Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Ion exchange to construct high-performance core-shell MnFe-PB@CuFe-PB cathode material for sodium ion battery

Hongyu Cheng[1], Yi-Nuo Liu[1], Zhuo-Er Yu[1], Yingying Song[1], Yinping Qin[1], Maomao Zhang[1], Yinping Qin[1], Riming Chen[1], Jingjing Zhou[1], Yang Liu[1,2,3]*, Bingkun Guo[1]*

1. Materials Genome Institute, Shanghai University, Shanghai, 99 Shangda Road, Baoshan District, Shanghai, China.
2. Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China.
3. Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jianghan University, No. 8, Sanjiaohu Rd., Wuhan, Hubei, 430056, P. R. China.

Corresponding Author

Yang Liu, email: liuyang81@shu.edu.cn

Bingkun Guo, email: guobingkun@shu.edu.cn

†These authors contributed equally to this paper.

Table S1. Elemental contents of MC-n samples (weight percentage)

Samples	Na	Mn	Fe	Cu
MC-0.04	28.09	34.27	35.76	1.9
MC-0.10 (MnFe-PB@CuFe-PB)	25.96	33.63	36.08	4.32
MC-0.19	24.82	30.98	35.77	8.41
MC-0.27	24.40	28.94	34.26	12.38
MC-0.38	23.18	25.43	33.35	18.03

Table S2. H_2O contents and chemical formula of MC-n samples

Samples	H_2O contents (wt%)	Chemical Formula
MC-0.04	11.50	$Na_{1.87}Mn_{0.96}Cu_{0.04}[Fe(CN)_6]_{0.98}\square_{0.02}\bullet 2.21H_2O$
MC-0.10 (MnFe-PB@CuFe-PB)	12.8	$Na_{1.66}Mn_{0.90}Cu_{0.10}[Fe(CN)_6]_{0.95}\square_{0.05}\bullet 2.42H_2O$
MC-0.19	13.13	$Na_{1.55}Mn_{0.81}Cu_{0.19}[Fe(CN)_6]_{0.92}\square_{0.08}\bullet 2.49H_2O$
MC-0.27	14.45	$Na_{1.47}Mn_{0.73}Cu_{0.27}[Fe(CN)_6]_{0.85}\square_{0.15}\bullet 2.74H_2O$
MC-0.38	17.27	$Na_{1.35}Mn_{0.62}Cu_{0.38}[Fe(CN)_6]_{0.80}\square_{0.20}\bullet 3.32H_2O$

Table S3. Elemental contents of MnFe-PB and MnFe-PB@CuFe-PB (weight percentage)

Samples	Na	Mn	Fe	Cu
MnFe-PB	29.33	35.04	35.63	—
MnFe-PB@CuFe-PB	25.96	33.63	36.08	4.32

Table S4. EIS fitting results of cycled MnFe-PB and MnFe-PB@CuFe-PB electrodes

Samples	R_s (Ω)	R_{ct} (Ω)
MnFe-PB	4.35	154.8
MnFe-PB@CuFe-PB	4.2	106.9

Table S5. Elements concentration of Mn^{2+}/Fe^{3+} in the electrolyte of MnFe-PB and MnFe-PB@CuFe-PB in 200 cycles

Samples	Mn^{2+} (mg L^{-1})	Fe^{3+} (mg L^{-1})	
MnFe-PB	0.5	0.1	In 200 cycles
MnFe-PB@CuFe-PB	—	—	In 200 cycles

Table S6. Comparison of PBAs in modification method, modified raw material and electrochemical performance

Materials	Modification method	Modified raw material	
PB/reduced graphene oxide conductive agent (RGO)	RGO as the conductive additive	RGO	
$Na_{1.7}MnFe(CN)_6 \cdot 2.38H_20$@Polymerization of polypyrrole (PPy)	Surface coated PPy	PPy	
$Na_{1.04}Fe_{0.83}Ni_{0.17}[Fe(CN)_6]_{0.76} \cdot 2.36H_2O$	Gradient nickel substitution	$NiCl_2 \cdot 6H_2O$	
$Na_{1.85}Ni_{0.40}Co_{0.31}Fe_{0.29}[Fe(CN)_6]_{0.97} \cdot 2.5H_2O$	Double doping with Co and Fe	$Ni(CH_3COO)_2 \cdot 4H_2O$ $Co(CH_3COO)_2 \cdot 4H_2O$	1
$Na_{1.20}Mn[Fe(CN)_6]_{0.79}$	A bottom-up approach	–	1
FeHCF@Ni-HCF	A co-precipitation method	$NiCl_2 \cdot 6H_2O$	
PB@Polyaniline (PANI)	Surface coated PANI	PANI	1
$Na_{1.38}Ni_{0.07}Mn_{0.93}[Fe(CN)_6]_{0.82} \cdot 1.4H_2O$	A slow nucleation method	$NiCl_2 \cdot 6H_2O$	
$Na_xK_yFe[Fe(CN)_6]$	K-doping at Na-site	$K_4Fe(CN)_6$	
$Na_{1.66}Mn_{0.90}Cu_{0.10}[Fe(CN)_6]_{0.98} \bullet 2.42H_2O$ (MnFe-PB@CuFe-PB)	An ion exchange mothd	$CuCl_2 \cdot 5H_2O$	1

