

## **High-entropy Prussian Blue Analogs with 3D Confinement Effect for Long-life Sodium-ion Batteries**

*Yichao Wang, Ning Jiang, Cheng Yang, Jiahe Liu, Shouyu Sun, Xinyu Wang, Jianhua Yang, Yu Liu\**

Yichao Wang, Ning Jiang, Cheng Yang, Jiahe Liu, Shouyu Sun, Xinyu Wang, Jianhua Yang, Cheng Yang, Yu Liu\*

<sup>a</sup>Shanghai Institute of Ceramics, Chinese Academy of Sciences

Shanghai 200050, China

<sup>b</sup>University of Chinese Academy of Sciences

Beijing 100049, China

**\*Corresponding Author**

Email: [yuliu@mail.sic.ac.cn](mailto:yuliu@mail.sic.ac.cn)

# 1. Experimental section

## 1.1 Synthesis of metal hexacyanoferrate

**1.1.1 Synthesis of Mn-PBAs and HE-PBAs:** HE-PBAs were synthesized using the saturated sodium citrate-chelating agent co-precipitation method. For the synthesis of HE-PBAs, solution A was first prepared by dissolving 200 mmol sodium citrate and 40 mmol  $\text{TM}\text{SO}_4$  mixture (TM = Fe, Mn, Co, Ni, Cu) into 600 mL deionized water, followed by 3 h magnetic stirring mixing. Secondly, solution B was obtained by dissolving 200 mmol trisodium citrate dihydrate and 80 mmol  $\text{Na}_4\text{Fe}(\text{CN})_6$  into 600 mL deionized 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. The obtained suspension was then aged for 40 h at room temperature. Before centrifugation, the obtained precipitates were washed with deionized water and ethanol and then dried in a vacuum oven at 120 °C for 24 h. For Mn-PBAs, all other steps are the same as HE-PBAs, except that the salt used is only  $\text{MnSO}_4$ .

**1.1.2 Synthesis of HE-PBAs@C:** For HE-PBAs@0.1C and HE-PBAs@0.2C, a mixture was prepared by adding 8g and 16g of conductive carbon composite paste (5wt%) to 200 ml of deionized water, respectively. Subsequently, 4g of HE-PBAs was introduced into the prepared suspension. To ensure thorough dispersion and integration of HE-PBAs with the carbon components, the suspension underwent vigorous stirring at 300 rpm for a duration of 2 hours. After this mixing process, the water was removed through a spray drying procedure, concurrently resulting in the formation of a conductive carbon layer encapsulating material HE-PBAs@C. The spray drying procedure was carried out at a temperature of 250°C, with the peristaltic pump set to deliver the suspension at a rate of 200 ml/h.

## 1.2 Materials characterization

X-ray diffraction (XRD) data were collected from 5° to 85° in Bruker D8 advance and Rigaku Ultima. The XRD refinements were conducted by Fullprof software. For ex-situ XRD experiment, electrode was charged and discharged at a current density of 10 mA g<sup>-1</sup>. The morphology and microstructure of sample was researched using transmission electron

microscopy (TEM) (JEOL-2100F). Thermogravimetry (TG) measurement was performed from 25 to 400 °C at a rate of 5 °C min<sup>-1</sup> in N<sub>2</sub>. Scanning electron microscopy (SEM, Hitachi S-4800) was used to represent the morphology, and spherically corrected transmission electron microscope (STEM, FEI Titan G2 80-200 ChemiSTEM) coupled with energy dispersive spectroscopy (EDS) was applied to obtain the information of lattice fringe and element distribution. To confirm the formula of PBAs, ICP-OES (Agilent 5110) was used to measure the concentration of Na, Fe, Mn, Co, Ni, and Cu. The UV-visible diffuse reflection spectroscopy (UV-vis DRS) were carried out on UV-2600 UV-visible spectrophotometer (Shimadzu, Japan). Surface compositions were determined by X-ray photoelectron spectroscopy (XPS, EscaLab 250xi). Fourier transform infrared spectroscopy (FTIR, Spectrum 100) was utilized to characterize the chemical bonds. Raman spectroscopy (LabRAM HR800) was used to characterize the graphitization degree of carbon layer.

