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# *Cathode Materials for Sodium-Ion Batteries: Limitations and Optimisation Strategies*

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***Abstract.*** Sodium-ion batteries are expected to be used in place of lithium-ion batteries because sodium resources are abundant, inexpensive and structurally compatible with aluminium current collectors. However, the main deficiencies in cell-level energy density, cycle life and interface stability are still with cathode materials. Layered transition metal oxides undergo irreversible phase transitions and are sensitive to the atmosphere of water and CO2. Polyanion compounds have a stable structure but are electronically insulating and lack capacity. Prussian blue analogues have open diffusion channels, but interstitial water and cyanide-derived precursors lead to side reactions and safety problems. The two most common ways to address the above problems are surface coating and elemental doping. Carbon, oxide and conductive polymer coatings promote interfacial charge transfer and mechanical buffering; sodium-site doping and transition-metal-site substitution stabilize the host lattice and suppress irreversible structural evolution. Systematically study the above deficiencies and optimisation paths in this paper, and discuss the remaining problems from the perspectives of energy density, scalable production, and compatibility with solid-state electrolytes.

***Keywords:*** Sodium-ion batteries, cathode materials, layered oxides, surface coating, elemental doping

## 1. Introduction

With the development of renewable energy and electric vehicles, more and more people want to use them, so storage devices that are inexpensive, long-lasting and reliable are needed. Lithium-ion batteries are currently used in portable electronics and electric vehicles, but lithium reserves are unevenly distributed and are becoming more susceptible to geopolitical and economic changes. Sodium-ion batteries have therefore gained the attention of researchers because sodium precursors are abundant and inexpensive, and aluminium foil can be used as the current collector for both electrodes. This will reduce material costs and simplify cell production. Sodium-ion batteries also have good thermal properties and a wide operating temperature range. The above attributes make sodium-ion technology suitable for stationary grid storage, backup power systems and low-speed electric vehicles.

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Despite the above advantages, the actual energy density and cycle stability of sodium-ion batteries are still limited by cathode materials. Layered oxides are easily subject to irreversible phase changes and air-induced surface degradation. Polyanion compounds are structurally stable but have low electronic conductivity and relatively small theoretical capacity. Prussian blue analogues have structural water and side reactions that reduce the extended cycle life. The problems of the traditional liquid electrolyte are flammability, leakage and a narrow electrochemical stability window. Solid-state electrolytes can inhibit dendrite growth, extend the operating temperature range, and improve intrinsic safety. Therefore, an excellent direction for high-performance sodium-ion batteries is the combination of optimised cathodes and solid-state electrolytes.

This paper studies the deficiencies of cathode materials for sodium-ion batteries and proposes corresponding optimisation strategies. Compare sodium-ion and lithium-ion batteries in terms of resource availability, cost, safety and energy density; analyze the main failure modes of layered oxides, polyanion compounds and Prussian blue analogues; examine surface coating and elemental doping as effective modification routes; discuss the remaining challenges; and summarize the main findings and future directions.

## 2. Sodium-ion batteries and their advantages over lithium-ion batteries

### 2.1. Resource abundance and cost advantage

The difference between sodium-ion and lithium-ion batteries is in the supply chain for the active material. Sodium is about 2.6% of the Earth's crust, and the concentration of lithium is only about 0.002%. Sodium carbonate and sodium chloride are already produced in large quantities for the glass, chemical and food industries, and their supply networks are geographically dispersed. Lithium resources, on the other hand, are concentrated in the lithium triangle of Chile, Argentina and Bolivia, as well as in Australia; this exposes the supply chain to geopolitical tensions, mining cycles and changes in trade policy. Lithium carbonate prices were around 40,000 yuan per ton in 2020, rose to about 600,000 yuan per ton during the 2022-2023 shortage, and then fell below 60,000 yuan per ton in 2025. Such fluctuations do not meet the requirements for a stable cost structure of grid-scale storage [1].

The other cost advantage is a current collector selection. Sodium does not alloy with aluminium at the anode potential, so aluminium foil can be used on both the positive and negative sides. Lithium forms Li-Al alloys at a potential of about 0.5V. Li/$Li^+$ will cause the anode to use copper foil. Copper foil is approximately three times more expensive per unit area than aluminium foil. Copper is thus not required, and production is simpler. Some cost models indicate that the theoretical lower bound for sodium-ion batteries could be about 20% lower than that for lithium-ion batteries, and solid-state sodium-ion designs could reduce costs by an additional 20%-30%. At present, commercial sodium-ion batteries have not been significantly cheaper than lithium iron phosphate batteries due to a small production scale. The cost advantage is structural, and it will be more pronounced with increased production scale [2].

