Supporting information

Investigation of high-entropy Prussian blue analog as cathode materials for aqueous sodium-ion batteries

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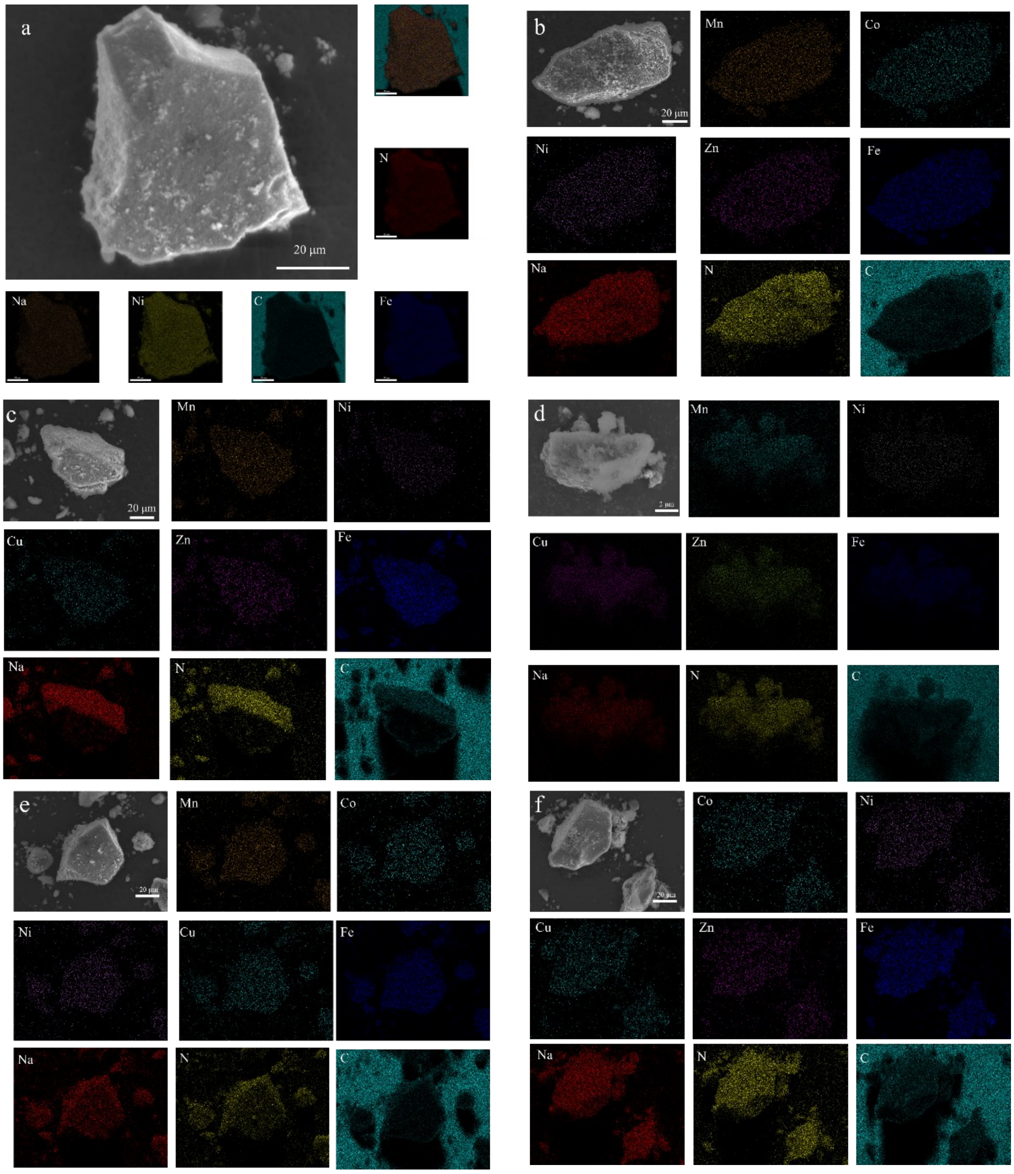


Figure S1 SEM and EDS element mapping of (a) NiHCF, (b) M4HCF-Cu, (c) M4HCF-Co, (d) M4HCF-Ni, (e) M4HCF-Zn, (f) M4HCF-Mn.