### **1.3 Electrochemical measurements**

For the fabrication of electrodes for electrochemical performance tests, the active materials, Super P, Ketjenblack and polyvinylidene fluoride (PVDF) with a weight ratio of 70: 15: 5: 10 were mixed in appropriate amount of 1-Methyl-2-pyrrolidinone (NMP) to make a slurry. The slurry was casted on Al foil and dried at 120 °C. After that, it was subjected to a hot rolling operation. Loading mass of active materials was in the range of 2.0 ± 0.5 mg cm<sup>-2</sup>. 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<sub>2</sub>O and O<sub>2</sub> levels are below 0.1 ppm. Na metal and glass fiber filters (Whatman, GF/D) were used as counter electrode and separator, respectively. 1M NaClO<sub>4</sub> dissolving in PC solution with 5 vol% addition of fluoroethylene carbonate (FEC) was used as the electrolyte for half battery. Cyclic voltammetry (CV) tests were performed at various scan rates of 0.2–1 mV s<sup>-1</sup>. The CV tests and Electrochemical impedance spectroscopy (EIS) were carried out by electrochemical workstation (PGSTAT302N, Metrohm Autolab, Netherlands). Electrochemical performance of the cells and galvanostatic intermittent titration technique (GITT) test were carried out on a Land battery testing system (CT3001A) within the voltage range of 4.0-2.0 V (vs. Na<sup>+</sup>/Na). As for full cell, HC and NTP electrodes consisted of 80 wt% NTP/HC, 10 wt% Super P, and 10 wt% PVDF, and the current collector

was Al foil. The HE-PBAs@0.1C cathode was matched with the hard carbon (HC) and NTP anodes in a glove box filled with Ar gas, and the electrochemical performance of the full cells were tested within the potential window of 3.8 – 1.8 V and 2.0 - 0.4 V, respectively. The electrolyte of HE-PBAs@0.1C/NTP full cell is similar to HE-PBAs@0.1C/Na half battery , 1 M NaClO<sub>4</sub> dissolved in ethylene carbonate diethyl carbonate and diethyl carbonate (EC: DEC = 1:1) with 2% FEC as additive (by volume) was used as the electrolyte for HE-PBAs@0.1C//HC full cell. The calculation of the specific capacity of the full cell was based on the mass of the cathode active material. Before assembling the HC//HE-PBAs@0.1C full cell, HC assembled a half cell with Na metal, and it was circulated for three cycles at a current density of 20 mA g<sup>-1</sup>.

## 2. Supporting Figures and Tables

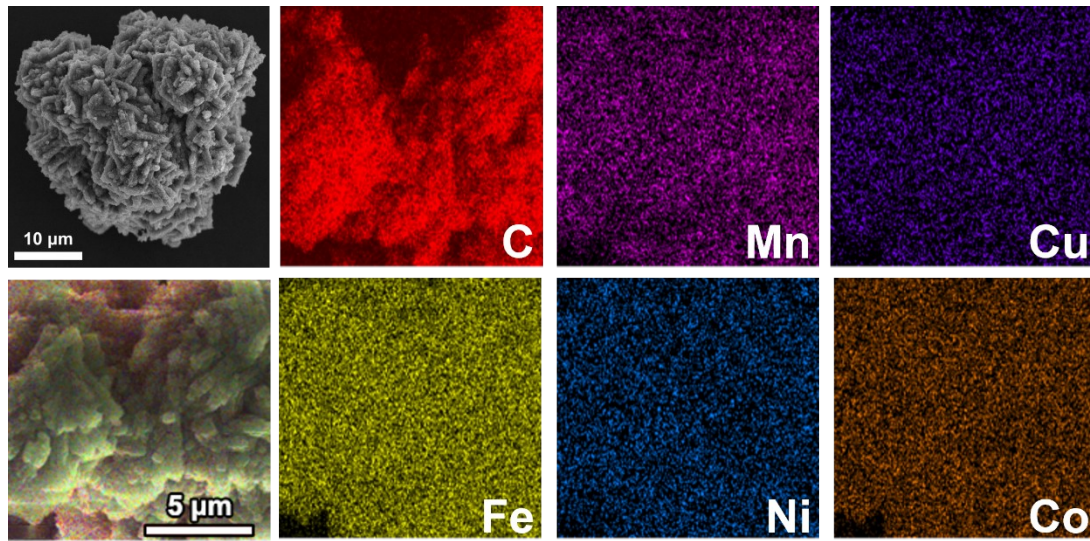


Figure S1. SEM micrograph and EDS mapping analysis for HE-PBAs.

