

Advances in Electrode Materials for High-Performance Sodium-Ion Batteries: Challenges and Future Prospects

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Abstract. Energy storage is crucial for modern technology, especially with the increasing reliance on renewable energy sources. While lithium-ion batteries (LIBs) dominate the market due to their high energy density, long cycle life, and widespread application, the growing scarcity and rising cost of lithium are driving the exploration of alternative materials. Sodium-ion batteries (SIBs) have emerged as a highly promising solution, offering significant advantages in terms of cost-effectiveness, abundance of sodium resources, and environmental sustainability. This review provides an in-depth examination of the working principles of SIBs, comparing their performance with LIBs and analyzing their potential in large-scale energy storage applications, including grid-level and stationary systems. Recent progress in the development of advanced cathode and anode materials is thoroughly discussed, with a particular focus on overcoming existing limitations related to energy density, cycle stability, and efficiency. Furthermore, the review addresses the prospects for SIB commercialization, along with the technical and economic challenges that remain. With continued material innovations and research, SIBs could play a vital role in creating sustainable and scalable energy storage solutions.

Keywords: Sodium-ion battery, electrode material, energy storage, sustainable energy.

1. Introduction

The emergency of power that is required globally, as well as the availability of renewable sources of energy, has made it important to have energy storage systems for a steady energy supply. Non-renewable energy sources are reliable and can supply energy on demand, while renewable energy sources are unreliable and can only supply energy when a certain condition persists [1]. Due to this, energy storage is important in the sense that it helps in storing excess energy in the event that generation is high and releases it in areas where there is low generation of energy [2]. The most popular energy storage system is batteries due to their flexibility, scalability, and energy density [3].

Lithium-ion batteries (LIBs) have dominated the market for energy storage systems for the last few decades due to factors such as high energy density, long cycle life, and their applicability in a wide range of applications, from consumer electronics to electric vehicles [3,4]. However, as the demand for lithium rises, some issues can be identified: firstly, there is a lack of lithium; secondly, the extraction cost is relatively expensive; and thirdly, mining of lithium is not environmentally friendly. Moreover, LIBs use cobalt in the cathode materials; this element has environmental, as well as ethically contentious concerns involving the processing of cobalt [2,3].

To this effect, Sodium-ion batteries (SIBs) can be regarded as one of the most promising candidate materials in replacement of LIBs because sodium is cheaper than lithium. As one may understand, unlike lithium ions, sodium ions can be extracted from seawater – and this is incredibly cheap and hardly affects the environment at all [5-7]. Besides, in sodium-ion technology, cobalt is not used in the cathode, and all the ethical and environmental problems mentioned above do not occur [1]. However, SIBs have lower energy density than LIBs, and the present research is sought to address these challenges through improved electrode material [5].

The symbiosis, which has been observed in the present day's trends towards energy diversification and the raised demand for the utilization of renewable energy sources does call for the search for new types of batteries. For these reasons, these applications are especially suitable for SIBs because of the low cost of developing such SIBs and the abundant availability of sodium materials. Since the world

is now adopting more and more sustainable energy, energy storage is becoming even more essential in the present world.

The purpose of this paper will be to provide the current state of knowledge of SIBs with emphasis placed on cathode and anode materials regarded to improve energy density, cyclability, and other characteristics. Likewise, as lithium is costlier than sodium, SIBs should be able to provide a wide opportunity in large-format battery storage, particularly in stationary applications where cost is a relatively more significant parameter than the gravimetric energy density [1-3].

2. Working Mechanism of SIBs

Similarly to the LIBs, SIBs work as well. In both types, the ions move from the anode to the cathode during the process of charging as well as discharging. The cycling of the cell involves the reduction of sodium ions (Na^+) from the cathode while discharging and the oxidation of the sodium ions and their insertion into the anode during charging [1,2].

Among the elements that distinguish SIBs from LIBs, it is vital to note that sodium has a larger ionic radius than lithium. This increased size affects the ion transport and, therefore, results in lower energy density of SIBs. It is also worth mentioning that sodium is larger, which only aggravates the issue of choosing appropriate electrode materials that could effectively insert and extract sodium ions without material degradation [3,5].