Fig S1. SEM images of MC-n (n = 0.04, 0.19, 0.27 and 0.38) (a-e), (f) XRD patterns of MC-n (n = 0.04, 0.19, 0.27 and 0.38).

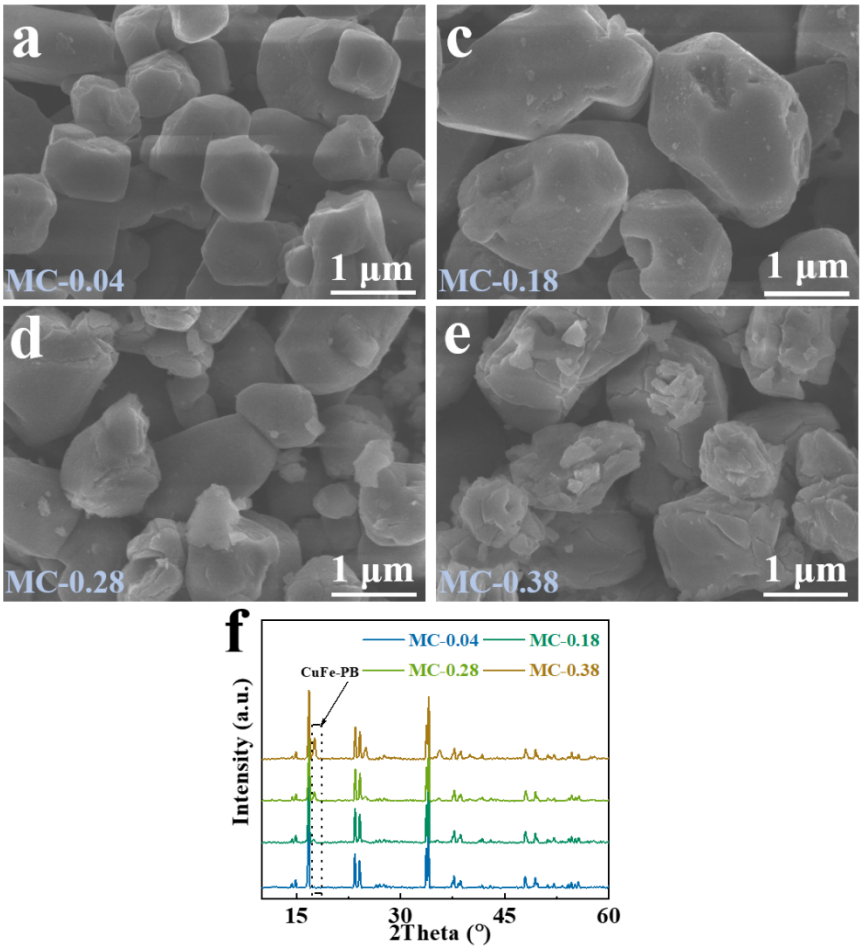


Fig S2. TGA curves of MC-n (n = 0.04, 0.19, 0.27 and 0.38).

