

Cite this: *Dalton Trans.*, 2024, **53**, 16128

Unlocking the structure and cation synergistic modulation of Prussian blue analogues with double redox mechanism for improved aqueous nonmetallic ion storage

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Prussian blue analogs (PBAs) exhibit high energy density and a good electrochemical stability window in aqueous non-metallic ion batteries, which is conducive to achieving high energy output and stable operation. Additionally, their synthesis process is simple and environmentally friendly, meeting the demands of sustainable development. However, the poor conductivity, structural stability issues, and inadequate ion diffusion pathways limit their application in batteries. To overcome these challenges, researchers have adopted various optimization strategies: enhancing the conductivity of PBAs by compositing with high-conductivity carbon materials such as graphite, carbon nanotubes, or graphene; optimizing synthesis conditions such as temperature and reaction time to improve the defect and structural water content of PBAs, thereby enhancing their stability and electrochemical performance; employing surface modification techniques, such as conductive polymer encapsulation and acid etching, to improve their electrochemical stability and ion transport performance; and optimizing ion diffusion efficiency and battery kinetics by selecting suitable electrolytes and additives. These comprehensive measures contribute to improving the electrochemical performance of PBAs and promoting the development of their commercial applications. Based on prior research advancements, we introduce a novel synergistic regulation strategy: the creation of multi-redox-active centers to augment the transport capability of non-metallic ions and the optimization of defect structures through the establishment of a metal ion concentration gradient, thereby enhancing both electrochemical stability and performance.

Received 3rd August 2024,
Accepted 6th September 2024

DOI: 10.1039/d4dt02212b

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1. Introduction

With the rapid development of renewable energy and the expanding market for new energy vehicles, there is an increasingly urgent need for efficient, safe, and environmentally friendly energy storage systems. Water-based non-metal ion batteries, a new type of energy storage technology, have attracted widespread attention due to their unique advantages in this field. With its unique structural characteristics and performance advantages, Prussian blue analogues (PBAs) have shown a wide range of application prospects in catalysis, sensors, biomedicine, environmental management, electrochemical energy storage and other fields. Prussian blue analogues are a class of inorganic compounds with special structures that have shown excellent energy density and electrochemical stability in non-metal ion batteries and

are considered to be one of the most promising electrode materials.¹⁻⁵

At present, there are Prussian blue analogues, excessive metal oxides and some other materials for electrode materials for aqueous batteries. The application of transition metal oxides in aqueous batteries shows a series of significant advantages, such as high conductivity, abundant redox active sites, and good structural stability, which together improve the charging and discharging efficiency and power density of the battery, and also endow the battery with long service life and environmentally friendly characteristics.⁶⁻¹⁰ However, their applications also face several challenges, including battery capacity decay over time, insufficient cycle stability, relatively low energy density, limited operating voltage, and potentially high cost. These problems limit the application potential of aqueous batteries in certain fields.

The 3D frame of Prussian Blue and its analogues has a large gap position, which facilitates the rapid insertion/expulsion of carriers.^{11,12} The chemical formula of the Prussian blue analogue is $A_xM_a[M_b(CN)_6]_z \cdot nH_2O$, where A is an alkali

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metal ion and M_a and M_b are transition metal ions. A can be partially or completely replaced by many different ions. PBAs are easy to synthesize, exist independently in aqueous solution, and have a wide variety of metal elements at M_a and M_b sites, so there are also many types of PBAs. For example, in recent years, our group has successfully synthesized electrode materials such as VOHCF and Mn-PBAs by manipulating the types and compositions of M_a and M_b metals, and applied them to APBs and AZIBs, respectively, and obtained excellent electrochemical performance.^{13–15} As shown in Table 1, some typical transition metal oxide or PBAs-based electrode materials are listed and their electrochemical properties in aqueous H^+ or NH_4^+ batteries are briefly summarized. Demonstrate the potential of PBAs materials for storing non-metallic charge carriers in their framework structures during insertion/extraction in aqueous electrolytes.

