

## Supporting Information

### **A Self-Preserving Pitted Texture Enables Reversible Topographic Evolution and Cycling on Zn Metal Anodes**

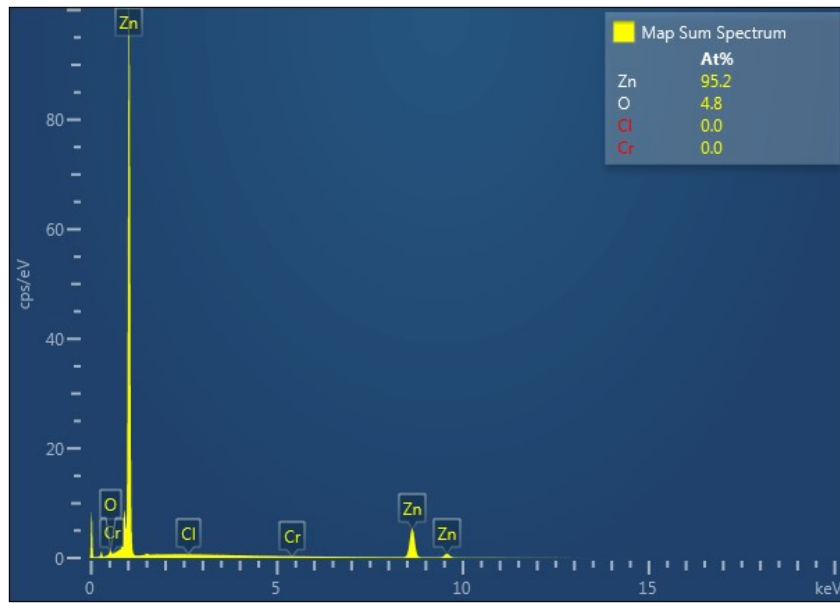
Yuanlin Xu,<sup>a</sup> Chen Wang,<sup>a</sup> Yu Shi<sup>b</sup>, Guoxing Miao,<sup>b</sup> Jing Fu<sup>a,c\*</sup> and Yunhui Huang<sup>a,d\*</sup>

<sup>a</sup> School of Materials Science and Engineering, Tongji University, Shanghai 201804, China. E-mail: jingfu@tongji.edu.cn; huangyh@hust.edu.cn

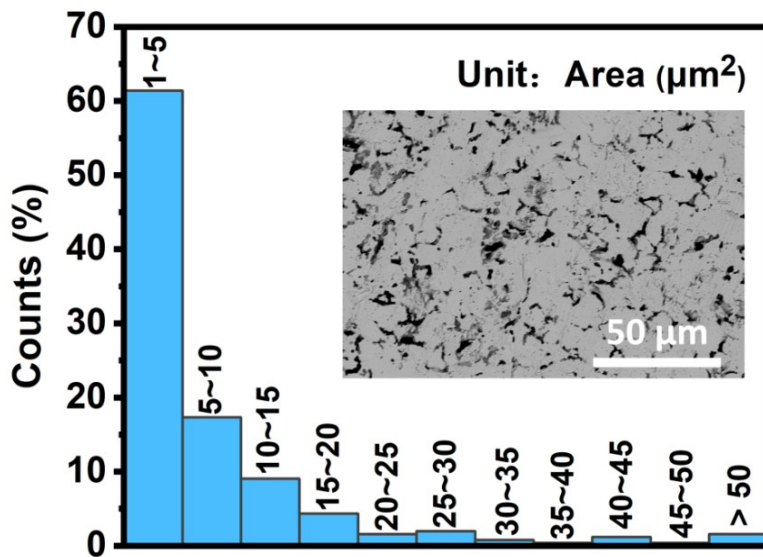
<sup>b</sup> Institute for Quantum Computing, Department of Electrical and Computer Engineering, University of Waterloo, Ontario N2L 3G1, Canada.

<sup>c</sup> Shanghai Key Laboratory of Development & Application for Metallic Functional Materials, Shanghai 201804, P. R. China.