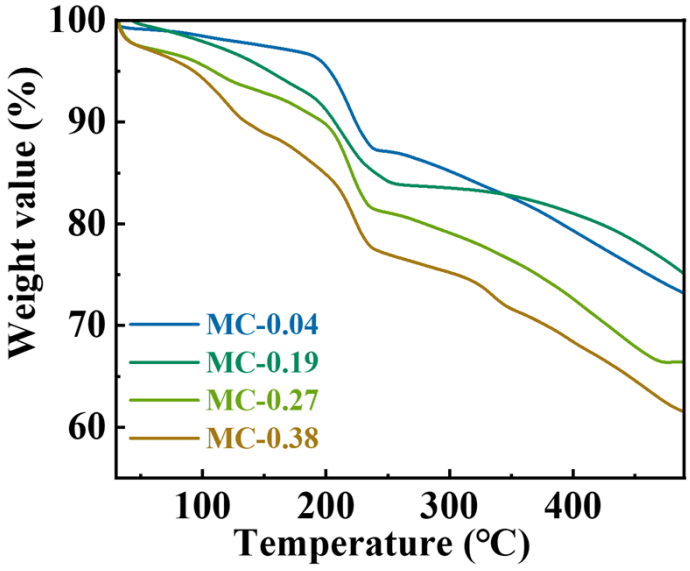


Fig S3. (a) Charge-discharge curves of MC-n at 0.1 C; (b) Cyclic voltammetry curves of MC-n at a scan rate of 0.1 mV s^{-1}; (c) Rate performance of MC-n at different rates; (d) Cycling performance within the potential window of 2.0 – 4.0 V vs. Na^+/Na of MC-n at 0.1 C; (f) Cycling performance of MC-n at 1 C.