Nowadays, the research on aqueous solution rechargeable batteries mainly focuses on metal carriers, such as Li^+ , Na^+ , K^+ , Zn^{2+} , and Al^{3+} , while there are relatively few studies on non-metallic carriers such as NH_4^+ and H^+ .^{22–24} The electrochemical behavior of non-metallic supports is different from that of metal ions. The type of charge carrier largely determines the electrochemical performance of a water-based rechargeable battery. As shown in Fig. 1, the small hydrated ionic radius of 0.3 nm, 0.331 nm and 0.15 nm are beneficial for the rapid diffusion of Cl^- , NH_4^+ and H^+ in aqueous electrolytes.^{25–27} Compared with other materials, PBAs materials, owing to their unique three-dimensional cubic structure and tunable chemical composition, serve as promising cathode materials for aqueous non-metallic ion batteries. The size of non-metallic ions can be well-matched with the cavities of these materials. The broad (100) crystal plane ion channels and the abundant carrier accommodation sites (with a diameter of approximately 4.6 Å) ensure the rapid insertion/extraction of ions. Moreover, many PBAs materials exhibit higher reaction potentials, ranging from 0.6 to 1.2 V. Theoretical studies indicate that during the entire reaction process, PBAs materials exhibit a volume change rate of less than 1%, classifying them as “zero-strain” materials. In contrast, the intercalation of hydrated sodium ions into PBAs can cause significant volume expansion, while the insertion of potassium ions tends to reduce structural symmetry, leading to lattice distortion.

However, PBAs-based batteries still encounter a range of challenges in practical applications, including inadequate conductivity, insufficient structural stability, and unsatisfactory ion diffusion pathways. These issues not only impact the battery's rate performance and cycle life but also have the potential to compromise battery safety. Consequently, effectively addressing these problems and further enhancing the performance of PBAs-based non-metal ion batteries has emerged as a current focal point and research challenge.^{28,29}

This frontiers article presents the challenges and possible countermeasures for the application of PBAs in non-metallic ionic aqueous batteries, aiming to provide valuable reference for researchers.

Table 1 Summary of the host materials and corresponding electrochemical performances of aqueous nonmetallic ion batteries

Materials type	Structure	Working potential range	Electrolytes	Capacity retention @ cycle number, current	Rate capability @ current	Ref.
VOHCF	Cubic	0.2–1.2 V vs. Ag/AgCl	1.0 M H_2SO_4	95.4% @ 10 000 cycles, 10 A g^{-1}		13
$Cu_{2.95}[Fe(CN)_6]_{1.69}$	Cubic	0.3–1.1 V vs. SCE	2.0 M NH_4NO_3	100% @ 3000 cycles, 1C	93.4% @ 50C	16
$NH_4Fe_4[Fe(CN)_6]_3$	Cubic	0.05–1.0 V vs. Ag/AgCl	Sat $(NH_4)_2SO_4$	87.5% @ 500 cycles, 1C 88.9% @ 2000 cycles, 30C	76% @ 20C	3
$(NH_4)_{1.81}Cu_{0.8}^{II}Cu_{0.2}^{I}$ $[Fe_{0.2}^{III}Fe_{0.8}^{II}(CN)_6]_{0.95} \cdot 1.14H_2O$	Cubic	0.3–1.1 V vs. SCE	2.0 M NH_4NO_3 + 0.01 M $Cu(NO_3)_2$	95.5% @ 700 cycles, 1C	98.3% @ 50C	4
$(NH_4)_{1.47}Ni[Fe(CN)_6]_{0.88}$	Cubic	0.2–0.9 V vs. Ag/AgCl	1.0 M $(NH_4)_2SO_4$	74% @ 2000 cycles, 5C	45% @ 10C	17
MnO_2	Monoclinic	0–1.0 V vs. SCE	1.0 M $(NH_4)_2SO_4$	60% @ 5000 cycles, 20 mA cm^{-2}		18
VO_2	Monoclinic	–0.7–0.3 V vs. Ag/AgCl	1.0 M $(NH_4)_2SO_4$	70% @ 10 000 cycles, 1 A g^{-1}	28% @ 5 A g^{-1}	19
MoO_3	Orthorhombic	–0.6–0.6 V vs. Ag/AgCl	$(NH_4)_2SO_4$	92.7% @ 5000 cycles, 20 A g^{-1}	44.1% @ 20 A g^{-1}	20
QA-COF		–0.6–0.6 V vs. SCE	0.5 M $(NH_4)_2SO_4$	76% @ 7000 cycles, 6 A g^{-1}	16.6% @ 10 A g^{-1}	21

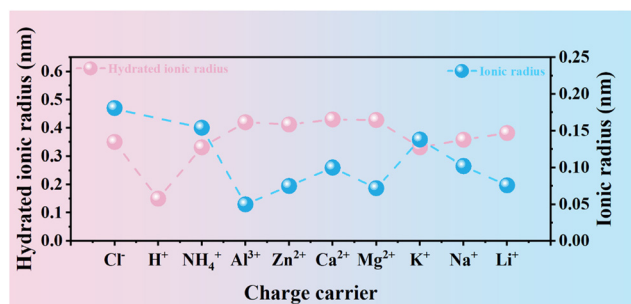


Fig. 1 The ionic radius and hydrated ionic radius of different charge carriers.