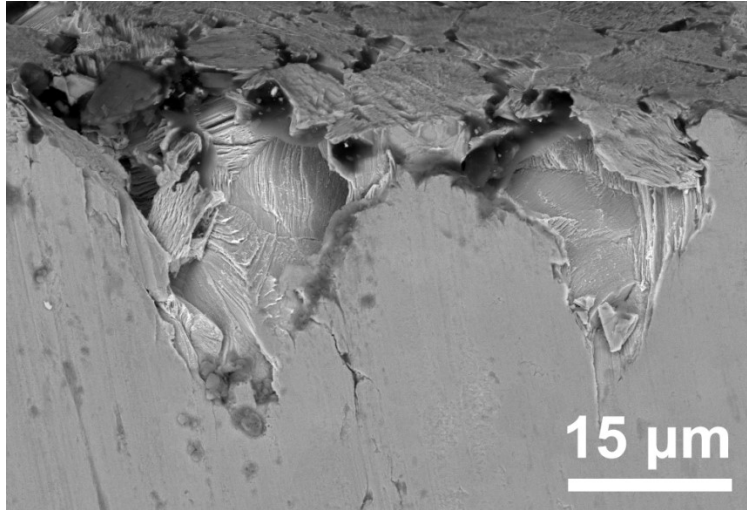
<sup>d</sup> School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China.



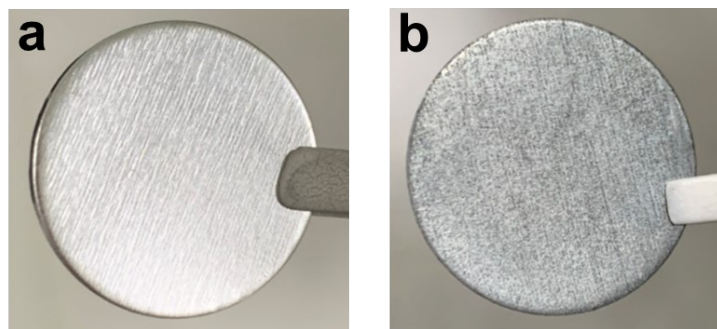
**Fig. S1** EDS spectrum of the pitted Zn.



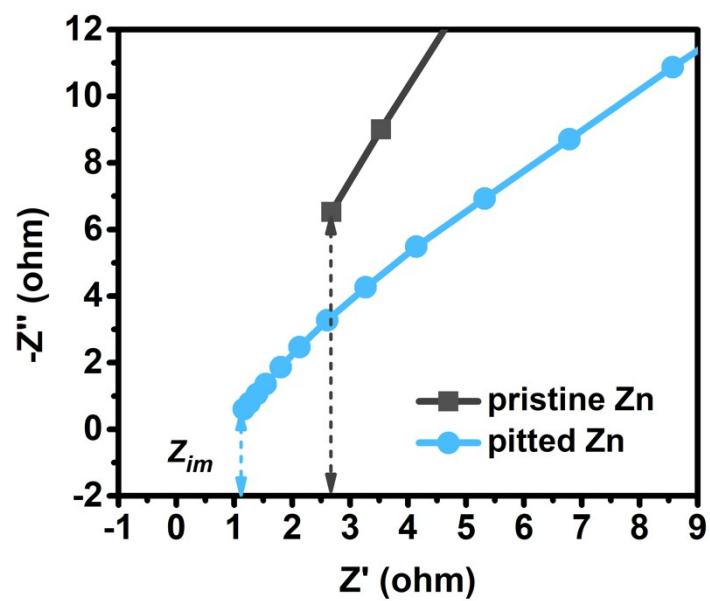
**Fig. S2** Size distribution of the micro-pits on the pitted Zn surface derived from digital image analyses based on the SEM image.



