# The Influence of Structural Stability of Prussian Blue-Based Cathode Materials on Sodium Storage Performance and Other Electrochemical Properties of Sodium-Ion Batteries

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**Abstract: This study focuses on the structural stability of Prussian blue analogue (PBA) cathode materials in sodium-ion batteries and its impact on sodium storage performance. This research has significant theoretical and practical value because PBA materials exhibit defects such as structural vacancies and incomplete coordination between crystal water and metals in practical applications. These factors directly affect the crystal stability of the material, thus determining the capacity retention, performance, and cycle life of sodium-ion batteries. Structural stability is not only a key factor for the industrialization of materials but also a scientific problem in sodium-ion battery systems that remains unresolved.**

**Most existing research focuses on the electrochemical performance testing or synthesis methods of PBA materials, but few studies systematically review the impact of structural stability on the sodium storage performance of sodium-ion batteries. This study employs a literature review and interdisciplinary approach, systematically organizing the relationships between different structural defect types, synthesis strategies, and electrochemical performance to analyze the influence of structural stability on sodium storage performance. This study will provide a systematic review of the impact of structural stability on sodium storage performance from the perspectives of crystal structure and electrochemical mechanisms, using literature analysis, comparative studies, and theoretical induction. This study aims to deepen our understanding of the structure-performance mechanism of PBA materials; promote the theoretical development of material structure design; and provide reference results for the optimization of cathode materials for sodium-ion batteries.**

**Keywords: Prussian Blue Analogue Cathode Materials; Sodium-Ion Batteries; Structural Stability; Sodium Storage Performance; Structure-Performance Relationship**

## 1. Introduction

### 1.1 Background and Demand for Sodium-Ion Batteries

Driven by the "dual carbon" goal, large-scale energy storage technology is a core support for promoting the consumption of renewable energy and building a new power system. Although lithium-ion battery technology is mature, the scarcity and uneven distribution of lithium resources lead to high costs, limiting its further popularization in grid-scale energy storage. In contrast, sodium-ion batteries, due to the abundant and widely distributed sodium resources in the Earth's crust(about 2.36%), low manufacturing costs, and high intrinsic safety, have become a strategic alternative technology for large-scale grid-scale energy storage scenarios, demonstrating irreplaceable application potential in areas such as wind-solar-storage integration and base station backup power.

### 1.2 Research Status of Prussian Blue-Based Cathode Materials

As a key factor in the energy density and cycle performance of sodium-ion batteries, the performance of cathode materials directly affects the commercialization process of the batteries. Among them, PBA materials are widely recognized as one of the most commercially promising sodium-ion battery cathode material systems due to their advantages such as low raw material cost, open three-dimensional framework structure that large ion channels are highly conducive to the rapid reversible insertion/extraction of large-radius $Na^+$ (1.02 Å), high theoretical specific capacity (possessing multi-electron reaction potential with a theoretical specific capacity of up to 170 mAh/g), and simple synthesis (usually using co-precipitation, a simple process that does not require high-temperature sintering and is easy to achieve low-cost large-scale production). Nevertheless, PBA materials still face severe challenges in their commercialization process, with the core issue being their structural stability. Problems such as vacancy defects, residual water of crystallization, and metal ion dissolution encountered in actual preparation and cycling severely limit their electrochemical performance.

### 1.3 How Structural Stability Determines Sodium-Ion Storage Performance

The electrochemical behavior of PBAs is dominated by the stability of their microcrystalline structure. Structural instabilities, such as increased $[Fe(CN)_6]^{4-}$ vacancy defects, changes in structural water content, metal ion dissolution, lattice distortion, and framework collapse, are frequent occurrences. These not only disrupt the effective diffusion pathways of $Na^+$ and damage the integrity of the electrode structure, but also directly lead to decreased battery cycle life, deteriorated rate performance, and reduced long-term energy storage reliability, becoming a core technological barrier restricting their commercialization. Therefore, overcoming this key bottleneck of "structural stability" and systematically elucidating the intrinsic relationship between PBA structural stability and sodium storage performance has become an urgent need to promote the large-scale application of sodium-ion battery technology.