2. Challenge and solution

PBAs has a unique layered structure and high ion diffusion channels, which makes it exhibit excellent energy density and electrochemical stability in non-metallic ion batteries. This stable electrochemical window facilitates high energy output and stable operation, meeting the requirements of modern energy storage systems.³⁰ For example, Li and his team discovered a zinc-ammonium double-ion cell, which performed a high cell voltage of 1.9 V and excellent rate capability.³¹

2.1 Challenge

Although PBAs has a high ionic conductivity, its own conductivity is poor, resulting in the obstruction of electron transmission, which seriously affects the rate performance and cycling stability of the battery. Therefore, how to improve the conductivity of PBAs is one of the keys to optimize its electrochemical performance. PBAs is prone to volume expansion and contraction during charging and discharging, resulting in insufficient structural stability, which affects the cycle life and safety of the battery. For example, manganese-based Prussian blue and its analogues are affected by the Jahn–Teller effect during charging and discharging, which causes the dissolution of manganese-based central atoms, which seriously affects its electrochemical stability and rate performance.^{32–35} Therefore, enhancing the structural stability of PBAs is essential to improve battery performance. The ion diffusion path in PBAs is often limited by its layered structure, resulting in low ion transmission efficiency, which further affects the charge–discharge performance of the battery. Therefore, optimizing the ion diffusion path is of great significance to improve the kinetic performance of the battery.^{36,37}

2.2 Solution

In order to solve the problem of poor conductivity of PBAs, researchers have tried to combine it with carbon materials with high conductivity, such as graphite, carbon nanotubes, or graphene.^{38,39} This composite material can not only improve the conductivity of the overall battery by taking advantage of the high conductivity of the carbon material, but also improve the structural stability of the PBAs through the three-dimen-

sional network structure of the carbon material. The experimental results show that the composite material significantly improves the rate performance and cycling stability while maintaining the high energy density of PBAs. Xue *et al.* used polypyrrole to encapsulate PBAs, which also improved the conductivity and electrochemical properties of the material.⁴⁰ In addition, Zhang *et al.* used density functional theory to study that the nominal cell voltage range of ammonium-ion batteries can be adjusted by changing the M_a element (M_a = Co, Cu, Fe, Mg, Mn, Ni, V, Zn) of iron-based PBAs (M_aFe-PBAs), showing excellent stability.⁴¹

By optimizing the synthesis conditions (such as temperature, reaction time and precursor concentration, *etc.*), the microstructure and morphology of PBAs can be effectively controlled, thereby improving its electrochemical properties and ion transport properties. The results show that PBAs materials with higher specific surface area, more uniform pore distribution and shorter ion diffusion path can be obtained under appropriate synthesis conditions, thereby improving the performance of the battery.⁴²

Surface modification technology is an effective way to improve the electrochemical stability and ion transport properties of PBAs. For example, the electron density and conductivity of the PBAs surface can be increased by coating with conductive polymers;³⁸ Acid etching removes surface impurities and defects, reducing resistance to charge transfer. These surface modification methods can significantly improve the electrochemical stability and ion transport properties of PBAs, thereby improving the overall performance of the battery.

