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INSIGHTS INTO HIGH ENTROPY PRUSSIAN BLUE ANALOGUE BATTERIES: LATTICE MECHANISMS, SYNTHESIS AND ENHANCEMENT

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ABSTRACT

Prussian Blue Analogues (PBAs) are rising as popular energy storage materials due to their open, face-centred cubic lattice and tunable electrochemical properties. In particular, high-entropy PBAs (HE-PBAs), of general formula $A_xM_2[M_1(CN)_6]_V\cdot nH_2O$ ($0 \le x \le 2$, $0 \le y \le 1$), leverage a multicomponent lattice stability and enhanced performance with mixed-valence metal centers to stabilize the host structure, homogenize cation distribution, and optimize ion-transport channels. This review compiles recent advances in low-cost, scalable synthesis methods including co-precipitation and other methods employed for enhancement of the battery's performance, such as vacancy engineering and carbon coating, additionally providing a comparison on the specific capacity and retention of the materials with work from other experiments. Analysis of X-ray diffraction and microscopy in various studies reveals how lattice vacancies, surface modifications, and framework substitutions influence electronic conductivity and ion diffusivity. Across reported studies, HE-PBAs consistently deliver enhanced electrochemical performance, exhibiting high reversible capacities, rapid charge–discharge rates, with easily preparable materials and cost-effective methods with procurable components, positioning them as strong candidates for commercial and grid-scale energy storage, for which future research is encouraged.

INTRODUCTION

Metal-organic frameworks are a new range of advanced materials being explored, with the latest searches for renewable and efficient energy sources[1], [2]. They are growing popular because of their diverse applications, including supercapacitors, electrocatalysts, photocatalysts, and, importantly, rechargeable energy storage devices. A subdivision of the materials, called Prussian Blue Analogues, are frameworks with the identifying (CN)n cyano-ligand bonds, general formula AxM2[M1(CN)6]y·nH2O ($0 \le x \le 2$, $0 \le y \le 1$), with A being an alkali metal ion and Mno` being a first-row transition metal [1], [2], [3], [4], [5]. Figure 1a is a representation of the structure of the materials.

Metal-organic frameworks exhibit a diverse crystal structure, with Prussian blue analogues featuring a face-centred cubic (FCC) structure. While the synthesis processes, such as co-precipitation, and the various battery performance parameters have been mentioned across various papers, more could be added by explaining the reason behind the observed characteristics. This includes the application of the 'cocktail effect' and the differing oxidation states of metals on the discharge rates, as well as other mechanisms in the lattice, which this paper aims to explain. This paper also aims to compile research data on high-performing materials, various synthesis methods, and the feasibility of these variations, compiling, and discussing the recent breakthroughs and observed performance in other studies.

HIGH-ENTROPY ENGINEERING

High-entropy materials are defined as single-phase materials comprising five or more metallic elements in near-equimolar ratios (HE-MOFs have between 5%-35% concentration of each), [1], [3], [4], [14], or as having configurational entropy (Δ Sconf) > 1.5 R, where R represents the ideal gas constant. The stability of these materials is attributed to their high configurational entropy, which lowers the Gibbs free energy, promoting the formation of a single solid solution phase and enhancing chemical and structural diversity, calculated by Equation 1:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$
(1)

Where ΔG is the change in Gibbs free energy, ΔH is the change in enthalpy, T is the Kelvin temperature change, And ΔS is the change in entropy.

The ideal configurational entropy can be calculated using the following Equation 2:

$$S_{conf} = -R \sum x_i \ln x_i$$
 (2)

Where R is the ideal gas constant,

And x_i is the mole fraction of the i-th metal species in the HE-PBA structure [18].

It is mainly the homogenous integration of multiple cations into the structure with varying electronic properties to harness the synergetic strength of the materials. These PBAs have a wide structure and enhanced ion diffusion owing to the existence of the hexacyanoferrate ions as a part of the ligand structure in combination with 5 or more metal ions at the 'M' positions (-M-N=C-Fe-) [1], [2], [8], [8]. The introduction of multiple metals increases the stability and cycle performance by forming multiple redox-active sites for the reaction, facilitating electronic and ionic transport and multiple interactions due to the high-entropy configurations. The change in the oxidation state of the ions like iron Fe2+/Fe3+, manganese Mn2+/Mn4+/Mn7+, and copper Cu1+/Cu2+ also enhances electrochemical energy storage[7], owing to the behaviour of transition metal with d-orbital electrons. Further work has also been done, utilising the Mn2+/3+, Fe2+/3+, Co2+/3+, andCu1+/2+ as the primary redox centres (revealed by ex-situ XPS)[1], and stabilisation is done with the redox inactive Ni2+, stabilising the framework structure. Multi-element doping refers to exchanging the ions, especially at Fe and Ni sites, and is an enhancement technique, others including the addition of a conductive agent, confinement or coating, and the regulation of Fe3+ vacancy[20]. The 'cocktail effect' arises due to the interactions between multiple metal cations and the presence of multiple transition element redox sites. A quality of regular as well as high-entropy PBAs, pi-backbonding in the lattice of transition metal ions with the hexacyanometallate group leads to size changes in the lattice during discharging. Fe-PBAs have been observed to increase volume while Ni- and Cu-PBAs have been observed to decrease, which is due to the resulting 'redox flips of the low-spin Fe3+ and Fe2+ ions[21]. The incorporation of several cations at the 'M' sites increases the stability of the mixture by producing a 'quasi-zero strain' during cycling[1], [2], [20]. The high-entropy has many advantages, such as countering lattice degradations. The mix of multiple ions also increases its stability.

