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论文题目：Epitaxial nickel-based
Prussian blue analogues (PBAs) Coating
Strategy for Durable Mn-Based PBAs in
Sodium-Ion Batteries

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Epitaxial nickel-based Prussian blue analogues (PBAs) Coating Strategy for Durable Mn-Based PBAs in Sodium-Ion Batteries

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1. Abstract

Manganese-based Prussian blue analogues (M-PBAs) are promising cathode materials for sodium-ion batteries owing to their high operating voltage and energy density. However, practical application is hindered by severe capacity fading caused by structural instability and transition-metal dissolution during cycling. In this work, we propose an epitaxial nickel-based Prussian blue analogue (Ni-PBAs) coating strategy to enhance the structural durability of M-PBAs. Owing to the lower formation energy of Ni-PBAs, a conformal Ni-rich protective layer spontaneously forms on the particle surface, effectively suppressing active-material dissolution and reinforcing framework stability. As a result, the coated material exhibits significantly improved electrochemical performance, retaining 91.8% of its initial capacity after 1,500 cycles at 10 C. This work provides an effective strategy for developing durable, high-energy-density PBA cathodes for advanced sodium-ion batteries.

Keywords: Sodium-ion batteries; Manganese-based Prussian blue analogues (M-PBAs) ; nickel-based Prussian blue analogue (Ni-PBAs) ; epitaxial coating

2. Introduction

Prussian blue analogues (PBAs) have attracted considerable attention as potential cathode materials for commercial sodium-ion batteries (SIBs) because of their open Na⁺ diffusion pathways, high theoretical capacity, and cost-effective synthesis.[1] The general chemical formula for PBAs can be expressed as Na_{2-x}M[Fe(CN)₆]_{1-y}□_y·nH₂O, where 'M'

represents transition elements, and '□' denotes vacancies in the $[\text{Fe}(\text{CN})_6]$ framework ($0 < x \leq 2$, $0 \leq y < 1$).^[2] Among these materials, manganese-based PBAs (M-PBAs) offer unique advantages, including dual redox-active centers ($\text{Mn}^{2+/3+}$ and $\text{Fe}^{2+/3+}$) that enable double-electron transfer and the highest operational voltage (3.4 V vs. Na^+/Na). These characteristics confer M-PBAs with the highest energy density within the PBA family, driving extensive research interest.

However, M-PBAs suffer from rapid capacity decay during cycling, primarily due to structural instability caused by the dissolution of electroactive species into the electrolyte. In this context, designing a structure to reinforce M-PBAs and minimize their dissolution tendency in the electrolyte is of great significance. Building on these observations, we propose a strategy to stabilize M-PBAs by coating them with an outer layer of nickel-based PBAs (Ni-PBAs). In contrast to Mn-PBAs, Ni-PBAs exhibit lower capacity but superior electrochemical stability. Their lower formation energy allows Ni atoms to spontaneously replace surface Mn sites during synthesis, forming a conformal Ni-PBAs protective layer.^[3] This epitaxial coating strengthens the structural integrity of the M-PBAs framework, inhibits transition-metal dissolution, and thereby markedly enhances the cycling stability of M-PBAs when used as cathodes in sodium-ion batteries.

3. Experiment procedure

3.1 Formation of M-PBAs and N-PBAs

In a typical process of M-PBAs, solution A was first prepared by dissolving 3.2 mmol nitrilotriacetic acid trisodium salt (NTA), 3.2 mmol MnSO_4 , 2 g ascorbic acid (VC) into 100 ml deionized (DI) water, followed by 30 min of magnetic stirring. Solution B was composed of 8 mmol $\text{Na}_4\text{Fe}(\text{CN})_6$, 1g polyvinyl pyrrolidone (PVP, k30) and 2 g VC in 100 ml DI water. Thirdly, solution A was slowly dropped into solution B with a peristaltic pump, and the liquid mixture went through an 8 h magnetic stirring at 60°C. The resulting suspension was then aged for 40 h at 60°C. Before centrifugation, the obtained precipitates were washed with deionized water and ethanol and then dried in a vacuum oven at 170 °C for 12 h. For

the Ni-PBAs modification, 0.1 g of NiCl_2 was dissolved in 60 mL of methanol, and 0.4 g of the as-prepared M-PBAs was added. The mixture was stirred at 60 °C for 12 h, followed by centrifugation and drying in a vacuum oven at 120 °C for 12 h to obtain the Ni-PBAs-coated product (N-PBAs).[4-5]