As an important part of non-metallic ion batteries, the properties of electrolyte directly affect the electrochemical performance and stability of batteries. By selecting the appropriate solvents, salts, and additives, parameters such as viscosity, ionic strength, and interfacial properties of the electrolyte can be adjusted, so as to optimize the ion diffusion efficiency and the kinetic performance of the cell. The results show that reasonable electrolyte regulation can significantly improve the performance and safety of PBAs-based non-metallic ion batteries.⁴³ Wang *et al.* reported a vanadium-ammonium oxide backbone (NVO) with excellent NH₄⁺ storage performance.⁴⁴ With NH₄Cl/PVA gel electrolyte, the capacitance and cycling performance of NVO have been greatly improved. The specific capacitance of the NVO electrode in the NH₄Cl/PVA electrolyte is 339 F g⁻¹ (610 C g⁻¹, 169 mA h g⁻¹) at a current density of 0.5 A g⁻¹ in the three-electrode configuration, which is much higher than that of 268 F g⁻¹ (483 C g⁻¹, 134 mA h g⁻¹) in the NH₄Cl electrolyte under the same conditions. After 14 000 cycles in NH₄Cl/PVA electrolyte, the capacitance retention rate was 71%. Tian and his team reported an electrolyte modulation strategy in which sucrose is added to the electrolyte,³⁶ which forms a sucrose-water hydrogen bond network in the electrolyte, disrupting the continuous water-hydrogen bond network and thus inhibiting the decomposition of water. In addition, the weak hydrogen bond interaction between ammonia ions and sucrose promotes the rapid migration of ions, improves the ionic conductivity, and enhances the

electrochemical performance. In addition, the assembled full battery has a wide voltage window of 2.2 V.

3. Perspectives

The insufficient conductivity and structural stability problems faced by PBAs materials in practical applications limit their application in high-energy-density batteries. In order to solve these problems, researchers have proposed an innovative strategy to construct multiple active sites by introducing additional active centers or functional groups to enhance the electrochemical activity and ion transport properties of PBAs materials. Specifically, active centers or functional groups introduced through chemical modification or structural design can be used as catalytic sites for electrochemical reactions, accelerating the charge transport process and thus improving the electrochemical activity of materials. At the same time, these active sites can also promote the rapid diffusion of ions in the material and enhance the ion transport performance, which is essential for improving the power density and cycling stability of the battery. In addition, by constructing multiple active sites, the volume expansion and structural damage of PBAs materials during charging and discharging can be effectively alleviated, so as to enhance the structural stability of PBAs materials. This strategy not only provides a new direction for the performance optimization of PBAs materials, but also opens up a new path for the development of high-performance non-metallic ion batteries. By finely adjusting the type, number and distribution of active centers or functional groups, it is expected that the electrochemical properties of PBAs materials can be precisely controlled, and then the development of non-metallic ion battery technology

will be promoted to meet the growing demand for high energy density, long cycle life and high safety energy storage.

The structure of PBAs was studied and analyzed in depth with the help of advanced characterization techniques and simulation calculation methods, and its structure was precisely regulated and optimized by artificial synthesis methods. This method can achieve precise control and optimization of the structure and performance of PBAs, and enhance its application potential in non-metallic ion batteries. Medium-entropy and high-entropy PBAs have garnered significant attention recently, which exhibit superior structural stability compared to low-entropy counterparts. The incorporation of multiple metal ions into the crystal lattice increases the configurational entropy, which helps in stabilizing the structure during cycling and under various environmental conditions. This leads to reduced phase transitions and less lattice distortion, which are critical for long-term performance. Moreover, the diversity of metal ions in medium- and high-entropy PBAs contributes to a wider range of redox-active sites. This can result in a broader operating voltage range and potentially higher capacity, as more redox reactions can take place simultaneously. The multiple metal ions also provide pathways for multi-electron transfer, which can enhance energy density.

In-depth exploration of the influence mechanism of electrolyte components on the electrochemical properties of PBAs materials and the development of new high-performance electrolyte systems have become the key paths to promote the release of the potential of PBAs materials and promote their development in practical applications. The composition of the electrolyte, which acts as a medium for ion transport in batteries, has a decisive influence on the electrochemical properties of PBAs materials. The solvents, salts and additives in the electrolyte not only affect the ion transport efficiency and