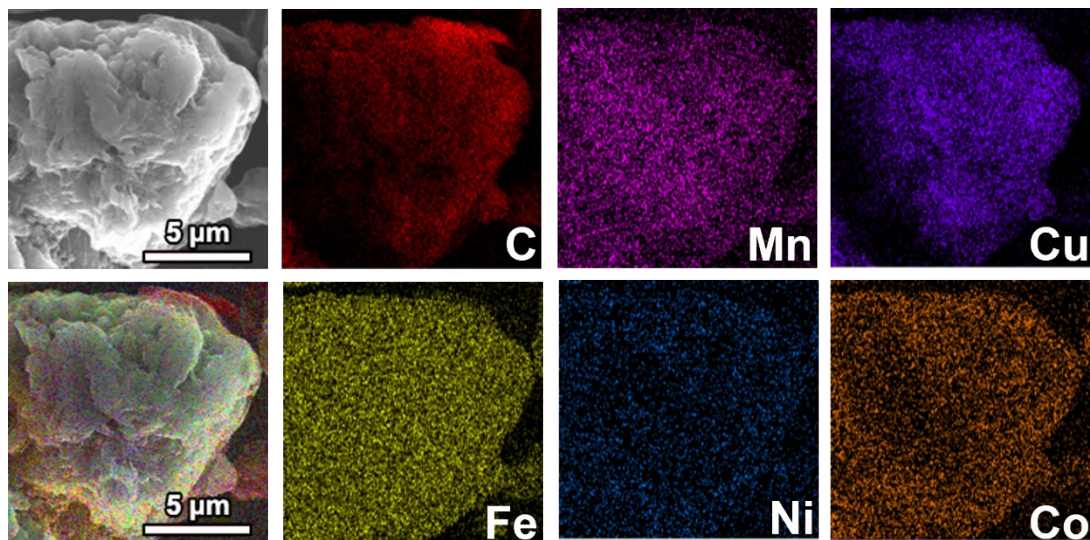


Figure S2. SEM micrograph and EDS mapping analysis for HE-PBAs@0.2C.

