

Current Research Directions of Sodium-Ion Battery Materials

Huang Chong

Xiamen University Malaysia, New Energy Science and Engineering, Malaysia

Abstract: The requirement for batteries has been steadily rising in recent years due to the advancement of electric vehicles and the growth of the energy storage industry. Sodium-ion batteries have attracted attention due to their inexpensive cost, wide distribution, and resemblance to lithium-ion batteries. The cathode material, anode material, and electrolyte system—the three main material technologies of sodium-ion batteries—are reviewed in this study along with a brief overview of the problems and developments in these areas of research.

Keywords: Sodium-Ion Batteries; Anode Materials; Cathode Materials; Electrolyte

1. Introduction

At present, lithium batteries are extensively utilized due to their cost-effectiveness and wide range of application scenarios. However, the majority of China's lithium resources need to be imported, and fluctuations in lithium prices may affect domestic industries. Additionally, the world still faces potential future shortages of lithium resources. To address the increasing demand for energy storage, both industry and academia are actively exploring sustainable solutions. For large-scale power storage uses, sodium-ion batteries have lately surfaced as a viable substitute for lithium-ion batteries. Despite the similarity in operating principles between the two types of batteries, sodium-ion batteries exhibit a significantly lower energy density compared to lithium-ion batteries when constructed from materials of analogous properties. Thus, directly applying lithium-ion battery technology to sodium-ion batteries is not appropriate. Therefore, finding suitable materials is one of the keys to making sodium-ion batteries practical.

In terms of material choice, sodium-ion metal oxides, polyanionic compounds, and Prussian blue analogs are the main subjects of study on cathode materials. Anode materials focus on carbon-based and titanium-based oxide materials.

These materials have demonstrated some sodium storage properties but still face varying degrees of challenges, such as limited capacity, poor cycle stability, and issues with environmental and structural stability [1]. Moreover, the lower capacity in commercial applications indirectly leads to higher costs. This paper provides a detailed review of several promising cathode, anode, and electrolyte materials, focusing on their electrochemical properties, scientific challenges, and solution strategies.

2. Cathode Materials

For different types of batteries, the cathode material is the primary point of distinction. The performance of these materials significantly influences a battery's energy density, safety, and cycle life. Sodium ions, compared to lithium ions, exhibit slower ion diffusion rates and have a larger mass and radius, leading to distinct behaviors. This results in slower theoretical capacity and reaction kinetics, along with lower structural stability [2]. To address these issues, advancements and changes in cathode materials are necessary. Currently, three promising approaches for cathode materials include layered oxides, polyanionic compounds, and Prussian blue analogs.

2.1 Layered Oxides

For sodium-ion batteries, layered oxides, which are the main cathode material used in the majority of lithium-ion batteries, are now the recommended option. Their advantages include ease of synthesis, high energy density, considerable reversible capacity, and efficient sodium ion intercalation and deintercalation properties. [3]. Extensive research has been conducted on sodium-based layered transition metal oxides (Na_xTMO_2) as ideal cathode materials for sodium-ion batteries. As the Na^+ content varies, different structures are formed, with common structures including O3, P3, O'3, and P2 phases. The O3 and P2 phase oxide materials are the two most widely reported types of sodium-ion layered cathode materials.

Their drawbacks, however, are also readily apparent: sodium ions may be removed during the charge and discharge procedures, which might result in layered metal oxides undergoing irreversible phase transitions or structural changes that would impair cycle performance. The O3 phase undergoes transitions between $O3 \leftrightarrow O'3 \leftrightarrow P3$ during charging, which worsens cycling performance [4]. The P2 phase, while more stable than the O3 phase, has a lower initial sodium ion content. When matched with sodium-free anodes, additional sodium sources are needed [5]. Addressing these two issues is a priority for layered oxides.

Currently, significant efforts are being made to overcome these challenges, primarily through surface modification and elemental doping. For instance, Li et al. found that the in-situ coating of NaSiO effectively suppressed the phase transitions of $O3\text{-NaNiMnFeO}$ during charge and discharge cycles by enhancing sodium ion migration, providing surface protection and mechanical support, and optimizing sodium ion distribution [5]. Additionally, doping various metals into the transition metal matrix has also enhanced stability. Jung et al. successfully synthesized Mg-doped O3-type NaNFM using a solid-state reaction method. The results indicate that the performance was significantly enhanced after Mg doping, as an appropriate amount of Mg in the layered structure stabilized the transition metal-oxygen bonding, thereby suppressing substantial structural changes and improving material stability. The optimized material can form a more stable O3 phase, which alleviates the structural collapse of high-voltage materials to some extent [6]. While these methods have improved battery stability to some extent, most only address individual issues, resulting in suboptimal electrochemical performance. Li et al. found that dual cation and anion doping, leveraging the strong electronegativity of F and the stability of Mo, further improved the initial discharge capacity and cycling stability of the batteries [5].

