

Electronic Supplementary Information

Unveiling the correlation between the thickness and uniformity of hydroxyethyl cellulose film and its protective efficiency on zinc electrode

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Reasons for the selection of HEC

In this study, we chose hydroxyethyl cellulose (HEC) with moderate molecular weight to construct the solid electrolyte layer (ASEI) for zinc metal electrodes with the following concerns: As a modified cellulose, HEC exhibits better dispensability in aqueous solutions compared to natural cellulose, making it suitable for preparing thin films from aqueous solutions. HEC contains abundant hydroxyl and ether groups, resulting in its solution having excellent viscosity. These characteristics enhance the adhesion between HEC film and zinc surface, and effectively inhibit the dispersion of HEC in aqueous electrolytes. Based on these reasons, the HEC Natrosol 250HBR (Ashland Company) was used in this work. It has good quality to ensure the repeatability of our results. The molecular weight of Natrosol 250HBR is about 1000000, allowing it to have a good solution processing capability in aqueous solution. At the same time, such a molecular weight can avoid the re-dispersion of ASEI in the aqueous electrolyte.

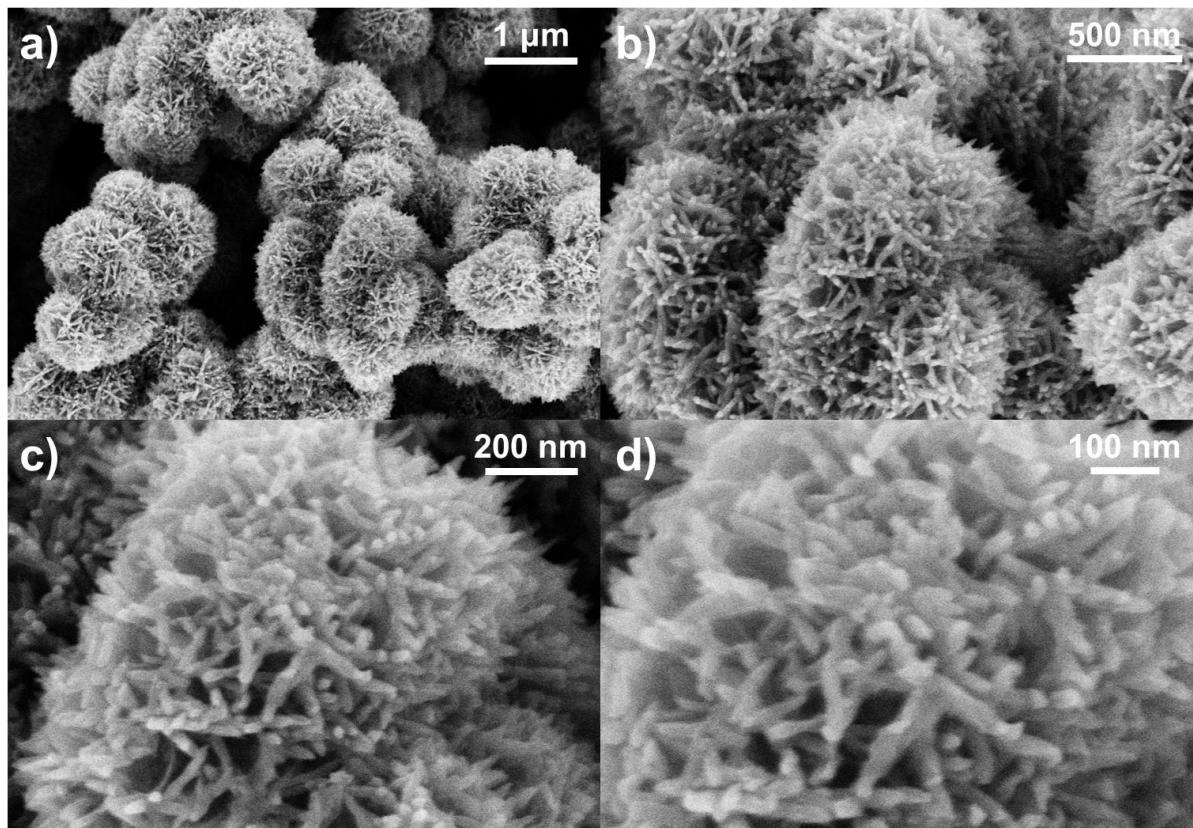


Figure S1. SEM images of α -MnO₂ at different scales.

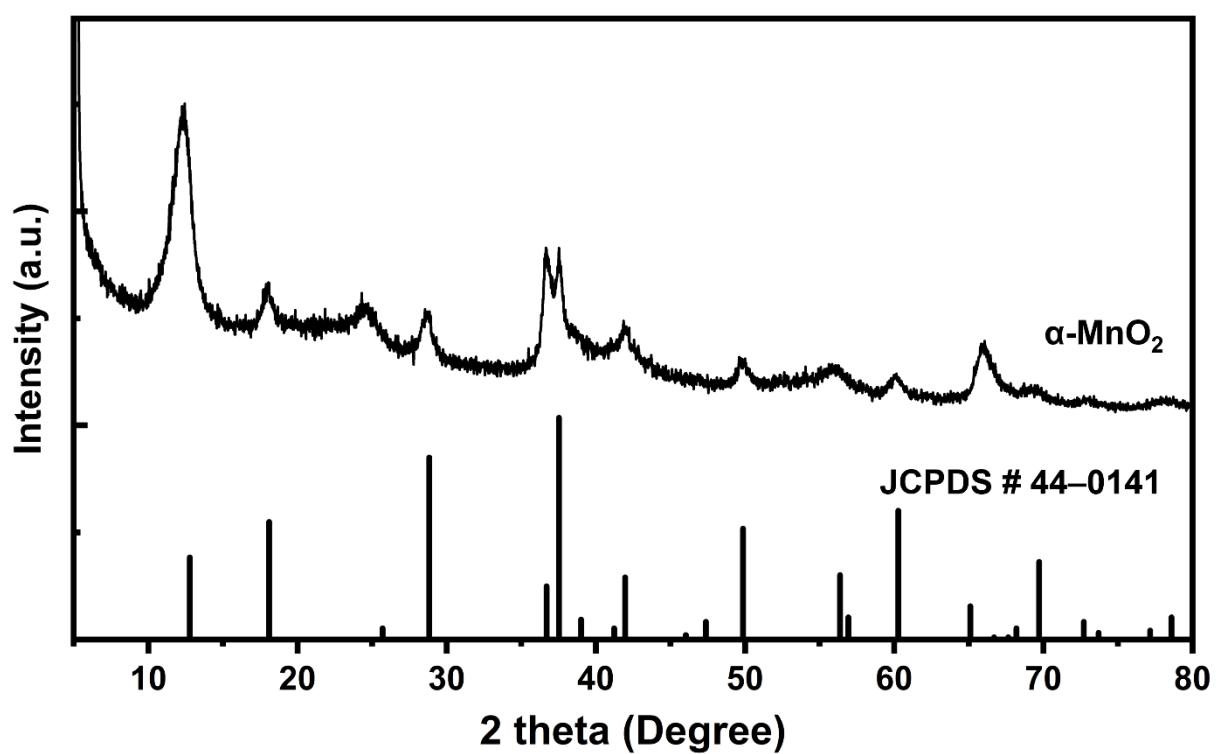


Figure S2. XRD patterns of α -MnO₂ in this work.