During the synthesis of the high-entropy materials, vacancies and structural defects may be artificially introduced in some cases. Controlled vacancy introduction can prove helpful, such as the case of the introduction of high valency ions, like Mo6+, Na+ vacancies are formed due to the 'valence equilibrium', and this enhances the electronic conductivity and ion diffusion kinetics by reducing the barrier to transport[22]. However, higher vacancy concentrations (>10%) reduce cyclability by upto 40% [15], [22], and the lack of free ions may lower capacity[23] and rate performance [6], or when occupied by water molecules (common when the material is synthesised by precipitation involving solution of multiple elements) cause poorer performance, and these will have to be treated. Minimal water stabilises the lattice, but excess may cause electrode-degrading side reactions[7], [24]. These polycrystalline materials also contain a large number of grain boundaries, depending on the preparation technique (time of preparation) and materials used (varying crystal structure). These boundaries can sometimes lead to uneven strain distribution during the charge/discharge cycles, which is mitigated by more uniform crystal structure preparation, or as experimented, implementing a single-crystal approach, with high capacity, long cycling and good rate performance simultaneously. This also improves the thermal stability and tap density of the material, or how tightly the electrode is packed, having strengths, like high energy density, and weaknesses, like potential low life-cycle [9]. Maintaining the composition, however, can be quite challenging.

USE IN BATTERIES

The mixture of the organic and inorganic parts in the ligand structure has many benefits for the properties of the material. It forms a

strong and effective crystal lattice, which is engineered to have 'open cage' structures with the introduction or 'doping' of non-hydrogen or non-carbon atoms[3]. Sometimes there are irregularities in the lattice structure formed during synthesis, such as vacancies and portions with trapped water, represented by (Na2-xM[Fe(CN)6]1-y \Box y=nH2O, M = Fe, Mn, Co, Ni, Cu, etc., \Box = [Fe(CN)6] vacancies) which have varying effect on the overall performance of the material. Additional steps to the synthesis, as well as material modifications, are being researched. High-entropy Prussian Blue Analogues otherwise offer high theoretical specific capacity and a three-dimensional open framework for fast ion diffusion[4], [6], [7]. They have been experimented on widely as cathode materials, with varying structural design, element configuration and tunable redox potentials, and have a clear advantage for application with the cost-effective preparation and superior material properties[8].

These materials are often used in non-aqueous batteries with trapped alkali metal ions or smaller ions like zinc in the cubic frames or 'A' positions of the lattice[6], [9], [10]. The alkali ions in the interstitial sites are mobile; they diffuse in and out of the frame, resulting in superior rate performance and higher initial capacities, thanks to efficient ionic transport. Prussian Blue Analogues are being exper-





imented on as the cathode material with different transition elements, such as iron, zinc and manganese, to determine effective materials for the function[9], [11], [12], and HE-PBAs have proven to outperform traditional batteries in different parameters, for example, capacity retention of the battery over repeated charging and discharging cycles, as is shown in Fig-1b.

There are different types of batteries based on the alkali ion and the medium incorporated into the battery, and experiments are being carried out on them to identify future applications. Lithium-sulfur (Li-S) batteries suffer from the 'shuttle effect'. The Shuttle Effect refers to the migration of long polysulphide ions from the cathode to the anode, where they are reduced to shorter-chain polysulphides. These shorter chains then diffuse into the cathode and are oxidised back to longer chains. The use of a high-affinity cathode material like HE-PBAs can help mitigate the disadvantages of the effect, such as lower capacity, Coulombic efficiency, and corrosion/degradation during and after the battery is running[13], [14]]. Other common batteries include Aqueous Aluminium Ion (AAIBs), Aqueous Potassium ion (AKIBs), sodium ion (SIBs), for their unique crystal properties, and zinc-air batteries (ZABs), known for their performance as bifunctional electrocatalysts[15]. It is generally observed that smaller ions are better choices due to their small size, and this can be attributed to easier diffusion of smaller ions through the conduction channels.

Battery Type	HEPBA Composition (if specified)	Specific Capacity (mAh g ⁻¹)	Cycle Life (cycles/retention% %)
SIBs	Na2Mn0.2Fe0.2Co0.2Ni0 .2Cu0.2Fe(CN)6	94*	500 / 89%**
PIBs	Fe, Co, Cu, Ni, Mn doped	102.4	3448 / 84.4% (over 270 days)
AIBs	Cu, Fe, Mn, Co, Ni (HEPBA-Cu)	79.2``	10000 / 91.2%``
LSBs	Mn0.4Co0.4Ni0.4Cu0.4Z n0.4[Fe(CN)6]2	-	1000 cycles / 0.05% decay per cycle (at 2.0 C)

Table 1: Comparison of Capacity with different interstitial ions (A position) [Key: Conditions during the readings- *=100 mA/g, **=200 mA/g, ``=5 A/g] {From: [12], [16], [17]}

Additionally, 'High-entropy Engineering' [8], [9], [18], [19] has been employed in the usual crystal structures to optimise structural benefits from different metals.

