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Review article

Recent achievements on polyanion-type compounds for sodium-ion batteries: Syntheses, crystal chemistry and electrochemical performance

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H I G H L I G H T S

- Recent progress on polyanion-type cathode materials for sodium-ion batteries is overviewed.
- Ortho-, pyro- and fluoro-phosphates are the main candidates.
- Mixed anions-type cathode materials are receiving increasing attention.

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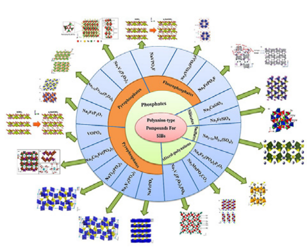

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In the past several years, many efforts have been made to develop polyanion-type cathode materials for sodium ion batteries by chemists and material scientists. These materials are one of the main types of promising cathodes though the studies are still in their infancy. This paper reviews almost all the important advances of polyanion-type cathodes on their syntheses, crystal structures, morphologies, electrochemical performance and Na redox mechanisms. It specifically focuses on their crystal chemistry and electrochemical behaviors. The contents are divided into several categories according to their chemical compositions. After introduction of the synthetic methods, phosphates (ortho-, pyro- and fluoro-), silicates, sulfates, and mixed anions type cathodes are summarized and discussed successively.

1. Introduction

Energy supply and consumption is an essential part of human life. The predominant choice of power supplier is fossil-type ones, including coal, petroleum and natural gas. Fossil-type power suppliers impose great pressure on environment, thus induce several problems negatively influencing human's life and health. So, exploring green power suppliers to replace fossil-type ones becomes a necessary and important topic. Nonetheless, the effective utilization of green power suppliers needs advanced energy storage and conversion devices or techniques. In the past, various types of such devices were developed, these include but not limit to batteries, supercapacitors, fuel cell, lead-acid cell, solar cell, and so on. Particularly, batteries represent a viable energy storage technology for integration of renewable resources providing intermittent energy into grid [1]. For portable electronic products such as phones and laptops, lithium ion batteries (LIBs) have been popularized as the power supplier. The available electrochemical performance of LIBs is enough to support their application in these products.

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However, further investigation of LIBs' applications in the fields of large-scale energy storage devices, such as hybrid or fully electric vehicles, and grid, pushes the price of lithium, the core materials of LIBs, continuously increase [2]. Moreover, the reserve of lithium in the earth's crust is low and its distribution on the world is not uniform [3]. All of these concerns make people explore new types of batteries with low cost and high reserves.

It is easy to turn eyes on the congener of lithium, namely, sodium. As highly abundant and easily available sodium has almost similar intercalation chemistry with lithium. Definitely, the gravimetric energy density of sodium ion batteries (SIBs) is lower than that of LIBs in view of the heavier mass of sodium. However, SIBs can be preferable to LIBs where gravimetric energy density is not the main concern, such as grid or mini-grid storage. Sodium has suitable redox potential 2.71 V (Na^+/Na), only 0.3 V above that of lithium, indicating that SIBs should be promising for electric energy storage (EES) applications. Though SIBs seem promising for energy storage, there are still some barriers must be overcome before their commercialization. The barriers are similar with those for LIBs when LIBs were in their infancy stage, including low energy density, unstable cycling performance, low power density et al.

It is known that cathode, anode, electrolyte and separator materials are the main components of batteries. Amongst them, many materials have been used as anodes for both LIBs and SIBs, such as transition metal oxides and sulfides. So, the lithiation and delithiation chemistry of LIBs can be applied to the sodiation and desodiation of SIBs. However, very few cathode materials can be served for both LIBs and SIBs as cathodes are usually the alkali-metal ions supplier. The cathode intercalation chemistry for LIBs can also be used for that of SIBs. Up to now, a large number of Na-containing compounds have been proposed as cathode materials, and some of them can deliver reversible capacities close to their theoretical values (Fig. 1). These compounds mainly include layered transition metal oxides, Prussian blue compounds, and polyanion-type compounds.4 For the last one, it includes orthophosphates $NaFePO_4$, $Na_3V_2(PO_4)_3$, $NaTi_2(PO_4)_3$, $Na_2M_2M'(PO_4)_3$, $NaVOPO_4$, $Na_xMV(PO_4)_3$, pyrophosphates $Na_2MP_2O_7$, $NaVP_2O_7$, $Na_2VOP_2O_7$, $Na_{3.12}Fe_{2.44}(P_2O_7)_2$, $Na_7V_3(P_2O_7)_4$, $(MoO_2)_2P_2O_7$, $(TiO)_2P_2O_7$, fluorophosphates Na_2MPO_4F, $Na_3(VO_{1-x}PO_4)_2F_{1+2x}$, $Na_4NiP_2O_7F_2$, $Na_7Fe_7(PO_4)_6F_3$, $Na_3Ti_2P_2O_{10}F$, silicates Na_2MSiO_4, sulfates $Na_{2+2x}M_{2-x}(SO_4)_3$, $M_2(SO_4)_3$, $NaMSO_4F$, $Na_2Mn_3(SO_4)_4$, $Na[Cu_2(OH)(H_2O)(SO_4)_2]$, $NaFe(SO_4)_2$, $Na_3Fe(SO_4)_2F_2$, and mixed polyanion-type compounds $Na_3M(PO_4)(CO_3)$, $Na_4M_3(PO_4)_2(P_2O_7)$, $Na_7V_4(P_2O_7)_4(PO_4)$, $NaFe_2(PO_4)(SO_4)_2$, where M, M′ stand for transition metals Fe, Co, Ni, and Mn. So far, there are lots of such compounds and their composites with various carbon materials have been extensively investigated as cathode materials for SIBs. The reason causes this hot topic is that polyanion-type compounds demonstrate versatile covalent open-frameworks, thermally stabilities, oxidation stabilities when charging, small volume changes, low-energy Na^+ migration pathways, high operating voltages induced by the inductive effects of polyanions, and tunable operating voltages by tuning local environments of polyanions. Inevitably, there are some disadvantages for polyanion-type structures. They have poor electron conductivities in view of the separation of the metal polyhedra and the strong electronegativity of the anions, resulting in their poor rate performance, and high operating voltages, which may influence the stability of electrolyte. Therefore, carbon incorporation is an effective and common strategy to improve their electrochemical performance [5].