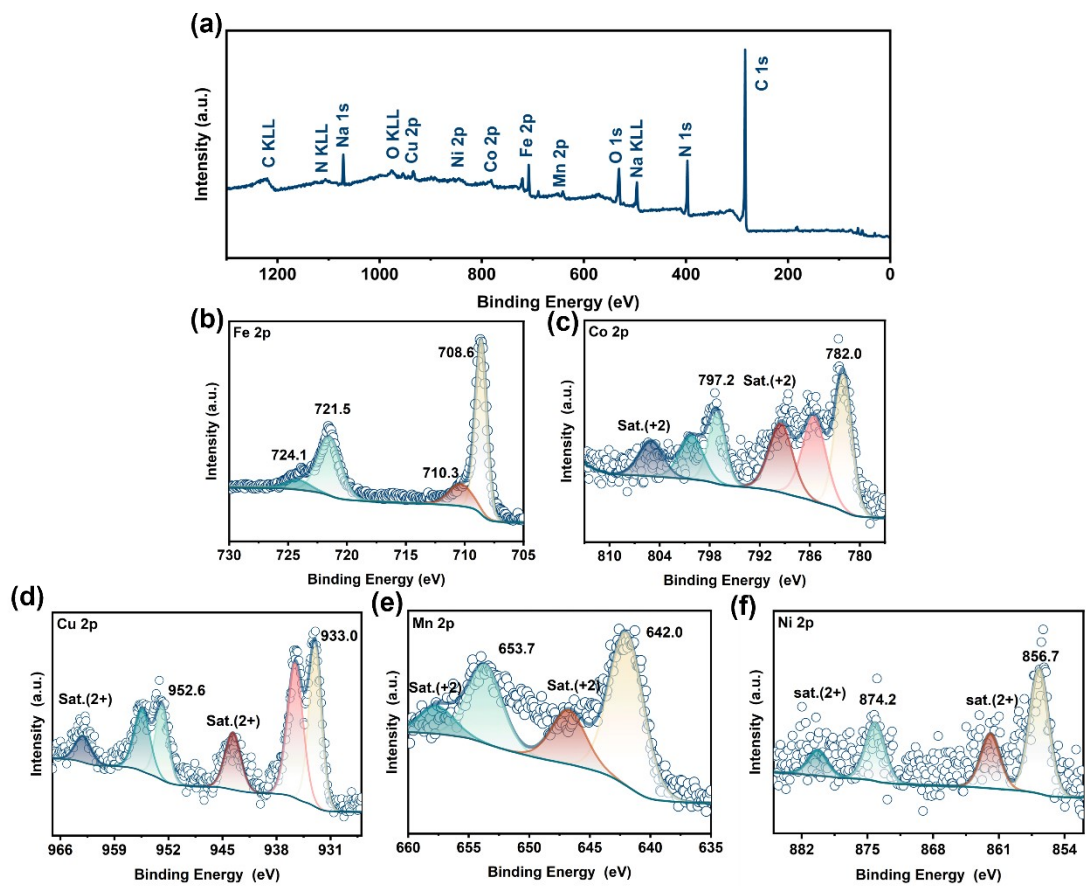


Figure S3. (a) The survey XPS spectrum for HEPBA@0.1C, (b) Fe 2p, (c) Co 2p, (d) Cu2p, (e) Mn 2p and (f) Ni 2p XP core-level spectra for HE-PBAs@0.1C.

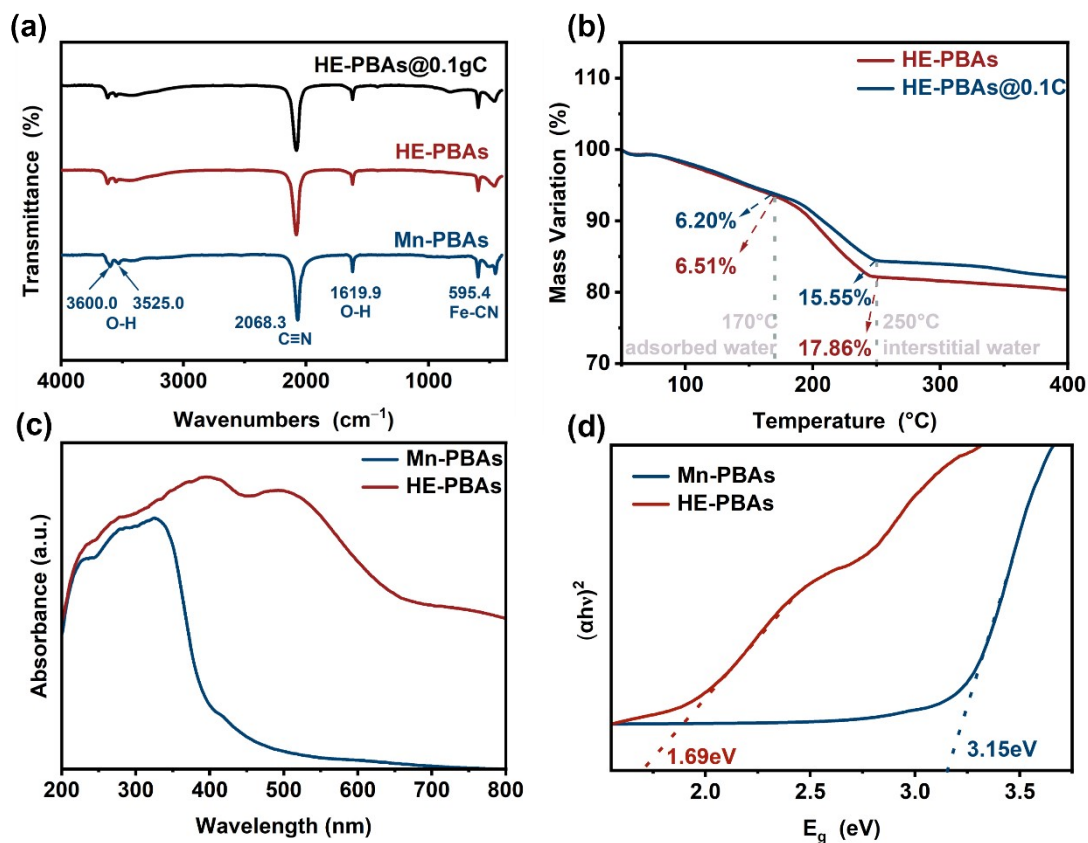


Figure S4. Structural characterization of as-prepared samples (a) FT-IR spectra, (b) TGA curves, (c) UV-vis diffuse reflectance spectra (d) Tauc plots.

