Proceedings of the 2023 International Conference on Functional Materials and Civil Engineering
DOI: 10.54254/2755-2721/26/20230824

Nanotechnology based on anode and cathode materials of sodium-ion battery

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Abstract. With the urgent need for carbon neutrality and the new energy vehicle industry's quick development around the world, the market demand for batteries is growing rapidly. At present, the batteries in the market are mainly lithium-ion batteries. However, the shortage and uneven distribution of lithium deposits worldwide result in high production costs. In recent years, sodium-ion batteries have developed rapidly for the sake of their similar principles and easy access to sodium resources, and are regarded as being able to replace lithium-ion batteries in the future. Nanotechnology is widely used in sodium-ion batteries to overcome the issue of extracting/inserting during charging/discharging due to the sodium ion’s large radius. This paper reviewed the application of nanotechnology in both anode and cathode materials of sodium-ion batteries. This paper covers widely used cathode materials such as layered transition metal oxides, polyanion compounds, and Prussian blue. Nanotechnologies employed in anode materials such as carbon-based materials and titanium-embedded materials are also introduced. It has turned out that sodium-ion batteries can improve the sodium storage capacity, energy density, and cycle performance efficiently via the application of nanomaterials.

Keywords: nanotechnology, sodium-ion battery, anode, cathode.

1. Introduction

Nowadays, people are facing serious energy and environmental problems. The fossil energy that mankind mainly controls is unable to meet the growing demand due to its limited reserves. Making renewable energy conversion, storage, and use more efficient is critical to reducing the energy challenges resulting from the overuse of fossil fuels. International demand for energy and supply are changing dramatically, and energy storage through the electrochemical method is now the most prevalent energy storage technology with the biggest growth potential. With the development of the battery industry, batteries based on sodium ions and lithium ions are two types of commonly used batteries. Although lithium-ion batteries occupy an important position in various battery fields, the quantities and price of lithium resources have forced the battery industries to worry about the future prospects of lithium-ion batteries [1]. Researches on both Na-ion batteries and Li-ion batteries were conducted essentially concurrently in the 1970s. The research on Na-ion batteries has gradually declined due to the successful commercialization of Li-ion batteries, while in recent years, scientists have been looking for new batteries that can replace Li-ion batteries, and Na-ion batteries have returned to people's vision, becoming an important breakthrough to solve this problem [2].

The Li-ion battery and the Na-ion battery both operate on the same principles [3-5]. Figure 1 depicts the process that Na ions insert/extract from the battery's negative electrode to the battery's positive electrode to realize the charge and discharge of the battery. In order to maintain charge balance, electrons are transferred to the negative electrode during charging while Na^+ is withdrawn from the battery's positive electrode material and incorporated into the battery's negative electrode material via the electrolyte. The electrical discharging is the contrary. However, the radius of Na ion is 1.02 Å which is larger than that of Li ion (0.76 Å), the diffusion rate of sodium ions in electrode materials is slow, and it is difficult to embed in electrode materials, and the volume effect is significant. These factors result in low specific capacity and insufficient cycle stability [6].

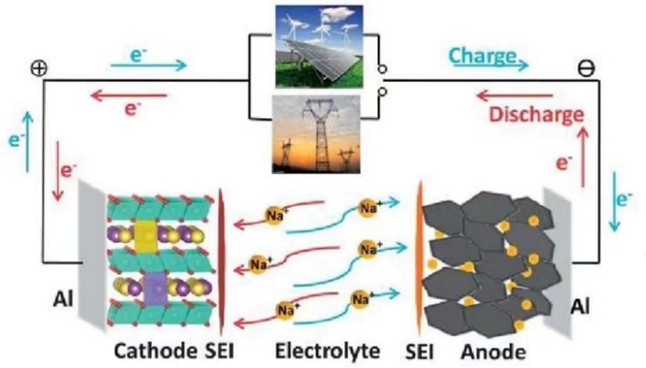

Figure 1. The sodium-ion battery's working principles [3].

In terms of operating temperature range and safety, sodium-ion battery operating temperature range is large compared to lithium battery, usually at -40 °C-80 °C. The ternary lithium-ion battery usually works at -20- 60°C. The performance of lithium-ion batteries will go down below 0 °C. In contrast, when sodium-ion batteries can work at -20 °C, the state of charge (SOC) retention rate is above 80% [7]. In terms of thermal runaway, sodium-ion batteries have higher internal resistance than Li-ion batteries, hence, the temperature of the battery will not rise easily during short circuit, guaranteeing the safety of the battery [7].