### 2.2. Safety and thermal stability

The main type of safety failure for lithium-ion batteries is thermal runaway. In commercial cells, the reaction between the litigated graphite anode and the electrolyte, along with oxygen release from the cathode at high temperatures, drives self-sustaining exothermic decomposition, and the onset is generally between 120 °C and 150 °C. Sodium-ion cells have a higher start-up temperature. Hard

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carbon anodes have a higher potential than graphite and thus reduce the driving force for electrolyte reduction. Aluminum current collectors are employed at both electrodes to prevent the exothermic alloying reaction of lithium and copper. Sodium-ion cells therefore have a lower risk of thermal runaway under similar conditions [3].

Operating Temperature Range is also convenient. Sodium-ion batteries can still maintain a usable discharge capacity and power at around -40 °C to 80 °C; however, lithium-ion batteries lose a considerable amount of capacity below -20 °C and age rapidly above 60 °C. This behaviour is due to the weaker solvation of sodium ions in carbonate electrolytes. Weaker solvation reduces the desolvation barrier at the electrode-electrolyte interface and enhances ion transport at low temperatures. Comparative tests show that the low-temperature discharge performance of sodium-ion batteries is significantly better than that of lithium iron phosphate batteries, and cycle life and safety are comparable. Stationary storage in cold climates and electric vehicles operating in winter can reduce the cost and parasitic energy consumption of active thermal management due to this feature [4].

### 2.3. Energy density and cycle life: the remaining gap

The primary defect of sodium-ion batteries is a low energy density. The ionic radius of sodium ions is 1.02 Å, about 34% larger than the 0.76 Å radius of lithium ions, and the atomic mass of sodium is 23 g/mol compared with 7 g/mol for lithium. Therefore, the upper bounds for both gravimetric and volumetric energy density are relatively low. Currently, commercial sodium-ion batteries deliver about 100-160 $Wh \cdot kg^{-1}$, lithium iron phosphate batteries reach 150-200 $Wh \cdot kg^{-1}$, and high-nickel layered oxide lithium-ion batteries can exceed 250 $Wh \cdot kg^{-1}$. For weight- and volume-sensitive applications such as passenger cars and portable electronics, the gap is relatively large and cannot be completely closed; otherwise, a larger sodium ion would require a more spacious host structure and thus reduce the charge stored per unit mass or volume [5].

The Cycle Life also has some problems. Optimisation of the cathode and electrolyte has achieved 1,000-4,000 cycles at 80% capacity retention for sodium-ion batteries, and some commercial prototypes have reported as high as 20,000 cycles. It is now comparable to lithium iron phosphate for stationary storage. Therefore, cycle life does not exclude sodium-ion batteries from the field of energy storage; instead, it determines the applications of these batteries. Stationary grid storage, backup power and low-speed electric vehicles are more concerned with cost per cycle and safety than with gravimetric energy density, and are therefore natural entry points for sodium-ion batteries. BloombergNEF predicts that by 2030, sodium-ion batteries will account for about 23% of the stationary storage market and have an annual demand of more than 50 GWh. With the development of industrialisation, their proportion of stationary storage is expected to rise substantially [5].

## 3. Limitations of cathode materials for sodium-ion batteries

### 3.1. Irreversible phase transitions

Layered sodium transition metal oxides have a high theoretical capacity and good rate capability, and are thus one of the most promising cathode materials for sodium-ion batteries. Repeated extraction and insertion of sodium ions can cause an irreversible phase change. This structural damage results in a rapid decline in capacity and shortens cycle life. Layered oxides are also susceptible to changes in the atmosphere. These materials are easily exposed to moisture and carbon dioxide, and sodium hydroxide and sodium carbonate are formed on their surface. The resulting

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surface layer causes slurry gelation during electrode fabrication and degrades electrochemical performance [6].

### 3.2. Low electronic conductivity and capacity limitations

Polyanion compounds, such as sodium iron phosphate and sodium vanadium phosphate, have a stable framework structure and are thermally stable. However, due to low electronic conductivity, they have poor rate capability in actual applications. These materials also have relatively low theoretical capacities compared to layered oxides. Good electrochemistry generally needs a conductive carbon coating or nanostructuring. Without such modification, polyanion cathodes often have poor active-material utilisation and unsatisfactory high-rate performance [6].

### 3.3. Structural water and side reactions

Prussian blue analogues are open-framework materials with fast sodium-ion transport properties. They also have a serious defect of interstitial or coordinated water. Structural water reacts with the electrolyte to produce an undesirable side reaction and poor cycling performance. Synthesis also uses toxic cyanide precursors and is thus environmentally and safely problematic for large-scale production. The possible release of hydrogen cyanide under conditions of abuse is an additional safety risk during battery operation [7].