## 2. Crystal Structure and Structural Stability of Prussian Blue Analogue Cathode Materials

### 2.1 Basic Crystal Framework and Chemical Composition of PBA

PBA belongs to a hybrid double perovskite structure with a highly open three-dimensional framework. Its crystal structure consists of two transition metal ions, M and Fe, alternately occupying the B-sites (metal ions coordinated with nitrogen (N)) and B'-sites (metal ions coordinated with carbon (C)) of a simple cubic lattice. These two types of metal ions are bridged by cyano ligands (–C≡N–), forming a rigid three-dimensional network of channels. This open architecture provides spacious ion channels and large interstitial sites, which is highly beneficial for the rapid migration and storage of large-radius sodium ions. Ideally, PBA exhibits face-centered cubic symmetry. However, the structure is complex. With increasing alkali metal ion content or the occurrence of octahedral co-tiling, crystal symmetry decreases. For example, sodium-rich PBA typically exhibits a rhombohedral phase, and this phase transition is usually reversible during charge and discharge.

The chemical composition of PBA is highly adjustable. Its general chemical formula can be represented as $A_xM[M'(CN)_6]_{1-y}\square_y \cdot nH_2O$, while the specific formula for sodium-ion batteries is often written as $Na_{2-x}M[Fe(CN)_6]_{1-y}\square_y \cdot nH_2O$. Interstitial sodium ions are located in the macropores of the framework. The sodium ion content not only determines the battery capacity but also directly affects whether the crystal structure is cubic or rhombohedral. The transition metal M is usually Mn, Fe, Co, Ni, etc., and is connected to the nitrogen end of the cyano group. The hexacyanoferrate ion $[Fe(CN)_6]^{4-}$ forms the anionic group of the framework, and Fe is connected to the carbon end. Vacancy defects are a key feature of the chemical composition of PBA. Due to the rapid nucleation during the precipitation process, $[Fe(CN)_6]^{4-}$ vacancy defects often exist in the crystal lattice. Water molecules exist in three forms: 1. Adsorbed water: physically adsorbed on the particle surface; 2. Coordinated water: occupying vacancy sites and directly coordinating with metal M to fill the coordination number; 3. Crystallization water: free in the interstitial channels of the crystal lattice. The presence of vacancies and water can disrupt the integrity of the structure, occupy $Na^+$ storage sites, and may lead to lattice distortion.

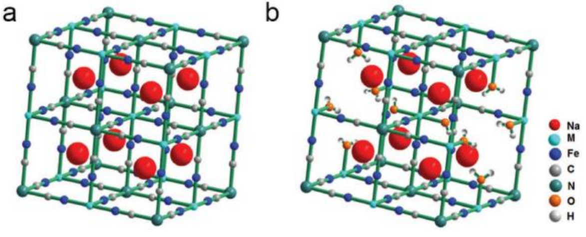

**Figure 1. a) an intact $Na_2M''[Fe''(CN)_6]$ framework without structural defects, b) a defective $NaM''[Fe''(CN)_6]_{0.75}\cdot\square_{0.25}$ framework with 25% $Fe(CN)_6$ vacancies existing in each unit cell.**

Location of coordinated water: Directly

coordinated with "suspended M ions" (M ions exposed due to $Fe(CN)_6$ vacancies) surrounding the vacancy.Location of water of crystallization: It fills alkali metal sites and octahedral interstices, and does not directly coordinate with lattice atoms [1].

### 2.2 Vacancy Defects

In Prussian blue analogues, vacancy defects are determined by the thermodynamic properties of the material and the synthesis kinetics. PBA is usually synthesized in aqueous solution by coprecipitation. Due to the extremely low solubility product constant of Prussian blue, the nucleation rate during the reaction is extremely fast, resulting in some $[Fe(CN)_6]^{n-}$ groups not having enough time to occupy the predetermined lattice positions during crystal growth, thus forming vacancies [2][3]. These vacancies are not true "vacuums," but are often occupied by water molecules to maintain the coordination saturation of metal ions, forming so-called "coordinated water." This “vacancy-coordinated water” structure disrupts the continuity of the -CN-bridge, leading to distortion of the local lattice environment [4].