For P2 phase oxides, their structure retains vacancies, allowing for reversible sodium ion incorporation to increase content. The insertion oxide electrodes that have been described thus far, the layered oxide $\text{Na}_2\text{Ti}_3\text{O}_7$ has the lowest operating voltage and can reversibly integrate 2 mol of sodium ions. For instance, $\text{P2-Na}_{0.547}[\text{Mg}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ has better structural stability and a solid electrolyte interphase. [7].

Additionally, Liang et al. proposed a new approach, using a mild wet chemical process to coat $O3\text{-NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ with $\text{P2-Na}_{2/3}\text{MnO}_2$. The O3 core serves as a considerable initial sodium store, while the P2 structure works as a strong protective shell. A single-layer coating adheres closely to the O3 material's surface, improving the cathode's structural integrity and stability by smoothing phase transitions and lowering lattice stress. Furthermore, electrochemical kinetics investigations show that the P2-NMO layer provides quick sodium ion diffusion paths, which promotes efficient charge transfer and increases the battery's rate capability. [8] Thus, half-cells with non-optimized heterogeneous structure cathodes demonstrate improved cycling stability and ultra-high rate capability.

2.2 Polyanionic Cathode Materials

Polyanionic compounds are typically composed of anionic groups and cations. In most polyanionic compounds, the anionic groups enable the rapid conduction of alkali metal ions within the framework and ensure the stability of the material structure during the metal redox process. Because polyanionic compounds exhibit greater redox potential compared to layered oxides and minimal structural rearrangement during Na^+ intercalation, they offer long cycle life, strong thermal stability, and good safety [9].

LE POUL et al. were among the first to replace lithium ions in the LiFePO_4 structure with sodium ions, initiating the study of NaFePO_4 . Research has shown that olivine-type NaFePO_4 exhibits a high theoretical capacity of 154 mAh/g [10]. According to TRIPATHI et al.'s work, sodium ions in NaFePO_4 have a lower conduction activation energy than lithium ions in LiFePO_4 , which means that sodium-ion batteries have a greater specific capacity [11]. The real capacity is, however, constrained by the imbalance that exists during operation. Conductive carbon materials can improve conductivity, however the creation of ultra-thin carbon layers is required since thick coatings obstruct Na^+ movement.

Furthermore, materials of the NASICON type have been examined for their rapid ion conductivity due to three-dimensional open ion transport channels. For example, batteries made with NASICON materials demonstrate good cycling stability and rate performance. Building

on this, HU et al. developed NVP@reduced graphene oxide (rGO) composites via spray drying, which exhibit excellent performance [12].

In the search for suitable materials, fluorinated phosphates have also gained attention as cathode materials for sodium-ion batteries and hybrid batteries. By introducing the highly electronegative F, the electronegativity of the anionic groups can be enhanced, thus improving the electrochemical reaction potential through inductive effects. Among these, NaVPO_4F and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, which mimic the structure of NASICON-type materials, are particularly notable. The structure of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ allows for the intercalation and deintercalation of three sodium ions. Meanwhile, the $(\text{PO}_4)^{3-}$ group and F[−] ions give $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ a higher operating voltage, resulting in an energy density that is very close to that of the currently commercialized LiFePO_4 . [13].

2.3 Prussian Blue (PB) and Its Analogues (PBAs)

The 18th century saw the invention of prussian blue as a painting medium, and in 1999 it was employed as a cathode material for lithium-ion batteries. It gained widespread attention after being used in sodium-ion batteries in 2012. PBAs have a unique open framework and three-dimensional large-channel structure, which are well-suited for sodium ion migration and storage, making them highly promising cathode materials for sodium-ion batteries.