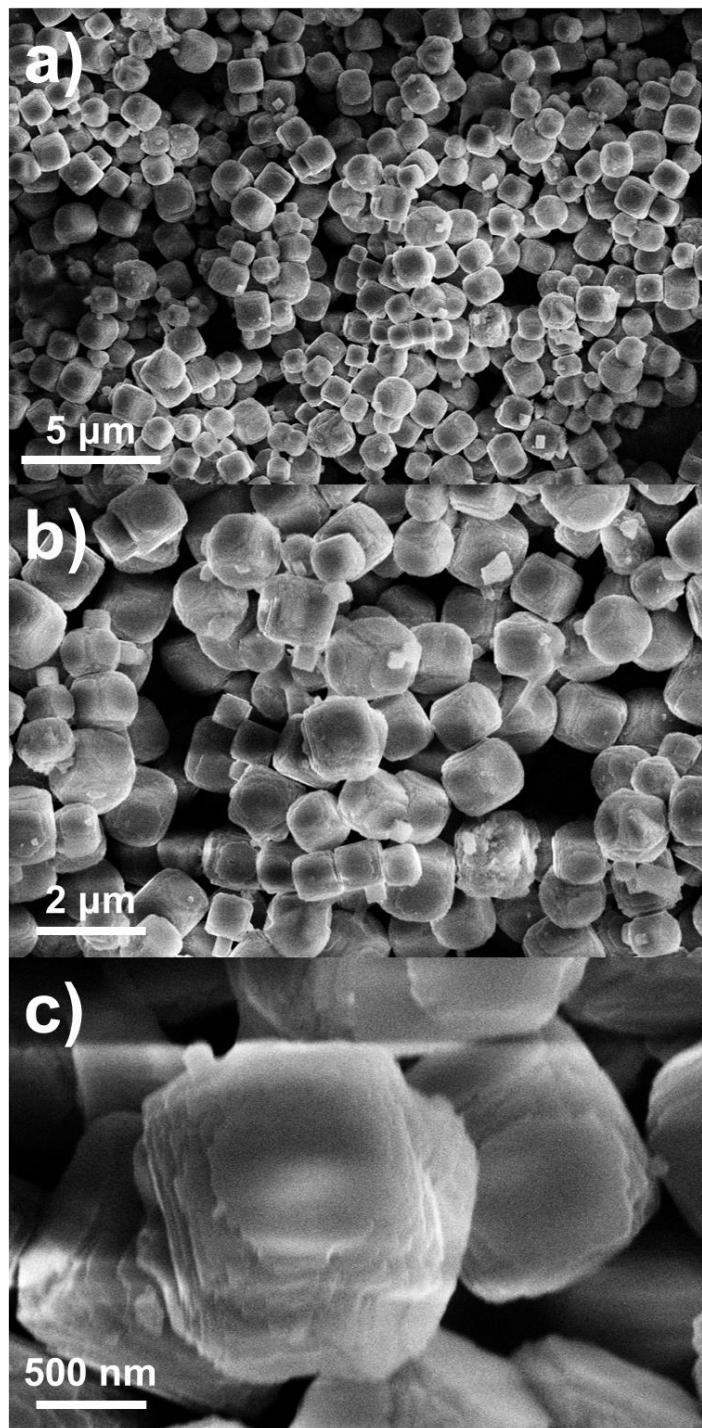


Figure S3. SEM images of PBAs at different scales.

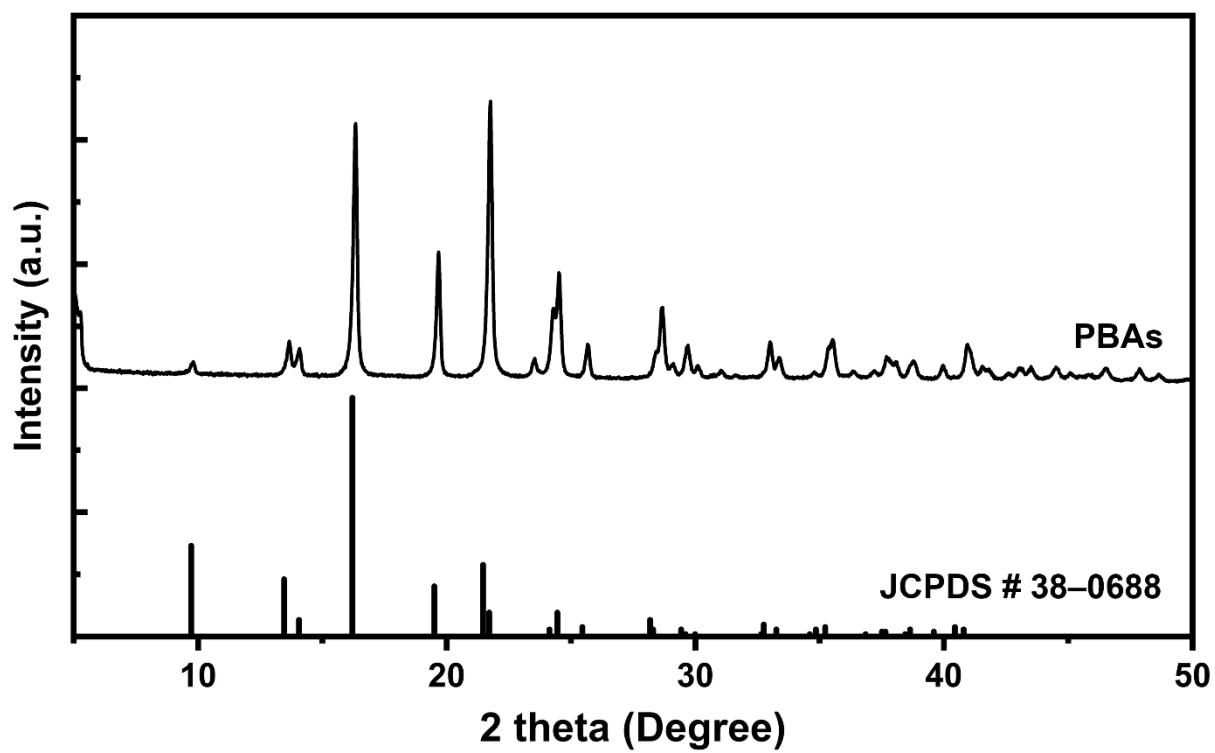


Figure S4. The XRD patterns of PBAs.