### 2.3 Structural Water and Framework Stability

Due to its unique aqueous coprecipitation synthesis environment, water molecules inevitably become part of the crystal structure of PBA. Water molecules in PBA mainly exist in three forms: adsorbed water, coordinated water, and crystallization water, and their content usually accounts for 10-20 wt% of the total mass [4][5]. The motion state of water molecules is closely related to the sodium content in the material. In PBA with high sodium content, water molecules diffuse in a spherical cavity with a radius of about 2.6 Å; while in PBA with low sodium content, the radius of the diffusion cavity shrinks to 1.8 Å. This indicates that water molecules are confined in the lattice pores. More importantly, some water molecules exhibit “oscillation” or rotational motion, indicating that they have a strong interaction and binding effect with sodium ions in the interstitial spaces [6].

Water molecules in the crystal framework of PBA are not merely impurities; they play a structural supporting role in maintaining a specific crystal phase. Fully hydrated sodium-rich PBA typically exhibits a monoclinic phase. The filling of water molecules in the lattice buffers volume changes, effectively providing the framework with a certain degree of mechanical stability. However, when moisture is removed through heat treatment, the crystal structure undergoes a significant transformation. Dehydration leads to a lattice volume shrinkage of approximately 20%, and the material transforms from a monoclinic phase to a rhombohedral or triangular phase. This dehydrated structure is in a metastable state and exhibits strong hygroscopicity, readily reabsorbing water and returning to its original state upon exposure to air [4][6]. Although PBA possesses an open three-dimensional framework structure, which facilitates rapid ion transport, its chemical stability faces challenges in aqueous environments. The integrity of the PBA framework is limited by the dissolution of transition metal ions. While the rigid framework can withstand lattice breathing during charging and discharging, low crystallinity or high defect states are often accompanied by high water content, making the framework more susceptible to chemical erosion and leading to the gradual disintegration of the crystal structure [7].

### 2.4 Metal Coordination Environment and Valence State Stability

PBA has a typical face-centered cubic structure, in which there are two distinct metal coordination environments:Fe: Located at the vertices or face centers of the unit cell, it forms an octahedral coordination with the carbon end of the cyano group. Due to the strong coordination field splitting energy of the carbon end, the iron ion at this position is usually in a low-spin state, and the electron configuration is highly delocalized.Transition metal M: Located at the complementary position of the unit cell, it coordinates with the nitrogen end of the cyano group. The coordination field at the nitrogen end is weak, which makes the metal ion at this position usually in a high-spin state [2][8]. This Fe-CN-M chain structure is not a simple connection, but rather has strong charge-spin-lattice coupling. For example, in NiHCF, the inductive effect of the coordination field can trigger the transfer of electrons from $Ni^{2+}$ to $Fe^{3+}$, thereby changing the local electron density distribution [8].

PBA materials usually contain two potential redox active centers, namely the $Fe^{2+}/Fe^{3+}$ pair and the $M^{2+}/M^{3+}$ pair. Ideally, these two active centers can provide abundant sodium storage sites. However, the valence state of metal ions is highly sensitive. Especially during the synthesis process, $Fe^{2+}$ is easily spontaneously oxidized to $Fe^{3+}$ in an aerobic environment. This valence instability causes the electronic structure of the material to deviate from the ideal stoichiometry before electrochemical cycling [9]. "Inert" metals in the PBA framework exhibit activation phenomena. It is traditionally believed that some metals (such as Ni) are electrochemically inert in the PBA framework, but through coordination field regulation and electron delocalization effect, $Ni^{2+}$ can be activated to participate in redox reactions, forming a "dual active site" mechanism [8].

The stability of the metal coordination environment directly determines the robustness of the framework. Coordination substitution: In actual crystals, the presence of some $[Fe(CN)_6]^{n-}$ vacancies leads to changes in the coordination environment of the $M_A$ site metal, and the original $M\text{-}N_6$ coordination is replaced by $M\text{-}N_{6-y}(H_2O)_y$. The introduction of this coordination water weakens the symmetry of the lattice field and changes the electronic spin state of the metal ions [2]. Chemical bond dissociation: Although the PBA framework is open, transition metal ions face a severe risk of dissolution in an aqueous electrolyte environment. This is essentially the breaking of metal-ligand bonds under solvation. This instability of coordination bonds leads to the loss of active metals and disrupts the local charge balance, which is a manifestation of the inherent structural fragility of PBA materials [7].

