. Among them, “A” represents an alkali metal ion (such as the lithium ion and sodium ion), M’ is typically Fe, denotes a vacancy, and M refers to a transition metal element [7].

Taking $Na_2M^{II}[Fe^{II}(CN)_6]$ as an example, it can be observed from Figure 3(a) that the Prussian blue analogues unit cell possesses a highly open framework structure, namely, a three-dimensional structure. After coordination, a very spacious ion channel can be formed, which allow rapidly insert and extract alkali metal ions, and the structure is not prone to change [1]. Nevertheless, the cathode of sodium-ion batteries faces significant difficulties and challenges when utilizing Prussian blue analogues. The first point is that its lattice structure will be intrinsic defects, mainly lattice vacancy, as depicted in Figure 3(b). During the process of charging and discharging, some heat will be inevitably generated due to the special lattice characteristics, which will lead to the decomposition of the cathode material. The second is that the formed crystal water, which is very easy to occur during the synthesis of the compound, will damage the crystal lattice and even the Na content, resulting in serious safety problems for sodium-ion batteries [6].

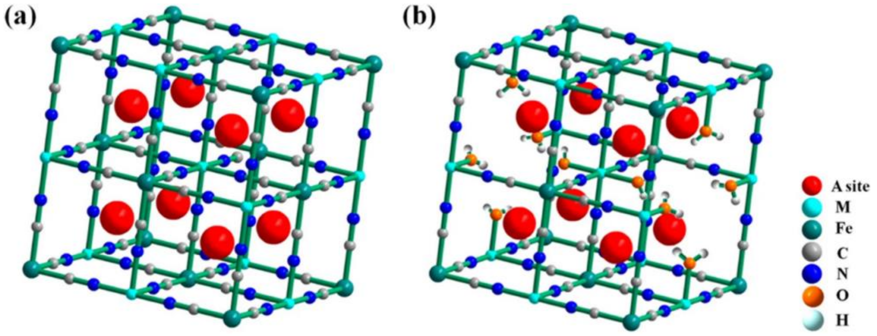

Figure 3. Schematic depiction of the crystal arrangement in Prussian blue analogs. (a) normal crystal structure; (b) defective crystal structure with permission from literature [7]

The main methods for synthesizing the Prussian blue analogues include co-precipitation, electrodeposition, ball milling and hydrothermal methods [7]. If prepared by the electrodeposition process, the synthesized Prussian blue analogues film has poor adhesion to conductive glass, resulting in poor cycle stability [8]. While prepared by the ball milling method, the inadequate reaction and easily aggregate particles will occur, leading to low capacity and cycle stability. The hydrothermal method demands overly complex experimental procedures and overly advanced instruments to prepare Prussian blue analogues materials. It is worth emphasizing that the co-precipitation method is straightforward and time-efficient compared with several other methods, the cathodes prepared by this method even show excellent electrochemical performance [7]. Therefore, the co-precipitation approach is currently predominantly utilized for the preparation of Prussian blue analogues. Nevertheless, no matter which method is used, the vacancies and lattice water that seriously interfere with sodium transport will inevitably be produced and are hard to eliminate. The lattice water and vacancies will occupy the positions of sodium ions, thereby influencing the electrode capacity.

High-quality Prussian blue analogues are usually fabricated with enhancing crystallinity, indicating the decreased content of lattice water and vacancies. In order to repair defects (vacancies and lattice water), some surfactants can be used to reduce the surface tension of Prussian blue analogues materials [9]. In addition, the reaction rate synthesizing Prussian blue analogues can also be inhibited by adding chelating agents to minimize the formation of vacancies. Crystallization water can also be eliminated through heat treatment. However, it is crucial to carefully control the temperature during heat treatment, as excessively high temperatures can result in structural damage, collapse, or other undesirable side reactions. To enhance the concentration of sodium ions, Prussian blue analogues can also be fabricated by establishing a sodium-abundant environment, thereby augmenting the specific capacity of the Li-ion battery [9]. Frequent utilization of raw materials containing excessive sodium in the preparation process, such as NaCl, contributes to the creation of a sodium-rich environment and the reduction of vacancies and crystal water. Some inactive metal ions or other structures can also be introduced to solve these problems [6]. Ion doping is an effective method for achieving high performance and is also the most commonly used approach. By introducing new atoms into the lattice in Prussian blue analogues, the original chemical properties can be modified to enhance the electrochemical performance of the material. For instance, Cr doping, which can perturb the original lattice structure, contributes to improved conductivity and structural stability in sodium-ion batteries, thereby enhancing their overall performance.