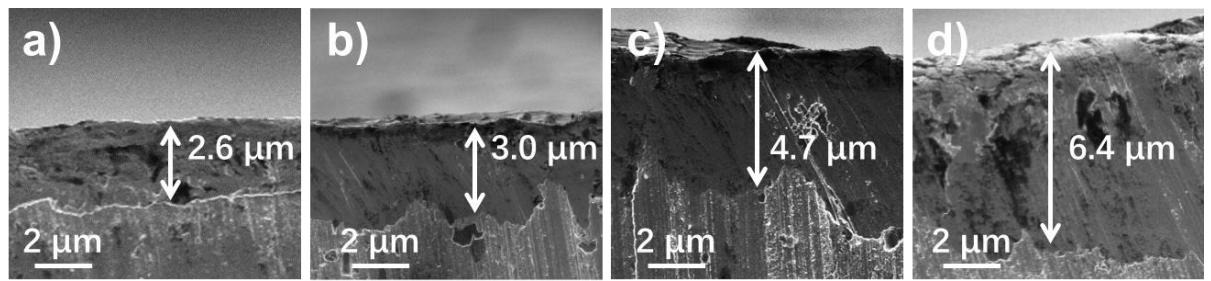


Figure S5. Cross-sectional SEM images of a) 0.5% HEC@Zn, b) 1.0% HEC@Zn, c) 1.5% HEC@Zn, and d) 2.0% HEC@Zn.

Table S1. The thickness of the HEC film on Zn foil

Sample	Thickness (μm)	Concentration of the HEC solution (wt.%)
0.5% HEC@Zn	2.7	0.5
1.0% HEC@Zn	3.1	1.0
1.5% HEC@Zn	4.5	1.5
2.0% HEC@Zn	6.0	2.0
2.5% HEC@Zn	15.0	2.5