However, the simultaneous nucleation and grain growth of PBAs usually lead to a large number of vacancies and crystalline water in the structure, resulting in lattice distortion and structural instability during the charge and discharge processes. These defects undermine structural integrity, reduce sodium storage sites, and deteriorate the electrochemical performance [14]. Therefore, optimizing the lattice and preparing materials with low vacancy structures are key strategies for improving the performance of PBAs.

One approach is to remove the crystalline water through heating. Goodenough et al. removed void and coordination water in a high vacuum oven. Although the heat-treated samples were prone to rehydration in air, they still exhibited stable cycling performance for over 2,000 cycles [15]. Another study by Zhou et al. used high-concentration citrate solutions as a

precipitation medium to control nucleation and grain growth, resulting in high-quality KMHCF with minimal crystalline water and defects, exhibiting excellent cycling and rate performance [16].

3. Anode Materials

3.1 Carbon-Based Sodium Storage Anode Materials

Currently, carbon-based anode materials are one of the main areas of research for sodium-ion battery anodes. Kim et al. discovered that the intercalation/extraction process of solvated sodium ions in natural graphite was accompanied by phase changes. The study indicates that solvated sodium ions can intercalate into the graphite lattice due to the low reduction resistance of ether-based electrolytes, which form a thin SEI layer on the graphite surface. However, the high intercalation potential and low reversible capacity resulted in reduced energy density, falling short of expectations. The intercalation of solvated sodium ions is hampered by the larger SEI layer that ester-based electrolytes create on the graphite surface. Consequently, it is not thought to be possible to use graphite as the main material for sodium-ion batteries. [17].

Moreover, hard carbon, as one of the key subjects of research, plays a significant role in development. It offers excellent overall performance, wide applicability, and comparatively low cost. Also, hard carbon derived from lignocellulose and other types of biomass waste exhibits better electrochemical performance compared to other sources. Jing et al. dissolved the lignin and hemicellulose from wood, and the anode material produced through subsequent high-temperature carbonization exhibited enhanced stability. [18].

3.2 Titanium-Based Oxide Anode Materials

Titanium-based electrode materials, known for their ultra-low voltage and high storage capacity, have also become important research objects in lithium-ion battery studies. TiO_2 , Na-Ti-O complexes, and titanium-based phosphates are the primary types of titanium-based electrode materials. Among titanium-based electrode materials, $\text{Na}_2\text{Ti}_3\text{O}_7$ stands out for its exceptional performance. However, compared to hard carbon, $\text{Na}_2\text{Ti}_3\text{O}_7$ has a lower theoretical capacity. Furthermore, titanium-based anodes, when

operating at low voltages, cause the electrolyte to undergo reductive decomposition, leading to the formation of a thick SEI layer on the anode surface, thereby reducing energy density. This irreversible reaction forms SEI, impacting the stability of the battery, with coulombic efficiency decreasing by 60% after 100 cycles at a capacity of 190 mAh/g [19].

$\text{Na}_2\text{Ti}_3\text{O}_7$ still faces numerous obstacles. First, it was discovered during preparation that the PVDF binder should be avoided since it may react with the sodium in the electrolyte to generate NaF [20]. Tsiamtsouri et al. improved sodium ion binding sites by exfoliating $\text{Na}_2\text{Ti}_3\text{O}_7$ nanosheets and restacking them under acidic and basic conditions. The results showed better Na^+ storage capacity and stable cycling behavior compared to the raw material [21].

4. Electrolytes

Sodium-ion batteries' electrolyte is made up of sodium salts, solvents, and additives. As a critical component of secondary batteries, the electrolyte connects the electrodes and facilitates ion transfer, playing a vital role in determining the functionality and security of the battery. Ideally, the sodium salt in the electrolyte should dissolve as much as possible, allowing ions to rapidly reach the surface of both the positive and negative electrodes for reactions without causing side reactions with electrode materials. Additionally, it should possess good electrochemical stability to ensure long-term battery operation.

Ether-based electrolytes are widely studied due to their low melting points, high conductivity, reduction resistance, and the formation of thin, stable SEI layers. But still their insufficient oxidation resistance causes intense reactions and decomposition when the battery voltage is too high, greatly reducing the battery's stability and capacity.

Moreover, the low flash point and flammability of ether-based electrolytes increase the risk of thermal runaway at elevated temperatures, thereby limiting their widespread use in sodium-ion batteries, especially since modern batteries often operate under high-temperature conditions. Luo et al. designed a fluorinated anion-containing ether-based electrolyte system. In this system, the additives can act as sacrificial agents, preferentially oxidizing before the solvent, significantly improving the oxidation resistance of the ether-based electrolyte.