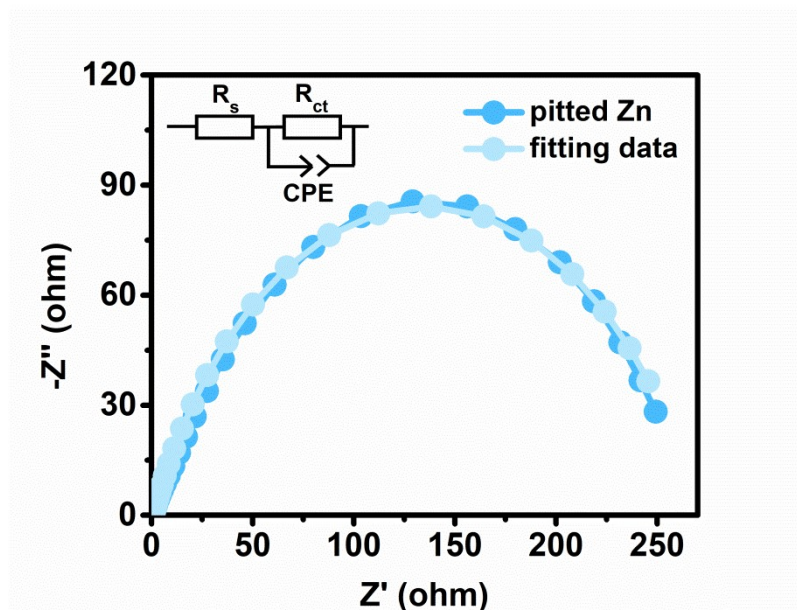
**Fig. S3** Cross-sectional SEM image of the pitted Zn.



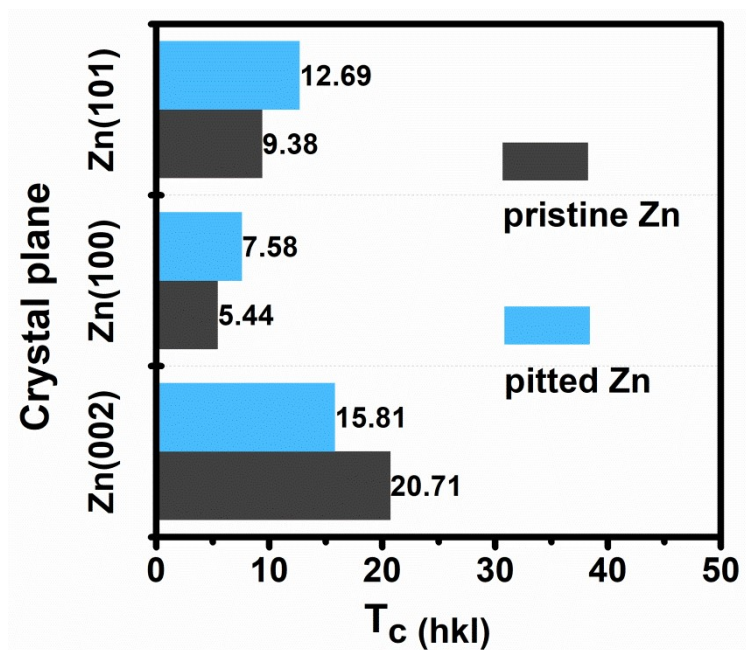
**Fig. S4** Digital images of the (a) pristine Zn and (b) pitted Zn.