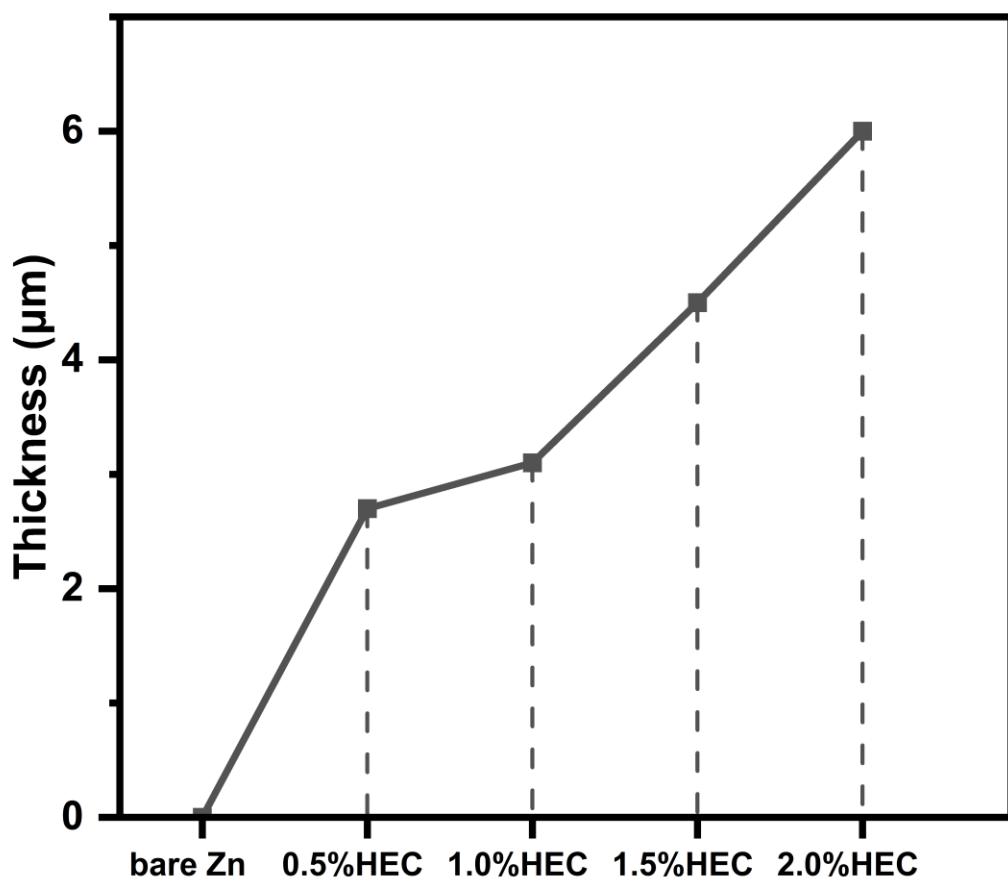


Figure S6. Thicknesses of the HEC films on Zn foils

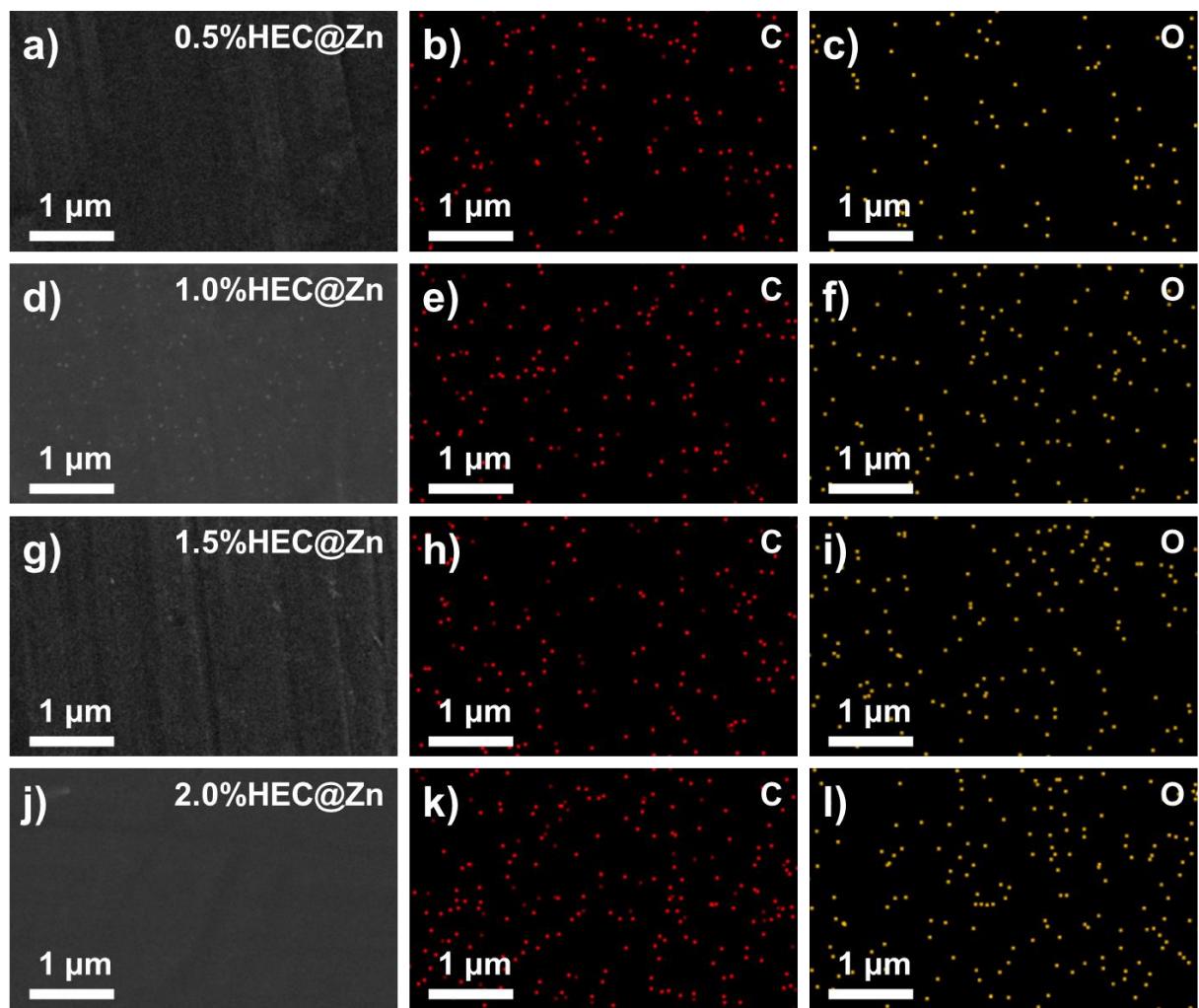


Figure S7. EDS mapping images of (a-c) 0.5% HEC@Zn, (d-f) 1.0% HEC@Zn, (g-i) 1.5% HEC@Zn, and (j-l) 2.0% HEC@Zn.

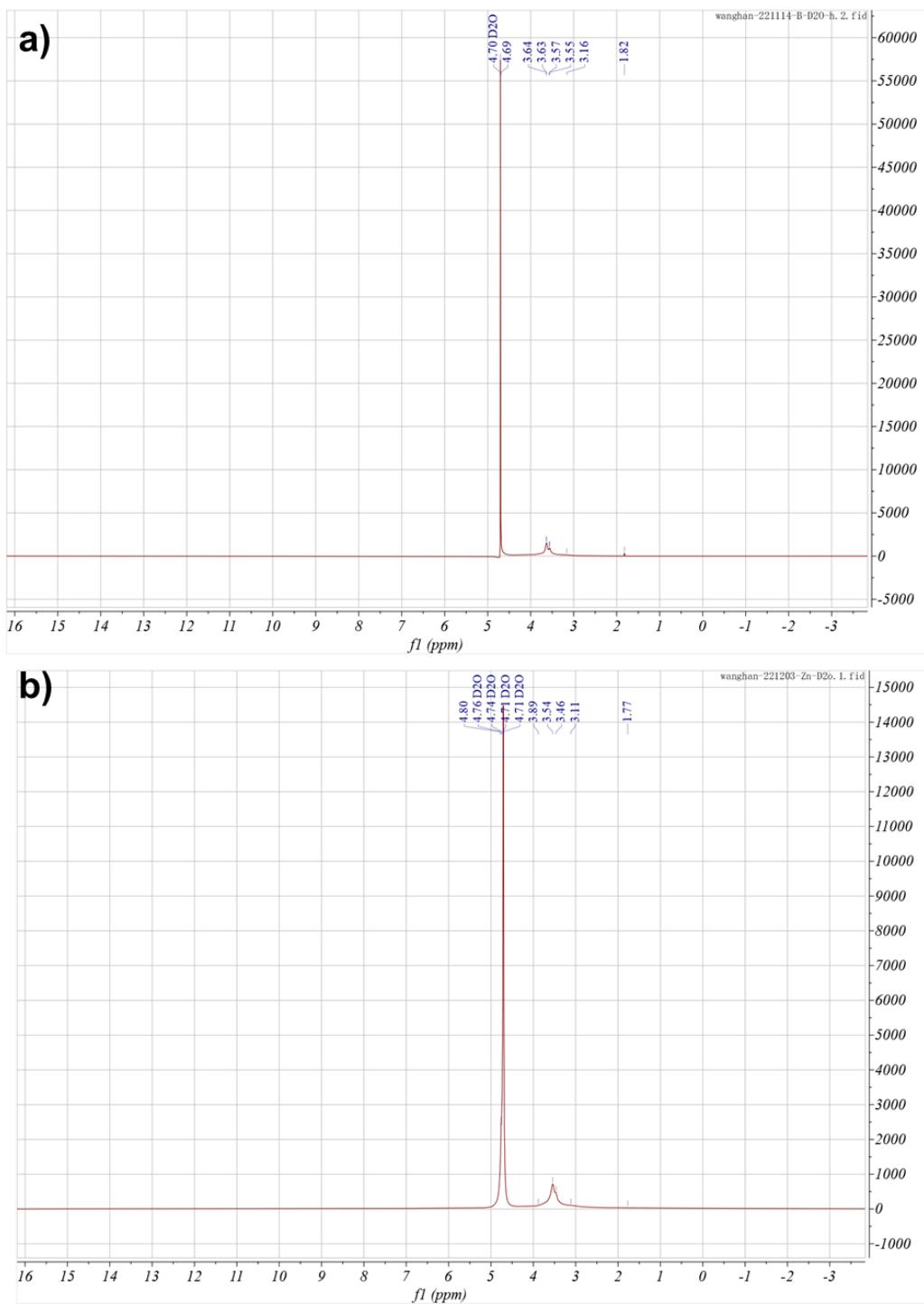


Figure S8. ^1H -NMR spectra of 2.0 wt.% HEC aqueous solution (a) before and (b) after the addition of ZnSO_4 .