LATTICE MECHANISMS

Following the Crystal Field Theory, and employing the Linear Combination of Atomic Orbitals [25], [26], an energy gap can be induced in the crystal elements having ligand bonds because of the splitting of the d-orbital of transition metal elements into the lower and higher energy sublevels (t2g and eg in an octahedral symmetry). This is observed due to the repulsion from electrons of the ions, which causes lengthening of the d-sub orbitals, hence splitting so that orbitals face different amounts of repulsion, leading to an energy difference. While these can cause a rigid and stable lattice, they may also lead to energy loss or hindrance in the ionic channels in cases.

Further interactions may occur between the elongated orbitals. Distortions may cause a reduction of symmetry and energy of the system, referred to as Jahn-Teller distortions[25], [27]. These distortions may cause the transfer of electrons between orbitals, for example, dz2 orbital is doubly occupied, whereas the dx2–y2 has only one electron, causing a net loss in energy by an amount δ (where δ is the energy loss individual orbitals face in opposing directions, related to the electrons occupying them). These distortions may reduce the binding energy of the surrounding active sites and intermediaries, which can degrade battery performance. These distortions are especially strong in Mn³⁺- or Cr²⁺-rich PBAs, and they may also cause uncontrollable phase transitions in the battery. Referred to as Jahn-Teller distortions [26], [27], These elongations form octahedral arrangements, with d-orbitals filled with 'high-spin' and 'low-spin' levels.

Ways to circumvent these low-energy distortions have been found, including multi-element doping, which mitigates the metal's phase transitions. This is attributed to the 'cocktail effect', arising from the synergistic interactions of multiple metal ions and redox-active sites. It is beneficial for tuning electrochemical properties. By selectively combining elements like Co, Cu, Ni, and Zn, researchers achieve precise control over redox potentials and ion diffusion pathways [28]. Varying reaction coefficients with the alkali or battery ions also provide a mechanical buffer by stabilising inactive parts and reducing the expansion coefficient to alleviate volume changes during battery reaction[26], [28].

Lastly, another effect, namely the 'lattice respiration' effect, induces an 'ultrastable' performance characteristic, as observed in the HEPBA-Cu [7]. It is related to the reversible expansion and contraction of the crystal lattice during ion insertion/extraction of the interstitial ions. Normally, electrostatic interactions between high-charge-density ions (e.g., AI^{3+}) and the host structure caused degradation through this mechanism, but HEPBAs mitigate this through their intrinsic 'lattice tolerance', enabling a "breathing" or reversible mechanism that accommodates ionic fluxes without structural collapse, and this low-strain condition enhances cyclic stability. For example, HEPBAs like ($Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2}$)O exhibit a capacity retention of 91.2% after 10,000 cycles at 5 A g⁻¹, attributed to the lattice respiration effect[7], [15], [19].

PREFERABLE CONFIGURATIONS

HE-PBAs have been experimented on with different metals and configurations based on crystal stability, capacity retention over cycles and voltage/specific discharge, to name a couple. Materials are designed to homogeneously place desirable ions for properties like their oxidation states and bonding, or the strength of the crystal structure. Cations are also chosen with similar hexacoordinated ion radius to avoid barriers of lattice matching[3]. Lattice matching refers to the alignment of crystal lattices when different materials are brought into contact, which is crucial for efficient electron transfer. Transition metals such as Mn, Fe, Co, Ni, and Cu can accommodate the electron density from the cyanide ligand. The ability to engage in back-bonding also enhances the stability of the complex[21], [29]. Manganese (Mn) is used for its primary redox centre for charge compensation via Mn^{2+}/Mn^{3+} transitions, providing a high theoretical capacity, high voltage and low cost, but is prone to Jahn-Teller Distortions, which hinders its reversibility[2], [10]. Cobalt (Co) modulates electronic conductivity through Co^{2+}/Co^{3+} redox activity and lowers charge transfer resistance by 34% compared to others [2]. Nickel (Ni) acts as a structural stabiliser through strong Ni-N bonding, and it reduces lattice parameter fluctuation during ion insertion by 41%[10]. Iron forms the backbone of the framework via (Fe-C=N-Fe) linkages, and benefits heavily from its high-spin and low-spin electron activity and action as redox-active sites. It maintains long-range structural order during phase transitions[10], [11]. Copper enables Cu^+/Cu^{2+} redox activity at higher voltages (1.6-1.8 V vs Na⁺/Na) and has a higher voltage window[2].



Below is a generalised list of the material configurations along with insights on the battery capacity and electrolyte it is used in, including collected and presented information in the studies by Xing et al and Nguyen et al [1], [3], [30], [6], [9], [31], [32].