The resources of sodium are widely distributed and rank fourth on earth, while the majority of lithium deposits are concentrated in South America. Na is abundant in the crust at around 2%, while Li is only present in the crust in amounts of about 20 ppm [4]. In addition, the ocean's sodium resources are unlimited. As a result, the cost of lithium sources was between \$5,000 per ton, while the cost of sodium sources was only about \$135-165 per ton [4]. Hence, compared with the lithium-ion battery, for the sake of the low cost of Na element, the sodium-ion battery is substantially less expensive.

However, sodium-ion batteries also have more prominent shortcomings that need to be solved, such as the sodium ions' large radius, which may result in the crack of the material when it is removed from the electrode material, thus affecting the battery's overall dynamic performance and the integrity of the electrode [8]. Compared to lithium, sodium has a higher standard electrode potential, resulting in sodium-ion batteries' lower energy density [8]. In order to solve the above problems, researchers conducted research deeply and made great progress. If the electrode material is narrowed to the nanoscale and utilized synergistic effects of composite materials and other modification methods, it can greatly improve sodium-ion batteries' capacity for energy. Researches about nanotechnology in Na-ion batteries are introduced in the next chapter.

2. Nanotechnology in Na-ion batteries

2.1. Cathode materials for Na-ion batteries

The practical application of the sodium ion battery requires suitable electrode composition, large sodium storage capacity, and good cycle stability. At present, the positive components of Na-ion batteries mainly include layered transition metal oxides, polyanion compounds, and Prussian blue [9,10].

2.1.1. Layered transition metal oxides. The layered transition metal oxide (Na_xMO_2, M is the transition metal element) has the advantages of convenient synthesis, simple structure, and sufficient raw materials, and is the most widely used material for the cathode of Na-ion batteries. According to the coordination structure of Na^+ in MO6 polyhedra and the stacking mode of O^{2-}, Delmas et al. separated layered oxides into the O3, O2, P3, and other structures [11]. O and P represent the coordination configuration of Na^+ as octahedral and triprism coordination, respectively, and the number represents the stacking layer number of the least repetitive units. At present, P2 and O3 structures are commonly used. Their crystal structures are depicted in Figure 2. In the course of charging and discharging, sodium ions are repeatedly extracted and inserted from the layered Na_xTMO_2 material, while transition metals and oxygen atoms are oxidized and reduced, respectively.

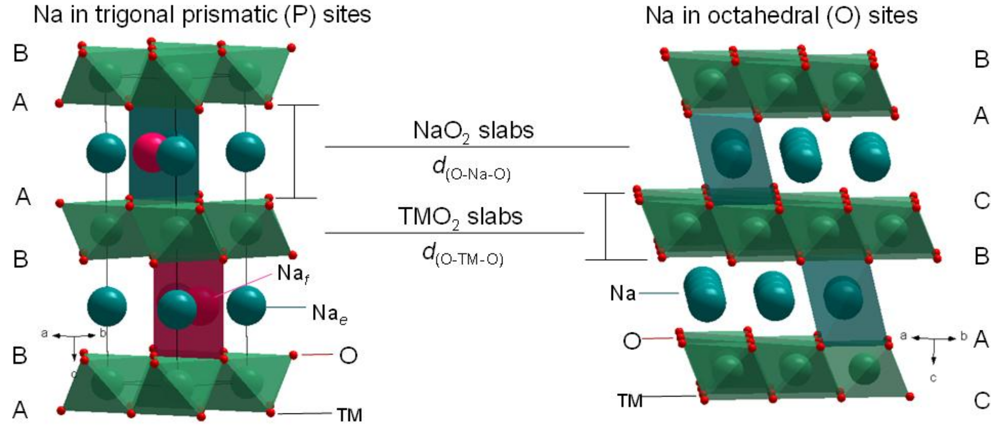

Figure 2. Crystal structure of common P2 and O3 sodium ions' layered oxides [12].

2.1.2. Polyanion compounds. The concept of "polyanionic materials" describes a group of compounds possessing tetrahedral $(ZO4)^{n-}$ anion units and their derivative units $(ZmO3m+1)^{n-}$ (Z refers to Si, S, etc.) and polyhedral units MO_x (M is the transition metal) in the structure of the compounds. The schematic figure of the structure of polyanion positive electrode is shown in Figure 3. Anions mainly include phosphate, pyroacid, fluorophosphate, and sulfate [13]. Due to the unique "induction effect" of polyanionic compounds, namely, the covalent bond represented by M-O can result in a stronger extent of ionization because X and O have a strong covalent bond., which leads to polyanionic electrode materials' high operating voltage.

