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The Application of Bismuth-based Compounds in the Anode of Sodium-ion Batteries

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Abstract:

The sodium ion battery (SIB) system has outstanding advantages such as high experimental specific capacity, chemical principles similar to lithium-ion batteries, as well as abundant resources, making it an ideal next-generation energy storage system. At present, research on SIBs cathode materials is relatively abundant and has been applied to SIBs. However, for the anode material of SIBs, since the size of the sodium ion is relatively large, there are few materials available for the sodium ion storage, so it is still necessary to explore materials that combine high capacity with good cycling performance. Among numerous anode materials, bismuth compounds are regarded as one of the candidate materials for the anode of SIBs due to their excellent rate performance, high capacity, and relatively good safety performance. This article first introduces the current battery system and analyzes bismuth compound materials as SIBs anode materials. Subsequently, the author outlines the synthesis methods and electrochemical properties of different bismuth-based anodes. Finally, various bismuth-based materials are compared and the challenges they will face in the future are analyzed.

Keywords: Sodium-ion batteries; Bismuth vanadate; Bismuth molybdate; Bismuth ferrite; Specific capacity

1. Introduction

In recent decades, the gradually diminishing fossil fuel supply worldwide has driven the global demand for a more reliable, sustainable energy source to an unprecedented level. Under this trend, traditional internal combustion engine (ICE) vehicles began losing their dominance and electric vehicles (EVs) started gaining popularity around the globe and appeared to be an ideal alternative to ICE vehicles. EVs took up 13 % of the sale of the new vehicle market in 2022 worldwide while in 2025, 13.66 million EVs have been sold to the public and 2.86 million charging stations for EVs have been built around the world [1]. Alongside with the environmental effects, another critical driven factor for this vehicle transition is the advancement of the energy supply of EVs, the lithium-ion battery (LIB) system. First explored

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in the early 1970s and commercially available in 1991 by Sony company, LIBs have been the crucial component in portable electronics, EVs, and grid-scale storage systems owing to their high energy density, long cycle life, as well as rapid charging and discharging efficiency [2]. Furthermore, improvements in manufacturing techniques like dry electrode processing and technical developments in battery chemistry like the creation of lithium iron phosphate (LFP) technologies have lowered the cost of LIBs and improved battery performance. The price of LIBs dropped 77% between 2010 and 2020. In 2020, pack-level LIBs priced around $132/kWh, while the price for cell-level was even lower ($99/kWh) [3].

Despite these advantages, lithium-ion batteries still exhibit certain serious drawbacks. As the demand and use of LIBs broadens, maintaining an adequate supply of essential materials becomes challenging [4]. Moreover, safety concerns related to LIBs are still quite severe, like the effective methods to dissipate the heat when LIBs are under operation. As heat continues accumulating, high-temperature environments will occur internally in the battery system, triggering unnecessary side reactions which might cause thermal runaway problem [4]. Hence, in recent years, researchers started developing sodium-ion battery (SIB) system.

SIBs operate similarly to LIBs, the main principle being that the mobile ions can shift between the two electrodes to achieve the goal of storing and releasing energy. However, SIBs have several advantages over LIBs. For example, the sodium resources are much more abundant in nature compared to lithium. Moreover, SIBs have more straightforward extraction process and are more cost-effective [5, 6]. Additionally, SIBs using sodium metal as the anode offer acceptable theoretic capacities (1166mAhg^{-1}, while typical LIBs only have a capacity of 372mAhg^{-1} [7]) and high energy densities [6]. Nevertheless, SIBs also have thermal safety issues which is similar to LIBs and the present research on this area is quite limited, so enhanced research efforts as well as significant cautions are required to address the thermal runaway challenges regarding SIBs [5]. Furthermore, in SIBs, the size of Na^+ is larger than that of Li^+. During the battery charging and discharging process, this size mismatch will directly result in slower chemical kinetics and huge volume expansion, which will cause low specific capacity and poor cycling stability. [8]. As a result, appropriate electrode materials for SIBs need to be explored and discovered.