Additionally, in order to solve the instability problem, the elements and organic matter can also be combined, which can integrate the outstanding properties of the stable characteristics of organic matter and the highly conductive features of inorganic matter [10]. For instance, inorganic materials exhibit relatively high conductivity, whereas the organic materials are comparatively stable despite their complex preparation. By harnessing the exceptional characteristics of both, we can achieve our desired outcomes. Metal-organic frameworks amalgamate these attributes and offer expansive channels for molecular entrapment. Ongoing exploration of alternative metal-organic frameworks has garnered significant attention owing to their innovative structures and stable redox potential. Utilizing metal-organic frameworks as templates for cathode material design is imperative.

3.2. Layered transition metal oxides

Generally, the layered transition metal oxide materials mainly refer to special oxides in the form of NaMO$_2$ which belong to the R3m space group, where "M" is the transition metal ion (Mn, Ni, etc.) [11]. There are two-dimensional channels in the lattice structure of the layered transition metal oxides for sodium ions diffusion, as shown in Figure 4, which allow sodium ions intercalated/deintercalated extremely rapidly from the cathode. In the 1980s, Delmas et al. categorized layered transition metal oxides into four types: O2, O3, P2, and P3, as illustrated in Figure 4, which has gained international recognition. Among them, "2" and "3" denote the number of transition metal oxide layers in one lattice unit, while the letters P and O signify that Na occupies the triangular prism (P) position and the octahedral (O) position, respectively [12].

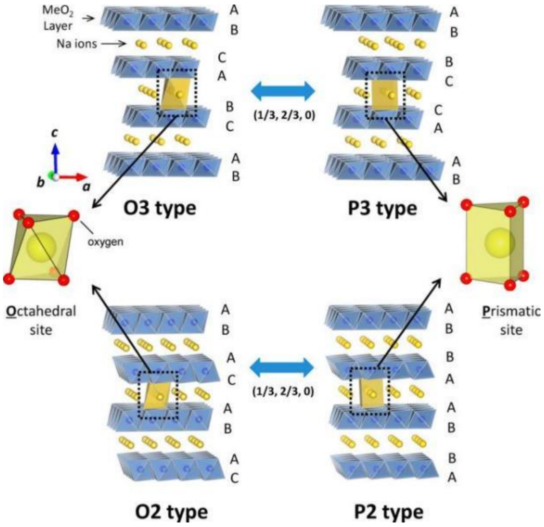

Figure 4. Crystal structures of different layered transition metal oxides [10]

Among these four types of layered transition metal oxide cathodes, the most common two are O3 and P2 [11]. They both have their own advantages. For example, the O3 type cathode has a relatively high sodium content, so the theoretical specific capacity is very high, while the P2 type has a larger spacing distance between the transition metal layers due to the triangular prism lattice unit, so the sodium ion transmission speed will be higher [10]. However, the layered metal oxides currently face many problems, such as extremely unstable structures. The main reasons are as follows: (1) The reaction between the cathode and electrolyte leads to the corrosion of the CEI film (cathode electrolyte interphase). (2) These cathodes are prone to undergo certain irreversible phase transitions, thereby causing irreversible damage to the material. (3) The cathode structure is unstable because the lattice is extremely sensitive to water and carbon dioxide, while their contact is inevitable during the manufacturing and charging/discharging process, thereby resulting in deliquescence [12].

For the layered transition metal oxides, it is necessary to minimize their irreversible phase transitions to the harmful rock salt or spinel phase and strive to achieve a stable structure. At present, cation doping is considered to be the most effective modification method [13]. The work done by Tan et al. involves doping Ti in layered metal transition oxide cathode, which ultimately leads to suppression in the irreversible phase transition compared with the undoped layered transition metal oxides [14]. At the same time, the structure has become more stable, and its stability in air and water has been greatly improved. The work conducted by Shi et al. was to dope Ti into NaNi$_{0.5}$Mn$_{0.5}$O$_2$ cathode and it was discovered that the vacancies were suppressed, the spacing between Na layers was increased, and the stability was significantly enhanced [15]. For this reason, the performance of the layered transition metal oxide cathodes for sodium-ion batteries can be enhanced by doping different transition metal elements even with different proportions. In addition to sole transition metal doping, inactive elements and co-doping substitution methods can also be employed to enhance the cycling stability of sodium-ion batteries. Furthermore, there is an expectation that sodium-ion batteries will find extensive use in small vehicles and facilities for storing energy in the future.