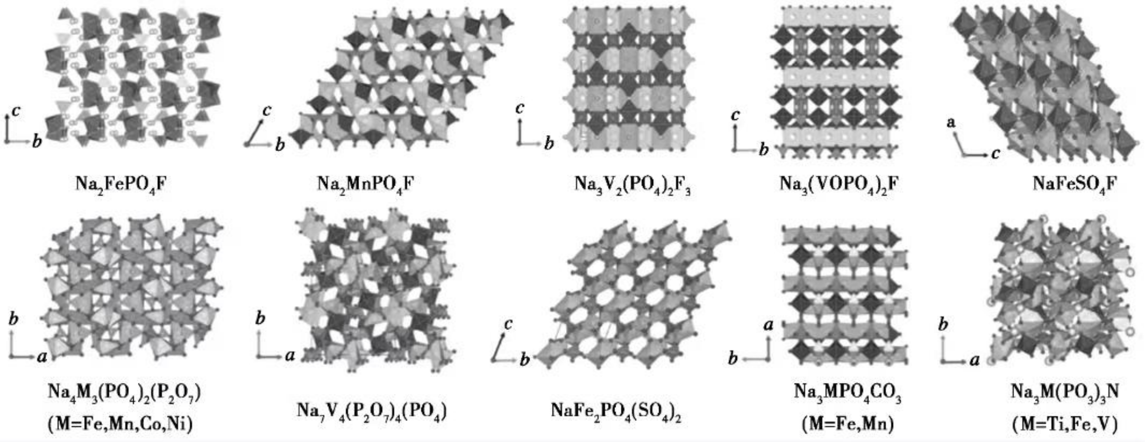

Figure 3. Structure's schematic diagram of polyanion positive electrode [13].

2.1.3. Prussian blue. Prussian blue ($Na_xFe[Fe(CN)_6]$) is of open frame structure formed by metal-cyanide coordination bonds. Figure 4 depicts the structure of Prussian blue. It is easy to insert and remove ions reversibly as the structures can provide enough space to contain sodium ions. They are among the few positive base materials capable of containing bigger basic cations like Na^+ and K^+ [12]. Although Prussian blue compounds have a lot of advantages, there are some problems such as poor magnification performance, unstable circulation, and low coulomb efficiency (≤90%) in practical studies. The main reason is the existence of $Fe(CN)_6$ vacancy and H_2O in the chemical compound. The vacancy caused by $Fe(CN)_6$ will lead to the deterioration of the material's electrochemical characteristics, structural degradation, and other problems, and H_2O will have side reactions with the electrolyte [14].

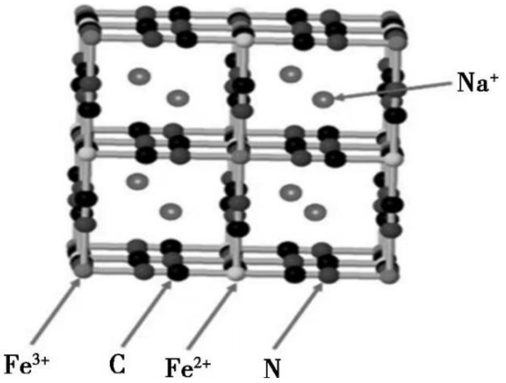

Figure 4. The structure of Prussian blue material [13].

2.1.4. The modification of sodium ion battery positive electrode. Compared with Li ion, Na ion has a larger radius, which will seriously damage the cycle capacity of the battery during the process of extraction and insertion. Meanwhile, some layered transition metal oxides have problems such as poor conductivity and weak rate performance. Therefore, a lot of scholars have concentrated on the modification of the positive electrode of Na-ion batteries in order to reduce structural changes in the process of discharging and improve the battery's conductivity and electrochemical performance. Morphology has a critical function in determining capacity performance of cathode material. Due to their high surface-to-volume ratio, which significantly affects sodium ions transport in the solid phase, materials with nanoscale features can boost the capacity of sodium ion batteries. Many scholars have modified the layered transition metal oxides by combining anode materials with nanotechnology to meet the requirements of battery applications.