The larger size of sodium ions (1.02 Å) compared to lithium ions (0.76 Å) presents both challenges and opportunities in battery design. While this size difference leads to slower ion diffusion and potentially lower energy density, it also allows for the exploration of a wider range of host materials that can accommodate the larger sodium ions. This aspect has spurred research into novel electrode materials that can effectively host sodium ions while maintaining structural integrity over multiple charge-discharge cycles.

There is also the problem of how to design electrolytes that will be compatible with sodium ions. Electrolytes must possess high ionic conductivity and chemical stability when the system operates at different temperatures and voltage conditions. The present studies also focus on the liquid, solid, and both liquid and solid electrolyte compositions so as to enhance the compatibility with sodium-ion systems [6].

Electrolyte development for SIBs has been a crucial area of research. Traditional organic liquid electrolytes used in LIBs, such as those based on carbonate solvents, have been adapted for use in SIBs. However, the larger size of sodium ions and their different chemical properties necessitate the development of tailored electrolyte formulations. Some promising directions include:

Fluorine-containing electrolytes: These have shown improved stability and performance in SIBs.
Ionic liquid-based electrolytes: Known for their high thermal stability and wide electrochemical window.
Solid electrolytes: Offering potential improvements in safety and energy density, though challenges in ionic conductivity remain.

However, there are certain challenges with SIBs, they are more economical and eco-friendlier and hence can be used effectively in grid energy storage systems where the performance requirements are comparatively less than electric vehicles [4,7]. Current efforts in developing new materials and electrolyte compositions for SIBs indicate that SIBs' performance can be enhanced to approach that of LIBs.

3. Merits and Applicability of SIB Technology

The following are the benefits of SIBs over LIBs especially on the aspect of cost and availability of resources. Sodium is the sixth most abundant element in the earth's crust and thus, its extraction is way much safer than that of lithium [2,3]. This means that SIBs are better suited for use in large-scale energy storage systems, where power density is not of the essence.

The abundance of sodium resources translates to significant cost advantages:

i) Raw material cost: Sodium carbonate, a key precursor for SIB materials, is approximately 20-30% of the cost of lithium carbonate.

ii) Extraction and processing: Sodium can be extracted from seawater, a process that is generally less energy-intensive and environmentally impactful than lithium extraction from brine or hard rock sources.

iii) Infrastructure: The ability to use aluminum current collectors instead of copper (as in LIBs) for the negative electrode further reduces material costs.

However, the major drawback of SIBs is their energy density and cycling stability in performance. The larger size of sodium ions leads to slower ion diffusion and lower overall energy storage capacity compared to lithium-ion systems [8]. This is a disadvantage as it limits the use of SIBs in high-performance sectors such as electric vehicles, where weight and energy density are a concern. Rather than that, SIBs are more appropriate for stationary applications where the energy density is not critical for achieving the goal, for example, for grid energy storage where the cost and cycle life are of paramount importance [5].

The applicability of SIBs also depends on the ability to create stable electrode materials to cope with mechanical strains resulting from sodium ion intercalation and de-intercalation processes. In the next sections, more improvements in the cathode and anode materials are presented, and these are important for the enhancement of the overall performance of SIBs and to make them as efficient as LIBs in different applications [7].

4. Advanced Cathode Materials

Cathode selection is a sensitive process in SIBs as it determines the energy density, voltage, and number of cycles in the battery. Significant progress has been made in attempts to identify suitable cathode materials that will host sodium ions between the charge and discharge stages. Thus, this section will further discuss various kinds of cathode materials, such as layered metal oxides, polyanionic compounds, and amorphous materials, to improve the performance of SIBs.

4.1. Layered Transition Metal Oxides

Transitional metal oxides (TMOs) are known and accepted widely today as one of the most effective candidates for use in SIB cathodes. The materials include a layer of stacked Na^+ ions and transition metals that enable sodium-ion 'swapping' during charge and discharge cycles. Of all the generic metals that are employed in these compounds, manganese, cobalt, nickel, and iron are common [3].

Several experiments have revealed that the phase state of the components has an impact on the properties of the layered metal oxides. It will be seen that O3 and P2 are the two most typical phases in the packing of oxygen slabs/planes. O3-phase material contains a higher amount of sodium and energy density but offers low structural coherency during cycling as compared to well-structured P2-phase material, which has a large interlayer gap to allow ion diffusion [1,2]. In an endeavor to enhance the structure stability and the reversible capacity of the layered oxides, other metals, such as iron, titanium, vanadium, etc., have been inserted [6].