3.3. Polyanionic materials

Polyanion compounds are usually defined as $Na_xM_y(XO_m)_zZ_w$, where “M” are usually the metal ions (Ti, Mn, Fe, Co, etc.), X are Si, P, B, S, etc., Z are F and OH^-, etc., which have been extensively studied. It can be observed from Figure 5 that the commonly used polyanions materials typically comprise stable tetrahedral structures and octahedral structures, such as PO_4^{3-}, $P_2O_7^{4-}$, etc., where oxygen atoms are not easy to detach from the oxygen-containing groups, making the cathode structure stable [4]. Moreover, the volume expansions of the lattice structure change little during the charging and discharging process, therefore demonstrating good safety, which is loved by people.

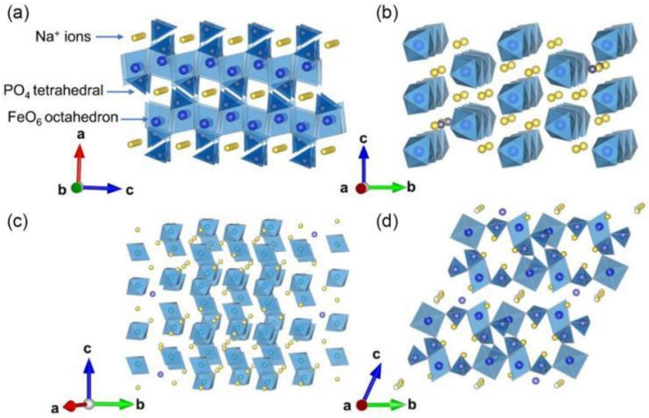

Figure 5. (a) $NaFePO_4$ (olivine-type) lattice structure, (b) $NaFePO_4$ (marokite−type) lattice structure, (c) $Na_2FeP_2O_7$ lattice structure, (d) $Na_3V_2(PO_4)_3$ lattice structure [16]

Referring to the lithium iron phosphate cathode materials employed in lithium-ion batteries, sodium iron phosphate can theoretically serve as the cathode material due to the similar chemical properties between sodium and lithium. However, generally speaking, sodium ion channels are inherently unstable on ferrite, thus alternative materials need to be investigated [6]. Therefore, people began to use vanadium to replace iron, hoping to compensate for the instability of sodium ion channels in iron-based phosphate compounds. However, vanadium is relatively expensive, which defeats the purpose of using sodium-ion batteries. So we have to give up using alum and look for new structures and substances.

At present, sodium ferric phosphate-pyrophosphate (NFPP) is attracting more attention because it possesses a dimer structure, which can compensate for the instability of the material and concurrently combines the characteristics of phosphate and pyrophosphate. So they provide stable charge and discharge performance. However, the issue lies in the fact that its conductivity is poor. In addition, during the synthesis process, it is difficult to obtain pure NFPP. When NFPP is impure, ion diffusion is inhibited due to the lack of chemical properties in the impurities, ultimately impacting performance. These problems still require to be addressed [17].

Its performance can be greatly improved through ion doping. The work carried out by Chen et al. was to doping Mo into sodium iron pyrophosphate, and it was found that its electrochemical performance, especially conductivity, would be significantly enhanced [18]. At the same time, Zhang et al. doped V into sodium iron pyrophosphate and ultimately discovered that it would possess high energy density and ultra-long cycle stability [19]. In order to address the impurity issue, lattice defects can be created as a solution. Zhao et al. successfully utilized spray drying to synthesize a range of NFPP samples with varying iron defect contents, and observed a reduction in local iron concentration during the material synthesis process, leading to significant suppression of $NaFePO_4$ impurities [20]. Improved by addressing these two issues, NFPP can serve as an excellent cathode material for sodium-ion batteries.

4. Conclusion and perspective

A variety of materials can serve as positive electrodes for sodium-ion batteries because of their specific structures, while the primary four categories-layered transition metal oxides, polyanionic compounds, and Prussian blue analogs-apply. All cathode materials usually face structural alteration and decreased capacity when they are in actual operation, which is attributed to the repeated insertion/deinsertion of Na^+. Therefore, it is necessary to enhance and optimize cathode materials by suppressing these defects. This article mainly discusses the advantages and disadvantages of the three main cathode materials for sodium-ion batteries. Prussian blue analogs, layered transition metal oxides, and polyanionic materials all have drawbacks, but the primary ones are related to lattice water/vacancies, irreversible phase transitions, and limited special capacity, in that order. The comprehensive overview aims to assist scholars in comprehending the characteristics of the three cathode materials and conducting associated studies, thereby advancing the progress of sodium-ion battery technology. Additionally, it is anticipated that sodium-ion batteries will have significant applications in compact vehicles and energy storage facilities in the coming years.

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