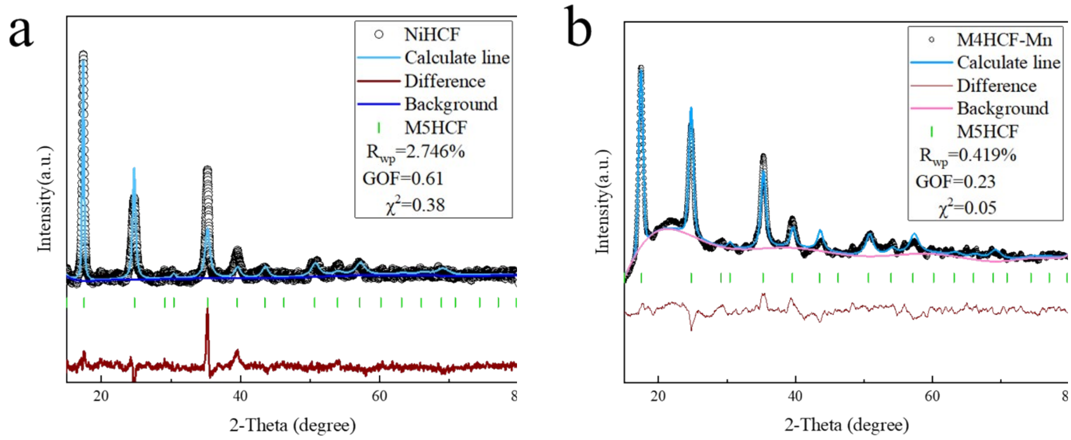


Figure S2 Rietived refinement of the (a) NiHCF, and (b) M4HCF-Mn.

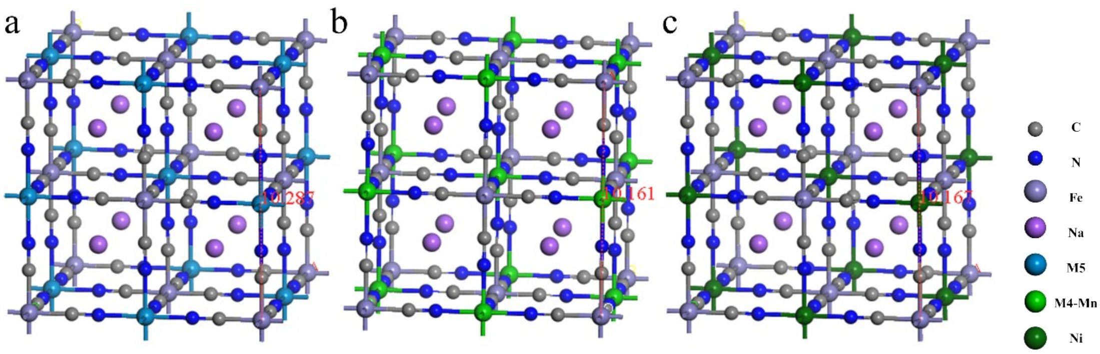


Figure S3 XRD refinement models of (a) M5HCF, (b) M4HCF-Mn, (c) NiHCF.

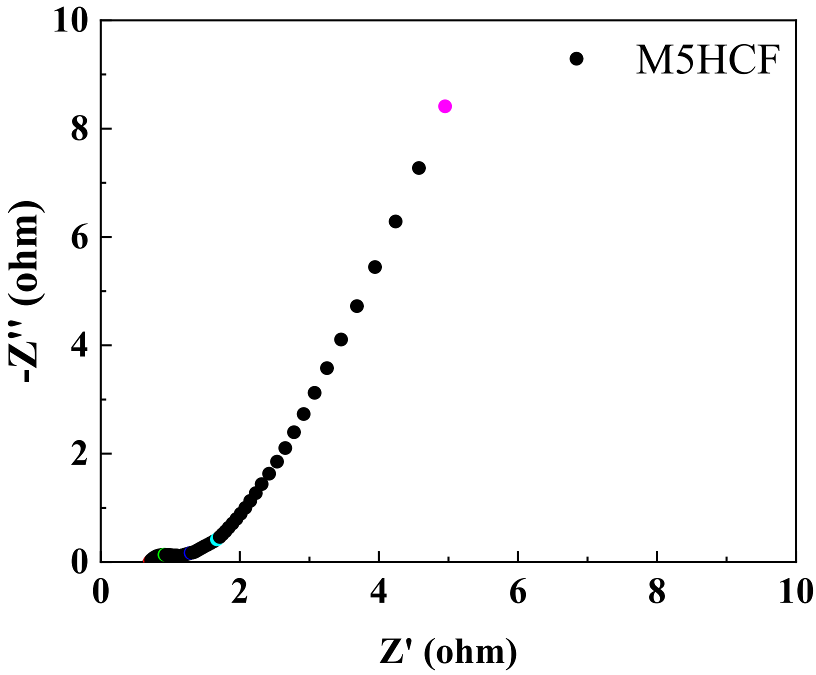


Figure S4 EIS spectrum of M5HCF.