3.2 Characterization methods

X-ray diffraction (XRD) data were collected from 10° to 80° in Bruker D8 Advance and Rigaku Ultima. Surface compositions were determined by X-ray photoelectron spectroscopy (XPS, EscaLab 250xi). For the fabrication of PBAs/N-PBAs electrodes for electrochemical performance tests, the active materials, Super P, Ketjenblack, and polyvinylidene fluoride (PVDF) were mixed with a weight ratio of 70: 15: 5: 10 in an appropriate amount of 1-Methyl-2-pyrrolidinone (NMP) to make a slurry. The slurry was casted on Al foil and dried at 170 °C. After that, it was subjected to a hot rolling operation at 120 °C. Loading mass of cathode materials was in the range of $1.7 \pm 0.5 \text{ mg cm}^{-2}$. All the electrochemical tests were carried out with CR2032 coin-type cells assembled in a high-purity argon-filled glovebox (Mikrouna Universal 2440/750), where both H_2O and O_2 levels were below 0.1 ppm. Na metal and glass fiber filters (Whatman, GF/D) were used as a counter electrode and separator, respectively. The electrolyte was 1 M NaClO_4 in PC+5% (vol%) FEC. The Electrochemical Impedance Spectroscopy (EIS) was carried out with an electrochemical workstation (PGSTAT302N, Metrohm Autolab, Netherlands), with $1\text{C}=170 \text{ mA g}^{-1}$.

4. Results and discussion

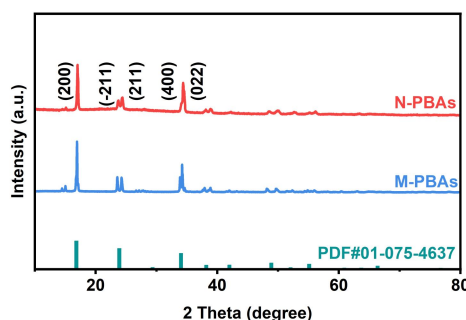


Figure 1. XRD patterns of N-PBAs and M-PBAs.

In Figure 1, we observed the XRD patterns of N-PBAs and compared them to those of the M-PBA. The normal M-PBAs have a sodium-rich monolithic structure with the $P2_1/n$ space group. After coating the M-PBAs with an outer layer of nickel-based PBA forming the N-PBA, the positions of the diffraction peaks remain the same. M-PBAs have diffraction peaks at 16.6° , 24.0° , and 34.4° corresponding to the (200), (-211)/(211), and (400)/(022) crystal planes. Similarly, the N-PBAs directly above the M-PBAs in Figure 1 have diffraction peaks at the same positions. This finding indicates that adding this coated layer of nickel does not alter the crystal's original structure.

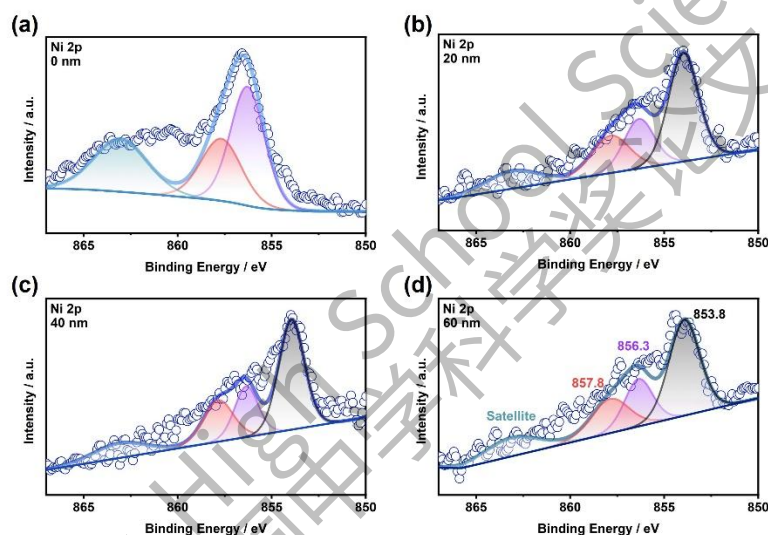


Figure 2. Ni element Monatomic ion beam etching X-ray photoelectron spectroscopy (MIBE-XPS) of N-PBAs.