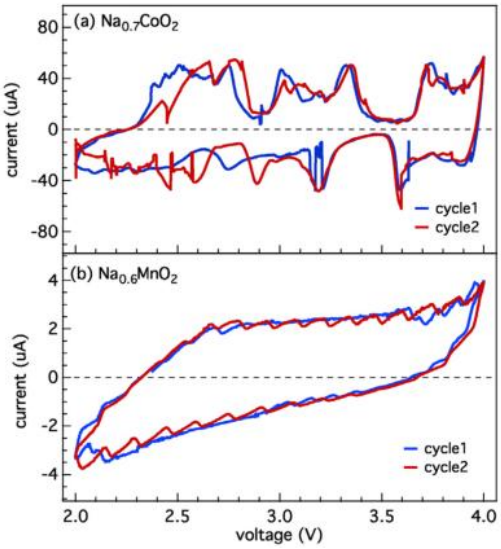

Figure 5. The cyclic voltammetry (CV) characterization of two types of coin cells— (a) $Na_{0.7}CoO_2$. (b) $Na_{0.6}MnO_2$, measured between 2.0 and 4.0 V at a scan rate of 0.1 mV/s using metallic Na as the counter electrode and $NaClO_4$ as the electrolyte [15].

Mahesh Chandra et al. synthesized stable P2 phase Na_xMnO_2 and Na_xCoO_2 nanostructures by sol-gel method and the electrochemical characteristics of coin batteries prepared with $Na_{0.7}CoO_2$ and $Na_{0.6}MnO_2$ as working electrodes and Na counter electrodes are studied and discussed [15]. The CV characterization of the two electrodes during the first several cycles is shown in Figure 5(a) and Figure 5(b). Several peaks in the anode and corresponding cathodic scans are consistent with the theory. This gives evidence of the reversibility of sodium ions, indicating that there are many intermediate valence states during the insert and extract of sodium ions in the $Na_{0.7}CoO_2$ solid matrix.

Jianhua Yan et al. successfully prepared large-scale Na_2FePO_4F/carbon nanotube (CNT) multilayer positive electrode samples by using LbL nanoassembly technology [16]. The sample's unique multilayer porous structure could provide adequate pathways for electron or ion conduction, as well as a strong affinity of Na_2FePO_4F nanoparticles. This kind of structure cannot be separated from conductive CNTs. Figure 6 (a) depicts that at 0.4 C, the initial discharge capacity of a sodium ion battery with a Na_2FePO_4F/CNT multilayer cathode reached 103.5 mAh/g, 82% of the theoretical value (126 mAh/g). After 100 cycles, the reversible capacity is 97.9 mAh/g, and the capacity retention rate reaches 94.6%. In the range of 0.4 to 2.0 C, the discharge capacity decreases as the current density increases, and at 2 C, the battery's capacity is 40mAh/g after 100 cycles. Meanwhile, as Figure 6 (b) shows, sodium ion batteries prepared by Na_2FePO_4F/CNT multilayer positive electrodes showed good cyclic stability. After 400 cycles at 0.4 C and a 74% capacity retention rate, the battery had a reversible capacity of 77.8 mAh/g. After 330 cycles, the capacity reaches 58.6 mAh/g and the capacity retention rate is 61% at 0.8 C. These results demonstrate that sodium ion batteries prepared by Na_2FePO_4F/CNT multilayer cathodes have good multi-cycle operation performance, good reversibility, and fast dynamics.