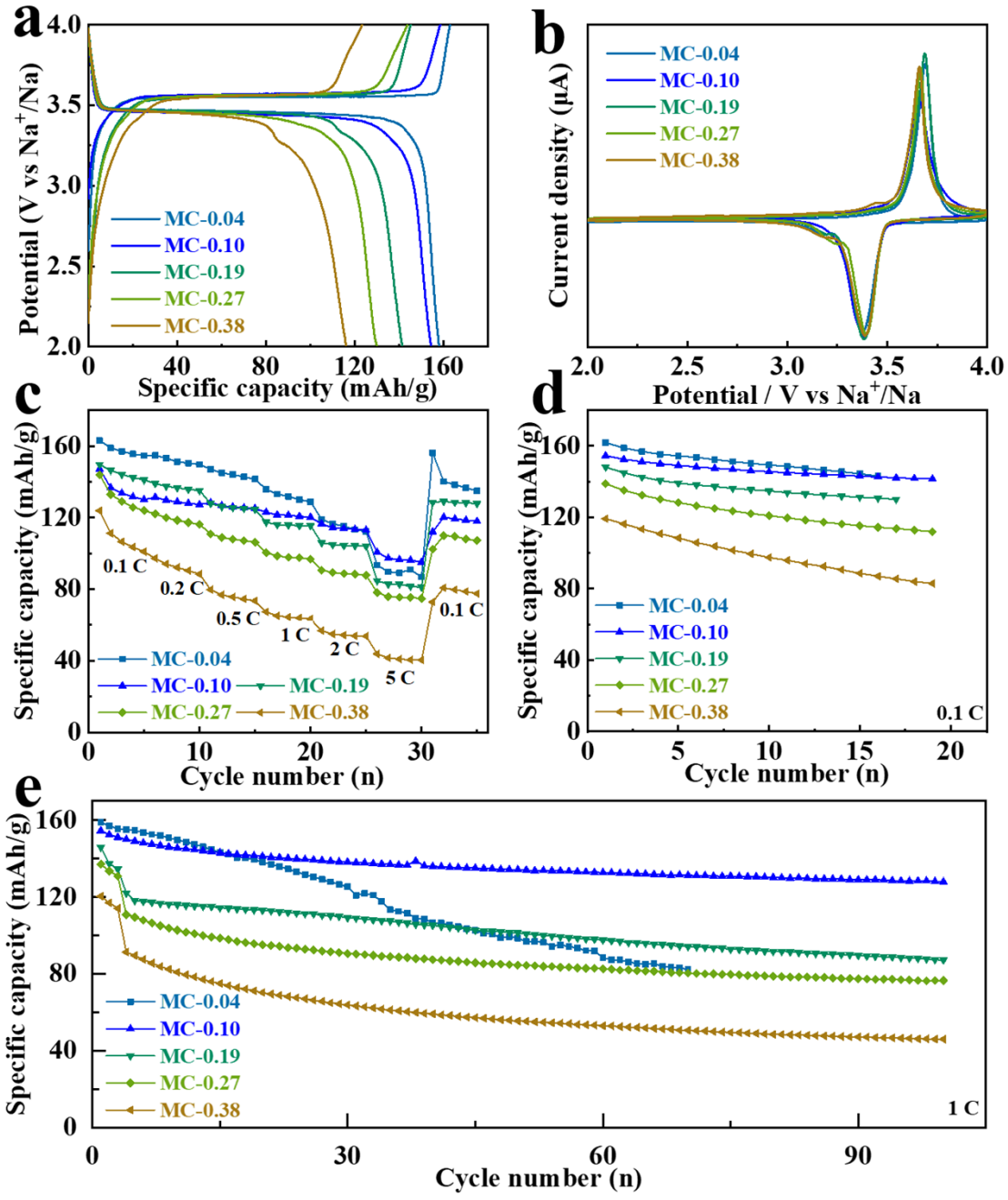


Fig S4. N_2 adsorption-desorption isotherms of (a) MnFe-PB and (b) MnFe-PB@CuFe-PB.

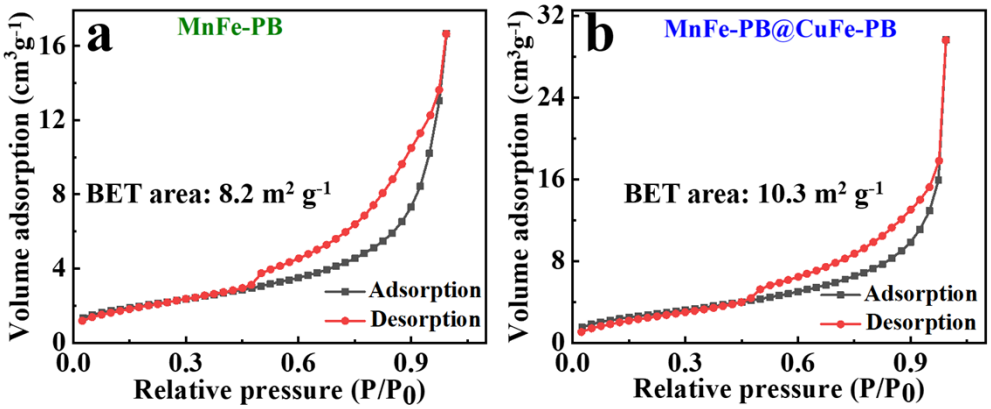


Fig S5. XPS depth profiles of Cu 2p peaks of MnFe-PB@CuFe-PB with increasing Ar^+ etching depth up to 200 nm.

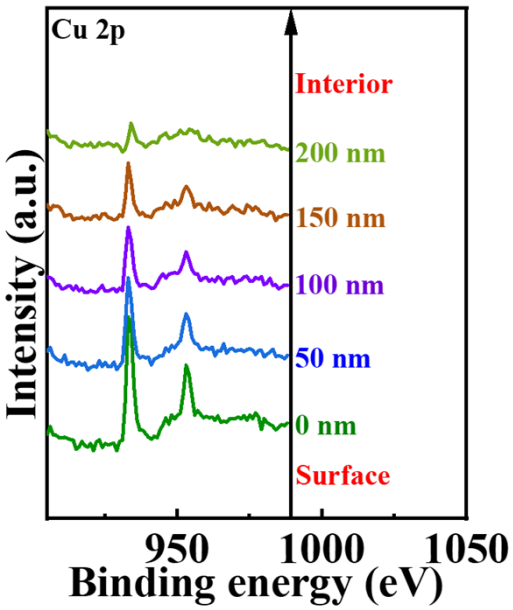


Fig S6. TGA carves of MnFe-PB and MnFe-PB@CuFe-PB.