There are plenty of breakthroughs in the cathode materials of SIBs, including polyanion materials, Prussian blue analogue materials, as well as layered oxides, but the development of SIBs anode materials with high theoretical specific capacity, better cycling stability, as well as high rate performance are still quite limited [8]. Nowadays, the research on SIBs anode materials mainly focuses on bismuth-based materials. Being one of the group V elements in the periodic table, bismuth has high specific capacity and relatively small volume expansions with sodium [9]. Guo et al., for example, discovered that carbon-caged micro-sized porous bulk bismuth particles (P-Bi/C) containing micro and nanoscale elements can serve as anodes for SIBs. A high rate capability of 153.2 mAhg^{-1} at 150C (1C = 400 mAg^{-1}), a high initial coulombic efficiency of 95.2%, and outstanding cycling stability for more than 20,000 cycles were achieved with this composite [10]. Besides, a mangosteen-like bismuth nanosphere coated with an N-doped carbon shell (Bi@NC) anode for SIBs was also created and constructed by Chen et al., showing excellent cycling stability (96.5% of capacity retention after 1000 cycles) and storage performance (392.8 mAhg^{-1}) [11]. These research advancements indicate the strong potential of bismuth-based materials in the materials for the anode of SIBs.

In this article, the author will discuss the current research progress of bismuth-based compound in the anode of SIBs. Then, a comparison between various kinds of bismuth-based materials will be analyzed and presented. Finally, a comprehensive suggestion and conclusion regarding the SIBs anode materials will be proposed.

2. Case

2.1 Bismuth Vanadate

Bismuth Vanadate ($BiVO_4$) is a yellow crystalline inorganic material. It is widely used in photocatalysis due to its high ionic conductivity and narrow optical band gap. In addition, bismuth vanadate also has three crystalline phases (monoclinic scheelite, tetragonal zircon, and tetragonal scheelite), making it ideal for water splitting, pollutants degradation, and chemical synthesis. Moreover, its nontoxicity and bright yellow color allow it to become optimal for the coating of traffic signs. In the anode material of SIBs, bismuth vanadate shows improved conductivity, shortened transport paths, fast kinetics, and larger interfaces for sufficient Na^+ insertion/extraction reaction.

2.2 Bismuth Molybdate

Bismuth Molybdate (Bi_2MoO_6) is a green to yellow (depending on the proportion of Mo), nontoxic compound. It has high thermal stability and excellent photocatalytic properties. As a result, it is widely used to purify the air, defend ultraviolet light, as well as disguise in military. In SIBs, it can be applied to the anode and significantly improve the specific capacity of the sodium-ion battery cell.

2.3 Bismuth Ferrite

Bismuth Ferrite ($BiFeO_3$) is a perovskite-like crystal with room temperature multiferroic properties (ferroelectric, antiferromagnetic, and ferroelastic). These properties make bismuth ferrite applicable in various situations such as sensors, memory devices, gas sensing, photosensing spintronics, and photovoltaics. When applied to SIBs, bismuth ferrite exhibits the properties of high specific capacity, good cycling stability, as well as good reversibility.

3. Analysis and Challenge

3.1 Bismuth Vanadate

In general, the preparation method of $BiVO_4$ anode of SIBs most came from the pulsed laser irradiation of colloidal nanoparticles (PLICN) method. For instance, a typical $BiVO_4$ anode synthesis method was described as follows [12]: firstly, the irregular block shaped $BiVO_4$ was placed in acetone solvent and it was dissolved through ultrasonic treatment. Then, the mixture was irradiated with 355 nm wavelength, 78 mJ $pulse^{-1}cm^{-2}$ laser fluence of pulsed laser beam for 10 minutes. $BiVO_4$ particles were observed to change into a vast number of 400 nm size average, homogeneous spherical particles (BVO-400) following this irradiation process. Then, 50 nm large particles (BVO-50) and nanocrystals with an average size of 5 nm (BVO-5) were produced when the laser fluence was raised to 156 and 260 mJ $pulse^{-1}cm^{-2}$, respectively. Typically, more energy was needed to attain the smaller particles because of their smaller optical cross-section. Therefore, BVO-5 nanocrystals obtained by laser evaporation usually maintained their stability under laser irradiation at the same laser. Therefore, no further aggregation would occur. Fig. 1 showed this process schematically.