## 3. Effect of Prussian Blue Structural Stability on Sodium Ion Storage Performance

### 3.1 Effect on Sodium Storage Specific Capacity

3.1.1 Vacancy defects leading to the loss of active sites

$[Fe(CN)_6]^{n-}$ vacancies are one of the main manifestations of structural instability. The generation of each vacancy essentially means the loss of a redox active center. Since the redox reaction of iron ions contributes a considerable portion of the total capacity of PBA, high concentrations of vacancies directly lead to a significant reduction in the theoretical capacity limit of the material [10]. Structural defects not only lead to the loss of physical sites, but also change the local electronic environment, making it difficult for some residual low-spin iron to be electrochemically activated, thus failing to contribute to the capacity [11].

3.1.2 Occupation effect of water molecules

The presence of structural water including crystal water and coordination water severely occupies the storage space of sodium ions. The large pores in the PBA framework should be the habitat of $Na^+$. However, due to the competition between water molecules in the lattice and Na+ for interstitial sites, the presence of a large number of water molecules directly reduces the total amount of $Na^+$ that can be embedded in the lattice [12][13]. Experimental data show that the lattice water content is negatively correlated with the capacity, and the sodium-rich phase with low water content exhibits a higher specific capacity than the sodium-poor phase with high water content. Structural water not only occupies space, but may also hinder $Na^+$ diffusion through hydrogen bond networks, resulting in some deep-layer capacity not being released within the normal voltage window [10].

### 3.2 Impact on Sodium Storage Reversibility

Sodium storage reversibility is a key indicator for measuring whether a battery can cycle stably for a long time and achieve high-efficiency energy conversion. Although PBA has an open framework, its reversibility in practical applications is often limited by its intrinsic structural fragility. Irreversible phase transitions caused by structural instability, interfacial side reactions, and loss of active materials constitute the three core mechanisms limiting its sodium storage reversibility.

3.2.1 Lattice distortion and irreversible phase transitions

PBA undergoes significant phase evolution during sodium storage. An ideal high-performance PBA should undergo a highly reversible phase transition mechanism of mutual transformation between cubic and rhombohedral phases. However, structural defects severely disrupt this reversibility. The presence of vacancy defects leads to uneven distribution of lattice stress. When a large amount of $Na^+$ is inserted, causing volume expansion, the high-defect framework cannot effectively buffer the stress, leading to plastic deformation of the lattice rather than elastic deformation, making it impossible for the structure to return to its original state during sodium removal [14]. In Mn-based PBA, the Jahn-Teller effect of Mn ions causes severe lattice distortion. This distortion is amplified in the presence of structural water, causing the material to gradually lose the order of the crystal structure during repeated charging and discharging, eventually leading to phase collapse, which physically blocks the insertion/extraction path of $Na^+$, resulting in irreversible capacity decay [15].

3.2.2 Interfacial side reactions induced by structural water

Structural water especially coordinated water is one of the main causes of reduced sodium storage reversibility. Coordinated water molecules occupying vacancies are unstable within the electrochemical window and are prone to inducing side reactions with the electrolyte. This reaction not only consumes the electrolyte but also generates a high-resistivity byproduct layer on the electrode surface [14][15]. The side reaction process is usually accompanied by the irreversible consumption of active $Na^+$. Furthermore, strong local charge interactions at structural defects may "capture" embedded $Na^+$, preventing it from escaping during charging and forming "dead sodium," thus permanently reducing the material's reversible capacity [16].

3.2.3 Framework disintegration and active metal dissolution

The most extreme manifestation of structural instability is the chemical disintegration of the framework. During cycling, PBA faces a serious problem of transition metal ion dissolution. Especially in the acidic local environment where structural water is present, metal-ligand bonds are more prone to breakage [15]. Dissolved metal ions shuttle to the negative electrode, damaging the negative electrode SEI film, while on the positive electrode side, the capacity continuously and irreversibly decreases due to the physical loss of active centers. This "electrochemically driven dissolution" phenomenon caused by structural instability is the fundamental reason why PBA materials are difficult to achieve long-life cycling.