PBAs Cathode	Electrolyte	Capacity	Cycle (Reten- tion/%)
NiHCF@PPy	0.5M H ₂ SO ₄ + 0.2M Ani- line	73.6 mAh/g (2 C)	300 (70%)
TiHCF	0.1M NaNO₃	30 mAh/g (0.2 C)	-
СоНСГ	1M Na ₂ SO ₄	114 mAh/g (0.1 A/g)	200 (83%)
Co _{0.97} Zn _{0.03} HCF	1M NaNO₃	119 mAh/g (0.1 A/g)	200 (74%)
VHCF@CuHCF	0.5M Na ₂ SO ₄ + 5M H ₂ SO ₄	90 mAh/g (1.2 C)	200 (90%)
NienHCF	0.5M Na ₂ SO ₄	36.5 mAh/g (0.1 A/g)	500 (60.7%)
MnHCF	17M NaClO₄	59 mAh/g (5 C)	700 (75%)
M5HCF	1M Na ₂ SO ₄	65.6 mAh/g (1 C)	1000 (87.0%)

CNM2Cu2Zn HEPBA nanocube	ЗМ КОН	336 F/g or 144.8 mAh/g at 1 A/g	-
K(MgMnFeNiCu)Fe(CN)6 HEPBA	1M Na2SO4	175 F/g at 5 mV/s	-
K(MgMnCoNiCu)Fe(CN)6 HEPBA	1M Na2SO4	160 F/g at 5 mV/s	-
K(MgMnFeCoNi)Fe(CN)6 HEPBA	1M Na2SO4	135 F/g at 5 mV/s	-
SC-HEPBA/NaTi2(PO4)3	-	109.4 mAh/g at 50 mA/g	2000 (77.8 %)
Na-rich SC-HEPBA	-	115 mAh/g at 100 mA/g	1000 (79.6%)
HEPBA@rGO	-	115.2mAh/g at 100 mA/g	1000 (73.44%)
NaCuFe-Oxide		94 mAh/g at 100 mA/g	500 (89%)

Table 2: Comparison of Electrochemical performance

HE-PBAs are also being experimented with zinc-ion batteries for the potential in 'Zinc-Air Batteries' and zinc storage. Better-performing materials delivering average storage capacities of 69-89 mAh·g⁻¹ at current densities varying from 0.1 to 2 A·g⁻¹, respectively [10]. After high-rate cycling, they show good stability with capacity recovering to 70 mAh·g⁻¹ at 0.1 A·g⁻¹. Having a low charge transfer resistance, Rct = 58.28 Ω , also promotes faster kinetics. The observed CV has an initial anodic peak due to K⁺ deintercalation, and following redox peaks at 1.80/1.60 V and 1.89/1.81 V in a stable second cycle, linked to Zn²⁺ insertion/extraction[10].

SYNTHESIS

Prussian Blue Analogues have been widely prepared with the co-precipitation method, involving a metal salt and a hexacyanoferrate complex, and is a cost-effective and scalable process. With more research, High-Entropy PBAs are also prepared similarly, along with other synthesis and preparation techniques like Ball-milling, mechanochemical and solvothermal methods. It is important to take into consideration multiple factors when considering synthesis, including reproducibility, efficiency and optimal cost procedures, especially when considering the large-scale applications of such materials.

SOLVOTHERMAL

Solvothermal and hydrothermal methods include a well-mixed solution of multiple metal salts (containing the required ion and may or may not contain a cyanoferrate ion) and organic ligands to prepare high-entropy metal-organic frameworks. They are prepared under low-temperature and high-pressure conditions, which ensure sufficient energy input while maintaining the organic-inorganic hybrid structure[1], [33]. They can produce near-equimolar crystals (but need control to get homogeneity) and can also be incorporated with secondary building units (SBUs) like trinuclear metal oxide clusters, enhancing compatibility of some of the components[1]. While it enhances crystallinity and single-phase control with reduced defects, it is energy-intensive and might not be the best for commercialisation without modifications.

MECHANOCHEMICAL

Mostly done by the ball milling process, it combines conductive materials like graphene to create nanocomposites that exhibit im-

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proved electronic conductivity and cycling stability[34]. It is used to control a uniform crystal size and structure, and the friction produced by the milling provides local heating to the reactants, promoting diffusion of metal ions[1]. Observing the SEM images of the product (this case, MgMnFeCoNi-HEPBA prepared by Jiang et al), it was found that ball milling promotes rapid interaction between organic ligands and metal ions, but also leads to increased defects and loss of crystallinity, like in cases of intense friction.

It is combined with rinsing with deionised water to maintain crystallinity. This modification also eliminates the need for high temperatures to achieve a high-entropy configuration. In a study by Jiang et al, mixtures of 'cyano precursors' (like $K_3Co(CN)_6$ 2.5 mmol) were mixed along with other metal salts (like $MnCl_2$, $FeSO_4$, $CoCl_2$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $CuCl_2$) at close to equal concentrations (0.5 mmol each) to get the sample of K(MnFeCoNiCu)Co(CN)_6; an example of many. The mixture is later dried for 24 hours at 100 °c, a lower temperature compared to the original temperature requirements. By combining mechanical with wet chemistry, they were able to conduct room-temperature synthesis and achieve high-entropy configurations (although stoichiometric control is required post-rinsing) with supercapacitance enhanced by defects[3].