**Fig. S5** Imaginary parts of the impedance from the Nyquist plots in Fig. 2h.

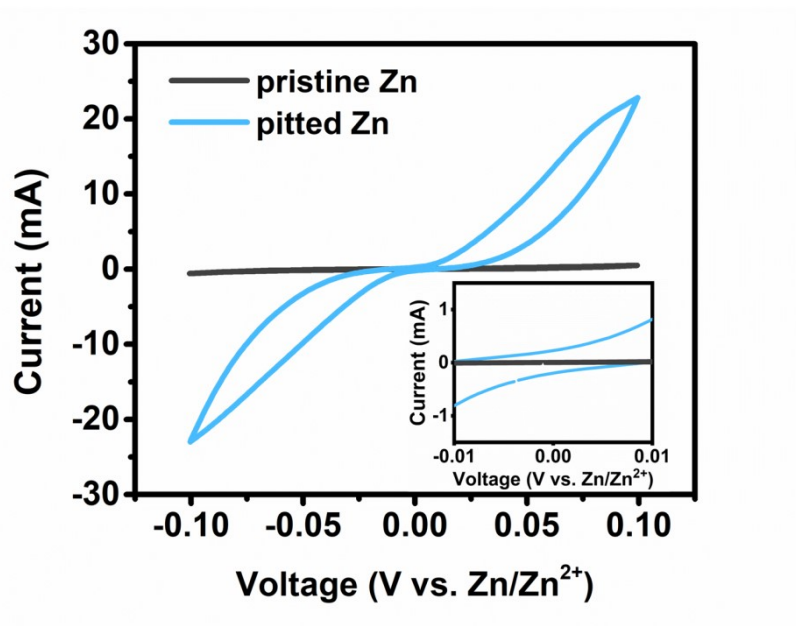


**Fig. S6** Nyquist plot and fitted plot with the corresponding equivalent circuit model of the pitted Zn.

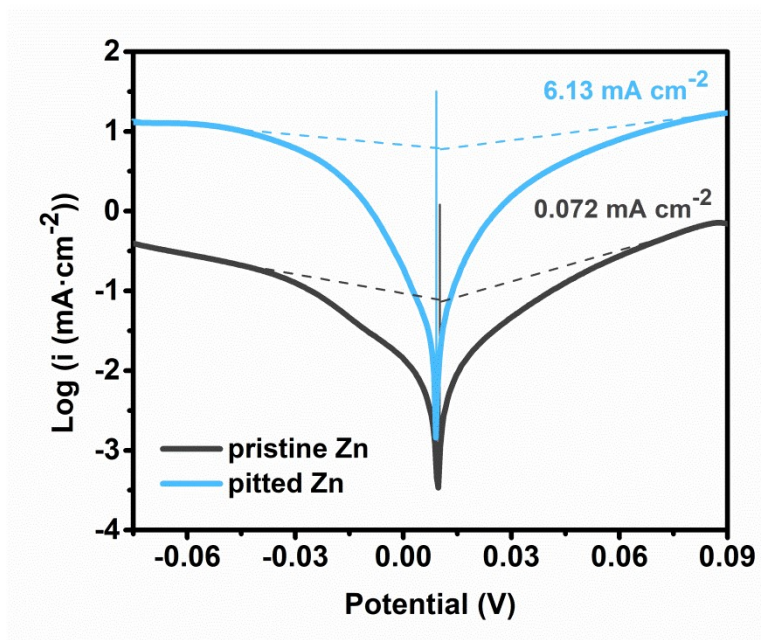


**Fig. S7**  $T_c$  value of Zn (002), Zn (100), and Zn (101) lattice planes of the pristine Zn and pitted Zn electrodes.