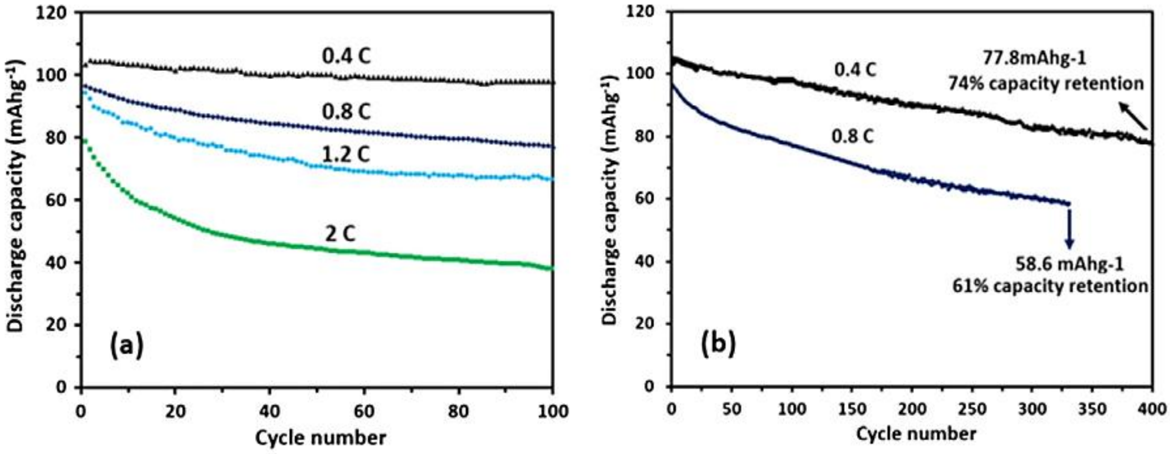

Figure 6. Cycle performance of Na-Na_2FePO_4F cells with multi-layered cathodes composed of Na_2FePO_4F/CNT (a) Rate effectiveness over 100 cycles. (b) Performance of plenty of cycles at 0.4 and 0.8 C [16].

Yu Jiang et al. reported that three-dimensional flower-like $Na_3V_2(PO4)_3$ composites with a carbon coating, as Figure 7 shows, allow for quick ions and electrons movement, high rate cycling, and high surface-controlled energy storage [17]. In addition to the layer structure, other nanostructures such as nanotubes, nano wires, nanofibers, nanocomposites, and other kinds of nanomaterials are employed to increase the positive electrode materials' rate capacity. Researches have shown that the preparation of nanoparticles of such cathode materials is not feasible, and that, in general, the use of nanocoatings to inhibit their chemical reactivity and the assembly of primary nanoparticles into secondary particles are two commonly used methods [17].

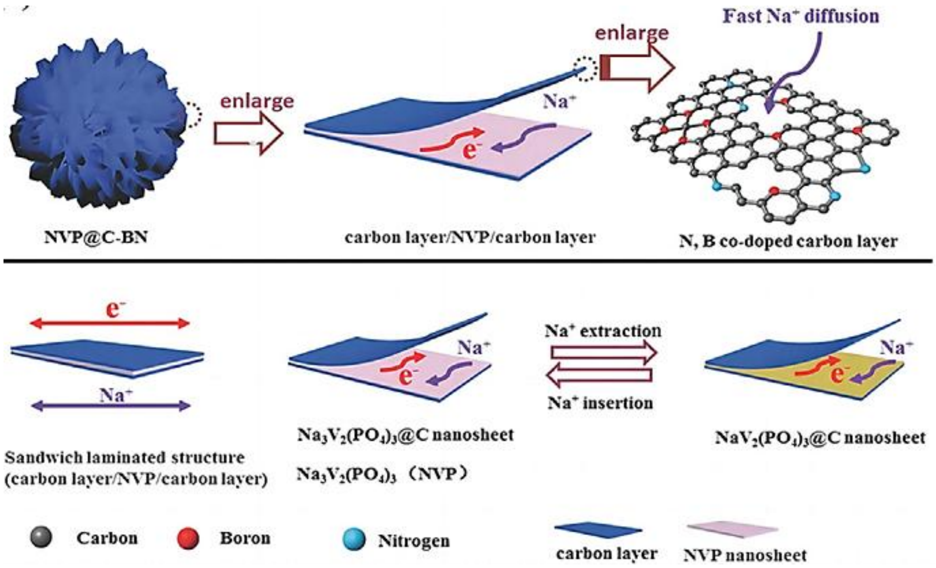

Figure 7. The graphical diagram of the illustration and structure of the NVP@C-BN electrode's extended cycle life at the high current density of 100 C for 2,000 [17].

2.2. Anode materials for Na-ion batteries

As one of the core components of a Na-ion battery, the negative electrode has an important effect on the energy density, rate performance, cycle performance, and first-cycle coulomb efficiency of the battery. Generally speaking, a good anode material for Na-ion batteries should be able to achieve a substantial specific sodium storage capacity while the structure changes as little as possible during the process of sodium ion removal. Compared with the positive electrode material, the research progress of negative electrode materials and industrialization for sodium-ion batteries are evidently slow, resulting in a relatively high cost. At present, the anode materials are primarily carbon-based materials and titanium-embedded anode.

2.2.1. Carbon-based materials. Because of the successful application of graphite materials in Li-ion batteries, the negative electrode of Na-ion batteries is first studied with graphite negative electrode, but the research shows that the sodium storage capacity of graphite is very low. The sodium embedding capacity of graphite materials is far less than the lithium embedding capacity due to the difference in the ion's radius. Due to its good strength and conductivity, nanotechnology is regarded as an important method for the enhancement of anode materials for sodium-ion batteries, like nanofibers, graphene, and carbon nanotubes.