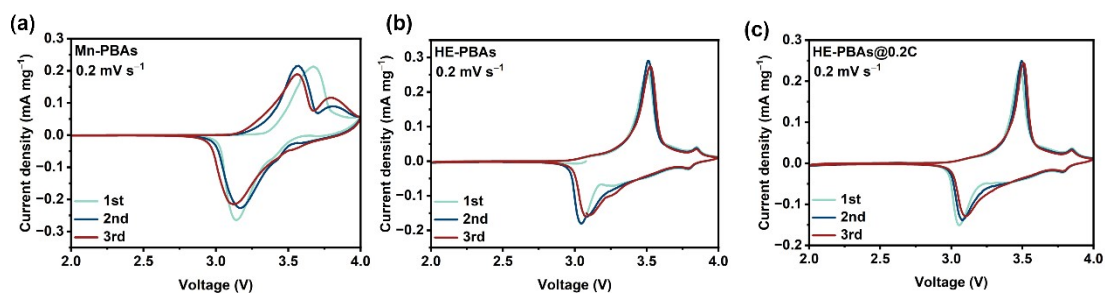


Figure S5. CV curves at first three cycles of (a) Mn-PBAs, (b) HE-PBAs, (c) HE-PBAs @0.2C.

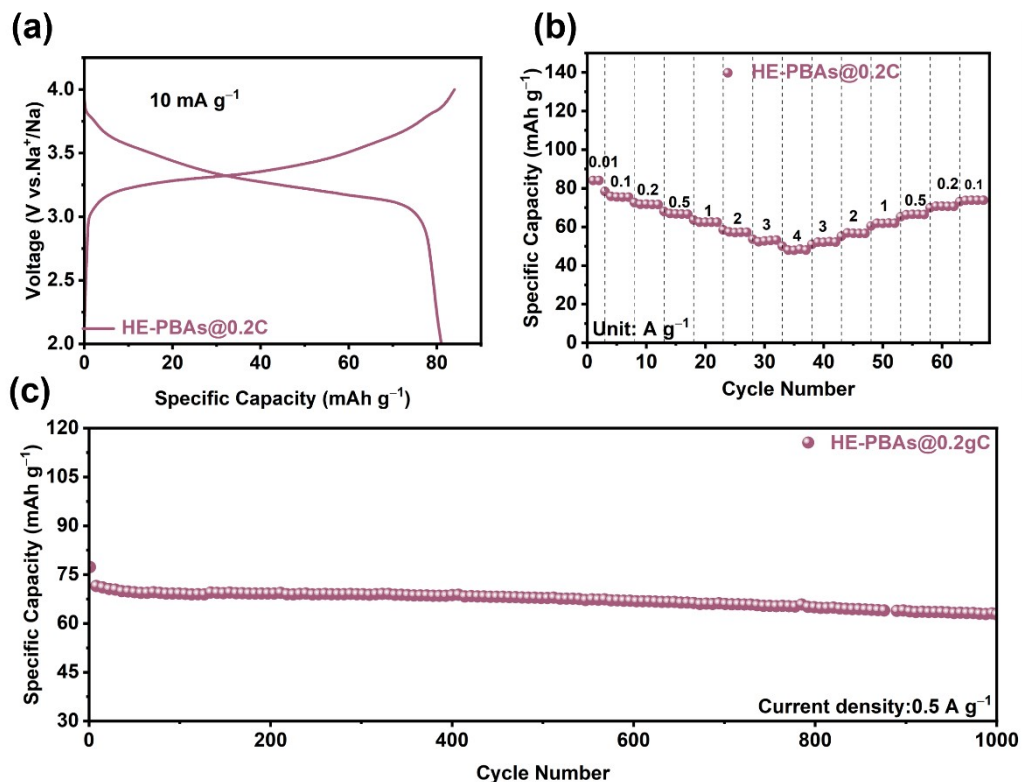


Figure S6. (a) First-cycle voltage profiles at  $0.01 \text{ A g}^{-1}$  of HE-PBAs@0.2C (b) Rate-capacity of HE-PBAs@0.2C, (c) Cycling performance of HE-PBAs@0.2C at  $0.5 \text{ A g}^{-1}$ .