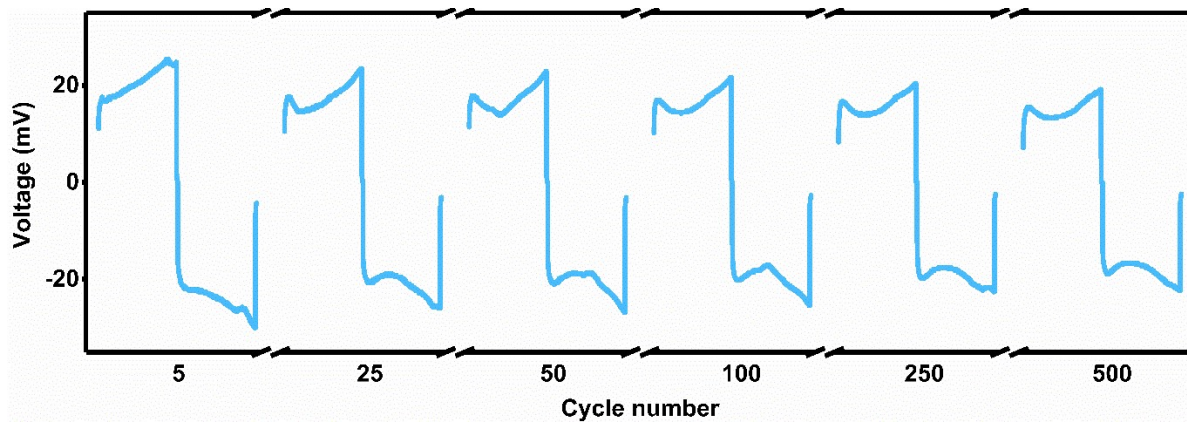




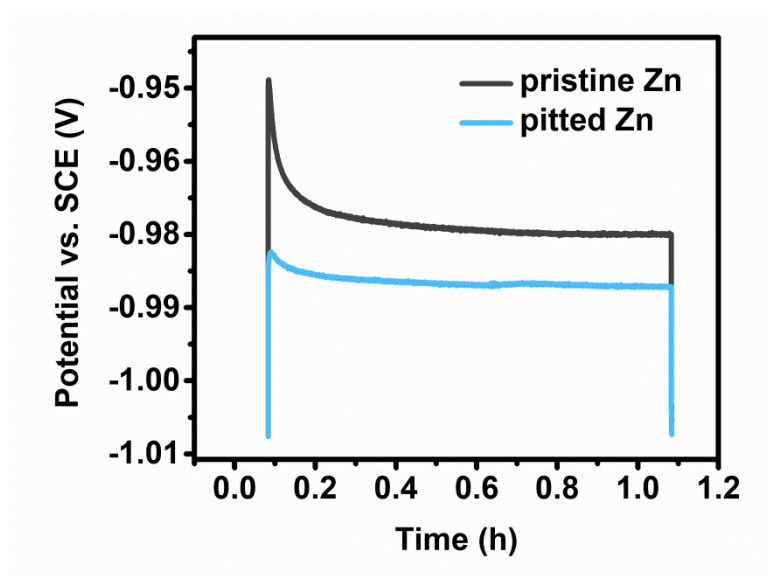
**Fig. S8** CV curves of the pristine Zn and pitted Zn symmetric cells.



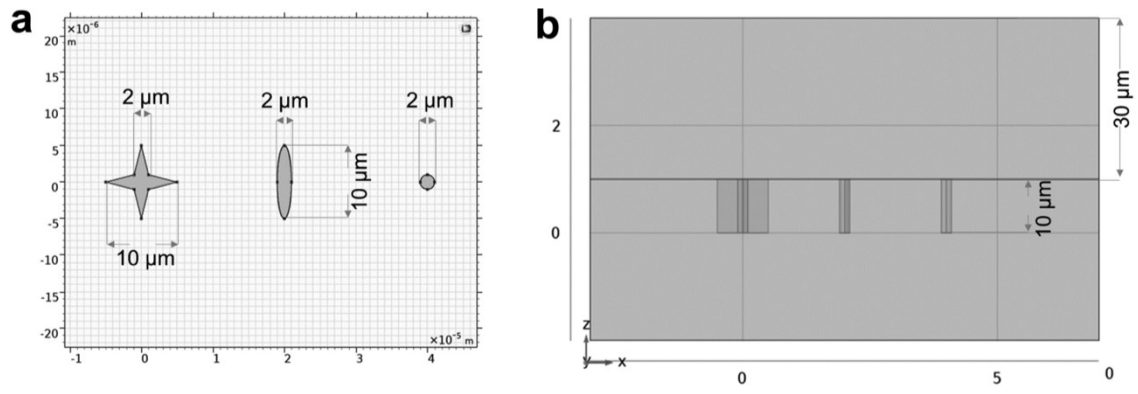
**Fig. S9** Linear polarization curves of the pristine Zn and pitted Zn symmetric cells.