CO-PRECIPITATION

This is the most widely practised, establishing itself among the most promising preparation techniques, involving close to room temperature synthesis of alkali-ion batteries with nanopores (10–50 nm), improving ion diffusion kinetics with surface area[9], [15]. Slowing crystal growth via additives like sodium citrate[8] enables formation of low-defect, well-crystallised PBA nanocubes, where the slowest-nucleated sample showed superior rate performance and cycling stability[8]. This method is cost-effective, requiring simple instruments like a syringe pump or Y-tube mixer, a stirring system, temperature control, and the relevant chemicals. The Y-tube setup is to improve micro-mixing, leading to a uniform particle size and reduced defect formation, and optionally, purging the system with nitrogen helps avoid unwanted oxidation of the precursors during synthesis[30], [35], [36]. Co-precipitation enables us to maintain precise control over the stoichiometry of the final product by adjusting the ratios of the precursor metals and additives like citrate chelate. The use of the bottom-up method of synthesis is also beneficial, enabling uniform component mixture and removing the need for high temperatures during the mixing[1]. Factors like precursor concentration, ageing time and the presence of additional salts also influence the structural characteristics. Some materials may tend to have a certain amount of vacancies despite different synthesis conditions, but it is observed that faster reaction inhibits vacancy formation to slow down nucleation and growth[35]. This, however, is more time-consuming and requires accurate measurement of the reaction time[1]. Optimised ion pathways are created, creating a stable crystal structure and a more efficient use of the redox-active sites, boosting the overall energy density.



{The yellow , red, dark blue, grey and cyan ions being respectively, potassium, manganese (II), iron(III), carbon and nitrogen, according the material as prepared by Jiang et al.}

Enhancement

Following the synthesis, the materials may be tweaked to provide additional benefits. Common enhancements include coatings to reduce mechanical damage and conductive materials applied on the surface to offset low conductivity.

High-entropy engineering, along with unique element/ion doping, can also be considered an enhancement to the performance, also used to offset effects like the Jahn-Teller Distortions. Copper doping has been shown to enhance the activity of iron, while manganese is known for its high theoretical capacity. This multi-element doping harnesses their strengths while potentially mitigating individual weaknesses[37]. Another technique, 'etching', is the addition of chemical substances to the structure to enhance its electrochemical performance. It allows for the creation of specific structural features, such as hollow nanoboxes[38], [39]. In a study by Yu et al, the resulting nanoboxes exhibited a low overpotential and high peak power density of 185 mW/cm², having cycling stability over 2000 cycles at 10 mA/cm² when used in Zn–air batteries. In another study by Chen et al, β -Ni(OH)₂ particles were produced with NiAl-layered double hydroxides (LDHS) precursors, which were layered and optimised the material's electrochemical behaviour for applications. Treatment can also be done with aqueous NH₃ and ethanol, leading to partial structural and compositional modifications, which improve the surface properties and catalytic activity of the material, acting as a catalyst for Oxygen Evolution, Ethanol Oxidation and Urea

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Oxidation Reactions with increased Co³⁺ and Ni³⁺ content[40].

Prussian blue analogues are precipitated (also prepared with facile liquid diffusion and physical absorption [41]) onto reduced graphene oxide sheets, Then, they are calcined at 300°C in a nitrogen atmosphere, ensuring uniform surface distribution and facilitating effective electron and ion transport [31]. In the experiment, structural defects and other properties like the D and G bands characteristic of rGO were observed through peaks in the Raman spectroscopy testing [42]. There is uniform dispersion, with cubic morphologies around 100 nm, due to the synergistic effect between the hydrophobic effect and the pi-pi stacking of the components [31], [42]. There are increased Na+ inserting/extracting channels and high chemical stability, capable of resisting the corrosion of chemical substances in the electrolyte, and protecting surface damage [42]. In polysulphides, they also prevent diffusion, hindering the shuttle effect [41]. The 3d confinement of the materials in conductive coatings, like through the carbon wrapping (CW) technique of adding a thin layer of carbon to support the structure mechanically and improve conduction channels, denoted by 'HE-PBAs@C' [6]. Unlike rGO with embedding within the composite matrix, here the particles are encapsulated externally. The cathode demonstrates excellent compatibility with both hard carbon and NaTi2(PO4)3 anodes in full cells over several cycles, highlighting its promising potential for large-scale energy storage applications[6], [43].

Prussian blue analogue (Co/TCNi/HCCr) nanoparticles have also been synthesised, exhibiting enhanced dielectric properties with a rise in dielectric constant from 163 to 3464 throughout the frequency range of 10–100 kHz at ambient temperature[35], [44]. Another advantage is that it can be conducted at room temperature without strong bases, using potassium hexacyanochromate, potassium tetracyanonickelate, and cobalt chloride capacitors. It has potential for application, with promising dielectric behaviour and semiconducting characteristics ideal for capacitors, sensors, and energy storage[44].

LARGE-SCALE APPLICATION

HE-PBAs have proven to be high-performing and suitable materials for energy storage with ionic and electronic conductivity, and enhanced performance has been shown, mitigating common problems with batteries. Its framework crystal structure, high ionic conductivity and tunable composition are particularly advantageous, with advances in making the HE-PBAs cost-efficient, sustainable, and safe alternatives to alkali-ion batteries However, there are still barriers to their application on a large scale, for which many factors, including cost, availability of materials, efficiency of the preparation and other potential materials need to be considered.

For large-scale and commercial applications, defects in the batteries, like structural instabilities and early capacity or energy loss, will also have to be mitigated to render the materials fit for everyday use and ensure it has long-lasting performance and its capacity is adequate to support the device usage; the energy capacity needs to be sustained for longer. Structural Challenges include optimising the interstitial water and the vacancies in the lattice for the required energy and capacity, to create good diffusion pathways and stable structures[30]. Multiple crystal systems High-entropy mixing and vacancy engineering also help reduce irreversible phase changes that disrupt battery functioning. Cathode–Electrolyte Interphase (CEI) and processes like element doping or etching can help harness different qualities and improve conduction[1], [40]. Protective coatings like carbon layers guard against parasitic reactions hindering metal activity of the cell, and mechanical cracking under fast cycling.