To verify the successful formation of the Ni-PBAs coating, N-PBAs were analyzed using monatomic ion beam etching X-ray photoelectron spectroscopy (MIBE-XPS). This technique not only provides detailed information on the chemical states and local environment of Ni at the bulk level but also enables monitoring of Ni distribution at various depths within the N-PBAs. As shown in Figure 2a, characteristic Ni peaks are clearly observed. The peaks at 856.3 and 857.8 eV are assigned to the Ni $2p_{3/2}$ and $2p_{1/2}$ states of Ni^{2+} , respectively, while the peak at 863.0 eV corresponds to the shake-up satellites. A new peak at 853.8 eV, corresponding to metallic Ni (Ni^0) 2p, emerges after Ar^+ etching, a result of the MIBE-XPS process (Figures 2b-d). Importantly, even after etching to a depth

of 60 nm, several characteristic Ni peaks remain detectable, indicating that the Ni-PBAs coating forms a substantial layer within the N-PBAs.

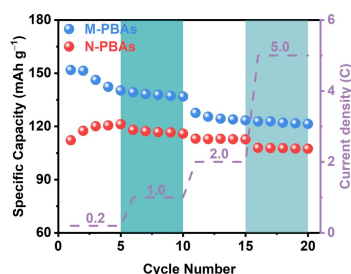


Figure 3. Rate performance of M-PBAs and N-PBAs.

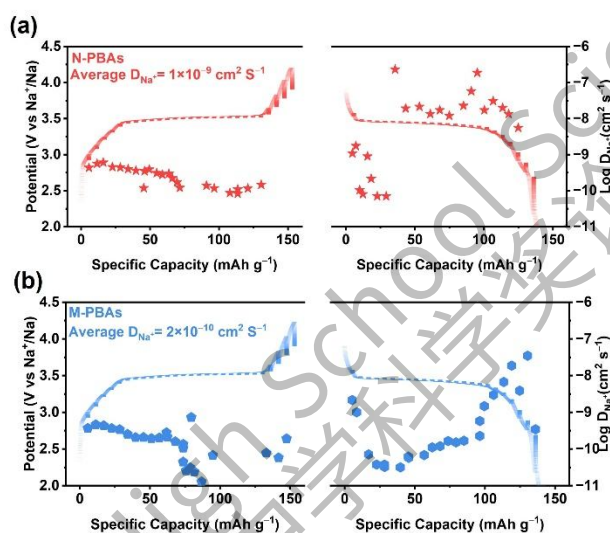


Figure 4. Calculated Na^+ diffusion coefficient of (a) N-PBAs and (b) M-PBAs.

The specific capacity of the two cathode materials was evaluated with a variable current density in Figure 1. At different levels of current density, 5 cycles were performed. In Figure 3 above, at a current density of 0.2C, M-PBA has a specific capacity of around 150 mAh/g while N-PBA has a specific capacity of around 120 mAh/g. This is because the coated N-PBA layer does not contribute to its specific capacity.[6] Based on this statistic, the N-PBA layer accounts for around 20% of the material's total mass. When the current density is increased to 5.0C, the specific capacity of M-PBA decreases to around 120 mAh/g, which is about 80% of its original value. On the other hand, N-PBA maintains around 89% of its original value. These results indicate that although the coated layer of N-PBA decreases its theoretical specific capacity, this is offset by an increase in its rate capability.

The Na^+ diffusion kinetics of both materials were also investigated using the galvanostatic intermittent titration technique (GITT). The average Na^+ constant (D_{Na^+}) calculated from the statistics in Figure 4 for M-PBA is $2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, while the constant for N-PBA is $1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. The diffusion constant for N-PBA is much larger than for M-PBA, indicating that the Ni coating allows Na^+ to diffuse at a faster rate than the original M-PBA. This allows Na^+ to travel faster within the PBA framework, reflecting a better rate capability as discussed in Figure 3.