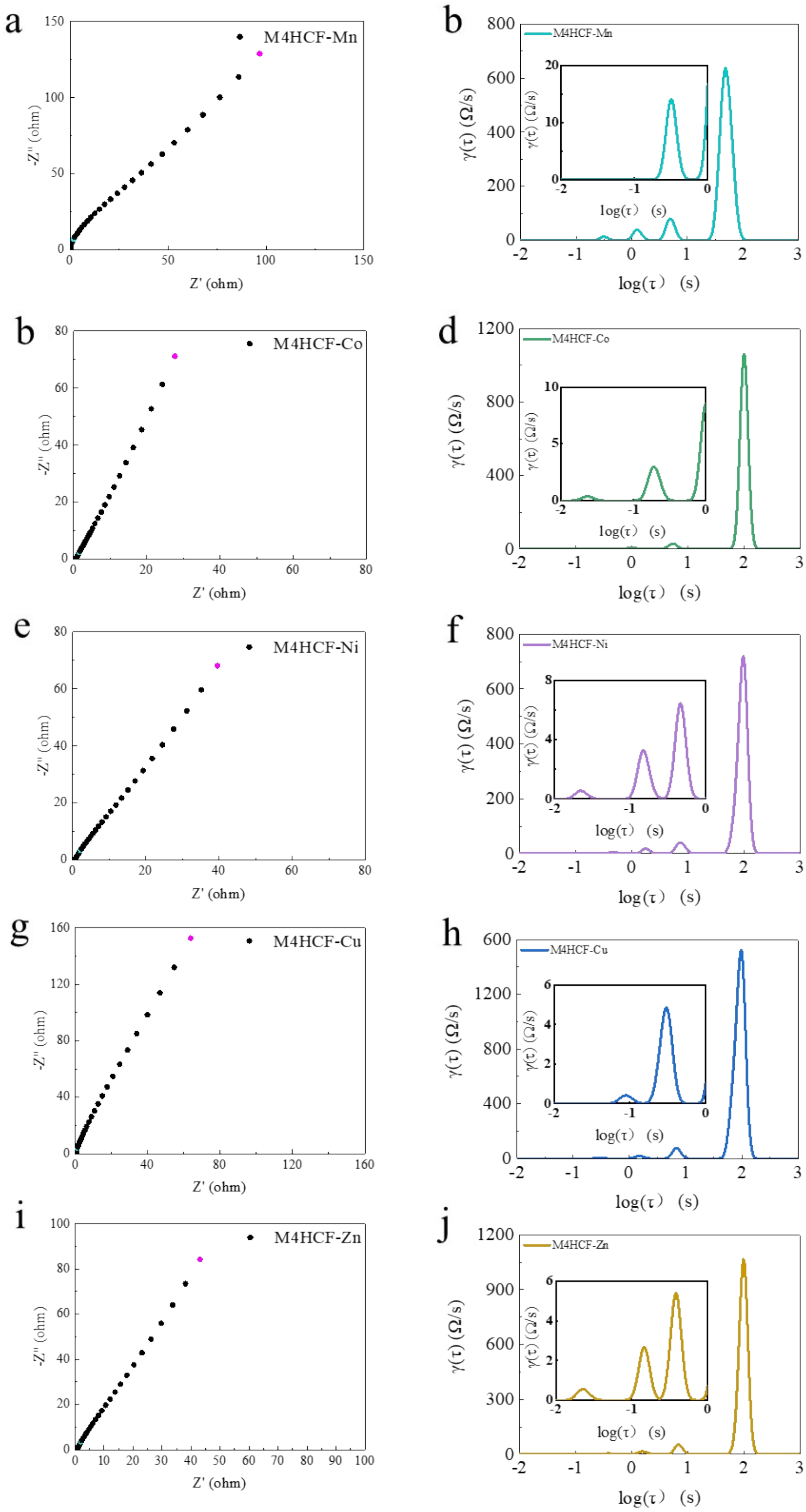
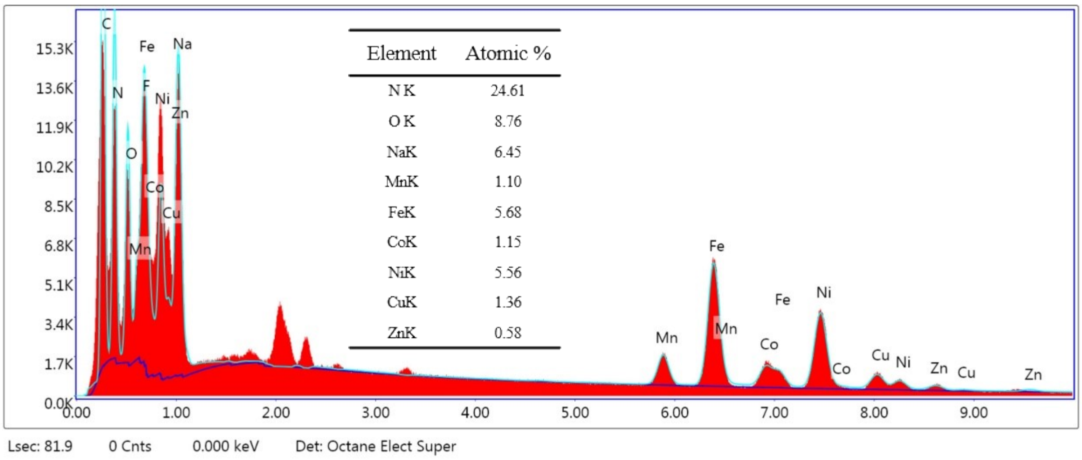