### 3.3 Effects on Sodium Storage Kinetics

3.3.1 Structural water blocking channels and diffusion barrier

The presence of structural water constitutes a significant steric hindrance effect on the migration of $Na^+$. Interstitial water molecules occupy the pores of the PBA framework, which should be the transport channels and storage sites for $Na^+$. In undehydrated samples, the migration of $Na^+$ in the hydrated framework requires overcoming the additional energy barrier brought about by the hydrogen bond network of water molecules, resulting in a decrease in the ion diffusion coefficient and thus exhibiting poor electrochemical kinetic performance. In contrast, materials that have undergone rigorous dehydration to transform into the rhombohedral phase have more open ion channels and exhibit superior rate response [17].

3.3.2 Truncation of electron transport paths by vacancy defects

PBA itself is a semiconductor or insulator, and its electronic conductivity mainly depends on the electron delocalization on the Fe-CN-M framework. Vacancy defects disrupt the continuity of the -CN- bridged ligands, greatly increasing the internal resistance of the material. Under rapid charge and discharge conditions, this low electronic conductivity leads to severe electrochemical polarization, causing a shift in the voltage plateau, and the effective capacity cannot be fully released before the cutoff voltage, thus significantly reducing the kinetic performance at high rates [18][19].

3.3.3 Lattice distortion and phase transition kinetics

The integrity of the crystal structure directly affects the energy barrier of the phase transition. Compare the kinetic differences between the sodium-rich rhombohedral phase (high crystallinity, low defects) and the sodium-deficient cubic phase (high defects). The structurally complete rhombohedral phase can support a highly reversible and rapid "rhombohedral-cubic-tetragonal" phase transition; while the high-defect structure is prone to irreversible structural collapse during $Na^+$ insertion/extraction, resulting in sluggish kinetic processes [10]. Operando technology reveals that the reaction of low-spin iron sites causes more severe local lattice distortion than that of high-spin iron sites. If the structure itself is unstable, this severe local distortion will hinder the advancement speed of the two-phase interface due to stress accumulation, thereby limiting the overall reaction kinetic rate [18].

### 3.4 Effect on Sodium Storage Stability

High concentrations of $[Fe(CN)_6]^{n-}$ vacancy defects severely weaken the integrity of the lattice. During charging and discharging, this defective structure is difficult to withstand the lattice stress caused by repeated $Na^+$ insertion/extraction, leading to irreversible structural transformations in the material [20]. Water molecules in the lattice undergo continuous side reactions with the electrolyte during cycling. This not only leads to electrolyte decomposition and SEI film thickening, hindering ion transport, but also generates gas that causes battery swelling and contact failure [20][21]. Studies have found that water molecules hydrate with sodium ions in the form of $(NaH_2O)^+$. This large hydrated ion migration causes cumulative distortion of the crystal structure, which eventually leads to structural failure as the number of cycles increases [21]. The small volume change of the hydrated phase allows water molecules to buffer the volume change to some extent, but water must be removed in order to achieve high voltage and chemical stability. However, dehydrated PBA such as cubic or rhombohedral phases undergoes huge lattice volume changes during cycling, with expansion/contraction ranging from 17% to 20% [6]. If the PBA lacks sufficient structural toughness or has a large number of defects, this violent volume breathing can cause cracks inside the particles, eventually leading to particle pulverization and detachment from the current collector [16]. This mechanical structural instability is an important reason for the increase in contact resistance and loss of active material during long cycling.

## 4. Effect on Voltage, Efficiency and Kinetic Properties

### 4.1 Effects on Voltage Characteristics

4.1.1 Crystal phase evolution and flatness of voltage plateau

An ideal PBA undergoes a clear phase transition during charge and discharge. Sodium-rich rhombohedral PBA exhibits a highly reversible "rhombohedral ⇋ cubic ⇋ tetragonal" three-phase evolution during sodium ion insertion and extraction. This ordered phase transition corresponds to multiple flat and clearly defined voltage plateaus on the constant current charge and discharge curve. However, when the structural stability is low, a large number of $[Fe(CN)_6]^{n-}$ vacancy defects in the lattice destroy the long-range order, causing the sodium ion insertion mechanism to change from a two-phase reaction to solid solution behavior. In the macroscopic manifestation of voltage characteristics, the voltage plateau gradually shortens or even disappears, turning into a sloping curve, resulting in unstable battery output voltage, which is not conducive to constant voltage power supply of electronic devices [10].

