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Recent Advances on Cathode Materials for Sodium-Ion Batteries

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Abstract. Sodium-ion batteries, owing to their advantages such as abundant sodium resources and low cost, have emerged as one of the most promising next-generation technologies for large-scale electrochemical energy storage. The cathode material plays a critical role in determining both energy density and cycle life. Currently research efforts are primarily focuses on three systems: layered oxides, Prussian blue analogues, and polyanion compounds. This review systematically summarizes the mechanism of three cathode materials in the sodium-ion battery, latest research progress in modification strategies such as element doping, interface modification, high-entropy design, and bottleneck problems of these cathode materials, aiming to provide perspectives on future development directions.

Keywords: Sodium-ion batteries, Cathode materials, Layered oxides, Prussian blue analogues, Polyanionic compounds.

1. Introduction

Traditional energy sources, such as coal and oil, are under intense pressure with the two strategic imperatives: of the global transition of energy systems and as the growing need for environment protection. More importantly, their non-renewable reserves are increasingly insufficient to meet the rising energy demands of human society. This demand has brought the development of sustainable new energy system as the key solution to the aforementioned challenges. Among various electrochemical energy storage technologies, lithium-ion batteries have become one of the hotspots in the past decades due to their high energy density. However, their further development is constrained by some notable limitations, such as the finite reserves of lithium resources and their uneven geographical distributions. In addition, the high reactivity of lithium rises concerns of operating safety. Researchers around the world actively seek alternative energy storage materials that can replace lithium. Sodium-ion batteries have emerged as a promising candidate due to the abundance low cost, and environmental compatibility the sodium resources, indicating the potential for future development and practical usage. Cathode materials are an important component of sodium-ion batteries. They are generally classified into three main categories, including layered oxides, polyanionic compounds and Prussian blue compounds. Layered oxides are characteristic by high theoretical specific capacity, low cost and tunable structure. However, the large radius of sodium ions results in high migration resistance. The polyanionic compounds have unique three-dimensional structure, high operating voltage and long cycle life. Nevertheless, they have low theoretical specific capacity. Prussian blue analogs offer advantages of broad ion migration channels and low production cost, which facilitat rapid sodium-ion mobility. But the presence of crystal water and lattice defects readily lead to the capacity loss. In general, these three categories of materials have a trade-off in a particular capacity, cycling stability, cost-effectiveness, and complexity of synthesis. This review summarizes the current developments on such cathode materials, and offers perspectives on the future development direction.

2. Layered metal oxide

Layered metal oxides (A_xMO_2)have a typical two-dimensional layered structure in the group of transition metal oxides. Among them, sodium-ion layered metal oxides (Na_xTMO_2) possess a crystal structure made out of the alternating layers of Na and transition metal oxide. Sodium ions are located in the interstitial positions formed by oxygen polyhedra, a structure that can facilitate the rapid sodium ions diffusion along planar pathways during charging and discharging. This enables reversible intercalation and deintercalation, allowing for efficient energy storage and release, thereby offering a high theoretical specific capacity and excellent rate performance. One notable advantage of this material lies in its compatibility with low cost metals like iron, manganese and nickel, owing to the abundant availability of these raw materials [1,2]. This design does not depend on the scarcity of cobalt metal, in line with the requirements of large-scale energy storage applications. Moreover, the structure diversity of the layered metal oxides enables performance optimization through strategies such as structural design, surface engineering, and element engineering, offering the highly tunable electrochemical properties. These advantagesmake layered metal oxide materials one of the most promising cathode materials in the present sodium-ion batteries (SIBs). Sodium-ion layered metal oxides [3] can be divided into P2-type and O3-type according to the different environments of coordination of sodium ions andstacking patterns of the crystals. P2-type materials have demonstrated superior rate capability and cycling stability owing to the reduced migration barrier and shorter diffusion pathways for sodium ions during charging and discharge [4]. On the contrary, O3-type materials possess a greater amount of sodium, which theoretically offers greater specific capacity. But in the deionization process, they frequently undergo multiphase transitions, leading to dramatic change in volume and the formation of minor cracks, which ultimately reduces their long-term repetitive ability [5].