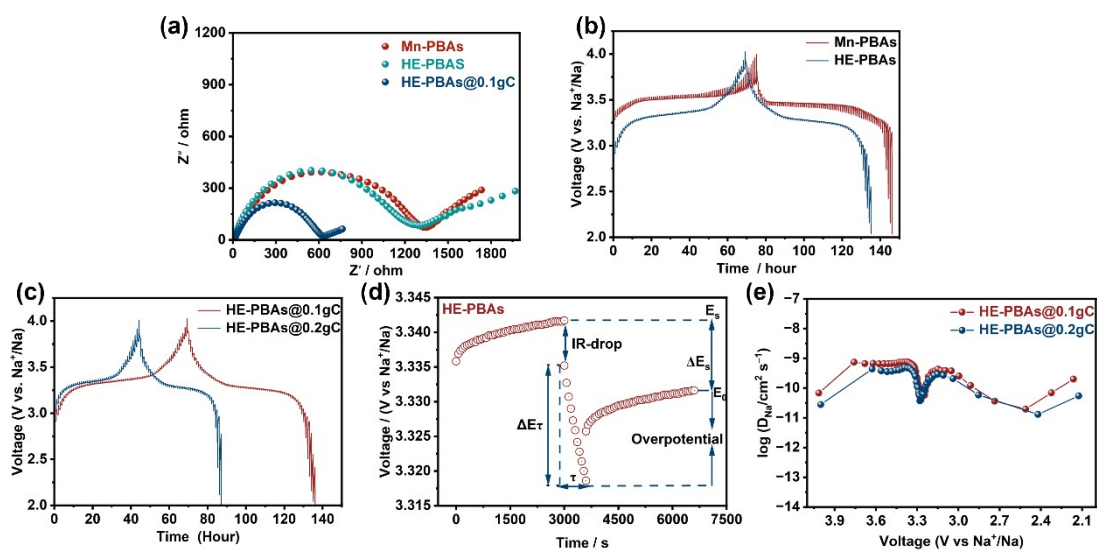


Figure S7. (a) EIS spectra of Mn-PBAs, HE-PBAs and HE-PBAs@0.1C, (b-c) GITT curves



of all the samples in the voltage range of 2.0–4.0 V during the sixth charge/discharge process, (d) single GITT step during the discharge process of HE-PBAs, (e) Calculated  $\text{Na}^+$  diffusion coefficient.