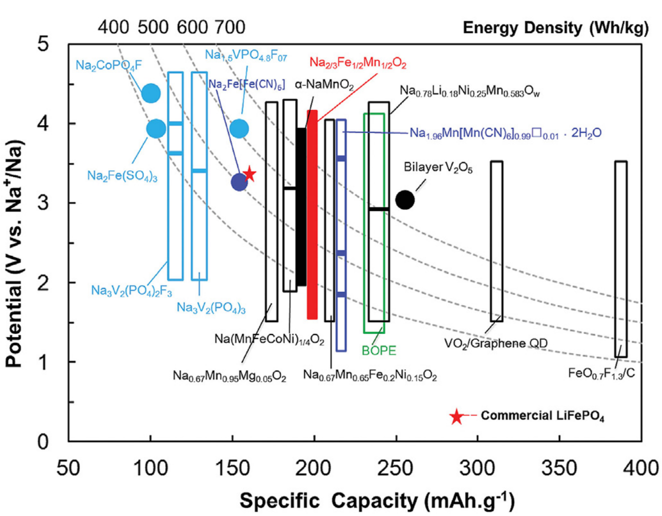

Fig. 1. Reported cathode materials for SIBs and their electrochemical performance, including energy density, operating voltage (vs Na^+/Na) and specific capacity (the solid squares represent the voltage plateaus or average voltage). Reproduced from Ref. [4] with permission. Copyright 2016, Wiley.

To our knowledge, there is no specialized summary addressed for polyanion-type cathode materials for SIBs though several summaries on SIBs have been presented recently [2,5–12]. In view of the vigorous development of this area, it is necessary and important to make a systematic summary, which pushes us to write this review. Most of polyanion-type compounds were synthesized using solid state methods, however, many other methods could also be used to obtain these compounds. So, the synthetic methods are given firstly. It is well known that materials' properties are mainly determined by their structures, so structure analyses of polyanion-type compounds are introduced firstly. Their electrochemical performance for SIBs are then introduced and analyzed according to their crystal structures and morphologies. Finally, some theoretical consideration and future concerns are proposed. The goal of this review is to address the sodium storage mechanisms in different structures, and provide insights for choosing and designing suitable polyanion-type cathode materials for SIBs.

2. Syntheses of polyanion-type compounds

Depending on the synthetic strategy, bulk- or diverse nano-polyanion type materials can be obtained. The synthetic conditions, such as the molar ratios of raw materials, choice of solvents, reactive temperatures, reactive times, and so on, have strong influences on the as-prepared samples' morphologies, further influence their electrochemical performance. According to different considerations, there are a lot of methods available to synthesize them, and the advantages and disadvantages of main methods are summarized in Table 1.

2.1. Solid-state reactions

Solid-state reaction is a conventional approach to synthesize various materials, such as ceramics and crystals. It is also a commonly employed method to synthesize polyanion-type materials for energy applications, and almost all the polyanion-type materials can be obtained by this method (Table S1). Compared with liquid or gas methods, it is an economic, efficient and easily scale up method. Generally speaking, solid-state reaction can be described as firstly grind the mixture of raw materials, and then load it in various reactive ampoules (crucible, glass tube, silica tube, metal tube, and so on) to heat it using a specific heating profile. For example, J. Kim et al. synthesized maricite $NaFePO_4$ powder using a simple solid-state method followed by ball-milling with conductive carbon [13]. W. D. Zhou et al. annealed powder mixture of sodium acetate, manganese acetate, vanadium acetylacetonate and