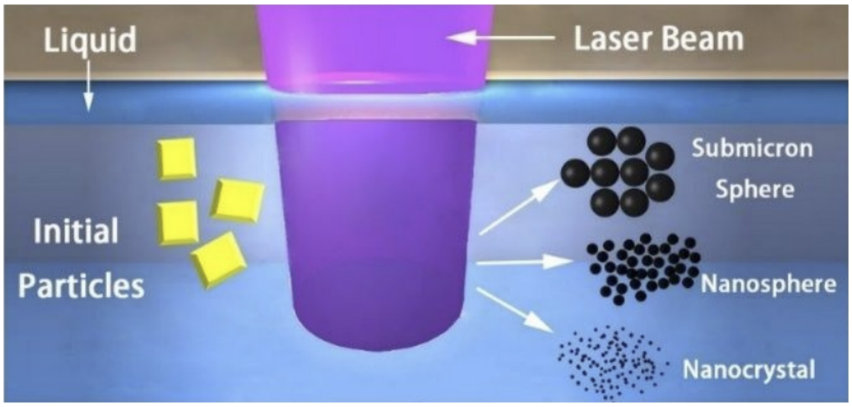

Fig. 1 Schematic illustration of the PLICN treatment of $BiVO_4$ particles [12].

The synthesized BVO-5 nanocrystals with rich oxygen vacancies were expected to display excellent electrochemical performances. In order to create the anode for SIBs, a simple facile hydrothermal process was carried out to anchor the BVO-5 nanocrystals on reduced graphene oxide (rGO). The BVO@rGO-5 electrode showed the best electrochemical performance among all BVO anodes. To begin with, an initial coulombic efficiency of 60.1% was showes. Additionally, BVO@rGO-5 always delivered highest, reversible, and most stable capacities throughout the whole cycle. After 200 cycles, a capacity of 470 $mAhg^{-1}$ was retained. Meanwhile, the rate capability of BVO@rGO-5 was quite striking. At current densities of 0.1, 0.2, 0.5, 0.8, 1.0, and 2.0 Ag^{-1}, respectively, it could produce the maximum capacities of 535, 491, 329, 392, 362, and 297 $mAhg^{-1}$. The capacity of BVO@rGO-5 rapidly recovered to 493 $mAhg^{-1}$ when the current density returned to 0.1 Ag-1, demonstrating its exceptional reversibility. Lastly, the excellent capacity retention ratio of 85.0% for BVO@rGO-5 indicated that the decay rate was only 0.076% each cycle. In summary, the reduced particle size is directly linked to the enhanced capacity, cycle performance, and rate capability, enabling a large contact area for the use of $BiVO_4$ particles and a shorter sodium ion diffusion path [12].

However, the significant volume change and the semiconductor property of $BiVO_4$ particles during sodiation and disodiation processes tend to cause shattered electrode, effecting poor cycling and rate performance of the anode. Although decreasing the size of $BiVO_4$ particles to nanoscale has been proved effective to solve these issues as their mechanical fracture can be suppressed and the ion transmission path can be decreased, the low electric conductivity of $BiVO_4$ still remains problematic. Recently, there has been studies on how to reduce the volume expansion and improve the electric conductivity of the $BiVO_4$ anode of SIBs by combining $BiVO_4$ with graphene or coupling with other unique materials. However, the current modified $BiVO_4$ materials' structure appears to be insufficient to handle the structural damage brought on by frequent Na^+ interposition or extraction. As a result, achieving high-rate capability and long-term cycling beyond 1000 cycles for the $BiVO_4$ anode is still difficult [13]. To put it briefly, more research is needed to discover the mechanism and principle of the structural changes of bismuth vanadate throughout the sodium storage process in order to enhance the specific capacity and energy conversion efficiency appropriately [8].

3.2 Bismuth Molybdate

The synthesis process of Bi_2MoO_6 anode in SIBs involved two main steps which were described as follows [14]: firstly, 15mL of ethylene glycol was measured and poured into a beaker. This process was repeated and then 1.26 g $Na_2MoO_4 \cdot 2H_2O$ and 5.06 g $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved separately in these two beakers which were later kept under stirring for 0.5 hour. Then, the two solutions from the two beakers were poured into a third container and 60 mL of ethanol was added dropwise. The container was allowed under stirring for 1.5 hours. Then, the solution in the container was transferred into a 180 mL stainless steel autoclave, heated in a 160 °C oven for 24 hours, and cooled down naturally to room temperature. Finally, through filtering, washing three times with ethanol, and drying in the air at 60 °C, Bi_2MoO_6 microspheres were obtained. For electrode preparation, Bi_2MoO_6, Super P, and Kynar polyvinylidene fluoride binder were mixed in an 8:1:1 weight percentage ratio in N-methyl-2-pyrrolidone in a mixer. A motorized K control coating machine (RK) with a 300 μm thick stainless-steel scraper was used to cast the slurry onto double-sided dendritic copper foil that was 10 μm thick. Following casting, the electrode (which had a 15 mm diameter and an active material concentration of about 2 mg cm^{-2}) was dynamically vacuum dried in a Buchi oven at 80 °C for 4 hours after being dried at ambient temperature for the whole night in a fume hood. The dry electrode was then placed in a glove box that contained argon gas (which had oxygen and water concentrations less than 0.1 ppm). Fig. 2 showed the SEM images of the synthesized Bi_2MoO_6 under different magnifications.