For example, Na_3MnO_2 , which belongs to the family of layered oxides, has attracted much attention because of the high specific capacity, cheapness, and availability of manganese. However, these materials possess certain shortcomings, including voltage depreciation and poor cyclability [2]. Therefore, researchers have tried to modify these materials and developed composites of these materials with cobalt and nickel to enhance both material stability and cycling performance. However due to the high cost of cobalt, this solution is not very viable for large-scale industrial applications.

Recent advancements in non-precious metal cathodes include $\text{Na}_3\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$: This material has exhibited nice characteristics, especially characterized by a capacity of approximately 190 mAh/g and cycling stability. $\text{Na}_3\text{Ni}_{0.3}\text{Fe}_{0.4}\text{Mn}_{0.3}\text{O}_2$: Nickel has been used in the development in order to enhance the energy density and cycle life. Prussian Blue Analogues: These materials with general

formula $A_3M[Fe(CN)_6]_y \cdot nH_2O$, where A is an alkali metal, and M is a transition metal, have attracted considerable interest because of their inherent open framework structure where it is easy to incorporate/exclude Na^+ ions.

4.2. Polyanionic Compounds

Polyanionic compounds are also labeled as potential cathode materials for SIBs, belonging to phosphates, sulfates, as well as fluorophosphates types. These materials offer high thermal stability, safety, and long cycle life and are, therefore, suitable for large-scale, utility-scale stationary energy storage applications. Regrettably, polyanionic materials possess relatively lower energy densities than layered metal oxides; this is not inherently favorable for high-energy-density batteries.

Among the polyanionic compounds, sodium iron phosphate ($NaFePO_4$) has received much attention, likely because of its stability, low cost, and environmental benignity. It has moderate energy density, high stability within the cycle, and undergoes a chemically stable phase change, hence suitable for use in grid energy storage applications [9]. Nonetheless, the energy density of $NaFePO_4$ appears to be less than those of Li-ion battery cathodes; this may be a disadvantage when using $NaFePO_4$ in high-power applications such as electric vehicles [4].

Other promising polyanionic compounds include:

- i) $Na_3V_2(PO_4)_3$: It operates at high voltages and exhibits excellent thermal characteristics.
- ii) Na_2FePO_4F : Fluorophosphates provide significantly enhanced ionic and electronic conduction compared with simple phosphates.
- iii) $Na_2Fe_2(SO_4)_3$: These sodium-ion materials have produced high operating voltages and rate capability using sulfate-based materials.

The best characteristics of polyanionic compounds include structural stability and safety elements. The significant covalent character of the anionic moieties (such as PO_4^{3-} , SO_4^{2-}) bonded to the metal centers prevents structural transformations during Na^+ uptake/release. Such properties lead to longer cycle life and enhancement of safety characteristics, and therefore, they are ideal for large-scale stationary storage applications, where long-term stability is of prime importance.

4.3. Amorphous Materials

SIB cathode application is not researched in amorphous materials as much as in crystalline ones, but the former does have certain benefits. As can be observed, the structures are disordered; hence, the diffusion of sodium ions is faster compared to the other structures, a factor that makes them ideal for high-rate applications. However, they have lower specific capacity and cyclic stability than crystalline materials, which does not allow the use of these materials [5].

The development of the characteristics of amorphous materials, such as stability and energy density, is mainly directed to the additives of nanostructures or hybrid materials. For instance, recent research has been carried out on hybrid cathodes that were made up of amorphous contents and layered oxides, and the result was enhanced energy density and cycling stability of the SIBs [2].

Recent developments in amorphous cathode materials include:

- i) Amorphous $FePO_4$: This material has demonstrated relatively high performance with a capacity of about 150 mAh/g and good rate capability.
- ii) Amorphous vanadium oxides: Most of these materials provide high energy density and acceptable structural integrity during cycling.
- iii) Glass-ceramic composites: With these characteristics, the incorporation of both amorphous and crystalline phases increases electrochemical performance and stability.

These materials have good Na^+ intercalative properties that could result in better cycle life for the same reason of structural change flexibility. However, challenges remain in terms of increasing their specific capacity and improving their long-term stability.