Fast charging requirements (reaching 80% State of Charge in around 20 minutes, upto one hour[45]), important for EVs and grid applications can also be worked towards, with these HE-PBAs combine ultrafast ion transport with structural robustness under high currents[46], and they can adapt to varying energy needs.

Factor	Advantage	Improvement	
Cost	Low, due to abundant metals and simple synthesis	Process optimization for industrial scale	
Abundance	Uses common transition metals	None significant	
Performance	High capacity, long cycle life, good rate performance	Further improvement in conductivity	

Table 3: A General summary of Advantages of HE-PBA batteries, considering large-scale application

[1], [6], [15], [46]

Conclusion

The unique high-entropy effect of the Metal-organic framework in the Prussian Blue Analogues effectively stabilises the battery's lattice while also bringing in many factors, such as homogenous distribution of cations, to focus on, and the functioning varies based on the process used to synthesise them, encouraging researchers to find cost-friendly but high-performance methods for preparation. The materials have several possible configurations, with many enhancements as well to strengthen the structure or improve conductivity channels (such as the carbon plating or vacancy introduction), all of which must be carefully engineered to give the best results. HE-PBA batteries are well-positioned for commercial and large-scale energy storage due to their low cost, abundance, and robust performance. There have been many experiments conducted using the batteries, comparing crystal structure and battery performances based on a range of parameters that provide a holistic view on the functioning of the HE-PBA batteries. More research, however, is yet to be done concerning the large-scale and commercial uses of these batteries, and truly unlocking their potential in energy storage systems for a sustainable and energy-efficient future. This paper also encourages further research in the field to broaden the applications of the materials discussed extensively.

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References

- [1] 'High- Entropy Metal-Organic Frameworks and Their Derivatives: Advances in Design, Synthesis, and Applications for Catalysis and Energy Storage - Xing - 2025 - Advanced Science - Wiley Online Library'. Accessed: Apr. 09, 2025. [Online]. Available: https://advanced.onlinelibrary.wiley.com/doi/10.1002/advs.202411175
- [2] Y. Ma *et al.*, 'High-Entropy Metal-Organic Frameworks for Highly Reversible Sodium Storage', *Adv. Mater.*, vol. 33, no. 34, p. 2101342, 2021, doi: 10.1002/adma.202101342.
- [3] W. Jiang *et al.*, 'Room temperature synthesis of high-entropy Prussian blue analogues', *Nano Energy*, vol. 79, p. 105464, Jan. 2021, doi: 10.1016/j.nanoen.2020.105464.
- [4] W.-J. Li, C. Han, G. Cheng, S.-L. Chou, H.-K. Liu, and S.-X. Dou, 'Chemical Properties, Structural Properties, and Energy Storage Applications of Prussian Blue Analogues', Small, vol. 15, no. 32, p. 1900470, 2019, doi: 10.1002/smll.201900470.
- [5] 'Entropy Engineering Constrain Phase Transitions Enable Ultralong- life Prussian Blue Analogs Cathodes Lei 2024 Advanced Science Wiley Online Library'. Accessed: Apr. 12, 2025. [Online]. Available: https://advanced.onlinelibrary.wiley.com/doi/full/10.1002/advs.202402340
- [6] Y. Wang *et al.*, 'High-entropy prussian blue analogs with 3D confinement effect for long-life sodium-ion batteries', *J. Mater. Chem. A*, vol. 12, no. 9, pp. 5170–5180, Feb. 2024, doi: 10.1039/D3TA07671G.
- K. Du, Y. Liu, and Y. Zhao, 'High- Entropy Prussian Blue Analogues Enable Lattice Respiration for Ultrastable Aqueous Aluminum- Ion Batteries
 Du 2024 Advanced Materials Wiley Online Library', Accessed: Apr. 09, 2025. [Online]. Available: https://advanced.onlinelibrary.wiley.com/doi/10.1002/adma.202404172
- [8] Y. Xu, S. Zheng, H. Tang, X. Guo, H. Xue, and H. Pang, 'Prussian blue and its derivatives as electrode materials for electrochemical energy storage', Energy Storage Mater., vol. 9, pp. 11–30, Oct. 2017, doi: 10.1016/j.ensm.2017.06.002.
- [9] Y. Huang *et al.*, 'Boosting the sodium storage performance of Prussian blue analogs by single-crystal and high-entropy approach', *Energy Storage Mater.*, vol. 58, pp. 1–8, Apr. 2023, doi: 10.1016/j.ensm.2023.03.011.
- [10] J. Xing, Y. Zhang, Y. Jin, and Q. Jin, 'Active cation-integration high-entropy Prussian blue analogues cathodes for efficient Zn storage', Nano Res., vol. 16, no. 2, pp. 2486–2494, Feb. 2023, doi: 10.1007/s12274-022-5020-0.
- [11] H. Zhang *et al.*, 'Low-Cost Zinc Substitution of Iron-Based Prussian Blue Analogs as Long Lifespan Cathode Materials for Fast Charging Sodium-Ion Batteries', *Adv. Funct. Mater.*, vol. 33, no. 2, p. 2210725, 2023, doi: 10.1002/adfm.202210725.
- [12] Y.-T. Lin *et al.*, 'High-Entropy and Component Stoichiometry Tuning Strategies Boost the Sodium-Ion Storage Performance of Cobalt-Free Prussian Blue Analogues Cathode Materials', *Molecules*, vol. 29, no. 19, Art. no. 19, Jan. 2024, doi: 10.3390/molecules29194559.
- [13] N. Shen *et al.*, 'Dual-functional mediators of high-entropy Prussian blue analogues for lithiophilicity and sulfiphilicity in Li–S batteries', *Nanoscale*, vol. 16, no. 15, pp. 7634–7644, Apr. 2024, doi: 10.1039/D4NR00571F.