Figure S5 EIS spectra, relaxation time distribution analysis and local magnification of (a, b) M4HCF-Mn, (c, d) M4HCF-Co, (e, f) M4HCF-Ni, (g, h) M4HCF-Cu, (i, j) M4HCF-Zn.



Element	Atomic %
N K	24.61
O K	8.76
NaK	6.45
MnK	1.10
FeK	5.68
CoK	1.15
NiK	5.56
CuK	1.36
ZnK	0.58

Figure S6 Sum Spectrum of EDS results for M5HCF.

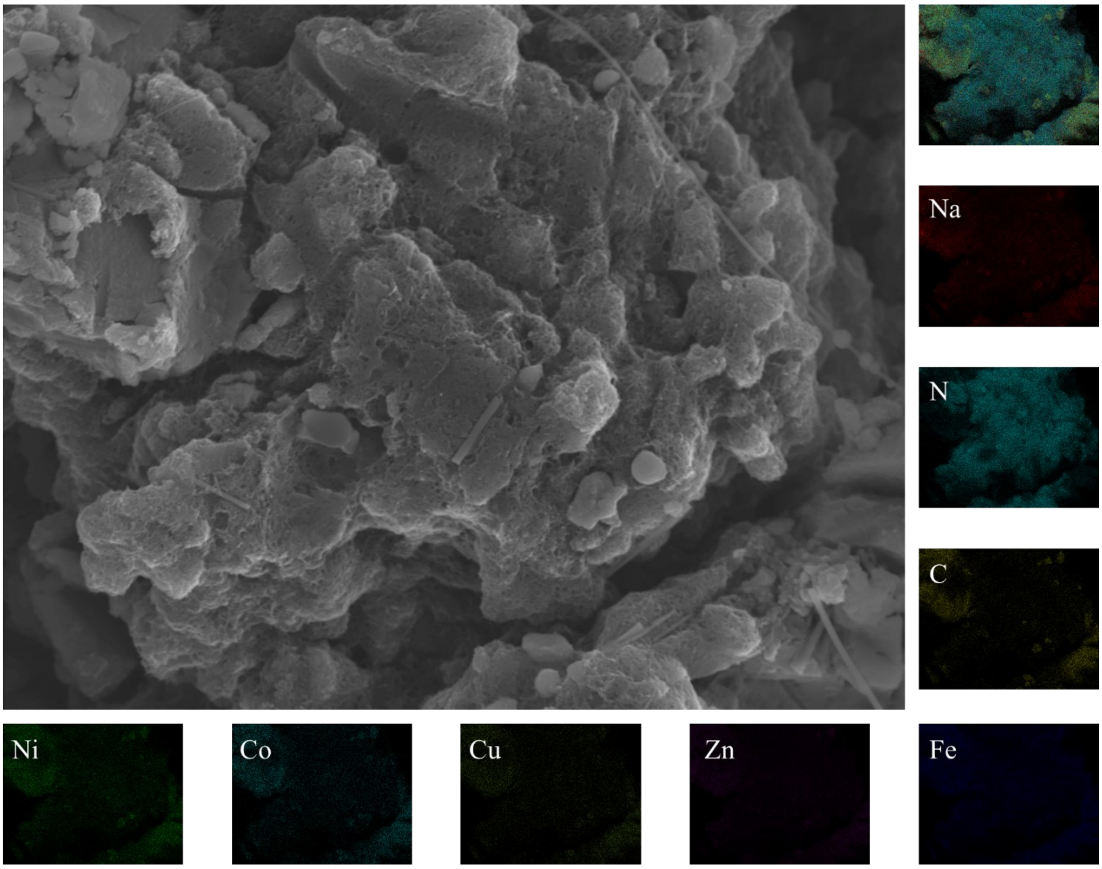


Figure S7 SEM image of and EDS mapping of M4HCF-Mn after 1000 cycles.