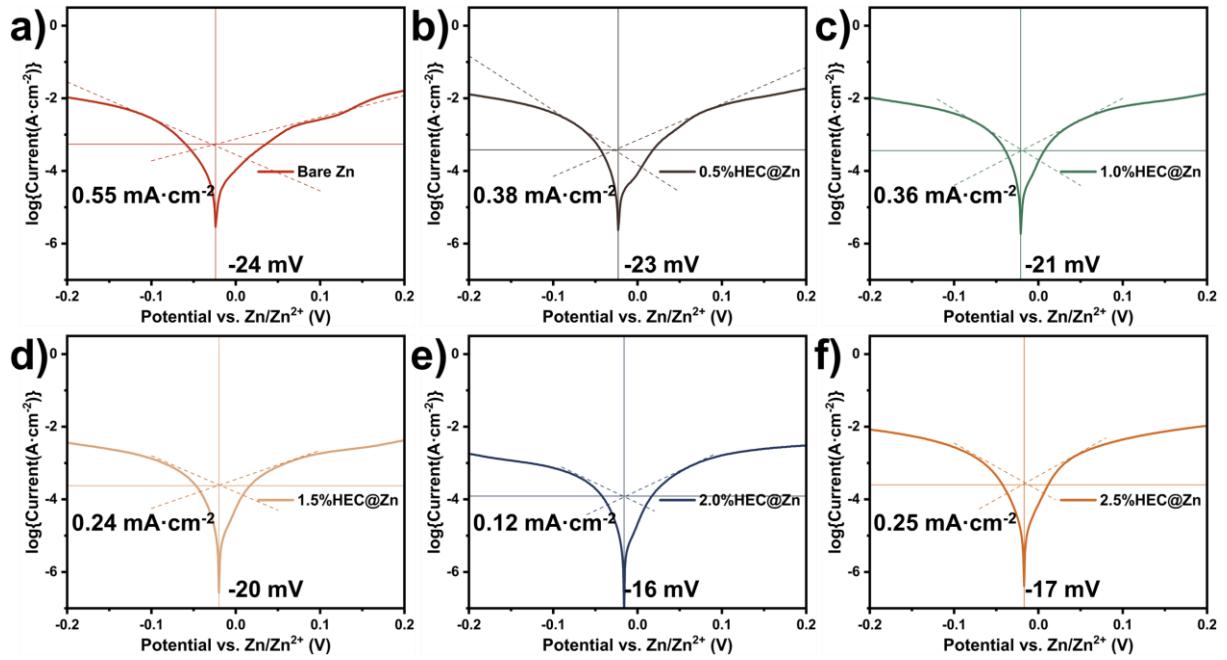


Figure S9. Hydrogen evolution current density for the symmetric cells with (a) bare Zn, (b) 0.5% HEC@Zn, (c) 1.0% HEC@Zn, (d) 1.5% HEC@Zn, (e) 2.0% HEC@Zn, and (f) 2.5% HEC@Zn as the electrodes.

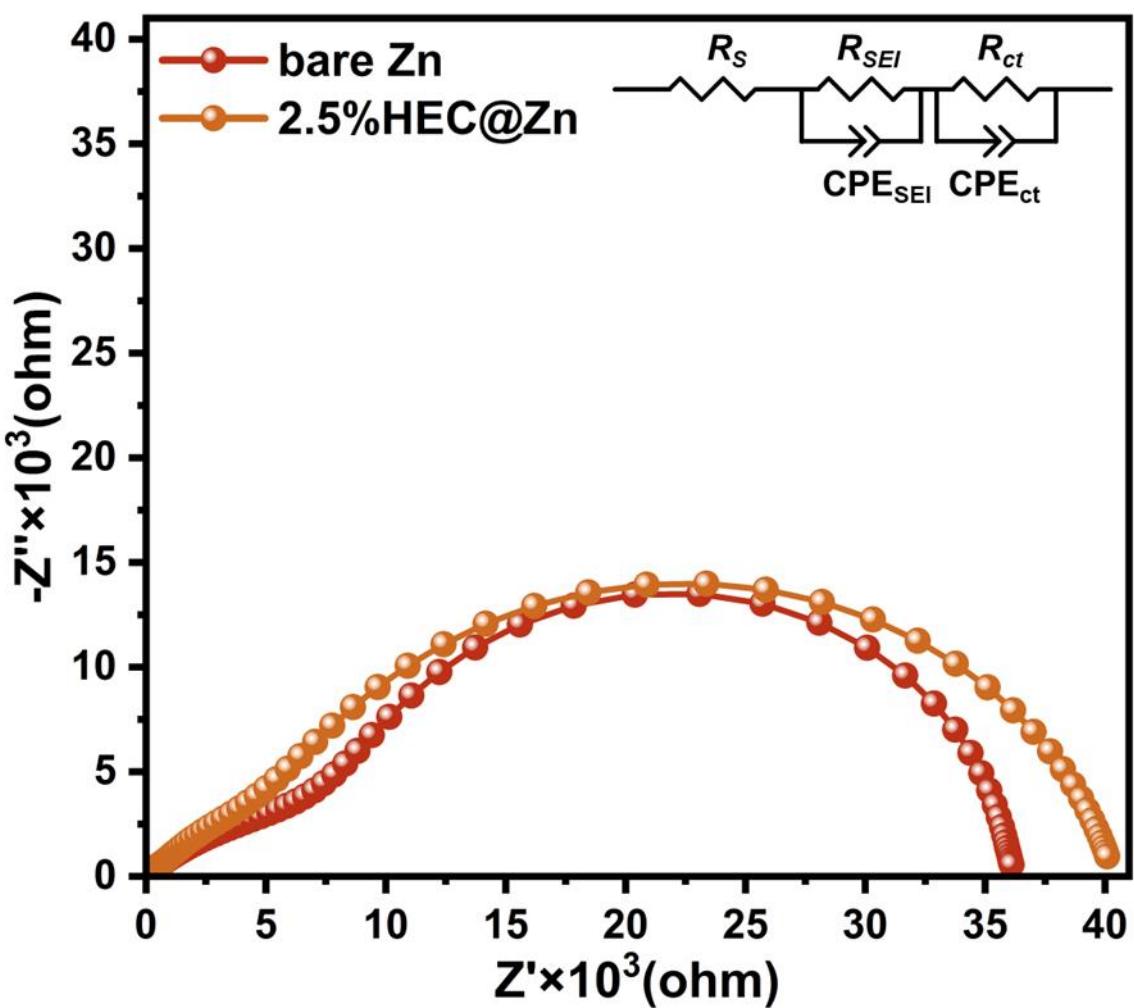


Figure S10. Nyquist plots of the symmetric cells with bare Zn and 2.5% HEC@Zn as electrodes (Inset: the equivalent circuit of the symmetric cells).

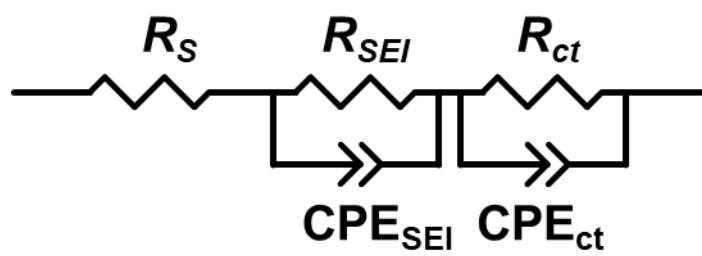


Figure S11. The equivalent circuit of the symmetric cells fitted.

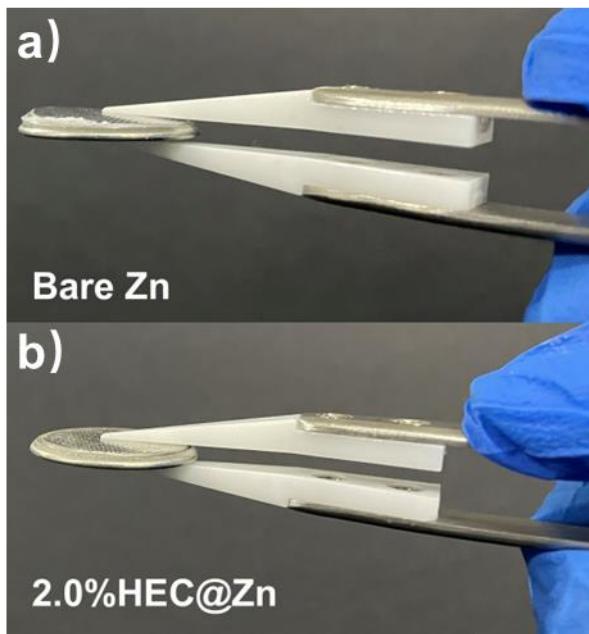


Figure S12. Digital images of the symmetric cells with (a) bare Zn and (b) 2.0% HEC@Zn as the electrodes after the cycling tests.