Recent studies on sodium-ion layered metal oxide cathode materials has primarily focused on enhancing structural stability, inhibiting phases transition during charging and discharging, air stability, and prolongation of the cycle life. One of several methods that have been used to address these challenges is element doping. Because it is a powerful tool to adjust the electronic structure and lattice parameters of host materials. For example, doping with high-valence Sb^{5+} not only strengthens the M-O covalent bonds but also facilittates the formation of a P2 / O3 biphase structure. This doping strategy consequently enhances electrochemical reversibility, particularly under high-voltage operating conditions [6].. Doping P2-$Na_{0.67}MnO_2$ with Zr provides enhances both ite structural stability and electrochemical performance. The $Na_{0.67}Mn_{0.9}Zr_{0.1}O_2$ electrode exhibits excellent cycle stability, retaining 86.5% of its initial capability after 500 cycles with a release capacity of 105 $mAh{\cdot}g^{-1}$. This doping strategy improves the Na^+ (de)intercalation kinetics and structural stability. Furthermore, Mg doping has been demonstrated to be effective in enhancing the air the stability of P2-type layered oxides. The introduction of Mg into P2-$Na_{0.67}O_2$ significantly enhances its structural stability in humid conditions, thereby improving battery performance. Mg doping shortens M-O bonds, stabilizes the crystal structure, excessive interlayer expansion, and inhibits the ordered phase transition of Na^+ vacancies. These combined effects consequently enhances the performance of the cycle [7]. There are also other structural modification and interface engineering techniques, which have had remarkable impacts. Surface coating is a widely employed strategy for interface stabilization. This approach serves as an effective strategy to inhibit detrimental side reactions at the electrode-electrolyte interface.. For example, an Al_2O_3 layer deposited via atomic layer deposition greatly improves the cycling stability of the $NaNi_{1/3}Mn_{1/3}Fe_{1/3}O_2$. Within a voltage window of 2.0 -4.2 V, the capacity retention of the coated material remains at 89% after 200 cycles as compared to 68% of its uncoated counterpart [8].

3. Prussian blue analogue

Prussian blue analogues (PBAs), with the chemical formula $A_xM_y{\cdot}nH_2O$, constitute a class of coordination compounds featuring an open three-dimensional framework. PBAs can also be used as positive electrode materials for sodium-ion batteries, and their advantages lie in: (1) Excellent ionic kinetics. The three-dimensional open framework composed of bridging metal ions and cyanide ligands contains wide channels and cavities that provide efficient pathway for the rapid insertion and extraction of sodium ions, resulting in outstanding rate and fast-charging performance; (2) Low cost. Their synthesis primarily relies on the utilization of earth-abundant metals such as iron and manganese, thus reduce the usage of rare materials like cobalt and nickel;(3) Capable of large-scale production. The PBAs are typically prepared through co-precipitation method under room temperature, which offers the advantages of facile scale-up and industrial viability; (4) Excellent structural stability. This three-dimensional framework exhibits minimal volume change (less than 1%) during repeated cycling, enabling an extend cycle life It has been reported that the optimized PBAs systems achieve enhanced cycling stability and capacity retention [9, 10]..

The electrochemical reaction in PBAs involves the redox of transition metals, denoted as M1 and M2. For instance, Fe^{2+}/Fe^{3+} redox couple is the major charge storage used. Nevertheless, the intrinsic water molecules and vacancies of the PBAs materials severely hinder Na^+ diffusion kinetics, thus inhibiting the specific capacity and cycling stability of the materials. Furthermore, the dissolution phenomenon of transition metal ions during the cycling process can lead to capacity degradation.