Additionally, the unique hydrogen bonding interactions between the perfluorinated anion additives and the ether solvents notably enhance the thermal stability of the electrolyte. After 100 cycles at 60°C, there was no significant change in capacity. [22]. The growth of sodium-ion batteries has been greatly aided by the invention of ether-based electrolytes, which have brought the technology closer to real-world use and expanded its potential for large-scale energy storage systems.

5. Conclusion

With the gradual development of the new energy sector, sodium-ion battery technology is also progressing toward industrialization. The current primary research direction for sodium-ion batteries is to build upon the foundation of lithium-ion battery technology and conduct more targeted studies. This has somewhat illustrated the capabilities and performance of sodium-ion batteries. Still, there are a lot of problems that need to be solved. As research on the batteries advances. First, the biggest factor limiting the practical development of sodium-ion batteries is their relatively low energy density. Improving the performance of sodium-ion batteries is the theoretical foundation for their widespread application. Second, safety issues are also one of the main reasons hindering the large-scale application of sodium-ion batteries at present. Currently, sodium-ion batteries need to be able to operate stably for extended periods under high-temperature conditions, so developing more stable and efficient materials is crucial. Finally, in the process of industrialization, although sodium is relatively abundant and inexpensive, other key materials for the batteries remain costly. At present, the synthesis methods for electrode materials are relatively limited, and there has been little research on the modification of electrode materials, which poses challenges in building an efficient and low-cost supply chain. Sodium-ion batteries will be utilized in large-scale energy storage systems in the new energy area at a relatively lower cost and with greater battery capacity and energy density compared to lithium-ion batteries.

References

- [1] Chen, X., & Zhang, Y. (2021). The main problems and solutions in practical application of anode materials for sodium ion batteries and the latest research progress.