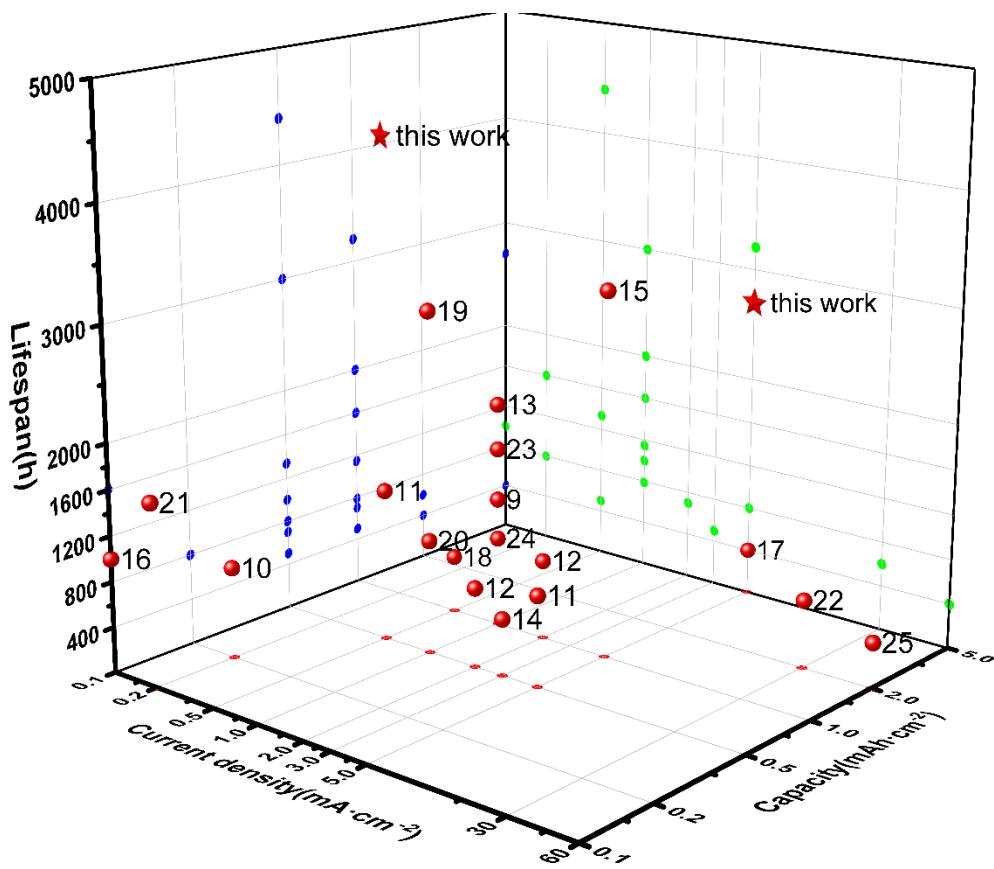


Figure S13. Comparison of the cyclic stabilities of the symmetric cells in this work with the recently reported Zn electrode protection strategies.

Table S2 Comparison of the performances of the symmetrical cells in this work with the recent reports.

Sample name	Current density (mA cm ⁻²)	Capacity (mAh cm ⁻²)	Lifespan (h)	Ref.
PANZ@Zn	1	1	1145	1
MZn-60	0.2	0.2	800	2
68E	0.5	0.5	1334	3
	5	0.5	800	
Zn@Zn-Mont	2	0.5	700	4
	2	1	700	
Zn-TSA@Zn	1	1	2000	5
MOF-PVDF-Coated Zn	3	0.5	500	6
MOF-CeO ₂ @Zn	5	1	3200	7
Zn@NGDY	0.1	0.1	1000	8
PSN-Zn	5	5	400	9
Zn@ZnF ₂	0.5	1	500	10
PPZ@Zn	1	0.5	3000	11
AA/DMSO@Zn	1	0.5	1000	12
MB@Zn	0.2	0.1	1600	13
ZnTA@Zn	30	2	600	14
SEI-Zn	1	1	1600	15
LM-Zn	1	1	788	16
Zn@ZBO	60	2	400	17
2.0% HEC@Zn	5	5	2700	This work