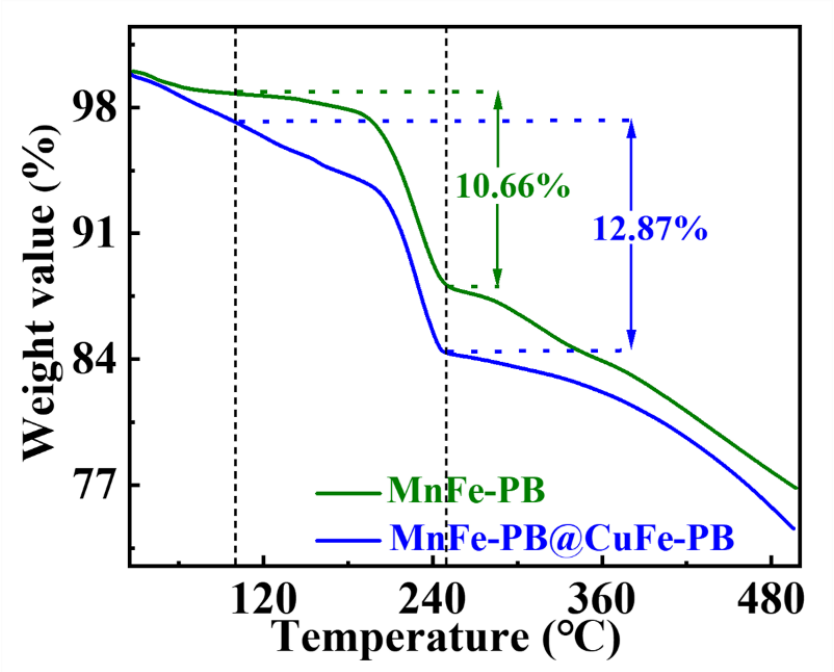


Fig S7. (a) Fe 2p and (b) Mn 2p XPS spectra of MnFe-PB.

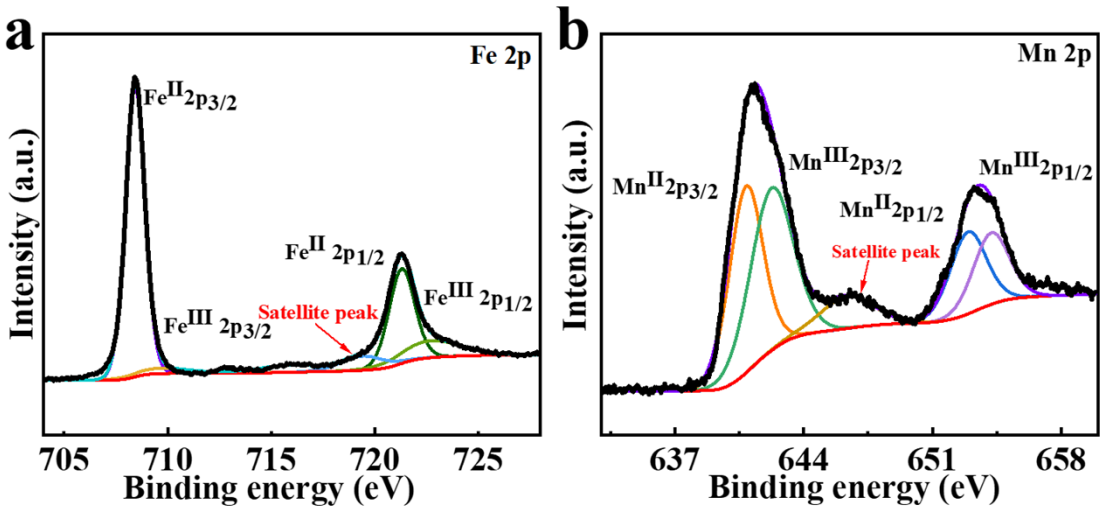


Fig S8. Rate performance of MnFe-PB and MnFe-PB@CuFe-PB at different rates.