4.1.2 Polarization and voltage hysteresis caused by structural defects

Structural stability directly determines the kinetic energy barrier of electrochemical reactions, and thus affects voltage polarization. The presence of crystal water and vacancy defects in the lattice results in extremely low intrinsic electronic conductivity of the material. Vacancies interrupt the electron transport framework of Fe-CN-M, while crystal water hinders the diffusion path of sodium ions. This structural obstruction leads to huge charge transfer impedance. In terms of voltage characteristics, this manifests as severe ohmic polarization and concentration polarization: the charging voltage plateau rises abnormally, and the discharging voltage plateau drops significantly, i.e., the voltage hysteresis continues to expand with cycling [22]. The discontinuous ion channels in traditional bulk PBA lead to stress concentration and diffusion lag. This dynamic "sluggishness" causes the voltage plateau to collapse severely at high rates, and the effective working voltage window is greatly narrowed [23].

4.1.3 Deactivation of surface redox centers and voltage decay

Structural degradation during long cycling leads to drift in the average working voltage. Deactivation of surface redox centers occurs in PBA during cycling. Structural degradation of the crystal surface and dissolution of transition metal ions lead to a reduction in the number of originally high-potential active sites or a change in the coordination environment from strong field CN coordination to weak field water coordination. This change in microstructure reduces the potential energy of the redox reaction, leading to a continuous decay trend in the average discharge median voltage of the battery during long cycles, thus weakening the energy output quality of the battery [24].

### 4.2 Effect on Efficiency Characteristics

4.2.1 Initial coulombic efficiency (ICE)

The initial coulombic efficiency reflects the utilization rate of active sodium ions during the battery formation stage. By comparing the performance of samples with different crystallinity, it can be found that the sodium-rich phase PBA with a complete structure has a very high ICE, while the ICE of samples with more defects is significantly reduced. During the initial charge and discharge process, some embedded sodium ions are "locked" by the strong local electric field of vacancy defect sites or lattice distortion, and cannot be released during the subsequent sodium removal process [10]. The structural water in the lattice undergoes an irreversible decomposition reaction at the high potential of the initial charge, consuming the charging current but not contributing to the discharge capacity, directly reducing the initial coulombic efficiency [22].

4.2.2 Cyclic coulombic efficiency (CE)

Cyclic coulombic efficiency measures the reversibility of the electrochemical reaction. Irreversible phase transitions and the dissolution of transition metal ions are the main causes of capacity decay. Unstable PBAs are prone to lattice collapse during cycling, leading to failure of the contact between the active material and the conductive agent, and these active materials cannot participate in subsequent reactions [24]. Structural defects and moisture exacerbate the erosion of the cathode material by the electrolyte, causing transition metal ions to dissolve into the electrolyte. This dissolution-deposition process not only consumes the active mass of the cathode but also corrodes the SEI film of the anode, making it difficult to maintain a high level of coulombic efficiency above 99.9% [22].

4.2.3 Energy efficiency (EE)

Energy efficiency is the ratio of discharge energy to charging energy, which comprehensively reflects the energy dissipation caused by voltage polarization and capacity loss. Ordinary PBA materials face huge volume changes and stress concentrations during charging and discharging, which leads to sluggish ion diffusion kinetics. The more unstable the structure, the higher the overpotential the battery must overcome in order to drive sodium ions through the distorted lattice and defects [23]. This means that more energy needs to be input during charging, while only less energy can be released during discharging. The high voltage hysteresis caused by structural instability converts a large amount of electrical energy into Joule heat dissipation, resulting in a significant reduction in the energy conversion efficiency of the entire battery. As structural degradation accumulates during cycling, polarization increases, and energy efficiency decreases at an accelerated rate, eventually leading to battery failure [24].

## 5. Strategies to Improve Structural Stability

### 5.1 Low-Vacancy Synthesis

5.1.1 Kinetic regulation assisted by chelating agents

Introducing sodium citrate as a chelating agent is one of the most effective means to inhibit rapid nucleation and reduce vacancy concentration. Citrate ions can form intermediate complexes with transition metal ions, thereby controlling the release rate of free metal ions and effectively delaying the kinetic process of precipitation reaction. This controlled crystallization environment allows crystals sufficient time to arrange themselves in an orderly manner, thereby significantly reducing the embedding of vacancies and water of crystallization, and generating low-defect crystals with regular morphology and high crystallinity [10][25]. The use of the inorganic chelating agent thiourea can also delay crystallization and optimize the nucleation process, significantly inhibiting the formation of defects [20].