## 4. Optimization of cathode materials

### 4.1. Surface coating modification

A relatively simple way to enhance the interface stability and electronic conductivity is surface coating. Carbon coating is often added to polyanion and Prussian blue analogues to form a connected conductive network and expand in volume during cycling. Carbon-coated sodium vanadium phosphate has reached a discharge capacity of about 110mAh/g at 1C and maintained 95% of its capacity after 500 cycles; the uncoated sample decays rapidly. Aluminium oxide and zirconium dioxide are examples of oxide coatings that can prevent the decomposition and irreversible phase change of layered oxides in the electrolyte. After 100 cycles, the aluminium oxide-coated sodium nickel manganese oxide had retained 85% of its initial capacity, and the pristine material had only retained 65%. Coatings of conductive polymers, such as poly(3,4-ethylenedioxythiophene) and polyaniline, have been modified to enhance their electronic conductivity, mechanical properties, rate performance and cycle life. Polyaniline-coated Prussian blue analogues showed a 30% increase in specific capacity at high rates compared with the uncoated ones [6, 8].

### 4.2. Elemental doping and substitution

Elemental doping is also used to stabilise the crystal structure and enhance electrochemical performance. Substitution of sodium ions by aliovalent ions, such as potassium, lithium and calcium, can suppress phase transitions and improve air stability through modification of the local coordination environment. For example, potassium-doped sodium manganese oxide had a 20% higher capacity retention after 200 cycles compared to the undoped material. Substitution of transition-metal sites with electrochemically inactive elements such as aluminium, magnesium and titanium helps to stabilise the layered structure and reduces lattice distortion during cycling.

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Magnesium-substituted sodium iron manganese oxide had a reversible capacity of 135mAh·g$^{-1}$ and retained 88% of the capacity after 150 cycles. Synergistic co-doping introduces several dopants at different sites to improve both structural reversibility and rate capability. Titanium and magnesium co-doped layered oxides had a discharge capacity of 150 mAh·g$^{-1}$ and good rate performance, with 100 mAh·g$^{-1}$ at 5C [6, 9].

## 5. Challenges

The energy density gap of sodium-ion batteries and lithium-ion batteries is inherent; therefore, new high-capacity cathode materials or solid-state electrolytes that expand the operating voltage window are needed. Layered oxides have suffered structural damage due to extended cycling, and are often not practical in practice because of irreversible phase changes. Polyanion compounds are thermally stable but have low electronic conductivity; thus, an additional carbon coating or nanostructuring is needed to enhance both the difficulty and cost of processing. Prussian blue analogues still have problems with structural water and cyanide precursors that affect both cycling stability and large-scale production. The interface resistance at the cathode-solid-state electrolyte interface is also not well known and often results in poor rate capability and a short cycle life [7].

The cost advantage of sodium-ion batteries has not yet been fully realised at the commercial scale. Manufacturing processes for cathode materials still need to be optimised to reduce production costs and improve batch consistency [10]. Air sensitivity of layered oxides and structural water in Prussian blue analogues needs to be addressed by scalable synthesis and post-treatment strategies. In addition, the compatibility of cathode materials with solid-state electrolytes also needs to be systematically studied, as interfacial reactions and loss of mechanical contact can occur. Therefore, cathode optimisation cannot be carried out in isolation from electrolyte design, electrode engineering and cell-level integration.

## 6. Conclusion

This paper has investigated the advantages of sodium-ion batteries over lithium-ion batteries and analyzed the main deficiencies of cathode materials, such as irreversible phase transitions and air sensitivity of layered oxides, low electronic conductivity and limited capacity of polyanion compounds, and structural water-induced side reactions of Prussian blue analogues. Surface coating and elemental doping have both been employed to some extent. Carbon coating, oxide coating and conductive polymer coating enhance the interfacial stability and electronic conductivity; sodium-site doping and transition-metal-site substitution stabilise the crystal structure and improve cycling performance. Reported results indicate that these measures are effective. Carbon-coated sodium vanadium phosphate delivered approximately 110 mAh·g$^{-1}$ at 1C with 95% capacity retention after 500 cycles. After 100 cycles, the aluminum oxide-coated sodium nickel manganese oxide retained 85% of the initial capacity; the undoped material was only at 65%. Magnesium-substituted sodium iron manganese oxide retained 88% of its capacity after 150 cycles, and titanium/magnesium co-doped layered oxides achieved 150 mAh·g$^{-1}$ and good rate performance.

However, there are still problems with energy density, air stability and manufacturing cost. Next, add new high-capacity cathode materials, develop large-scale synthesis routes, and combine them with solid-state electrolytes in future work. High-entropy oxides and cobalt-free/nickel-free compositions are relatively promising routes for reducing cost and improving structural stability. In combination with new synthesis and in-situ characterisation techniques, the mechanism of phase transition will be elucidated more effectively, and rational design of next-generation cathodes will be

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achieved. Moreover, academia-industry collaboration is essential to transfer laboratory achievements to commercial products, and policy support for raw material supply chains will further promote industrialization. With continuous progress in material design, interface engineering and manufacturing technology, sodium-ion batteries are expected to be widely used for stationary energy storage and low-speed electric vehicles in the future, promoting a sustainable and low-cost energy system.

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