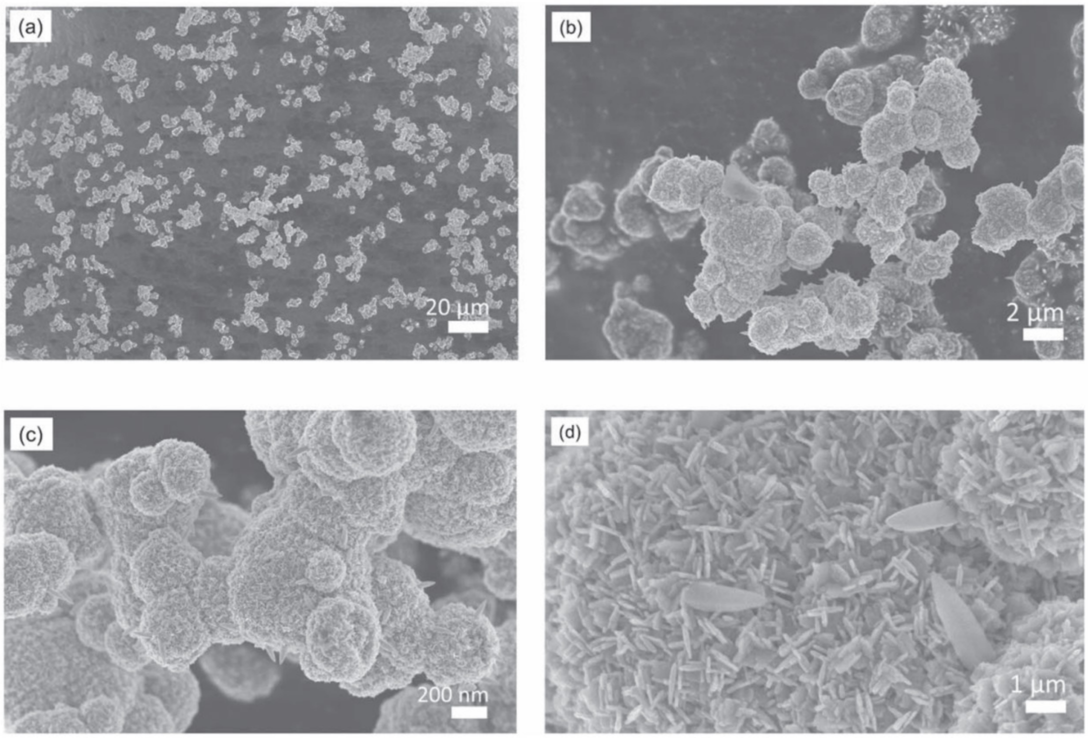

Fig. 2 SEM images of Bi_2MoO_6 particles generated by secondary electrons at different magnifications: (a) ×500, (b) ×5000, (c) ×10,000 and (d) ×50,000 [14].

The synthesized Bi_2MoO_6 anode possessed excellent specific capacity of 650 $mAhg^{-1}$ in the first cycle. Then, the capacity underwent a significant drop in the second as well as the third cycle. Subsequently, the capacity became stable in the fourth to tenth cycle, achieving a specific capacity range of 245-285 $mAhg^{-1}$. The reactions during the fourth to tenth cycle were:

$$\mathrm{Na} + \mathrm{Bi} \ \square \ \mathrm{NaBi} \tag{1}$$

$$2Na + NaBi \square Na_3Bi \quad (2)$$

The sum of the theoretical capacities for reactions (1) and (2) is 264 $mAhg^{-1}$, which significantly lower than the capacities during the first three cycles (>300 $mAhg^{-1}$). The Mo-containing matrix produced by the irreversible conversion of Bi_2MoO_6 in the anode will undergo reduction and oxidation reactions during the operating cycle of the cell, possibly explaining the extra capacity in the first three cycles[14].