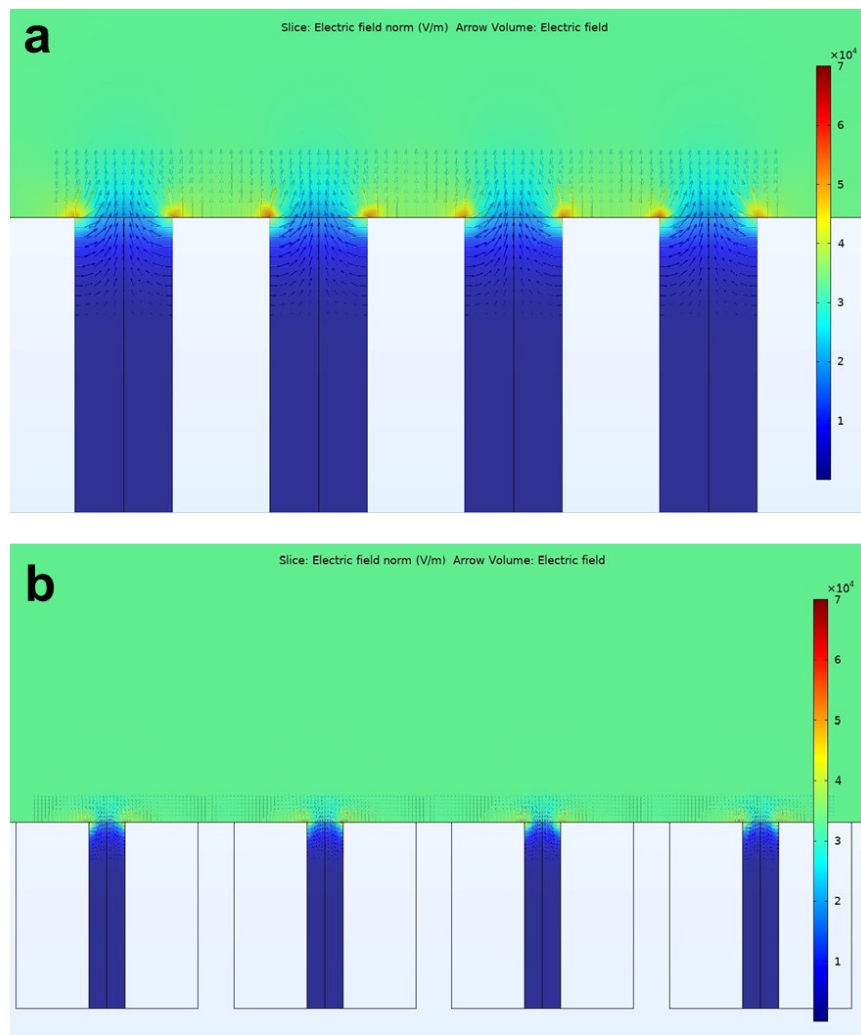
**Fig. S10** Voltage file of the pitted Zn at different cycles under  $1.0 \text{ mA cm}^{-2}/1.0 \text{ mAh cm}^{-2}$ .



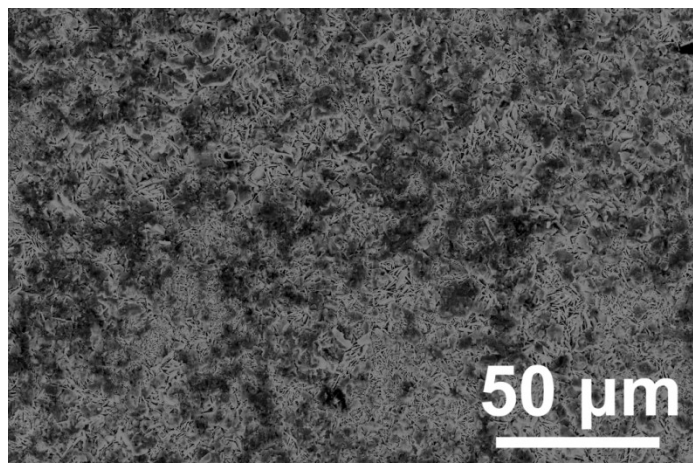
**Fig. S11** CP curve of the pitted Zn during the initial stripping process at  $1.0 \text{ mA cm}^{-2}$ .