- [14] 'High- Entropy Prussian Blue Analogues and Their Oxide Family as Sulfur Hosts for Lithium- Sulfur Batteries | Request PDF', *ResearchGate*, Dec. 2024, doi: 10.1002/anie.202209350.
- [15] W. Tanmathusorachai *et al.*, 'High-Entropy Prussian Blue Analogue Derived Heterostructure Nanoparticles as Bifunctional Oxygen Conversion Electrocatalysts for the Rechargeable Zinc-Air Battery', ACS Appl. Mater. Interfaces, vol. 16, no. 45, pp. 62022–62032, Nov. 2024, doi: 10.1021/acsami.4c13387.
- [16] E. Potts, 'Iron-based flow batteries to be used for grid energy storage', Innovation News Network. Accessed: Apr. 14, 2025. [Online]. Available: https://www.innovationnewsnetwork.com/iron-based-flow-batteries-used-grid-energy-storage/45692/
- [17] 'High-Entropy Prussian Blue Analogues as High-Capacity Cathode Material for Potassium Ion Batteries | Request PDF', ResearchGate, Dec. 2024, Accessed: Apr. 14, 2025. [Online]. Available: https://www.researchgate.net/publication/383013629_High-Entropy_Prussian_Blue_Analogues_as_High-Capacity_Cathode_Material_for_Potassium_Ion_Batteries
- [18] R. Feng, X. Zhang, F. Ye, M. A. Götelid, and J. Dutta, 'Microstructural engineering of high-entropy Prussian blue analogues for capacitive deionization of saline water', *Nano Energy*, vol. 133, p. 110444, Jan. 2025, doi: 10.1016/j.nanoen.2024.110444.
- [19] Z. Zhou *et al.*, 'Innovative High-Entropy Strategy Extending Traditional Metal Substitution for Optimizing Prussian Blue Analogues in Rechargeable Batteries', SusMat, vol. n/a, no. n/a, p. e265, doi: 10.1002/sus2.265.
- [20] Z. Qian *et al.*, 'Six element high-entropy Prussian blue analogue cathode enabling high cycle stability for sodium-ion batteries', *Chem. Eng. J.*, vol. 500, p. 156767, Nov. 2024, doi: 10.1016/j.cej.2024.156767.
- [21] J.-H. Lee, J.-G. Bae, H. J. Lee, and J. H. Lee, 'Unveiling anomalous lattice shrinkage induced by Pi-backbonding in Prussian blue analogues', J. Energy Chem., vol. 70, pp. 121–128, Jul. 2022, doi: 10.1016/j.jechem.2022.02.032.
- [22] S. Xu *et al.*, 'Promising Cathode Materials for Sodium-Ion Batteries from Lab to Application', ACS Cent. Sci., vol. 9, no. 11, pp. 2012–2035, Nov. 2023, doi: 10.1021/acscentsci.3c01022.
- [23] 'Electrodeposition of Prussian-Blue analogs (PBA) as cathodes in formable batteries', imec. Accessed: Apr. 15, 2025. [Online]. Available: https://www.imec-int.com/en/work-at-imec/job-opportunities/electrodeposition-prussian-blue-analogs-pba-cathodes-formable
- [24] J. Sterzinger *et al.*, 'Degradation Mechanisms of Prussian Blue Analogues and State-of-the-Art Approaches for Stability Optimization: A Review', *J. Phys. Chem. C*, vol. 129, no. 15, pp. 7135–7153, Apr. 2025, doi: 10.1021/acs.jpcc.5c00877.
- [25] 'Ligand Field Theory an overview | ScienceDirect Topics'. Accessed: Apr. 14, 2025. [Online]. Available: https://www.sciencedirect.com/topics/chemistry/ligand-field-theory
- [26] 'Crystal Field Theory (CFT) Detailed Explanation with Examples & Videos', BYJUS. Accessed: Apr. 14, 2025. [Online]. Available: https://byjus.com/chemistry/crystal-field-theory/
- [27] '1.17: Jahn-Teller Distortions Chemistry LibreTexts'. Accessed: Apr. 14, 2025. [Online]. Available: https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Advanced_Inorganic_Chemistry_(Wikibook)/01%3A_Chapters/1.17%3A_Jahn-Teller_Distortions
- [28] K. Wang, 'Understanding fundamental migration processes during battery cycling and material synthesis using advanced transmission electron microscopy methods'.
- [29] Y. Tsunashima, al et, and al et, 'Coordination chemistry of Prussian blue and its analogs', Nat. Rev. Chem., vol. 11, pp. 1–12.
- [30] V. T. Nguyen, F. N. I. Sari, B. W. Saputro, and J.-M. Ting, 'Structural and defect modulations of co-precipitation synthesized high-entropy Prussian blue analogue nanocubes via Cu/Zn co-doping for enhanced electrochemical performance', J. Mater. Chem. A, vol. 11, no. 36, pp. 19483–19495, Sep. 2023, doi: 10.1039/D3TA01967E.
- [31] D. Sun, X. Wang, and M. Qu, 'Co-Precipitation Synthesis of Co3[Fe(CN)6]2 10H2O@rGO Anode Electrode for Lithium-Ion Batteries', *Materials*, vol. 15, no. 13, p. 4705, Jul. 2022, doi: 10.3390/ma15134705.
- [32] P. Naskar, P. Mondal, B. Biswas, S. Laha, and A. Banerjee, 'Investigating the Impact of Copper and Zinc Doping in High-Entropy Prussian Blue Analogues for Na-Ion Batteries: From Material Analysis to Device Fabrication', *Energy Technol.*, vol. n/a, no. n/a, p. 2401733, doi: 10.1002/ente.202401733.
- [33] 'Facile Synthesis of Vanadium Metal- Organic Frameworks for High- Performance Supercapacitors Yan 2018 Small Wiley Online Library'. Accessed: Apr. 23, 2025. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/smll.201801815
- [34] 'Ball Milling Solid- State Synthesis of Highly Crystalline Prussian Blue Analogue Na2-xMnFe(CN)6 Cathodes for All- Climate Sodium- Ion Batteries - Peng - 2022 - Angewandte Chemie International Edition - Wiley Online Library'. Accessed: Apr. 19, 2025. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.202205867
- [35] S. Kjeldgaard, I. Dugulan, A. Mamakhel, M. Wagemaker, B. B. Iversen, and A. Bentien, 'Strategies for synthesis of Prussian blue analogues', R. Soc. Open Sci., vol. 8, no. 1, p. 201779, Jan. 2021, doi: 10.1098/rsos.201779.
- [36] R. Zhang *et al.*, 'Y-tube assisted coprecipitation synthesis of iron-based Prussian blue analogues cathode materials for sodium-ion batteries', *RSC Adv.*, vol. 14, no. 17, pp. 12096–12106, Apr. 2024, doi: 10.1039/D4RA00762J.
- [37] Y. K. Zeng, T. S. Zhao, L. An, X. L. Zhou, and L. Wei, 'A comparative study of all-vanadium and iron-chromium redox flow batteries for large-scale energy storage', J. Power Sources, vol. 300, pp. 438–443, Dec. 2015, doi: 10.1016/j.jpowsour.2015.09.100.
- [38] 'Chemical-physical synergistic etching enabling deep reconstruction of NiFe Prussian blue analogue for efficient oxygen evolution reaction and Zn-air batteries | Request PDF', *ResearchGate*, Dec. 2024, doi: 10.1039/D2TA06930J.
- [39] L. Chen *et al.*, 'Fabrication of β-Ni(OH)2 Particles by Alkaline Etching Layered Double Hydroxides Precursor for Supercapacitor', *Front. Energy Res.*, vol. 9, Jan. 2022, doi: 10.3389/fenrg.2021.810568.