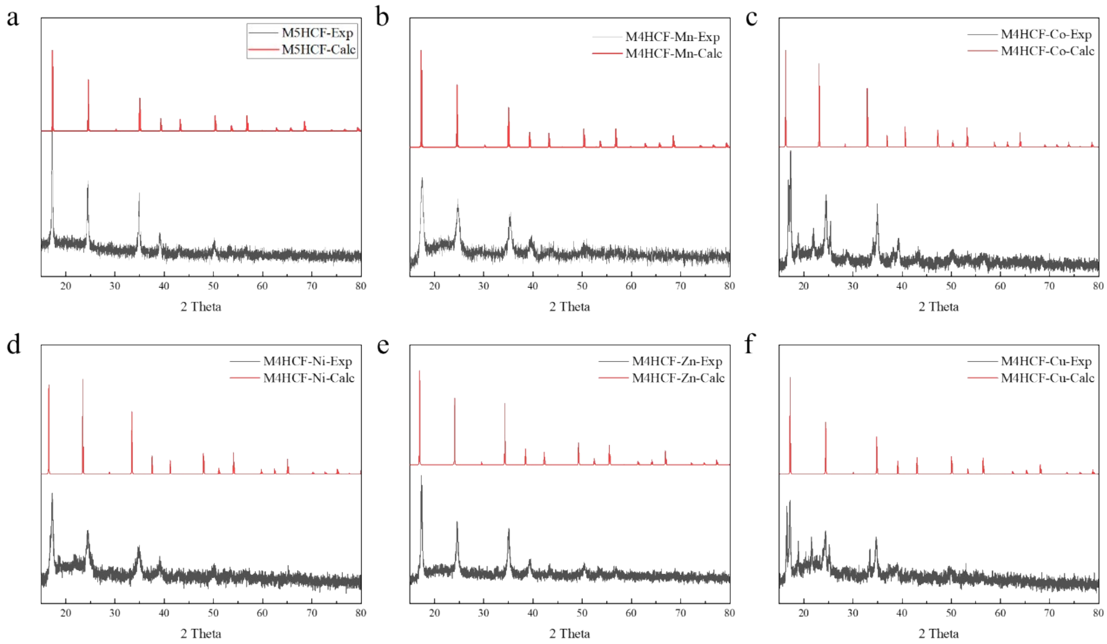


Figure S8 The comparisons of calculated XRD with experimental patterns for (a) M5HCF, (b-f) M4HCF.

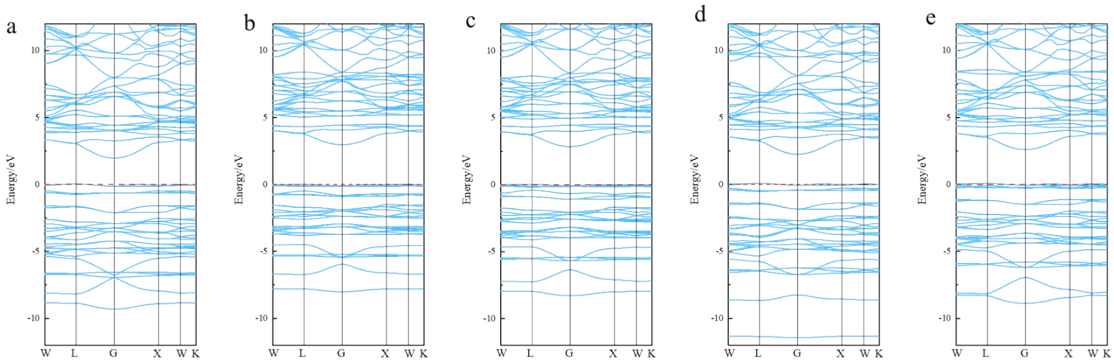


Figure S9 energy bands of (a) M4HCF-Mn, (b) M4HCF-Co, (c) M4HCF-Ni, (d) M4HCF-Cu, (e) M4HCF-Zn.