The main intrinsic issue with Bi_2MoO_6 anode is the cycling stability. Reaction (1) gradually becomes irreversible, and Bi no longer forms during the sodium removal process after the 8th cycle. In the following cycles, reaction (2) also exhibits similar irreversibility as a gradually increasing number of NaBi particles are converted to Na_3Bi during the sodiation process, but do not recover during the sodium removal process. That process is accompanied by the formation of the hexagonal phase Na_3Bi (h-Na_3Bi) and cubic phase Na_3Bi (c-Na_3Bi). Since h-Na_3Bi has poor cycling stability compared to the cubic phase owing to a structural mismatch with NaBi and the reversibility of cycling to or from c-Na_3Bi is also greatly reduced in later cycles, a rapid capacity decay occurs as the Bi–NaBi and NaBi–Na_3Bi reactions become more irreversible followed by the formation of h-Na_3Bi [14]. Therefore, the short cycle life of Bi_2MoO_6 anode in SIBs limited its wide application.

3.3 Bismuth Ferrite

The fabricating process of $BiFeO_3$ mainly involves the electrospinning technique. For example, a typical $BiFeO_3$ nanotube preparation method was described as follows [15]: 2.02g $Fe(NO_3)_3 \cdot 9H_2O$ and 2.425g $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 10 ml N, N-dimethylformamide (DMF) solution. A suspension solution would form and 1.0 g of polyvinylpyrrolidone (PVP) was added to the solution once it became transparent. The mixture was then stirred until it returned to transparency. At the same time, a solution of polymethyl methacrylate (PMMA) with a concentration of 20-30% in DMF was prepared for the formation of the core during electrospinning. Under the conditions of room temperature and relative humidity of less than 30%, the mixed solution was pumped at a speed of 0.6 mlh^{-1} using a double hole needle located 15 cm away with a voltage of 18 kV. The obtained nanofibers were then preheated at 100 °C for 2 hours, and then heated up to 350 °C at a heating rate of 1 °C/minute. After holding at 350 °C for 30 minutes, the fibers were calcinated at 550 °C for 3 hours in air atmosphere at a heating rate of 5 °C/minute. Eventually, the PVP and PMMA solution would be burnt away during the calcination process and the BFO fibers were obtained. In order to create hollow nanotubes, the produced BFO was combined with graphene at a mass ratio of 10:1 to create BFO/graphene (BFO/Gra) composite materials using ultrasound. The mixer was thereafter subjected to drying and centrifugation procedures. Finally, the BFO/Gra product was obtained for the subsequent manufacture of the electrode slurry. Fig 3. depicted this process schematically.

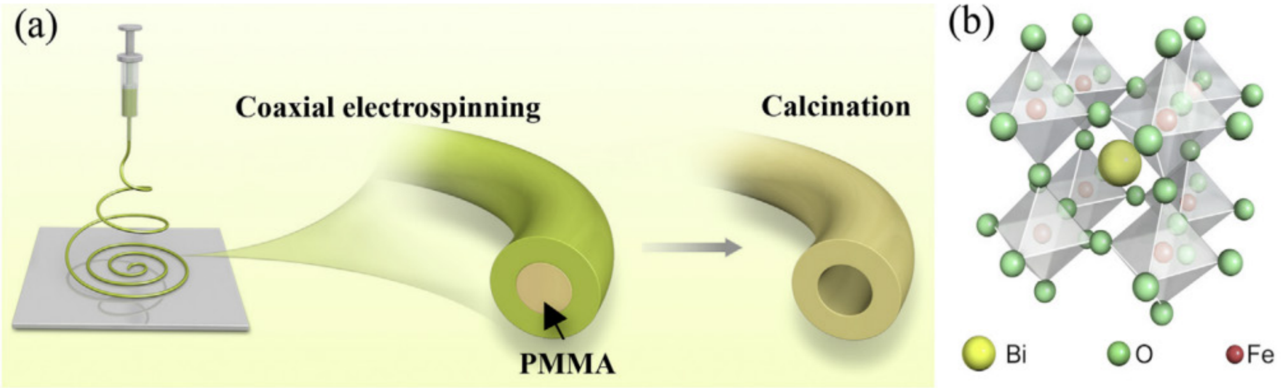

Fig. 3 (a) Schematic fabrication process, (b) Crystal structure of unit cell, of the $BiFeO_3$ nanotube [15].

When utilized as SIBs anode materials, BFO/Gra composite materials show excellent cycling stability and specific capacity, with a specific capacity of roughly 600 mAhg-1 and an 89% capacity retention rate after 200 cycles. Furthermore, the produced BFO anodes have specific capacities of 600, 520, 480, 420, 370, 350, and 320 $mAhg^{-1}$, respectively, when the current density rises from 50, 100, 150, 200, 300, 400, and 500 mAg^{-1}. The specific capacity reverted to 450 $mAhg^{-1}$ when the current density was brought back to 150 mAg^{-1}, suggesting that the produced electrode had good reversibility [15].

