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Supporting Information

A High-Performance Free-Standing Zn Anode for Flexible Zinc-Ion Batteries

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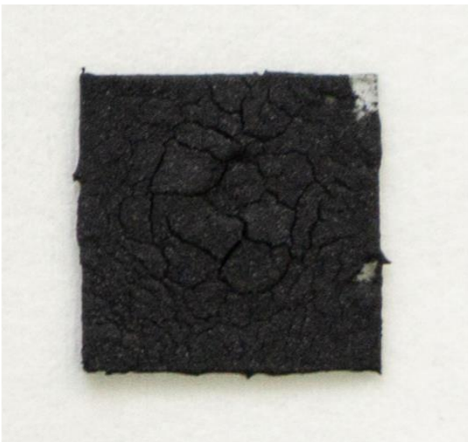

Figure S1. Photograph of Zn anode without PVDF-HFP

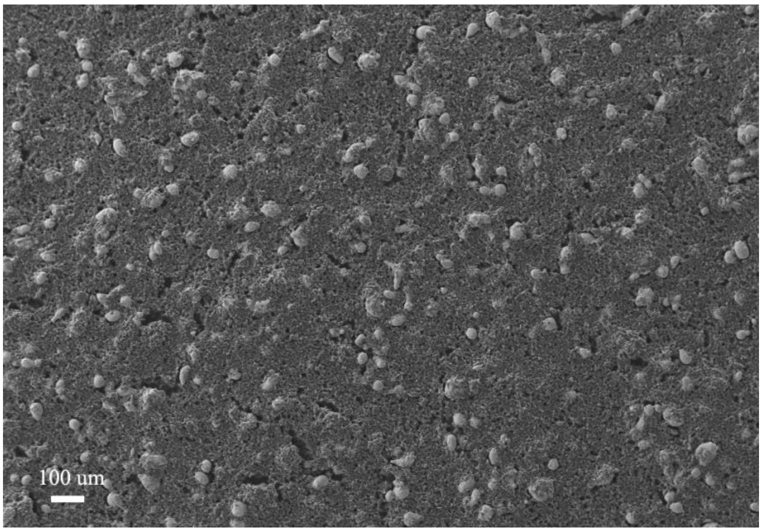

Figure S2. SEM image of the free-standing Zn anode (80:12:8).

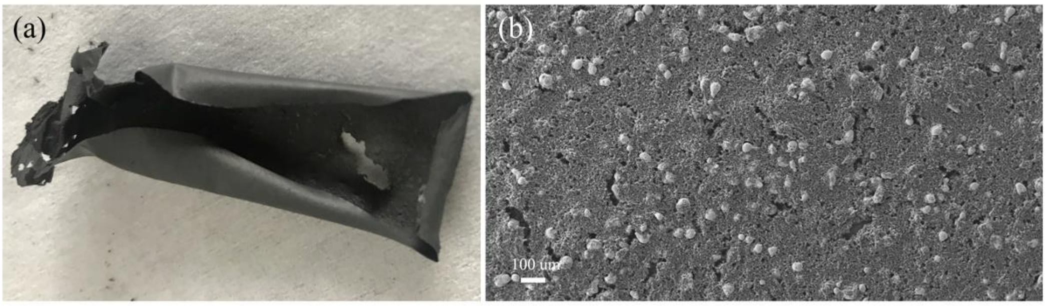

Figure S3. (a) Photograph and (b) SEM image of the free-standing Zn anode (ratio 88:4:8).