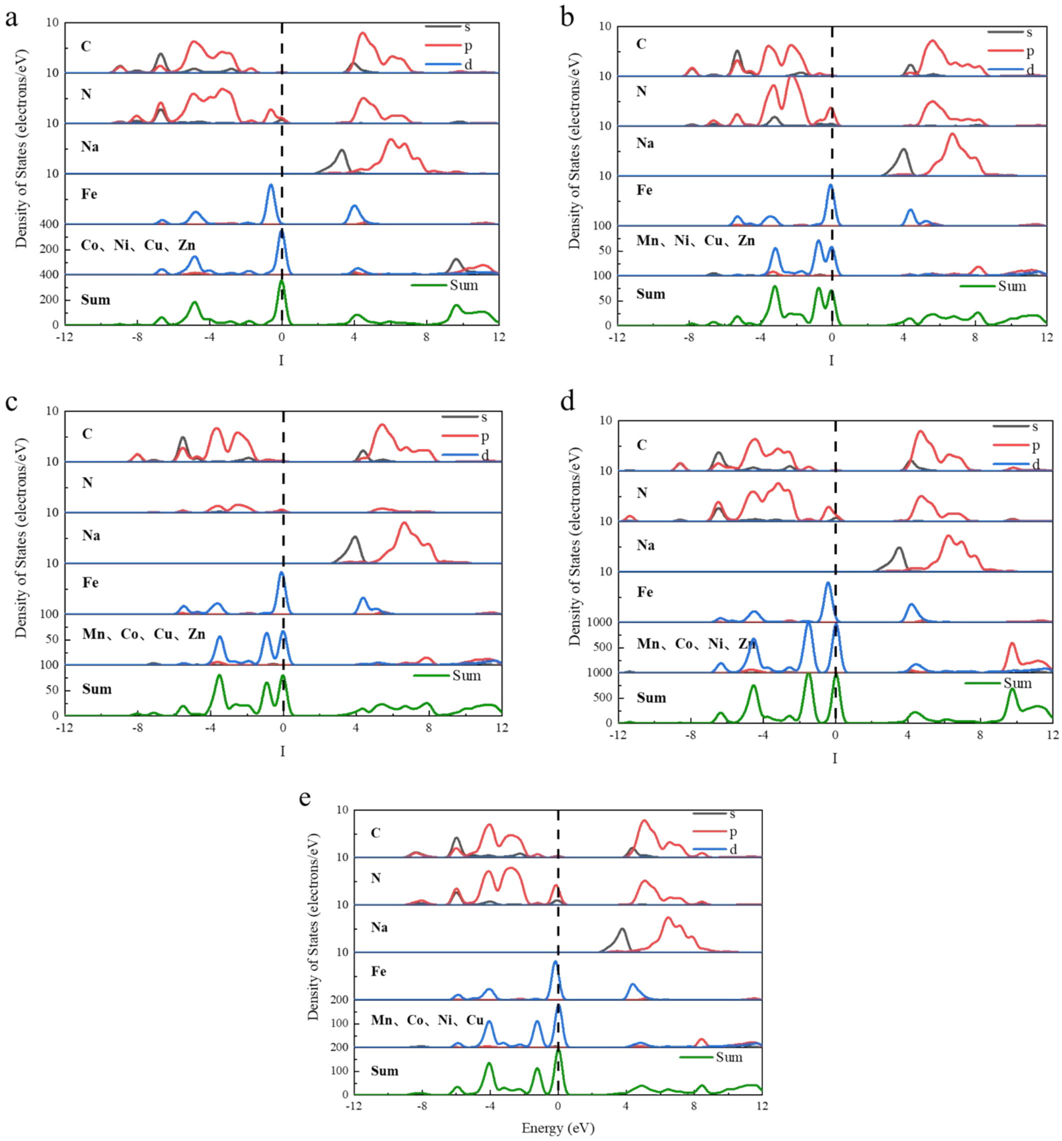


Figure S10 Total density of states, partial density of states plots of (a) M4HCF-Mn, (b) M4HCF-Co, (c) M4HCF-Ni, (d) M4HCF-Cu, (e) M4HCF-Zn.