5.1.2 Reaction atmosphere and valence state protection

Atmosphere control in the synthesis environment is crucial for maintaining the low valence state of metal ions and reducing defects. An inert atmosphere can effectively prevent $Mn^{2+}$ and $[Fe(CN)_6]^{4-}$ from being oxidized to a high valence state by oxygen in the air. Maintaining a low valence state not only helps maintain charge balance, thereby adsorbing more $Na^+$ into the lattice to form a sodium-rich phase, but also avoids structural defects caused by oxidation, ultimately obtaining high-purity PBA with low $[Fe(CN)_6]^{4-}$ vacancies [25].

5.1.3 Stoichiometric ratio and reaction parameter optimization

Precise control of the molar ratio and concentration of reactants is another important way to reduce defects. Studies have found that when the Fe:Mn ratio is controlled at 1:2, and the Mn ion concentration is low (0.02 mol/L) and the reaction time is long (12 h), the best crystal quality can be obtained [20]. This Mn-rich environment and slow reaction conditions are conducive to the formation of a structurally complete cubic phase MnHCF, which significantly reduces the content of interstitial water molecules and the $[Fe(CN)_6]^{4-}$ vacancy density.

## 5.2 Regulation of Structural Water

### 5.2.1 Heat treatment dehydration and phase transformation control

Through precise temperature control under an inert atmosphere, interstitial water and strongly bound coordination water can be effectively removed [4][26]. The dehydration process is accompanied by significant crystal structure evolution. High-water-content PBA is usually cubic or monoclinic, but after dehydration, it transforms into a more thermodynamically stable and more crystalline rhombohedral or triangular phase. This low-water-content structure can activate the redox activity of low-spin Fe, significantly improving cycle stability.

### 5.2.2 Vacuum and rehydration kinetics

By studying the effect of vacuum on the dehydration phase transition, it was found that under high vacuum ($10^{-2}$ mbar), the temperature of the monoclinic phase to rhombohedral phase transition is lower and more complete than under low vacuum (20 mbar). However, this study also revealed the extremely rapid rehydration characteristics of the dehydrated phase: the dehydrated rhombohedral PBA has extremely strong hygroscopicity and can reabsorb moisture and degenerate back to the monoclinic phase within minutes of exposure to air. This finding highlights the necessity of battery assembly and testing in a completely dry environment [17].

### 5.2.3 Ligand pre-exchange strategy

In conventional synthesis, $Fe^{2+}$ forms $[Fe(H_2O)_6]^{2+}$ in aqueous solution, which inevitably leads to the entry of coordinated water into the lattice. This strategy introduces ethylene glycol (EG) as a strong ligand to pre-replace water molecules around $Fe^{2+}$, forming the $[Fe(EG)_x(H_2O)_{6-x}]^{2+}$ precursor. Due to the introduction of EG, the coordinated water content in the final synthesized PBA is significantly reduced, and the $[Fe(CN)_6]^{4-}$ vacancy defect is also suppressed. The low-water-content PBA prepared by this method exhibits excellent structural rigidity, with a capacity retention of up to 70% after 1000 cycles [27].

## 5.3 Metal Doping and Framework Strengthening

Metal element doping is a key strategy to enhance the intrinsic framework rigidity of PBA, suppress structural degradation during cycling, and synergistically improve capacity and stability. Introducing copper dopants into the iron-vacancy-rich PBA framework for synergistic modification can effectively solve the problem of poor cycling stability of PBA materials. In this strategy, electrochemically inactive Cu elements are designed to replace some of the high-spin iron sites in the lattice. Although the Cu dopant itself does not contribute the main redox capacity, it plays the role of a "structural stabilizer" in the lattice. During the repeated insertion/extraction of $Na^+$, which induces valence state changes ($Fe^{3+}/Fe^{2+}$) in high-spin iron and low-spin iron, Cu doping enhances the framework's tolerance to volumetric strain, effectively preventing lattice collapse during long cycles and thus significantly improving capacity retention. Metal doping not only strengthens the internal lattice but also profoundly affects the evolution of microstructure. Undoped PBA samples have small particles (400-1000 Å), while the introduction of Cu doping significantly promotes the regular growth of crystals, forming larger (3000-4000 Å) and uniformly distributed cubic particles. This optimized microstructure, combined with a robust doped framework, not only provides a stable host structure but also improves the diffusion dynamics of $Na^+$ [16].

