Supporting Information

Stable cycling of Prussia blue-based Na/Zn hybrid battery in

aqueous electrolyte with a wide electrochemical window

Chunli Liu,^a Yunpo Sun,^a Jianbo Nie,^b Dong Dong,^c Jian Xie^{*a,d} and Xinbing Zhao^{a,d}

^a State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: xiejian1977@zju.edu.cn; Fax: +86-571-87951451; Tel: +86-571-87952181

^b State Grid Zhejiang Integrated Energy Service Co., Ltd., Hangzhou 310000, P. R. China

^c Zhejiang Huayun Information Technology Co., Ltd., Hangzhou 310008, P. R. China

^d Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Hangzhou 310027, P. R. China



Fig. S1 HAADF-STEM image and EDX mapping of FeHCF.



Fig. S2 (a) EDS spectra and (b) XRD patterns of FeHCF electrodes at various charge and discharge

states.



Fig. S3 Cycling performance of symmetric Zn cell with PA-coated Zn and VC-added electrolyte at a current density of 1 mA cm⁻² and an areal capacity 0.5 mAh cm⁻².



Fig. S4 Photos of zinc anode and separator after 500 cycles in full cell with (a) bare Zn and (b) PA-coated Zn.





Fig. S5 SEM images of zinc anode after 500 cycles in full cell with (a) bare Zn and (b) PA-coated

Zn, and (c) FTIR spectra of PA-coated zinc before and after cycling.

Cathode	Anode	Capacity (mAh g ⁻¹)	Cycle number	Capacity retention	Reference
Na _x FeFe(CN) ₆	Zn	70	1000	77%@1000 mA g ⁻¹	This work
Na _x FeFe(CN) ₆	Zn	70	4000	60%@1000 mA g ⁻¹	This work
NiHCF	Zn	~60	1000	>81%@500 mA g ⁻¹	[1]
$Na_2MnFe(CN)_6$	Zn	~130	2000	75%@800 mA g ⁻¹	[2]
$Na_{0.61}Fe_{1.94}(CN)_6 \cdot \Box_{0.06}$	Zn	~73	1000	80%@300 mA g ⁻¹	[3]
$Na_2NiFe(CN)_6$	NaTi ₂ (PO ₄) ₃	_	250	88%@500 mA g ⁻¹	[4]
$Na_2CuFe(CN_{)6}$	NaTi ₂ (PO ₄) ₃	_	1000	88%@1000 mA g ⁻¹	[5]
Na _{1.24} Mn[Fe(CN) ₆] _{0.81} · 1.28H ₂ O	NaTi ₂ (PO ₄) ₃	117	50	81%@2 mA cm ⁻²	[6]

Table S1. Comparison of electrochemical performance of PB-based cathodes in aqueous cells

Table S2. Fitting results of the Nyquist plots using the equivalent circuit

Full cell system	Sample	$R_{\rm e}(\Omega)$	$R_{\rm f}(\Omega)$	Q_1		P(0)	Q_2	
				Y	n	$\Lambda_{\rm ct}(22)$	Y	n
Bare Zn &pristine	10 th cycle	4.9	19.1	2.6×10 ⁻⁴	0.64	61.0	1.1×10 ⁻³	0.73
electrolyte	500 th cycle	4.6	20.4	9.1×10 ⁻⁴	0.82	119.3	3.8×10 ⁻³	0.88
Coated Zn & pristine	10 th cycle	5.1	83.6	1.3×10 ⁻⁴	0.96	302.7	2.4×10 ⁻³	0.54
electrolyte	500 th cycle	1.9	38.2	1.2×10 ⁻⁴	0.99	204.7	1.5×10^{-3}	0.55
Coated Zn & VC	10 th cycle	1.7	187.2	2.4×10-4	0.83	295.3	2.9×10 ⁻³	0.56
added electrolyte	500 th cycle	9.6	49.4	1.1×10 ⁻⁴	0.99	170.7	1.7×10 ⁻³	0.59

References

- 1 K. Lu, B. Song, J. T. Zhang and H. Y. Ma, J. Power Sources, 2016, **321**, 257–263.
- Z. G. Hou, X. Q. Zhang, X. N. Li, Y. C. Zhu, J. W. Liang and Y. T. Qian, *J. Mater. Chem. A*, 2017, 5, 730–738.
- L. P. Wang, P. F. Wang, T. S. Wang, Y. X. Yin, Y. G. Guo and C. R. Wang, *J. Power Sources*, 2017, 355, 18–22.
- 4 X. Y. Wu, Y. L. Cao, X. P. Ai, J. F. Qian and H. X. Yang, *Electrochem. Commun.*, 2013, **31**, 145–148.
- 5 X. Y. Wu, M. Y. Sun, Y. F. Shen, J. F. Qian, Y. L. Cao, X. P. Ai and H. X. Yang, *ChemSusChem*, 2014, 7, 407–411.
- 6 K. Nakamoto, R. Sakamoto, M. Ito, A. Kitajou and S. Okada, *Electrochemistry*, 2017, **85**, 179–185.