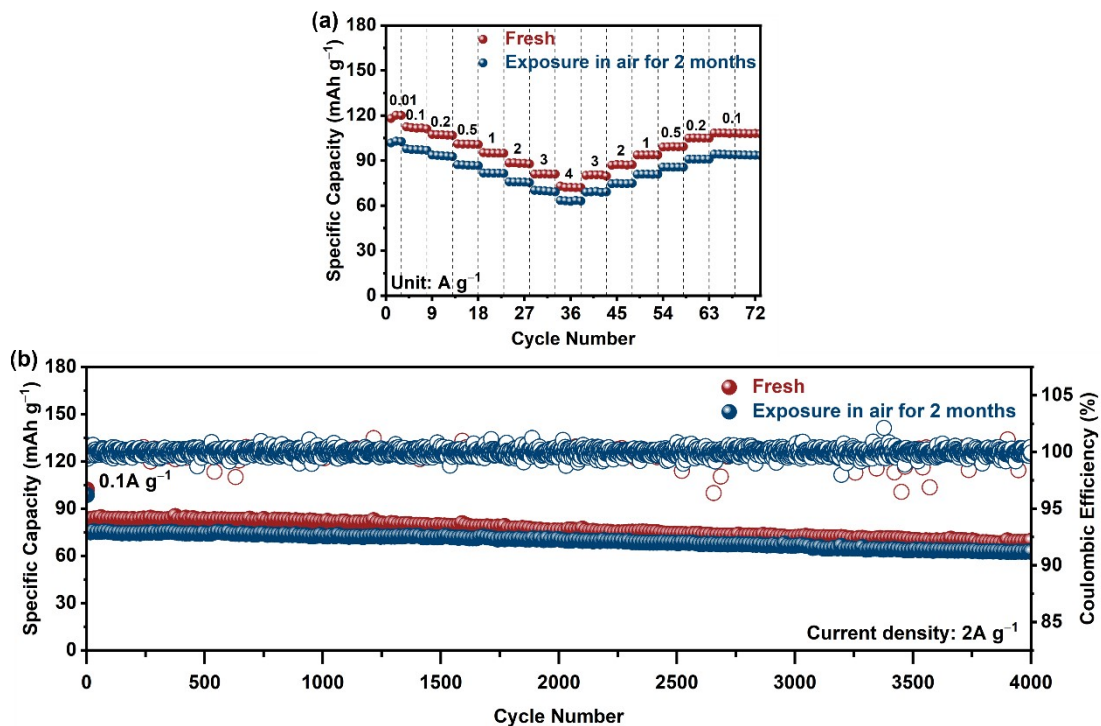


Figure S8. (a) Rate performance of the fresh and air-exposed HE-PBAs@0.1C, (b) Cycling performance of the fresh and air-exposed HE-PBAs@0.1C at  $2 \text{ A g}^{-1}$ .

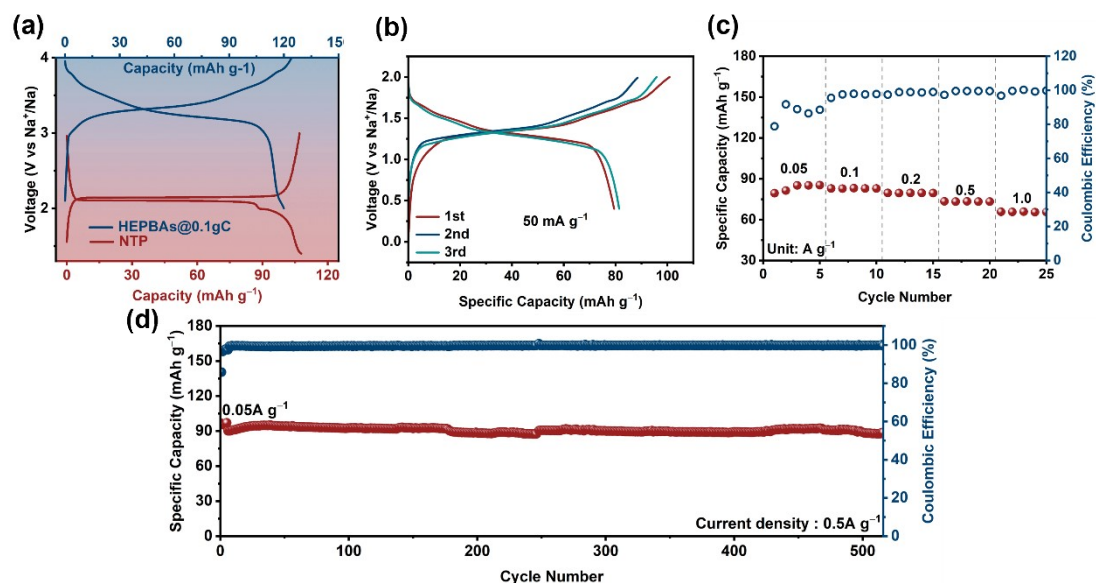


Figure S9. (a) The voltage match-up by the charge/discharge galvanostatic curves of HE-PBAs//Na and NTP//Na (b) The first three charge-discharge curves of HE-

PBAs@0.1C//NTP full-cell, (c) The full-cell charge/discharge curves at various rates of HE-PBAs@0.1C//NTP, (d) Long-cycle performance of HE-PBAs@0.1C//NTP full-cell (specific capacity calculated by active mass of HE-PBAs@0.1C).

Table S1. Atomic coordinates for HE-PBAs, obtained by Rietveld refinement with the Fullprof software.