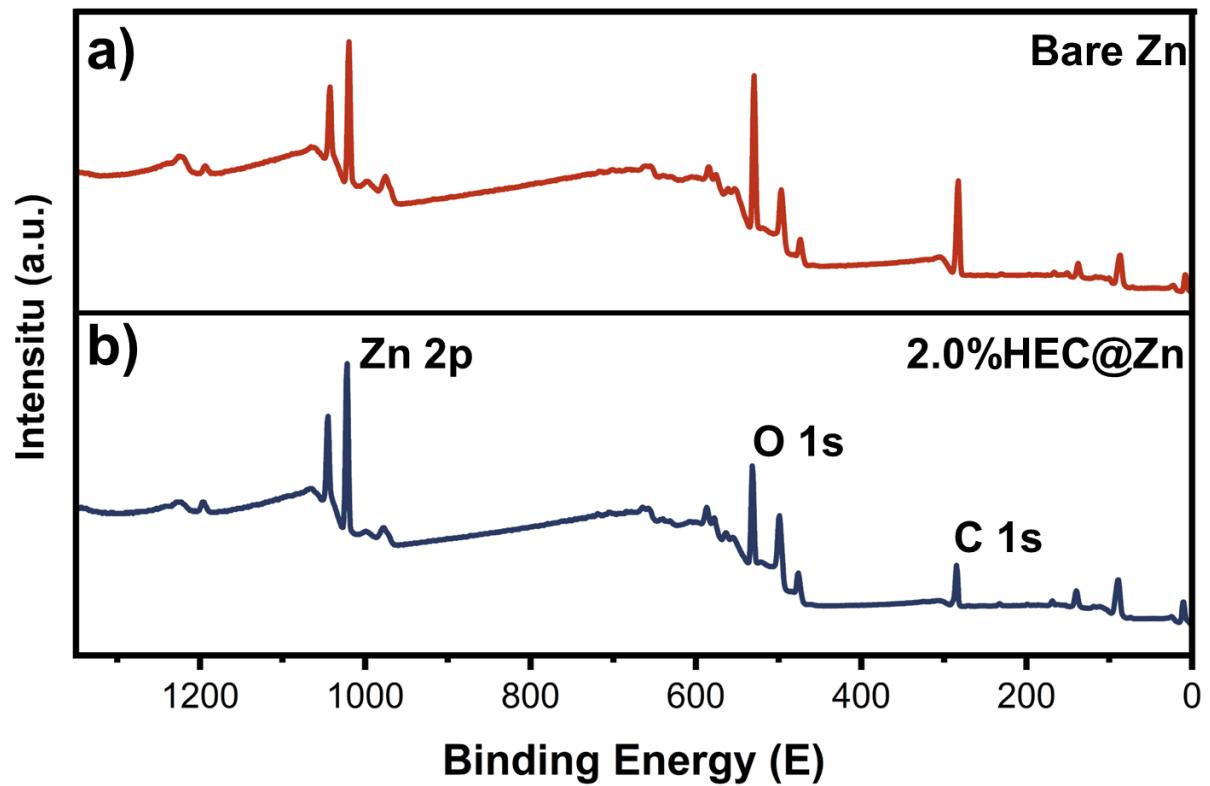


Figure S14. The full scale XPS spectra of bare Zn foil (a) and 2.0% HEC@Zn (b) after plating/stripping.

Table S3 the information for the peak at each binding energy of bare Zn and 2.0%HEC@Zn.

		bare Zn	2.0% HEC@Zn		
C1s	binding energy(eV)	284.7	288.9	284.8	286.3
	Area (CPS*eV)	156191.8	11552.8	113045.8	91498.8
O1s	peak identify	C-C/C-H	C=O	C-C/C-H	C-O
	binding energy(eV)	531.7		531.6	532.5
Zn2p	Area (CPS*eV)	391519.9		131532.5	212671.4
	peak identify	ZnO/Zn(OH) ₂		ZnO/Zn(OH) ₂	Organic O
	binding energy(eV)	1022.3	1045.2	1022	1045.1
	Area (CPS*eV)	807233.7	409814.7	440388.8	256541.7
	peak identify	Zn 2p3/2	Zn 2p1/2	Zn 2p3/2	Zn 2p1/2

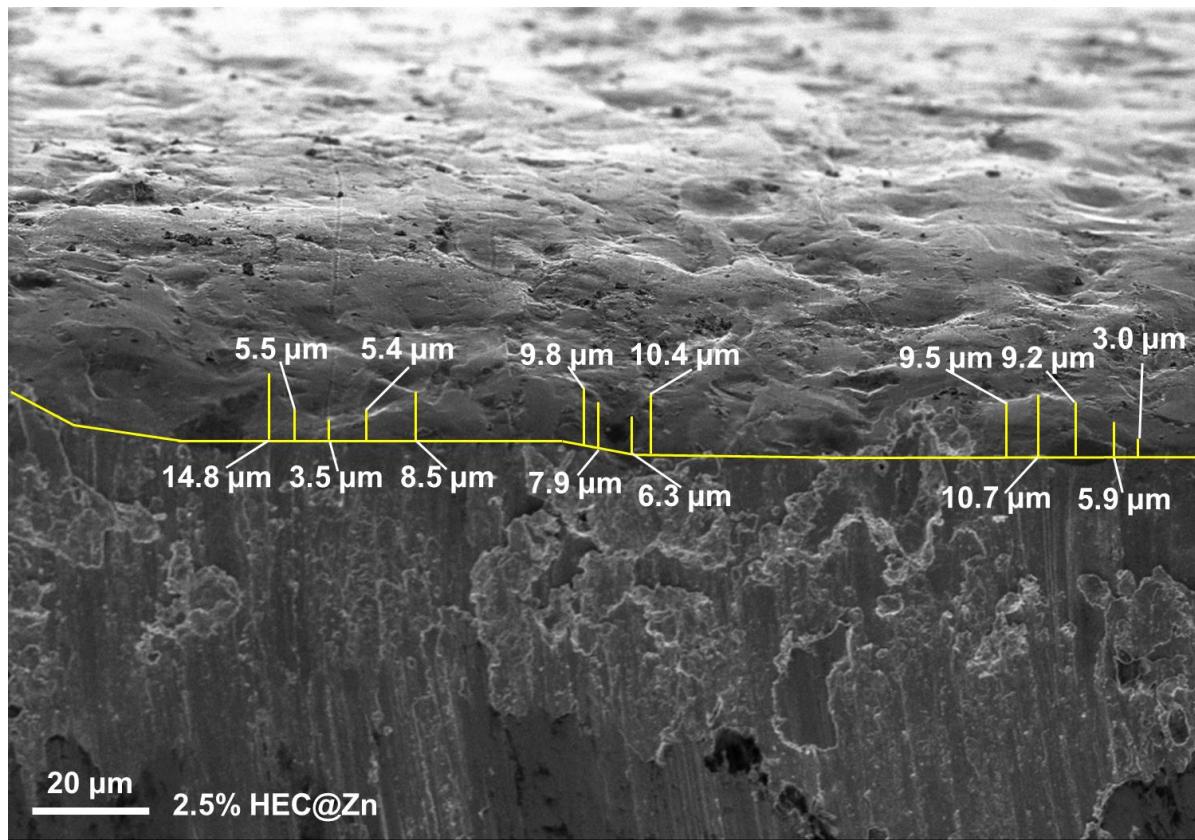


Figure S15. SEM image of 2.5% HEC@Zn. The region below the yellow line is Zn, while the region above the yellow line is the HEC coating. In the image, the thickness changes of uneven several areas on the surface is measured to illustrate the thinnest thickness of 2.5% HEC@Zn.

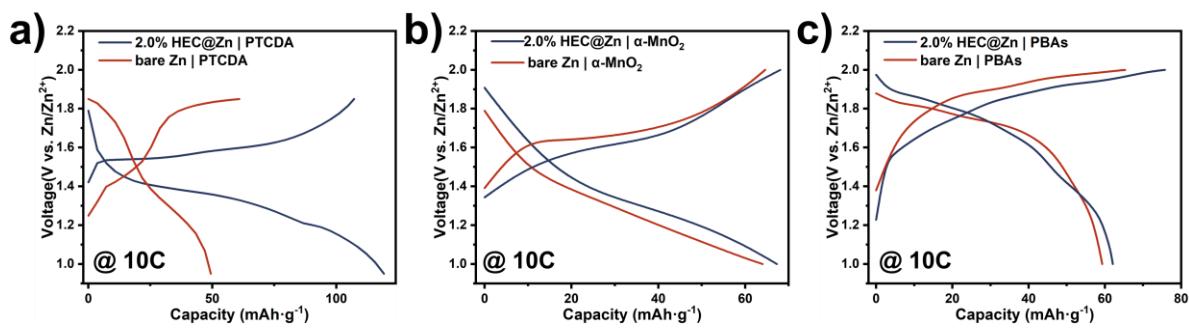


Figure S16. GCD curves of the cells consist of 2.0% HEC@Zn or bare Zn and PTCDA (a), α -MnO₂ (b) or PBAs (c).