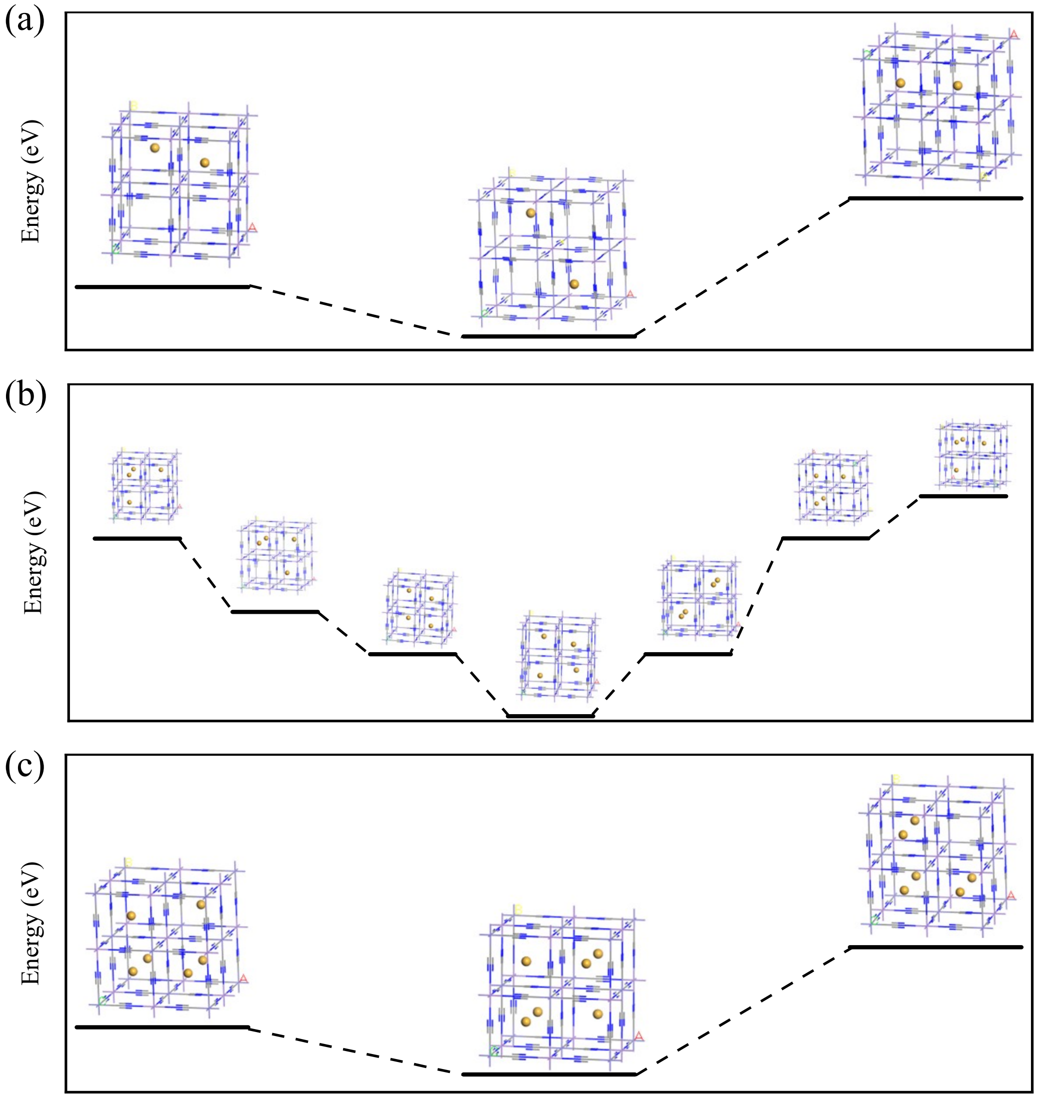


Figure S11 Binding energy relationship of (a) $Na_{0.5}M5Fe(CN)_6$, (b) $NaM5Fe(CN)_6$, (c) $Na_{1.5}M5Fe(CN)_6$.

Table S1 ICP-OES results of element ratios for NiHCH, M5HCF and M4HCF-Mn.

	Na	Fe	Ni	Mn	Co	Cu	Zn
NiHCF	1.231(2)	0.792(3)	0.813(2)	0	0	0	0
	$Na_{1.23}Ni_{1.0}[Fe(CN)_6]_{0.79}\square_{0.21}\cdot 1.13H_2O$						
M5HCF	1.193(2)	1.125(3)	0.185(4)	0.191(3)	0.182(3)	0.212(2)	0.234(2)
	$Na_{1.19}(Zn_{0.23}Mn_{0.19}Ni_{0.19}Cu_{0.21}Co_{0.18})[Fe(CN)_6]_{0.81}\square_{0.19}\cdot 1.15H_2O$						
M4HCF-Mn	1.196	0.782(2)	0.250(3)	–	0.251(4)	0.252(2)	0.252(3)
	$Na_{1.2}(Zn_{0.25}Ni_{0.25}Cu_{0.25}Co_{0.25})[Fe(CN)_6]_{0.78}\square_{0.22}\cdot 1.15H_2O$						