- International Journal of Energy Research, 45(7), 9753–9779. <https://doi.org/10.1002/er.6500>
- [2] Ahsan, Z., Cai, Z., Wang, S., et al. (2024). Recent Development of Phosphate Based Polyanion Cathode Materials for Sodium-Ion Batteries. *Advanced Energy Materials*, 14(27), 2400373. <https://doi.org/10.1002/aenm.202400373>
- [3] Mamoor, M., Li, Y., Wang, L., et al. (2023). Recent progress on advanced high energy electrode materials for sodium ion batteries. *Green Energy and Resources*, 1(3), 100033. <https://doi.org/10.1016/j.gerr.2023.100033>
- [4] Lin, C., Liu, H., Kang, J., et al. (2022). In-situ X-ray studies of high-entropy layered oxide cathode for sodium-ion batteries. *Energy Storage Materials*, 51, 159–171. <https://doi.org/10.1016/j.ensm.2022.06.035>
- [5] Li, N., Wang, S., Zhao, E., et al. (2022). Tailoring interphase structure to enable high-rate, durable sodium-ion battery cathode. *Journal of Energy Chemistry*, 68, 564–571. <https://doi.org/10.1016/j.jechem.2021.12.018>
- [6] Jung, K.-N., Choi, J.-Y., Shin, H.-S., Huu, H. T., Im, W. B., & Lee, J.-W. (2020). Mg-doped $\text{Na}[\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ with enhanced cycle stability as a cathode material for sodium-ion batteries. *Solid State Sciences*, 106, 106334.
- [7] Wang, D., Xu, S., Wang, J., et al. (2022). $\text{P2-Na}_{0.55}[\text{Mg}_{0.25}\text{Mn}_{0.75}]\text{O}_2$: An SEI-free anode for long-life and high-rate Na-ion batteries. *Energy Storage Materials*, 45, 92–100. <https://doi.org/10.1016/j.ensm.2021.11.031>
- [8] Liang, X., Yu, T., Ryu, H. (2022). Hierarchical O3/P2 heterostructured cathode materials for advanced sodium-ion batteries. *Energy Storage Materials*, 47, 515–525. <https://doi.org/10.1016/j.ensm.2022.02.043>
- [9] Yan Q., Lan Y., Yao W., et al. (2021). Recent development of polyanionic cathodes for second ion batteries. *Energy Storage Science and Technology*, 2095-4239 (2021) 03-872-15
- [10] Le Poul, N. (2003). Development of potentiometric ion sensors based on insertion materials as sensitive element. *Solid State Ionics*, 159(1–2), 149–158. [https://doi.org/10.1016/S0167-2738\(02\)00921-9](https://doi.org/10.1016/S0167-2738(02)00921-9)
- [11] Tripathi, R., Wood, S. M., Islam, et al. (2013). Na-ion mobility in layered $\text{Na}_2\text{FePO}_4\text{F}$ and olivine $\text{Na}[\text{Fe,Mn}]\text{PO}_4$. *Energy & Environmental Science*, 6(8), 2257. <https://doi.org/10.1039/c3ee40914g>
- [12] Hu, P., Zhu, T., Wang, X., et al. (2019). Aqueous $\text{Zn}//\text{Zn}(\text{CF}_3\text{SO}_3)_2//\text{Na}_3\text{V}_2(\text{PO}_4)_3$ batteries with simultaneous $\text{Zn}^{2+}/\text{Na}^{+}$ intercalation/de-intercalation. *Nano Energy*, 58, 492–498. <https://doi.org/10.1016/j.nanoen.2019.01.068>
- [13] Liang, K., Wu, D., Ren, Y., et al. (2023). Research progress on $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ -based cathode materials for sodium-ion batteries. *Chinese Chemical Letters*, 34(6), 107978. <https://doi.org/10.1016/j.cclet.2022.107978>
- [14] Li, W., Chou, S., Wang, J., et al. (2015). Facile Method To Synthesize Na-Enriched $\text{Na}_{1+x}\text{FeFe}(\text{CN})_6$ Frameworks as Cathode with Superior Electrochemical Performance for Sodium-Ion Batteries. *Chemistry of Materials*, 27(6), 1997–2003. <https://doi.org/10.1021/cm504091z>
- [15] Song, J., Wang, L., Lu, Y., et al. (2015). Removal of Interstitial H_2O in Hexacyanometallates for a Superior Cathode of a Sodium-Ion Battery. *Journal of the American Chemical Society*, 137(7), 2658–2664. <https://doi.org/10.1021/ja512383b>
- [16] Qiao, Y., Guo, S., Zhu, K., et al. (2018). Reversible anionic redox activity in Na_3RuO_4 cathodes: A prototype Na-rich layered oxide. *Energy & Environmental Science*, 11(2), 299–305. <https://doi.org/10.1039/C7EE03554C>
- [17] Kim, H., Hong, J., Yoon, G., et al. (2015). Sodium intercalation chemistry in graphite. *Energy & Environmental Science*, 8(10), 2963–2969. <https://doi.org/10.1039/C5EE02051D>
- [18] Jing, W., Wang, M., Li, Y., et al. (2021). Pore structure engineering of wood-derived hard carbon enables their high-capacity and cycle-stable sodium storage properties. *Electrochimica Acta*, 391, 139000. <https://doi.org/10.1016/j.electacta.2021.139000>
- [19] Rudola, A., Saravanan, K., Mason, C. W., & Balaya, P. (2013). $\text{Na}_2\text{Ti}_3\text{O}_7$: An intercalation based anode for sodium-ion battery applications. *Journal of Materials*

- Chemistry A, 1(7), 2653. <https://doi.org/10.1039/c2ta01057g>
- [10] Nagulapati, V. M., Lee, J. H., Kim, H. S., et al. (2020). Novel hybrid binder mixture tailored to enhance the electrochemical performance of SbTe bi-metallic anode for sodium ion batteries. *Journal of Electroanalytical Chemistry*, 865, 114160. <https://doi.org/10.1016/j.jelechem.2020.114160>
- [21] Tsiamtsouri, M. A., Allan, P. K., Pell, A. J., et al. (2018). Exfoliation of Layered Na-Ion Anode Material $\text{Na}_2\text{Ti}_3\text{O}_7$ for Enhanced Capacity and Cyclability. *Chemistry of Materials*, 30(5), 1505–1516. <https://doi.org/10.1021/acs.chemmater.7b03753>
- [22] Hou, X., Li, T., Qiu, Y., et al. (2024). Interfacial Chemistry of Perfluorinated-Anion Additives Deciphering Ether-Based Electrolytes for Sodium-Ion Batteries. *ACS Energy Letters*, 9(2), 461–467. <https://doi.org/10.1021/acsenergylett.3c02811>