Table S4 Comparison of the performances of the AZIBs in this work with the recent reports.

Electrode	Cathode	Current density (A g ⁻¹)	Charge/discharge rate (C)	Lifespan (cycles)	Ref.
68E	ZnVO	0.5	\	500	3
Zn@Zn-Mont	MnO ₂	\	2	1000	4
Zn-TSA@Zn	V ₂ O ₅	2	\	1500	5
PVB@Zn	MnO ₂	\	5	1500	18
ILG-Zn	MnO ₂	\	2	600	19
FCOF-Zn	MnO ₂	\	3	1000	9
AEC-Zn	MnO ₂	\	2	300	20
SEI	MnO ₂	\	10	700	21
PDMS/TiO _{2-x}	MnO ₂	\	1	400	22
PSN-Zn	MnO ₂	0.3	\	100	23
PANZ-Zn	MnVO	0.5	\	1050	1
Zn@ZnF2	MnO ₂	0.5	\	250	10
ZCS-Zn	MnO ₂	5	\	600	24
Zn@SIP	MnO ₂	2	\	1200	25
AA/DMSO@Zn	NaVO	2	\	2000	12
MB@Zn	MnO ₂	0.5	\	200	13
SEI-Zn	MVO	5	\	800	15
LM-Zn	MnO ₂	1	\	1000	16
Zn@ZBO	MnO ₂	\	10	2000	17
	α -MnO ₂	3	10	10000	
2.0% HEC@Zn	PTCDA	1.3	10	10000	This work
	PBAs	1.7	10	1300	

References

1. P. Chen, X. Yuan, Y. Xia, Y. Zhang, L. Fu, L. Liu, N. Yu, Q. Huang, B. Wang, X. Hu, Y. Wu and T. van Ree, *Adv. Sci.*, 2021, **8**, 2100309.
2. N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao and Z. Niu, *Angew. Chem.-Int. Edit.*, 2021, **60**, 2861-2865.
3. R. Qin, Y. Wang, M. Zhang, Y. Wang, S. Ding, A. Song, H. Yi, L. Yang, Y. Song, Y. Cui, J. Liu, Z. Wang, S. Li, Q. Zhao and F. Pan, *Nano Energy*, 2021, **80**, 105478.
4. L. Hong, X. Wu, C. Ma, W. Huang, Y. Zhou, K.-X. Wang and J.-S. Chen, *J. Mater. Chem. A*, 2021, **9**, 16814-16823.
5. Z. Tao, Y. Zhu, Z. Zhou, A. Wang, Y. Tan, Z. Chen, M. Yu and Y. Yang, *Small*, 2022, **18**, 2107971.
6. M. Liu, L. Yang, H. Liu, A. Amine, Q. Zhao, Y. Song, J. Yang, K. Wang and F. Pan, *ACS Appl. Mater. Interfaces*, 2019, **11**, 32046-32051.
7. P. Li, J. Ren, C. Li, J. Li, K. Zhang, T. Wu, B. Li and L. Wang, *Chem. Eng. J.*, 2023, **451**, 138769.
8. A. Naveed, H. Yang, Y. Shao, J. Yang, N. Yanna, J. Liu, S. Shi, L. Zhang, A. Ye, B. He and J. Wang, *Adv. Mater.*, 2019, **31**, 1900668.
9. Z. Zhao, R. Wang, C. Peng, W. Chen, T. Wu, B. Hu, W. Weng, Y. Yao, J. Zeng, Z. Chen, P. Liu, Y. Liu, G. Li, J. Guo, H. Lu and Z. Guo, *Nat. Commun.*, 2021, **12**, 6606.
10. Y. Yang, C. Liu, Z. Lv, H. Yang, Y. Zhang, M. Ye, L. Chen, J. Zhao and C. C. Li, *Adv. Mater.*, 2021, **33**, 2007388.
11. X. Wang, J. Meng, X. Lin, Y. Yang, S. Zhou, Y. Wang and A. Pan, *Adv. Funct. Mater.*, 2021, **31**, 2106114.
12. C. Huang, W. Deng, X. Yuan, Y. Zhou, C. Li, J. Hu, M. Zhang, J. Zhu and R. Li, *ACS Appl. Mater. Interfaces*, 2023, **15**, 2341-2350.
13. T. Huang, K. Xu, N. Jia, L. Yang, H. Liu, J. Zhu and Q. Yan, *Adv. Mater.*, 2023, **35**, 2205206.
14. P.-F. Zhang, Z. Wu, S.-J. Zhang, L.-Y. Liu, Y. Tian, Y. Dou, Z. Lin and S. Zhang, *Nano Energy*, 2022, **102**, 107721.
15. N. Wang, Y. Zhang, J. Yuan, L. Hu, M. Sun, Z. Li, X. Yao, X. Weng and C. Jia, *ACS Appl. Mater. Interfaces*, 2022, **14**, 48081-48090.
16. C. Liu, Z. Li, X. Zhang, W. Xu, W. Chen, K. Zhao, Y. Wang, S. Hong, Q. Wu, M.-C. Li and C. Mei, *Adv. Sci.*, 2022, **9**, 2202380.
17. D. Wang, H. Liu, D. Lv, C. Wang, J. Yang and Y. Qian, *Adv. Mater.*, 2023, **35**, 2207908.

18. J. Hao, X. Li, S. Zhang, F. Yang, X. Zeng, S. Zhang, G. Bo, C. Wang and Z. Guo, *Adv. Funct. Mater.*, 2020, **30**, 2001263.
19. D. Lee, H.-I. Kim, W.-Y. Kim, S.-K. Cho, K. Baek, K. Jeong, D. B. Ahn, S. Park, S. J. Kang and S.-Y. Lee, *Adv. Funct. Mater.*, 2021, **31**, 2103850.
20. R. Zhao, Y. Yang, G. Liu, R. Zhu, J. Huang, Z. Chen, Z. Gao, X. Chen and L. Qie, *Adv. Funct. Mater.*, 2021, **31**, 2001867.
21. D. Li, L. Cao, T. Deng, S. Liu and C. Wang, *Angew. Chem.-Int. Edit.*, 2021, **60**, 13035-13041.
22. Z. Guo, L. Fan, C. Zhao, A. Chen, N. Liu, Y. Zhang and N. Zhang, *Adv. Mater.*, 2022, **34**, 2105133.
23. S. Zhou, Y. Wang, H. Lu, Y. Zhang, C. Fu, I. Usman, Z. Liu, M. Feng, G. Fang, X. Cao, S. Liang and A. Pan, *Adv. Funct. Mater.*, 2021, **31**, 2104361.
24. Y. Chu, S. Zhang, S. Wu, Z. Hu, G. Cui and J. Luo, *Energy Environ. Sci.*, 2021, **14**, 3609-3620.
25. M. Zhao, J. Rong, F. Huo, Y. Lv, B. Yue, Y. Xiao, Y. Chen, G. Hou, J. Qiu and S. Chen, *Adv. Mater.*, 2022, **34**, 2203153.