5. Advanced Anode Materials

In SIBs, the anodes in the system are also of great importance in determining the ability of the system to work fluidly. Sodium ions have to be incorporated and de-inserted into the anode materials during cycling with lower changes in the volume of the anode materials since large changes in the volume of the material lead to mechanical failure and reduced capacity. This section discusses the types of anode materials that are being contemplated for use in SIBs, which include carbon-based anodes, alloy-based anodes, and conversion anodes.

5.1. Hard Carbon

The anode materials for SIBs are especially hard carbon most of the time. This material has relatively good sodium-ion intercalation and is less expensive than some other anode materials. However, some issues associated with hard carbon anodes include a short cycle life as well as capacity fading, and these challenges are being addressed by changing the materials and fine-tuning the electrolytes [2,3].

Sodium ions are located in two ways in hard carbon: intercalation between the individual graphene layers and in the micropores. However, this process also leads to significant volume change of hard carbon during cycling, which can give rise to the degradation of structure [1].

For example, the limitations mentioned above are an area of active research for researchers to understand how the structure of hard carbon, for instance, the pore size and specific surface area, is regulated. They have pointed out that with these approaches, the electrochemical performance and the cycling stability of the hard carbon anodes can be improved [9].

5.2. Alloy-Based Materials

The actual capacity of the alloy-based anodes, especially tin, antimony, and phosphorus anodes, is much higher compared to the carbon anodes. These materials can intercalate more sodium ions, and that is why they are useful for high-capacity applications [10-12].

However, alloy anodes face major challenges, like the creation of large volume changes during the Na ion intercalation and deintercalation process, leading to mechanical failure and capacity deterioration. For example, the tin-based anodes can expand as much as three times their size during cycling, which is detrimental to the cycle life of the anodes [7].

To overcome these problems, researchers have developed alloy anodes containing a combination of carbonaceous or binder materials to improve the anodes' mechanical characteristics. Such an approach has the rationale of prolonging the cycle life of alloy anodes and concurrently achieving high capacities of these hybrid materials [4].

5.3. Conversion-Type Anodes

Various conversion types of anodes, such as TMOs and sulfides, have especially attracted consideration because of their high theoretical capacities. During the cycling process, these materials undergo conversion reactions where sodium ions directly react with metal oxide to form a new phase to accommodate a large number of sodium ions [6].

While conversion-type anodes have high capacity, they demonstrate low electrical conductivity and experience substantial volume change within the course of cycling, thus limiting the application of these anodes. The researchers are studying some strategies for improving the conductivity and stability of these materials; these include the incorporation of nanostructures and conductive surface layers [3].

Lai et al. have also proposed iron oxide, Fe_3O_4 , as a potential candidate for conversion-type anodes for SIBs. It has high capacity, but some drawbacks include poor cycling stability and low conductivity compared to other types of materials, which have not made it popular. However, nanostructuring and the use of conductive carbon layers have been shown to produce improvements to the efficiency of the iron oxide anodes [11].

6. Conclusion

SIBs have, therefore, gained attention as a possible replacement for LIBs, especially in applications such as grid energy storage, where factors such as cost and availability of materials are important. Sodium, which is more available and cheaper than lithium, obtainable from seawater, has some benefits over lithium. Nevertheless, SIBs have issues regarding energy density, ion diffusion and cycling stability, which are ascribed to the larger size of sodium ions as compared to lithium ions.

Improvement in the design of the cathode and anode has been identified as a way of overcoming such drawbacks. Among the layered metal oxides, manganese-based compounds have been identified to have the ability to be used as cathode materials, which are both economical, efficient and, most importantly, stable. At the same time, polyanionic compounds, including phosphates, are known to be safe and have long cycle life, which is appropriate for stationary energy storage. Nevertheless, higher energy density is necessary to enable SIBs to rival LIBs in high-power applications, including electric vehicles.

On the anode side, hard carbon is still the predominant material despite problems like capacity decay and volume change. Tin-based and metal oxide materials, which are alloy and conversion-type anodes, provide higher capacities but suffer from mechanical failure and conductivity issues.

However, material optimization for solid electrolyte, electrolyte, and electrode design is still under research and may bring a better future for SIBs. The next stage of development may see SIBs taking up the mantle of energy storage solutions in the shift towards green energy, with the batteries being cheaper and more eco-friendly than LIBs for use in grid storage and other stationary applications.

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