Atom	Wyckoff Pos.	Atomic Position			OCC
		X	Y	Z	
Fe1	4a	0	0	0	0.082
Fe2	4b	0	0	0.5	0.034
Mn	4b	0	0	0.5	0.015
Ni	4b	0	0	0.5	0.004
Cu	4b	0	0	0.5	0.02
Co	4b	0	0	0.5	0.014
C	24e	0.20076	0.79924	0.09261	0.5
N	24e	0.15542	0.84458	0.08705	0.5
Na	8c	0	0	0.24585	0.162

Space group = R - 3m, a = b = 7.43133 Å, c = 17.62605 Å  $\alpha = \beta = 90^\circ$   $\gamma = 120^\circ$ ,  
and V = 842.982 Å<sup>3</sup>, R<sub>wp</sub> = 4.41 %

Table S2. ICP-OES for Mn-PBAs, HE-PBAs and HE-PBAs@0.1C.

Sample	Na(wt%)	Fe(wt%)	Co(wt%)	Cu(wt%)	Mn(wt%)	Ni(wt%)
<b>Mn-PBAs</b>	12.4372%	16.9579%	0.0022%	0.0040%	18.0302%	0.0018%
<b>HE-PBAs</b>	11.6379%	15.8379%	3.8611%	6.9648%	6.3330%	1.0236%
<b>HE-PBAs@0.1C</b>	9.6815%	14.2002%	3.3799%	6.3876%	5.7329%	0.9410%

Table S3. Representative performance of reported PBAs in organic electrolyte SIBs.

Material	Capacity (mAh g <sup>-1</sup> @ mA g <sup>-1</sup> )	Cycle life (cycles, retention%@ mA g <sup>-1</sup> )	Rate performance (mAh g <sup>-1</sup> @ mA g <sup>-1</sup> )	Reference
HE-PBAs@C	118.0@10	2000, 80.0@500	73.0@4000	This Work
ZnFe-PBAs	132.4@15	500, 76.5@500	57.3@6000	[1]
MnNi-PBAs	93.9@15	700, 85.3@500	69.4@1000	[2]
MnFe-PBAs	123.0@10	300, 80.2@50	21.0@2000	[3]
FeNi-PBAs	117.0@10	90, 86.3@200	52.0@1000	[4]
Mn-PBAs	120.0@25	500, 70@200	73.8@600	[5]
CoNi-PBAs	140.0@30	600, 83@750	88.0@1500	[6]
Fe-PBAs	116.0@10	500, 71@100	70.0@2000	[7]

## References

- [1] H. Zhang, J. Peng, L. Li, Y. Zhao, Y. Gao, J. Wang, Y. Cao, S. Dou, S. Chou, *Adv. Funct. Mater.* **2023**, 33.
- [2] Z. Xu, Y. Sun, J. Xie, Y. Nie, X. Xu, J. Tu, J. Zhang, L. Qiu, T. Zhu, X. Zhao, *Acs Sustainable Chemistry & Engineering* **2022**, 10, 13277.
- [3] W. Li, C. Han, W. Wang, Q. Xia, S. Chou, Q. Gu, B. Johannessen, H. Liu, S. Dou, *Adv. Energy Mater.* **2020**, 10.
- [4] H. Fu, C. Liu, C. Zhang, W. Ma, K. Wang, Z. Li, X. Lu, G. Cao, *J. Mater. Chem. A* **2017**, 5, 9604.
- [5] Y. Tang, W. Li, P. Feng, M. Zhou, K. Wang, Y. Wang, K. Zaghbi, K. Jiang, *Adv. Funct. Mater.* **2020**, 30.
- [6] J. Peng, J. Wang, H. Yi, W. Hu, Y. Yu, J. Yin, Y. Shen, Y. Liu, J. Luo, Y. Xu, P. Wei, Y. Li, Y. Jin, Y. Ding, L. Miao, J. Jiang, J. Han, Y. Huang, *Adv. Energy Mater.* **2018**, 8.
- [7] W. Wang, Y. Gang, Z. Hu, Z. Yan, W. Li, Y. Li, Q.-F. Gu, Z. Wang, S.-L. Chou, H.-K. Liu, S.-X. Dou, *Nat. Commun.* **2020**, 11.