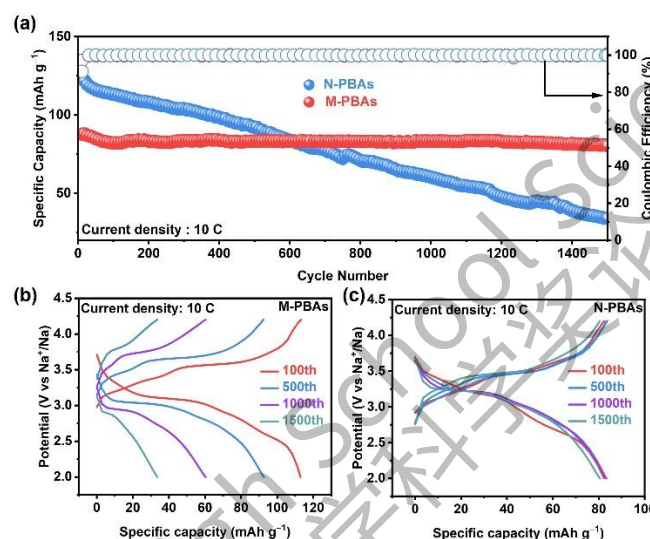


Figure 5. (a) Cycling performance of M-PBAs and N-PBAs at 10C; Charge-discharge curves of (b) M-PBAs and (c) N-PBAs after different cycles at 10C.

In Figure 5a, the specific capacity of N-PBA and M-PBA is compared over a large number of cycles at a constant current density of 10. At this current density, N-PBA retains 91.8% of its specific capacity over 1500 cycles while M-PBA retains only 26.3%. This reflects that the N-PBA layer enables the battery to maintain a more stable structure capable of withstanding a large number of cycles. In Figures 5b-c, the discharge plateau remains stable at 3.25V even after 1500 cycles for N-PBAs, while it is not clearly observable in M-PBA. [7] This result, as mentioned above, justifies that N-PBA has a much more stable structure than M-PBA even under different potential environments.

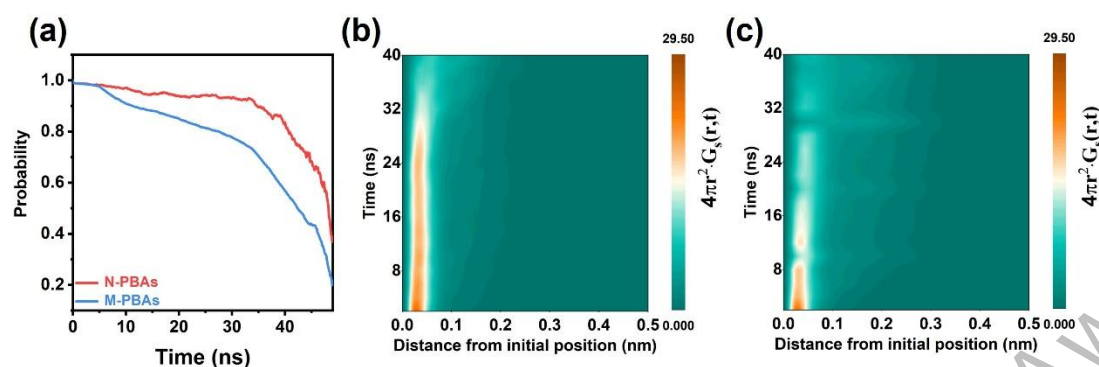


Figure 6. (a) Evolution of probability of N-PBAs/M-PBAs molecules' moving distance; Counter plots of the G_s part of the van Hove correlation function for (b) N-PBAs and (c) M-PBAs.

The Van Hove correlation function was employed to investigate the migration behavior of PBA in the electrolyte. The function gives the probability of a particle appearing at a distance (r) from its original position in the time interval (t). This provides insight into the tendency a material to diffuse and dissolve in the electrolyte. In Figure 6a, the probability distribution of M-PBA decreases faster than that of N-PBA, indicating that M-PBA is more likely to diffuse and dissolve in the electrolyte.[8]

Figure 6b-c shows the distribution of cathode materials over a time interval (t). For N-PBA, most of the material remains around 0.1 nm from its original position even after the first 40 ns. In contrast, M-PBAs display a broader spatial distribution, with particles moving by more than 0.16 nm in the first 40 ns. The significantly suppressed molecular displacement observed in N-PBAs indicates a lower tendency to dissolve and stronger structural stability in the electrolyte environment. This result can be explained by the Ni-PBA coating layer. The Ni layer contained in the M-PBA suppresses the interaction between the cathode and the electrolyte, decreasing the cathode's tendency to dissolve. As a result, the material's superior long-term performance is explained.