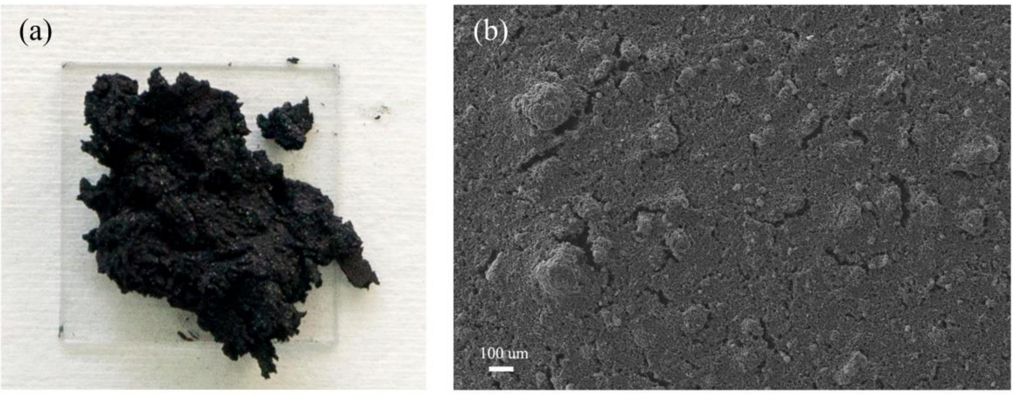

Figure S4. (a) Photograph and (b) SEM image of the free-standing Zn anode 88:8:4.

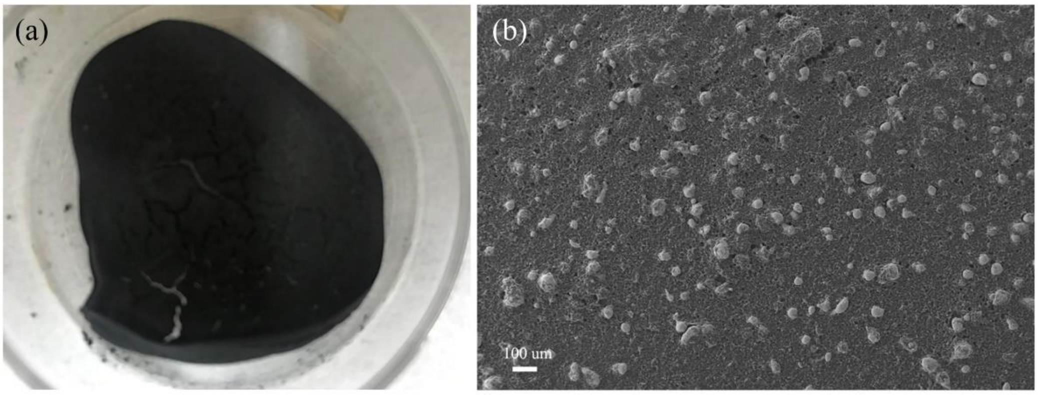

Figure S5. (a) Photograph and (b) SEM image of the free-standing Zn anode (ratio 80:10:10).

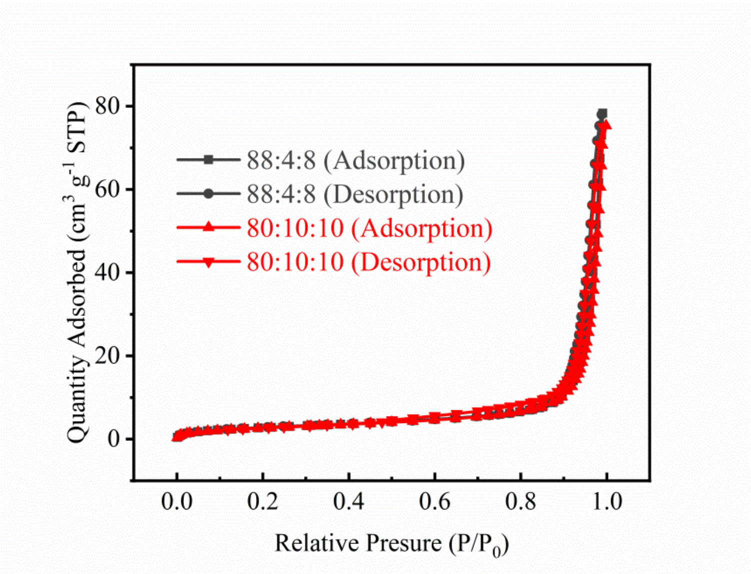

Figure S6. Nitrogen adsorption/desorption isotherm of the 88:4:8 and 80:10:10 free-standing Zn anode.