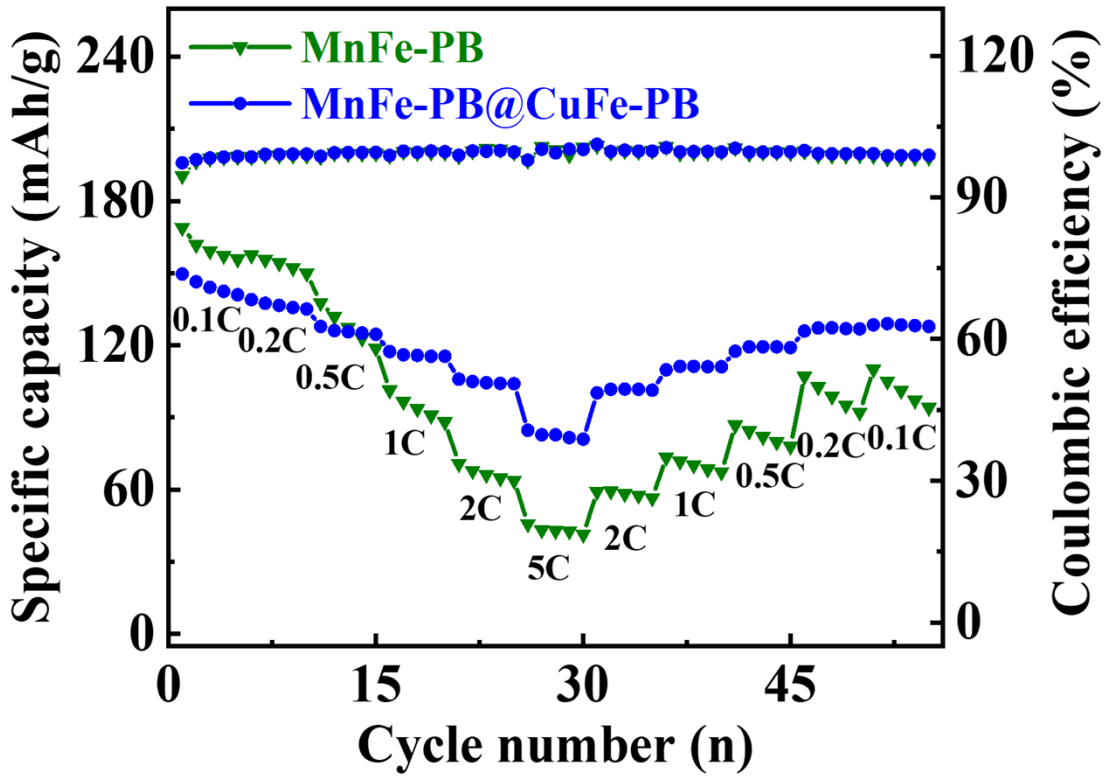


Fig S9. (a) GITT carves and (b) diffusion coefficients of sodium ions during the charging and discharging process of two samples.

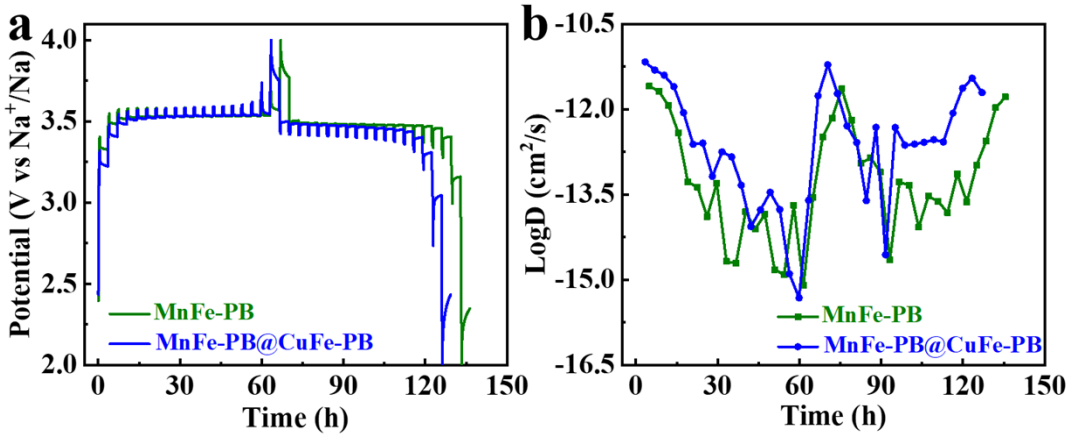


Fig S10. Ex situ XRD results of MnFe-PB (a) and MnFe-PB@CuFe-PB (b) during the first cycle under 0.1 C; Different colored lines correspond to the numbers 1 to 11 for different charging and discharging states.