## 5.4 Carbon Coating and Surface Engineering

Conductive polymers are widely used to buffer the volume expansion of PBA and modify the interface due to their good flexibility and conductivity. Through in-situ polymerization, a polydopamine (PDA) film can be coated on the surface of NaFeHCF. PDA not only has extremely strong surface adhesion, but also significantly improves the diffusion kinetics and electron transport efficiency of $Na^+$. As a protective layer, it effectively isolates the direct contact between the electrolyte and the active material, thereby improving the cycle stability [28]. Gas phase molecular self-assembly technology: This method uses gas phase pyrrole monomers to form a polypyrrole (PPy) layer on the surface of PBA through in-situ polymerization. This solvent-free process not only maintains the stoichiometric integrity of PBA crystals, but the generated PPy layer also acts as a physical barrier, effectively inhibiting the dissolution and phase change of iron ions during cycling, so that the material still retains 85.6% of its capacity after 500 cycles, overcoming the defects of traditional liquid phase coating that easily lead to $Fe^{2+}$ oxidation and $Na^+$ loss [29]. 5.4.2 Molten salt-assisted carbon encapsulation strategy The molten salt-assisted carbothermal reduction strategy uses molten sodium chloride as a floating template to guide the iron core to shuttle through the pores of the carbon matrix. First, Fe/C composite intermediates are synthesized, and then in-situ converted into carbon-encapsulated Prussian blue. This carbon encapsulation structure not only endows the material with excellent electronic conductivity, but the robust carbon skeleton also provides mechanical support for the volume breathing of the internal PBA microcrystals, limiting the pulverization and aggregation of particles, thereby achieving excellent structural stability[30].

## 6. Conclusions and Outlook

### 6.1 Major Challenges in Current Research

Despite significant progress in the structural modification of PBA, the field still faces serious challenges. First, the contradiction between low defects and low cost remains unresolved. Currently, the preparation of PBA with low vacancies and low water content often relies on expensive chelating agents, complex non-aqueous solvothermal methods, or stringent atmosphere control, making it difficult to meet the low-cost requirements of large-scale energy storage. Second, interfacial stability remains a weakness. Even with framework reinforcement, the dissolution problem of transition metal ions in organic electrolytes remains unresolved.

### 6.2 Future Development Directions

Future research should focus on precisely constructing highly robust frameworks at the atomic scale, mainly including the following three aspects: 1) Zero-strain material design: Developing PBA materials with minimal volume changes during sodium insertion/extraction processes through multi-component high-entropy metal doping or lattice pillar effects, fundamentally solving the mechanical pulverization problem caused by lattice breathing. 2) Advanced in-situ characterization techniques: Combining Operando XRD/TEM and neutron scattering techniques to capture vacancy evolution and the dynamic migration paths of water molecules in real time, providing a theoretical basis for structural design. 3) System-level Interface Engineering: Moving beyond simple cathode modification, developing functional electrolytes with better compatibility with PBA, constructing a stable cathode/electrolyte interface (CEI), and synergistically inhibiting metal dissolution.

### 6.3 Industrialization Trends

The industrialization of PBA cathodes will involve developing continuously produced modified aqueous co-precipitation processes, combined with efficient spray drying or microwave dehydration post-treatment technologies to balance material performance and production energy consumption. Addressing the low density of PBA powder, the industry will focus on microsphere morphology control and gradation technology to improve electrode compaction density, thereby increasing the volumetric energy density of the battery. With its excellent rate performance and low-temperature characteristics, the highly structurally stable PBA cathode will be the first to achieve large-scale application in grid frequency regulation, residential energy storage, and low-speed electric vehicles, becoming an important supplement to lithium batteries.

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