5. Materials

5.1 Materials for M PBA and N PBA synthesis

No.	Material Name	Amount Used	Purpose
1	Nitrilotriacetic acid	3.2 mmol	Solvent A; Complexing agent
2	Manganese sulfate MnSO ₄	3.2 mmol	Solvent A; Manganese source
3	Ascorbic Acid (VC)	4 g	Solvent A and solvent B each 2 g
4	Deionized water	At least 200 mL	Solvent A and solvent B each 100 mL; also used for washing
5	Sodium ferrocyanide	8 mmol	Solvent B
6	Polyvinylpyrrolidone (PVP)	1 g	Solvent B surfactant
7	Ethanol	10-20 ml	Washing
8	NiCl ₂	0.1 g	Ni PBA coating
9	Methanol	60 mL	Dissolve NiCl ₂ to enter coating reaction

5.2 Materials for Battery

No.	Material Name	Purpose	Ratio and other purposes
1	M PBAs and N PBAs	Cathode Active Material	Proportion of ingredient 70 wt%
2	Super P	Conductive Agent	Proportion of ingredient 15 wt%
3	Ketjenblack	Conductive Agent	Proportion of ingredient 5 wt%
4	Polyvinylidene difluoride PVDF	Adhesive	Proportion of ingredient 10 wt%
5	NMP	Pulping solvent	Proportion of ingredient not specified
6	Aluminum foil	Current collector	Coating electrode slurry
7	Sodium (Na)	Counter electrode	Sodium ion battery
8	High concentrated Argon	Laboratory glove box	H ₂ O and O ₂ lower than 0.1 ppm

No.	Material Name	Purpose	Ratio and other purposes
9	NaClO ₄	Electrolyte salt	electrolyte concentration 1 mol L ⁻¹
10	Propylene carbonate PC	Electrolyte solvent	Solvent
11	4-Fluoro-1,3-dioxolane FEC	Electrolyte additive	5% of volume

5.3 Experiment equipment

No.	Device	Purpose	Condition
1	Magnetic stirrer	Preparing solutions and stirring reactions	30 min; 60 °C for 8 h
2	Thermostatic heater	Reaction and aging temperature control	60 °C; aging for 40 h
3	Peristaltic pump	Slowly pour solution A into solution B	N. A
4	Centrifuge	Separate M PBAs and N PBAs precipitates	N. A
5	Vacuum drying oven	Powder drying	170 °C 12 h; 120 °C 12 h
6	Hot roll press	Positive electrode sheet pressing	120 °C

No.	Device	Purpose and comment
1	X-ray Powder Diffractometer XRD	XRD test; scanning angle 10 to 80 degrees
2	X-ray Photoelectron Spectroscopy	Surface composition and chemical property analysis
3	Ar ion gun or etching module	Etching depth up to 60 nm
4	Laboratory glove box	Assemble CR2032 battery; H ₂ O and O ₂ lower than 0.1 ppm
5	Coating machine	Electrode coating

No.	Device	Purpose	Condition
6	Oven	Dry powder	
7	Battery charge and discharge testing system	Electrochemical tests	

6. Conclusion

In summary, an epitaxial Ni-PBA coating strategy was developed to enhance the structural stability of M-PBAs. The lower formation energy of Ni-PBAs facilitates spontaneous formation of a conformal Ni-rich protective layer on the particle surface, effectively suppressing transition-metal dissolution and reinforcing framework integrity. Consequently, N-PBAs demonstrate remarkable cycling stability, retaining 91.8% of their initial capacity after 1,500 cycles at 10 °C, significantly outperforming pristine M-PBAs (26.3%). The stable discharge plateau and preserved Mn redox activity further validate the effectiveness of the coating layer.

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