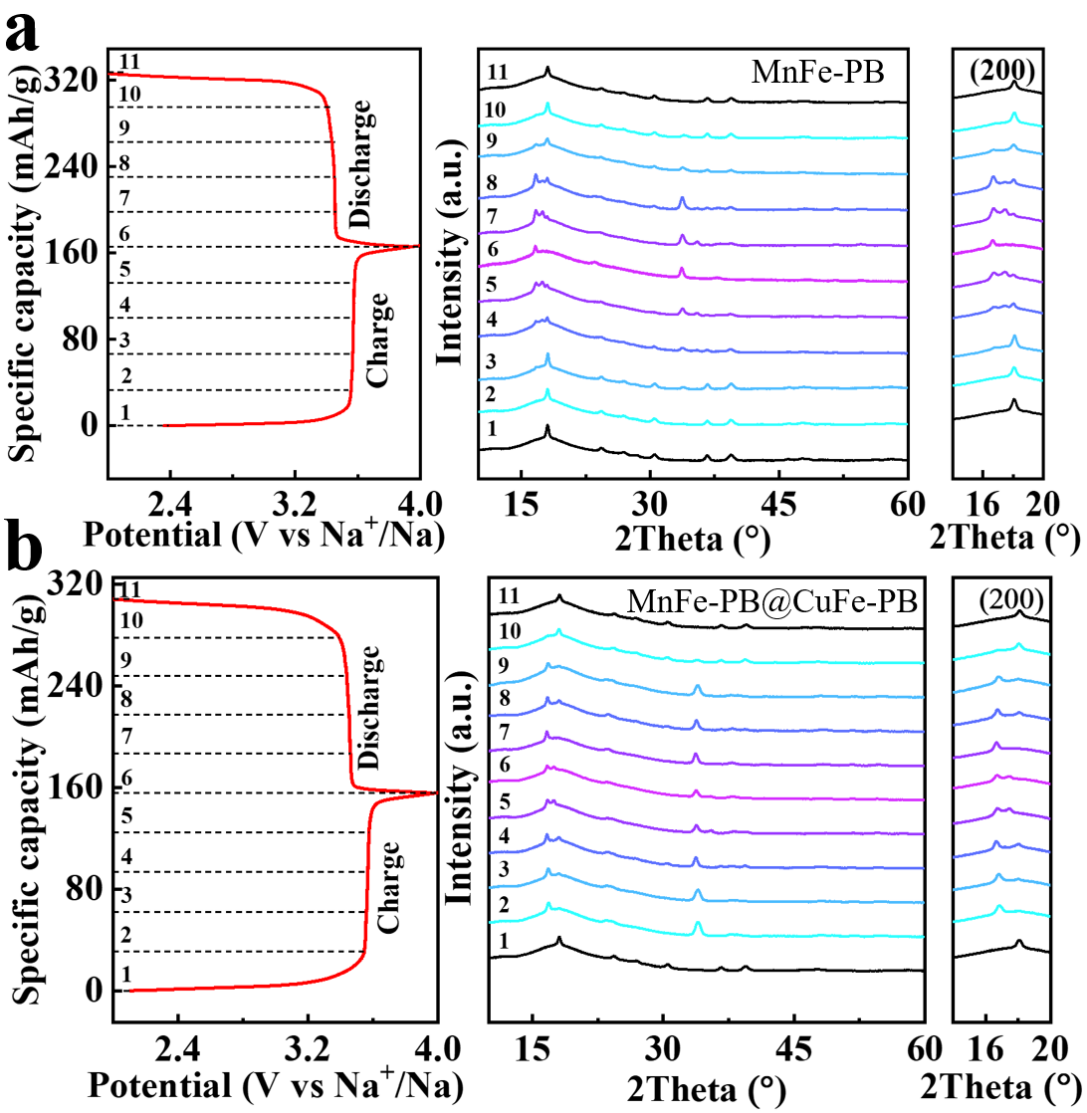


Fig S11. EIS spectra of cycled MnFe-PB and MnFe-PB@CuFe-PB electrodes (the inset shows the corresponding equivalent circuit).