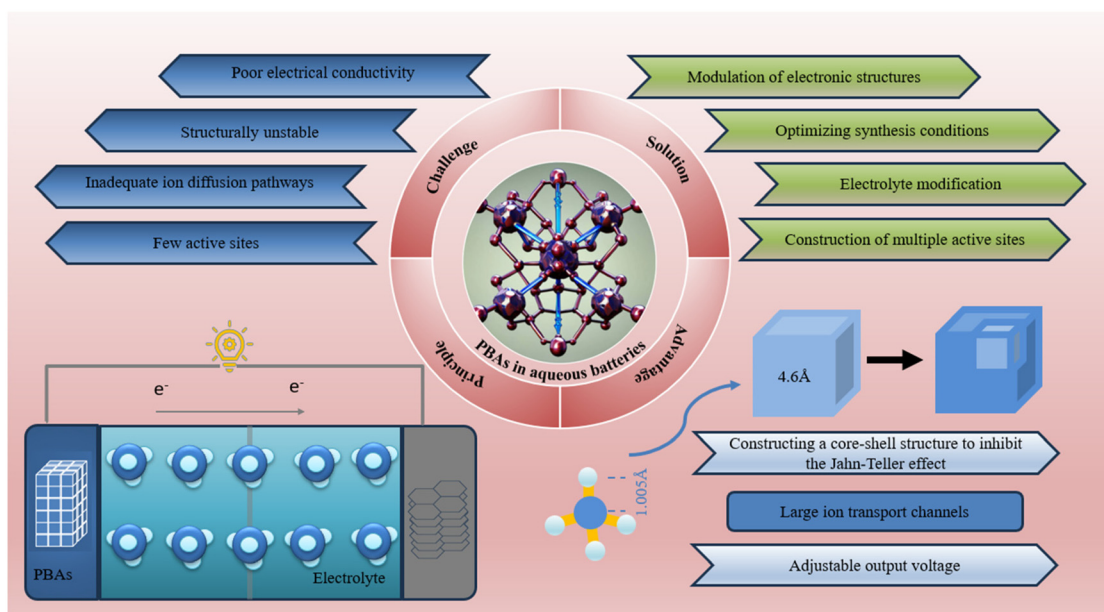


Fig. 2 Summaries of PBAs for aqueous batteries.

charge transfer kinetics, but also directly affect the stability of the electrode material and the overall safety of the battery. By studying the effects of different solvent systems, electrolyte salt types, concentrations and additives on the electrochemical properties of PBAs materials, the interaction mechanisms between electrolytes and electrode materials can be revealed, such as interfacial charge transfer, electrolyte decomposition voltage window, electrochemical window and structural stability of electrode materials. Understanding this mechanism is critical for designing and optimizing electrolyte systems to meet the electrochemical needs of PBAs materials. Based on the in-depth understanding of the electrolyte-electrode material interaction, the development of new high-performance electrolyte systems has become the key to promote the application of PBAs materials. This includes, but is not limited to, the design of solvents with a wider electrochemical stabilization window, the selection of electrolyte salts that are more compatible with PBAs materials, and the introduction of functional additives that can improve the stability of the electrode interface. Through these strategies, the new electrolyte system can not only improve the ion transport efficiency and electrochemical activity of PBAs materials, but also effectively alleviate the side reactions in the process of charging and discharging, and enhance the cycling stability and safety of batteries, so as to achieve the high-performance performance of PBAs materials in non-metallic ion batteries. In conclusion, in-depth study of the influence mechanism of electrolyte composition on the electrochemical properties of PBAs materials and the development of new high-performance electrolyte systems are the core strategies to promote the development of PBAs materials in practical applications. This can not only promote the optimization of PBAs material properties, but also promote the application of PBAs in non-metallic ion batteries, providing an important material basis and electrolyte solution for energy storage devices with high energy density, high power density and long cycle life (Fig. 2).

4. Conclusion

Prussian blue analogues show great potential in non-metallic ion batteries as a material with high energy density and a good electrochemical stabilization window. However, its practical application performance is still restricted by its poor electrical conductivity, insufficient structural stability and unsatisfactory ion diffusion path. Some progress has been made in optimization strategies such as compounding with high-conductivity carbon materials, optimizing synthesis conditions, surface modification technology, and electrolyte manipulation, but it is still necessary to explore new research strategies and methods to further improve the performance of PBAs non-metallic ion batteries and promote their commercial application. The review presents a novel approach to synergistically regulate the structure of PBAs through active sites and cation doping, enhancing their adaptability for non-metallic charge carrier storage in aqueous electrolytes. This method effectively

improves their aqueous non-metal ion storage capacity. For future research, several issues deserve in-depth exploration: (1) How to balance defects and structural water in the synthesis of PBAs using hydrothermal or co-precipitation methods; (2) The influence of *in situ* addition of other ions, and even the synthesis of high-entropy compounds, on the structure of PBAs during the synthesis process; (3) *In situ* electrochemical characterization of multiple redox-active centers; (4) The spatial hindrance reaction of the framework on the insertion/extraction of non-metallic charge carriers and the efficient utilization of active sites.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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