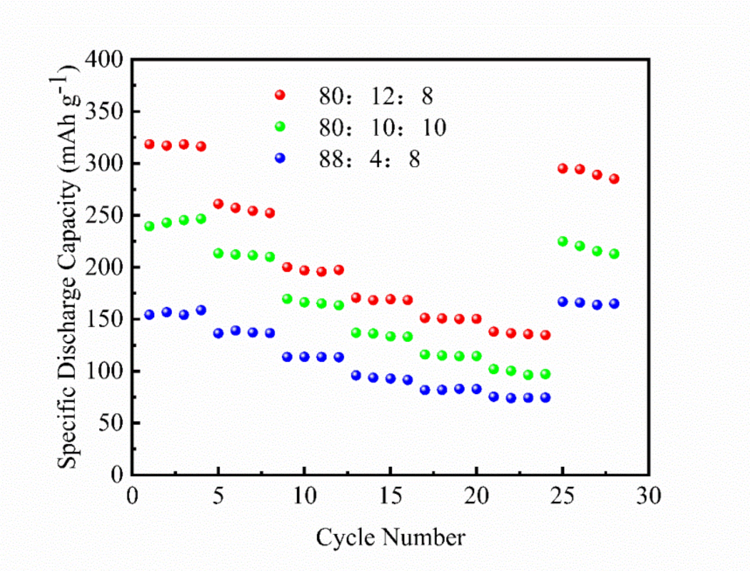

Figure S7. Rate capability of Zn-MnO_2 batteries with free-standing Zn anode (ratio 80:12:8, 80:10:10 and 88:4:8)

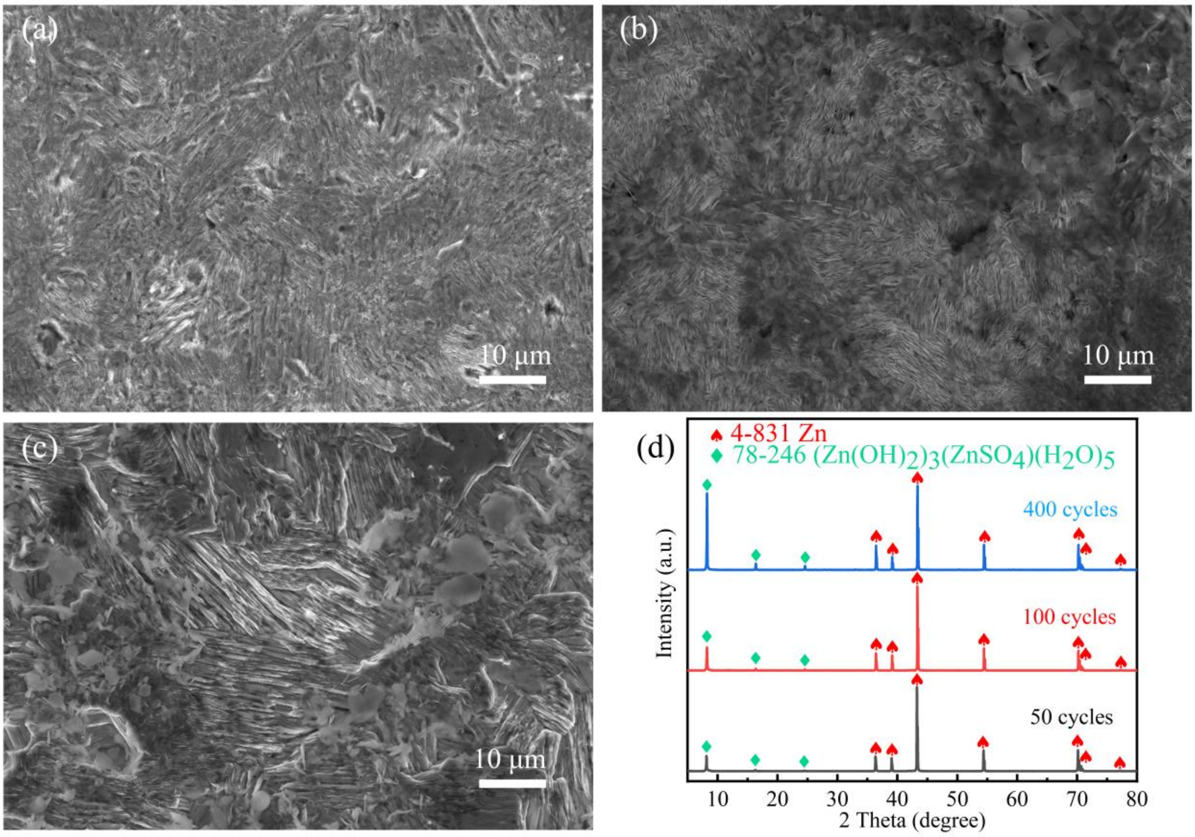

Figure S8. SEM images of the zinc foil after (a) 50, (b) 100, and (c) 400 cycles. (d) XRD patterns of the zinc foil after cycling.