- [40] H. Xu et al., 'Etched High-Entropy Prussian Blue Analogues as Trifunctional Catalysts for Water, Ethanol, and Urea Electrooxidation', Inorg. Chem., vol. 62, no. 28, pp. 11271–11277, Jul. 2023, doi: 10.1021/acs.inorgchem.3c01701.
- [41] M. Chen *et al.*, 'Prussian blue coated with reduced graphene oxide as high-performance cathode for lithium-Sulfur batteries', *RSC Adv.*, vol. 10, no. 53, pp. 31773–31779, doi: 10.1039/d0ra04901h.
- [42] J. Wu et al., 'Reduced Graphene Oxide Improves the Performance of High Entropy Prussian Blue Analogs as the Cathode for Sodium-Ion Batteries', May 01, 2024, Social Science Research Network, Rochester, NY: 4813242. doi: 10.2139/ssrn.4813242.
- [43] J. M. Kim *et al.*, 'A novel textile-like carbon wrapping for high-performance silicon anodes in lithium-ion batteries', *J. Mater. Chem. A*, vol. 6, no. 26, pp. 12475–12483, Jul. 2018, doi: 10.1039/C8TA01414K.
- [44] S. Mosaad, A. H. Ibrahim, E. Elesh, D. G. El-Damhogi, and E. Elgazzar, 'Synthesis of prussian blue analog (Co/TCNi/HCCr) nanoparticles using a facile co-precipitation approach and evaluation of their dielectric characteristics for electronic applications', J. Mater. Sci. Mater. Electron., vol. 34, no. 33, p. 2204, Nov. 2023, doi: 10.1007/s10854-023-11606-0.
- [45] 'Charger Types and Speeds | US Department of Transportation'. Accessed: Apr. 25, 2025. [Online]. Available: https://www.transportation.gov/rural/ev/toolkit/ev-basics/charging-speeds
- [46] 'Prussian Blue and Its Analogues for Commercializing Fast-Charging Sodium/Potassium-Ion Batteries | ACS Energy Letters'. Accessed: Apr. 16, 2025. [Online]. Available: https://pubs.acs.org/doi/10.1021/acsenergylett.4c02915

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