PBAs can be classified the into low-, medium- and high-entropy categories according to the entropy of their elemental composition. Traditional PBAs, such as $Na_2FeFe(CN)_6$ and $Na_2MnFe(CN)_6$ [11], belong to the low-entropy type. In recent years, high-entropy PBAs have emerged as a new class of materials. Researchers have successfully incorporated five or more principal elements in a high-entropy PBAs [12], including composite systems with Fe, Mn, Ni, Co, Cu, etc. The high-entropy design enhances structural stability as well as thermodynamic tolerance. Moreover, this design further enhances the configurational entropy effect of the material and effectively suppresses Jahn-Teller distortion and local phase transitions. This strategy provides a promising pathway to the next generation sodium-ion cathodes featuring better performance and enhanced safety [13].

4. Polyanionic

Polyanionic compounds represent an important class of cathode materials for sodium-ion batteries, characterized by a structural framework composed of multiatomic anionic groups (e.g., PO_4^{3-}, SO_4^{2-}, SiO_4^{4-}) connected by strong covalent bonds. These materials have attracted considerable research interest due to their excellent thermal stability, elevated operating voltage, and low volume strain characteristics. As sodium-ion battery cathode materials, their working principle is similar to that of PBAs. During charging, Na^+ is released from the lattice while transition metal ions (e.g., Fe^{2+}/Fe^{3+},

V^{3+}/V^{4+}) [14] are oxidized,, releasing electrons; the reverse occurs during discharge. Due to the presence of strong M–O–P covalent bonds, the electronic state of oxygen atoms is effectively stabilized, substantially mitigating oxygen release at high temperatures and thereby enhancing safety. Compared with layered oxides and Prussian blue analogues, the rigid three-dimensional framework and low strain characteristics of polyanionic compounds confer superior structural stability making them suitable for high-power and long-life application. Moreover, the "induction effect" exerted by polyanionic compounds enables tuning of the redox potential of transition or nonmetal elements, which can lead to higher output voltages and improve energy density. Based on the different crystal structure and anion types, polyanionic materials are classified into three major categories: NASICON type [15], olivine type, and sulfate/silicate systems. NASICON type materials (such as $Na_3V_2(PO_4)_3$) are highly regarded due to their three-dimensional open framework structure. It is composed of VO_6 octahedra and PO_4 tetrahedra sharing oxygen atoms, forming continuous Na^+ diffusion channels, and providing excellent ion conductivity (up to 10-3 $S·cm^{-1}$). Nevertheless, the toxicity and high costs of vanadium have motivated the development of vanadiumfree alternatives, e.g., iron-based $Na_3Fe_2(PO_4)_3$ or manganese-based derivatives, which retain the favorable NASICON structure [16,17]. Olivine-type phosphate, (such as $NaFePO_4$), adopt a stable two-dimensional layered network. However, their main drawbacks are low electronic conductivity and tendency to form amorphous phases during synthesis. To address these issues, strategies such as carbon coating and nanostructuring have been widely employed. Carbon coating is an effective modification strategy, which involves constructing a conductive carbon layer on the surface of $NaFePO_4$ active material particles. The nanomization strategy aims to reduce the particle size of the active material to the nanoscale to fully utilize the advantages of nanomaterials [17]. Other polyanionic systems including pyrophosphate ($Na_2MP_2O_7$), sulfate ($Na_2Fe_2(SO_4)_3$), and silicate (Na_2MSiO_4) often exhibit higher theoretical voltages or lower raw material costs. However, their practical application is hampered by slow ion diffusion kinetics and insufficient cycling stability [18].

5. Conclusion

This review systematically summarizes recent advances in three types of cathode materials for sodium-ion batteries: layered oxides, PBAs, and poly-anionic compounds. Layered oxides offer high capacity and low cost, yet are hindered by structural phase transitions and sensitivity to ambient air.; PBAs exhibit excellent rate performance and potential for low cost production, but their performance is compromised by crystalline water and inherent lattice defects; Poly-anionic compounds are known for their high voltage and high safety, but they have issues such as low conductivity and limited capacity. Future research efforts should prioritize precise structural control, elucidation of key degradation mechanisms, and optimization of large-scale preparation processes. Through various synergistic effects, the comprehensive performance can be further enhanced, accelerating of sodium-ion batteries towards the practical applications that meet the demands of high energy density, long cycle life, enhanced safety, and low cost.

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