Using carbon nanotubes or graphene alone can achieve good cycle stability, but its capacity is relatively low. In recent years, the preparation of high-performance anode materials by combining graphene or carbon nanotubes with conversion materials has become a popular field of research. The conversion reaction materials are mainly transition metals and compounds composed of oxygen, sulfur, selenium, and phosphorus. Unlike graphite, the above compounds show a certain sodium storage activity. The reaction principle is to react with Na^+ to generate transition metals and corresponding sodium oxide, sodium sulfide, sodium selenide, and sodium phosphide.

However, due to the high electronegativity of O, the chemical bond formed with the transition metal or Na^+ is very stable, and the Na_2O generated by the reaction is difficult to achieve complete reversibility in the electrochemical process. Therefore, the transition metal oxide also has the problems of voltage hysteresis and low Cullen efficiency in sodium ion batteries. To this end, most researchers have focused on transition metal sulfur/seleniumide. On the one hand, S and Se have slightly better conductivity and their electronegativity is lower than O. Na_2S and Na_2Se can be reversible in the reaction process, thus improving Cullen's efficiency. On the other hand, the transition metal sulfur/selenium is a layered material, the layer spacing is large, and Na^+ can be inserted and extracted easily. Therefore, good electrochemical properties can be obtained.

Jiangling Luo et al. improved the fabrication process of the negative electrode of nanotubes by employing a simple one-step selenization process to prepare a three-dimensional carbon net with high conductivity consisting of V_5Se_8 with self-intercalation structure and one-dimensional multi-walled carbon nanotubes (MWCNTs) [6]. The reversible storage capacity and structural stability of this three-dimensional structure of sodium ions during the cycle can be effectively increased. The V_5Se_8/MWCNTs electrode has a magnification capacity of 250 mAh/g at 10 A/g and an initial reversible capacity of 353 mAh/g at 0.2 A/g. It can be seen that this structure can provide excellent magnification capacity and a large reversible capacity. At the same time, they also obtained sufficient cyclic stability, after 1,000 cycles at 2 A/g, the cyclic stability is 323 mAh/g.

2.2.2. Titanium embedded materials. Titanium-based materials and their compounds are considered to be very helpful for sodium ion embedding because of their low cost, non-toxicity, low operating voltage, low strain, and excellent cycle performance. Therefore, Titanium-based material has been widely used in the study of sodium-ion battery electrode materials. In addition, this kind of material has a low charging and discharging voltage platform in sodium-ion batteries, so its application in the field of negative electrodes has received a lot of attention. TiO_2 mainly includes four crystal forms (anatase, rutile, titanite, and TiO_2(B)). Anatase phase TiO_2 has a channel size suitable for sodium ion diffusion, stable structure, and excellent electrochemical performance, and can achieve reversible sodium ion embedding and removal [18, 19].

Chunlin Ye et al. synthesized TiO_2@MWCNTs nanocomposites by sol-gel method, assembled sodium-ion batteries using TiO_2@MWCNTs nanomaterial as the negative electrode, and tested its electrochemical performance [18]. The battery's initial capacity of discharging can reach 477 mAh/g at 0.1 A/g current density. After 1,000 cycles, the discharge capacity can still be maintained at 181 mAh/g, showing excellent long-cycle performance.

3. Conclusion

Unlike lithium, sodium has sufficient resources to be developed, hence, sodium-ion batteries are likely to become the next generation of new energy sources. However, at present, sodium ion batteries are relatively lacking in both materials and technology, these materials have a dramatic change of volume when charging and discharging, which is far below commercial standards. It is necessary to explore new electrode materials of sodium-ion batteries. In terms of cathode materials of sodium ion battery, as nanomaterial has a large surface-volume ratio, it can provide large space for sodium ions to diffuse. Researchers have successfully made use of nanotechnology to modify the positive electrode in order to reduce structural change effectively. Therefore, the nanostructure of materials is an effective strategy to solve the structural problem and increase the capacity of the battery. In addition, the electrodes with nanotechnology can improve the capacity of the battery, cycle performance, and energy density, verifying the feasibility of replacing lithium-ion batteries.

However, sodium-ion batteries still lack large-scale application in the market at present. Firstly, sodium-ion batteries do not have a significant price advantage over lithium-ion batteries via the present technology. Secondly, the industry chain is not mature enough that there are many potential performance defects. Therefore, low cost of production and industry optimization should be focused on in the future.

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