As shown in Fig. S8a, some flakes emerged on the surface of the zinc foil after 50 cycles. With increasing cycle number, the flakes became large and the surface of the zinc foil became textured (Fig. S8b and Fig. S8c). After 50 charge/discharge cycles, XRD measurements exhibited typical Zn (JCPDS:4-831) and $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ (JCPDS:78-246) peaks (Fig. S8d). Those peaks were also detected after 100 and 400 cycles, and the peak intensity of $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ was significantly increased after 400 cycles. The flakes observed in Fig. S8a-c are related to the formation of $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$. The increasing peak intensity of $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ during long cycling is consistent with the evolution observed in the SEM images.

Table S1. EIS fitting results of the Zn-MnO_2 batteries with free-standing Zn anode or zinc foil anode.

Samples	$R_S(\Omega)$	$R_{ct}(\Omega)$
free-standing Zn anode	3.412	6.576
zinc foil anode	3.885	44.26

Table S2. BET data of the free-standing Zn anode (ratio 88:4:8 and 80:10:10).

Sample	BET surface area ($m^2\ g^{-1}$)
free-standing Zn anode (88:4:8)	10.407
free-standing Zn anode (80:10:10)	10.083

Table S3. Comparison of Zn-MnO_2 batteries based on free-standing Zn anode with ZIBs based on other composite Zn anode in terms of electrochemical performance.

Anode	Cathode	Current collector	Rate performance	Cycling performance	Refs.
Free-standing Zn anode	MnO_2	none	318.5 mAh g^{-1} at 0.3 A g^{-1} 138.0 mAh g^{-1} at 3 A g^{-1}	65% after 1000 cycles at 3 A g^{-1}	This work
flexible Zn/stainless steel mesh composite anode	Layer-expanded $V_2O_5·2.2H_2O$	stainless steel	450 mAh g^{-1} at 0.1 A g^{-1} 222 mAh g^{-1} at 10 A g^{-1}	85% after 3000 cycles at 5 A g^{-1}	1
Zn@carbon fibers anode	MnO_2	carbon fibers	248.2 mAh g^{-1} at 0.3 A g^{-1} 119.3 mAh g^{-1} at 1.5 A g^{-1}	86.8% after 140 cycles at 0.3 A g^{-1}	2
active carbon-modified Zn anode	MnO_2	stainless steel	none	85.6% after 80 cycles at 0.2 A g^{-1}	3
Zn/CNT anode	$LiMn_2O_4$	black paper	none	~46% after 80 cycles at 0.24 A g^{-1}	4
Zn/active carbon anode	$LiMn_2O_4$	black paper	none	40% after 210 cycles at 0.24 A g^{-1}	4
Zn/acetylene black anode	$LiMn_2O_4$	black paper	none	~63% after 80 cycles at 0.24 A g^{-1}	4
Zn/rGO anode	Ag_2O/rGO	Cu tape	none	~65% after 160 cycles at 42 mA g^{-1}	5

Reference

1. J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas Jr, J. Ma, W. Fang and Y. J. N. E. Zheng, *Nano Energy*, 2019, **62**, 94-102.
2. W. Dong, J.-L. Shi, T.-S. Wang, Y.-X. Yin, C.-R. Wang and Y.-G. J. R. a. Guo, *RSC advances*, 2018, **8**, 19157-19163.
3. H. Li, C. Xu, C. Han, Y. Chen, C. Wei, B. Li and F. J. J. o. t. E. S. Kang, *J. Electrochem. Soc.*, 2015, **162**, A1439.
4. H. Tao, X. Tong, L. Gan, S. Zhang, X. Zhang, X. J. J. o. A. Liu and Compounds, *Journal of Alloys and Compounds*, 2016, **658**, 119-124.
5. D. Ozgit, P. Hiralal, G. A. J. A. a. m. Amaratunga and interfaces, *ACS Appl. Mater. Interfaces*, 2014, **6**, 20752-20757.