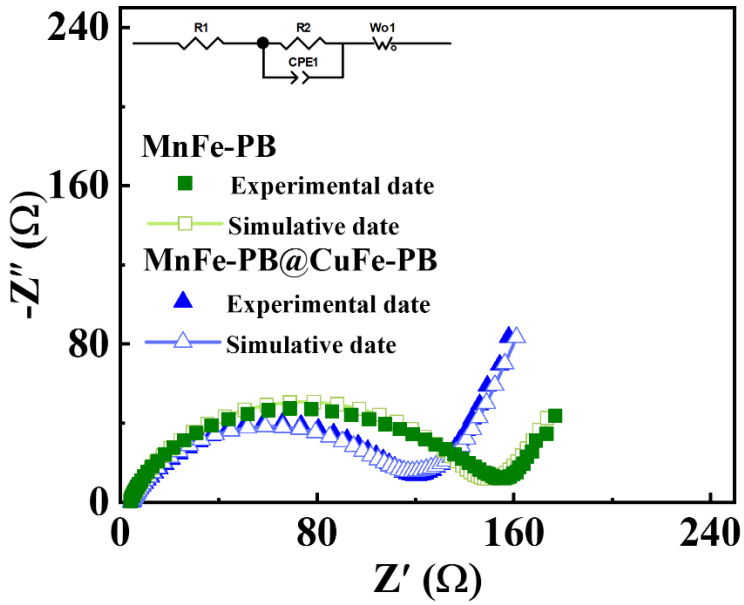
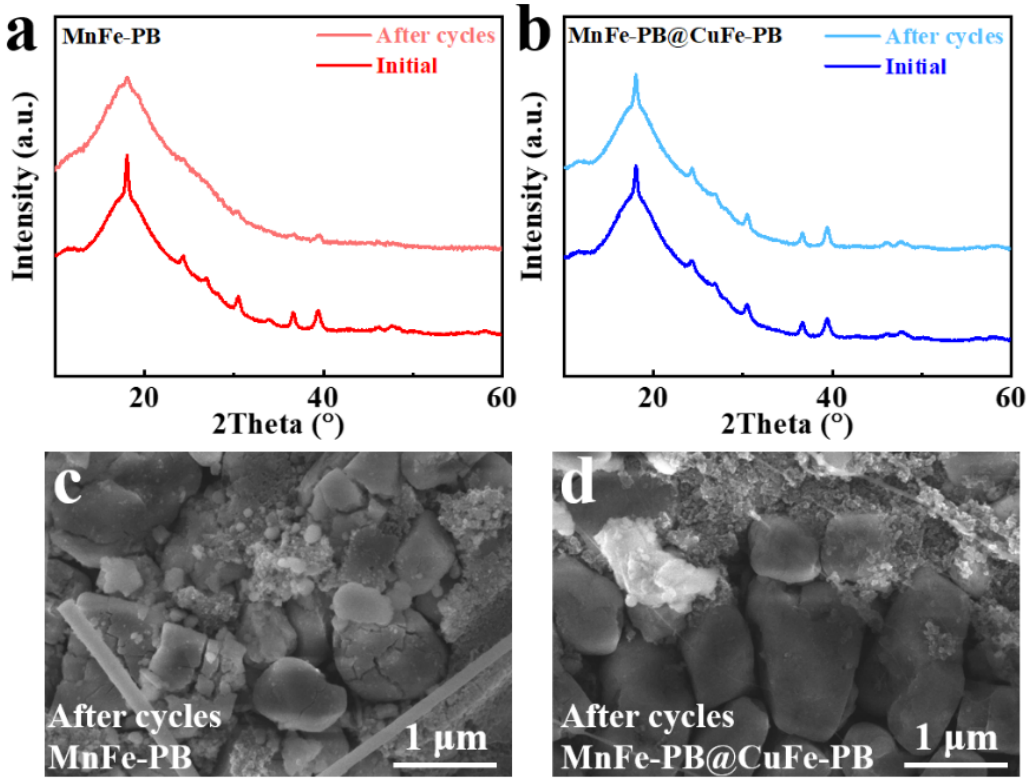


Fig S12. The initial and after cycles of XRD patterns and SEM images of (a and c) MnFe-PB and (b and d) MnFe-PB@CuFe-PB cathodes.



References

1. W. Zhuo, J. Li, X. Li, L. Ma, G. Yan, H. Wang, S. Tan and W. Mai, *Surfaces and Interfaces*, 2021, **23**, 100911.
2. W.-J. Li, S.-L. Chou, J.-Z. Wang, J.-L. Wang, Q.-F. Gu, H.-K. Liu and S.-X. Dou, *Nano Energy*, 2015, **13**, 200-207.
3. B. Wang, Y. Han, Y. Chen, Y. Xu, H. Pan, W. Sun, S. Liu, M. Yan and Y. Jiang, *Journal of Materials Chemistry A*, 2018, **6**, 8947-8954.
4. L. L. Zhang, C. Wei, X. Y. Fu, Z. Y. Chen, B. Yan, P. P. Sun, K. J. Chang and X. L. Yang, *Carbon Energy*, 2021, **3**, 827-839.
5. Y. Xi and Y. Lu, *Chemical Engineering Journal*, 2021, **405**, 126688.
6. M. Wan, Y. Tang, L. Wang, X. Xiang, X. Li, K. Chen, L. Xue, W. Zhang and Y. Huang, *Journal of Power Sources*, 2016, **329**, 290-296.
7. Q. Zhang, L. Fu, J. Luan, X. Huang, Y. Tang, H. Xie and H. Wang, *Journal of Power Sources*, 2018, **395**, 305-313.
8. Y. Huang, M. Xie, Z. Wang, Y. Jiang, Y. Yao, S. Li, Z. Li, L. Li, F. Wu and R. Chen, *Small*, 2018, **14**, 1801246.
9. J.-Y. Liao, Q. Hu, B.-K. Zou, J.-X. Xiang and C.-H. Chen, *Electrochimica Acta*, 2016, **220**, 114-121.