The higher initial discharge capacity of BFO negative electrode is mainly attributed to the participation of B-site ions (such as Fe) and the coexistence of multiple sodium

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storage mechanisms. But the main problems with BFO anodes are their short cycle life and very low Coulombic efficiency, which surely restricts their use. Furthermore, the alloying reaction between Bi and Na and the oxidation-reduction of BFO with Na can both result in notable volume changes, which often cause the active material to crack and lose capacity [15]. Numerous attempts have been made to address this issue, such as altering binders and electrolytes, creating nanostructures, and choosing better B elements. Future studies, according to the author, will advance these fields and improve the cycle life of perovskite-type anode materials [8].

4. Summary and Suggestion

Table 1. Comparison of various bismuth-based anode materials

SIBs Anode Materials	Advantages	Disadvantages
$BiVO_4$	High capacity Good initial coulombic efficiency Excellent reversibility Good economic viability Environmental friendliness	Low cycle life Low rate capability after certain charging & discharging cycles Potential significant volume change and structural damage
Bi_2MoO_6	Extremely high capacity Relatively good economic viability Environmental friendliness	Extremely low cycle life Irreversible alloying of Bi and Na
$BiFeO_3$	High capacity Good economic viability Environmental friendliness	Low cycle life Low coulombic efficiency

Bismuth-based anode materials were listed and concluded in Table. 1. When $BiVO_4$ is applied to the anode of SIBs, it demonstrates good specific capacity and initial coulombic efficiency. In addition, the restored capacity after the rapid change of the current density indicates its excellent reversibility. For its wide application, $BiVO_4$ is relatively easy to have access to and is environmentally friendly, making it a good candidate for the anode material of SIBs. Nevertheless, drawbacks of $BiVO_4$ such as low cycle life and low rate capability limit its wide application. Additionally, the structural damage and volume change caused by the insertion and detachment of Na^+ ions is one critical issue that needs to be solved. Therefore, the changes of the $BiVO_4$ anode during the sodiation and desodiation processes needs to be fully explored to achieve higher cycling stability.

For Bi_2MoO_6, it owns extremely high specific capacity in the first several cycles. In addition, similar to $BiVO_4$, it has relatively good economic viability as well as environmental friendliness. However, the disadvantages are quite severe. The extremely poor cycling stability caused by the alloying of Na and Bi to form the hexagonal phase Na_3Bi is the major impediment of its ommercial application. Therefore, in order to further enhance the electrochemical performance, future study should concentrate on the synergistic interaction between other metal components.

Last but not the least, $BiFeO_3$, similar to other bismuth-based materials, have several advantages such as high specific capacity, good economic viability, as well as nice environmental friendliness. Notwithstanding, its low cycle life, which is the common issue with bismuth-based anode of SIBs, and low coulombic efficiency. These drawbacks significantly affect the cell's electrochemical performances and negatively influence its wide application. Thus, electrolyte modification, the addition of a binder, as well as nanostructure construction might improve the performance of BFO anode.

5. Conclusion

This article introduced and analyzed several bismuth-based materials that might be potential candidates for the anode of SIBs. All of those bismuth-based materials own an excellent property which is the high specific capacity, making them ideal for future exploration. In addition, these materials are easy and relatively cheap to purchase or synthesize, and they are environmentally friendly, indicating the possibility of wide research and practice. However, these materials all possess some essential drawbacks such as significant volume expansion and reduction as well as low cycling stability that significantly limit their wide application. As a result, several suggestions regarding the future research on bismuth-based materials for the anode of SIBs are presented as follows.

1). The operating principle of several bismuth-based anode of SIBs needs to be fully investigated to achieve higher capacity, energy conversion efficiency, and safety.

2). The irreversible structural evolution of bismuth-based materials, such as the alloying of Na and Bi and the insertion and extraction of the large Na^+ ions, can lead to significant volume changes. This significant volume change may have potential defects in battery design, electrode preparation, as well as in the processes of sodiation and desodiation, and should be given sufficient attention.

3) In order to be widely used in society, battery systems must withstand harsh environmental tests, such as changes from high temperature to low temperature, and traditional single component electrolytes often cannot meet such usage standards. Future research and development of binary or ternary electrolyte systems will be required to increase the batteries' operating temperature range while maintaining the structure stability of the anode of SIBs.

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