Table S2 Element content of C, H and N for three samples (wt %)

	C	H	N
NiHCF	19.678	2.276	20.365
M5HCF	19.682	2.231	20.442
M4HCF-Mn	16.817	2.497	19.501

Table S3 Electrochemical performance of different element-doped PBAs cathode materials in aqueous sodium ion full cells

PBAs cathode	Electrolyte	Capacity/ (mAh/g)	Cycle (Retention/%)	Ref.
NiHCF@PPy	0.5M H_2SO_4 + 0.2M Aniline	73.6 (2 C)	300 (70%)	[1]
TiHCF	0.1M $NaNO_3$	30 (0.2 C)	-	[2]
CoHCF	1M Na_2SO_4	114 (0.1 A/g)	200 (83%)	[3]
$Co_{0.97}Zn_{0.03}$HCF	1M $NaNO_3$	119 (0.1 A/g)	200 (74%)	[4]
VHCF@CuHCF	0.5M Na_2SO_4 + 5M H_2SO_4	90 (1.2 C)	200 (90%)	[5]
NienHCF	0.5M Na_2SO_4	36.5 (0.1 A/g)	500 (60.7%)	[6]
MnHCF	17M $NaClO_4$	59 (5 C)	700 (75%)	[7]
M5HCF	1M Na_2SO_4	65.6 (1 C)	1000 (87.0%)	This work

References

[1] P. Naskar, S. Debnath, A. Maiti, B. Biswas, A. Banerjee, *Chemphyschem*, 2023, **24**, e202200588. https://doi.org/10.1002/cphc.202200588.

[2] M. Li, A. Bina, M. Maisuradze, M. Giorgetti, *Batteries*, 2021, **8 (1)** : 1. https://doi.org/10.3390/batteries8010001

[3] J. Kim, S-H. Yi, L. Li, T.V. Thu, S-E. Chun, *Int. J. Energy Res.*, 2022, **46 (15)**, 22717-22729. https://doi.org/10.1002/er.8574.

[4] J. Kim, S-H. Yi, L. Li, S-E. Chun, *J. Energy Chem.*, 2022, **69**, 649-658. https://doi.org/10.1016/j.jechem.2022.01.034.

[5] T-U. Choi, G. Baek, S.G. Lee, J-H. Lee, *ACS Appl. Mater. Interfaces*, 2020, **12, 22**, 24817–24826. https://doi.org/10.1021/acsami.0c05458.

[6] D. Zhang, L. Sun, C. Wang, Q. Xue, J. Feng, W. Ran, T. Yan, *ACS Appl. Mater. Interfaces,* 2022, **14, 14,** 16197–16203. https://doi.org/10.1021/acsami.2c00143.

[7] S. Qiu, X. Wu, M. Wang, M. Lucero, Y. Wang, J. Wang, Z. Yang, W. Xu, Q. Wang, M. Gu, J. Wen, Y. Huang, Z.J. Xu, Z. Feng, *Nano Energy,* 2019, **64**, 103941. https://doi.org/10.1016/j.nanoen.2019.103941.

Table S4 EDS results of two samples before and after cycling test (at.%)

		Na	Mn	Fe	Co	Ni	Cu	Zn
M5HCF	before	33.5	6.7	30.7	7.8	6.0	6.3	9
	after	63.1	2.4	38.1	0.9	7.7	2.2	2.3
M4HCF-Mn	before	29	–	32	10	9	10	11
	after	45	–	30	0	15	3.6	6.1

Table S5 Convergence test data for high and medium entropy doped PBAs

Materials	Truncation energy/eV	k-point
M5HCF	780	4×4×4
M4HCF-Mn	750	4×4×4
M4HCF-Co	800	4×4×4
M4HCF-Ni	780	5×5×5
M4HCF-Cu	780	4×4×4
M4HCF-Zn	780	3×3×3

Table S6 Energy formation and voltage plateau during discharging of M5HCF cathode material

Materials	Binding energy E_f/eV	Voltage plateau/V
$FeM5(CN)_6$	—	—
$Na_{0.5}FeM5(CN)_6$	-1.29332	2.58665
$NaFeM5(CN)_6$	-1.98945	1.39225
$Na_{1.5}FeM5(CN)_6$	-2.54984	1.1208
$Na_2FeM5(CN)_6$	-2.90225	0.7054