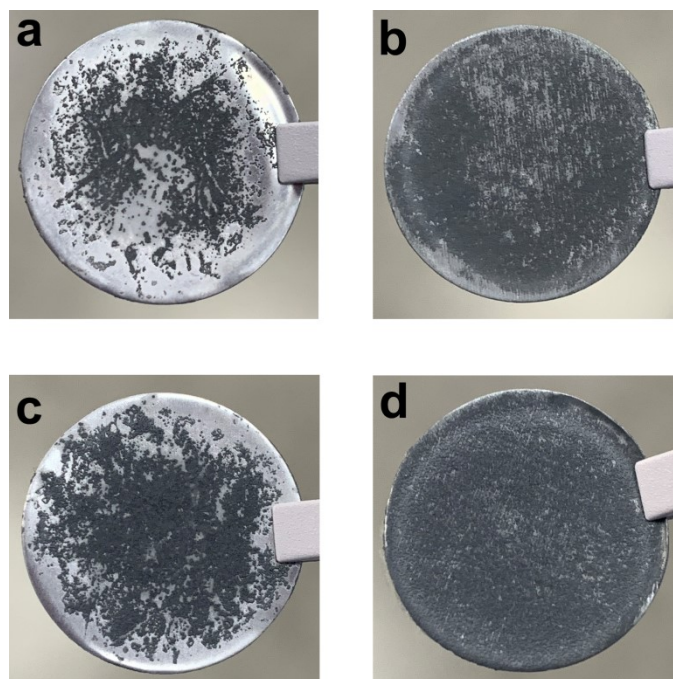
**Fig. S12** Finite element method models of the pitted Zn. (a) Top view; (b) Side view.



**Fig. S13** Electric field distribution on the pitted Zn surface. (a) Ellipse-shaped micro-pits; (b) Star-shaped micro-pits.

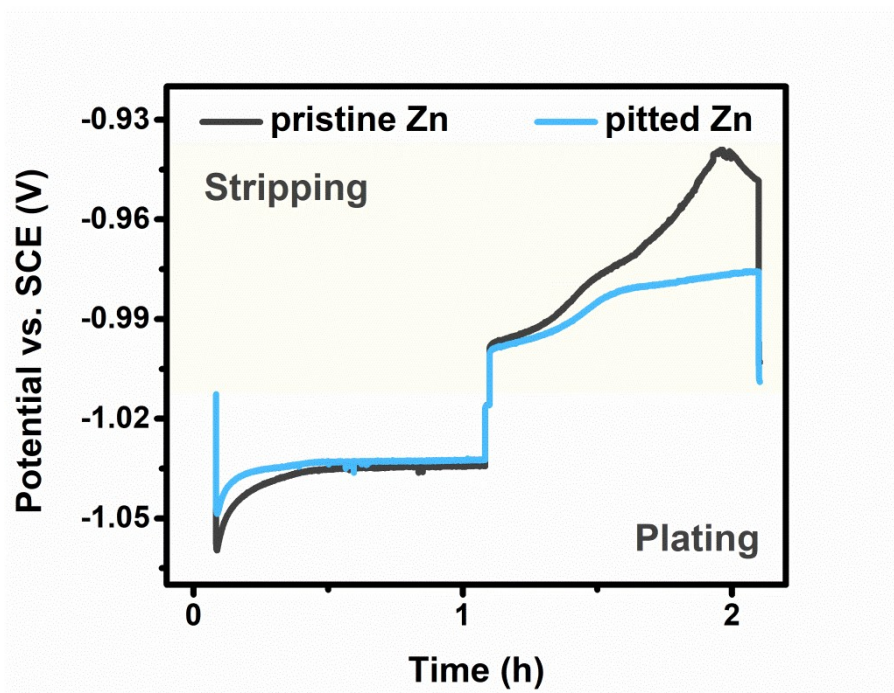


**Fig. S14** SEM image of the pitted Zn after plating at 1.0 mA cm<sup>-2</sup> for 5 h.

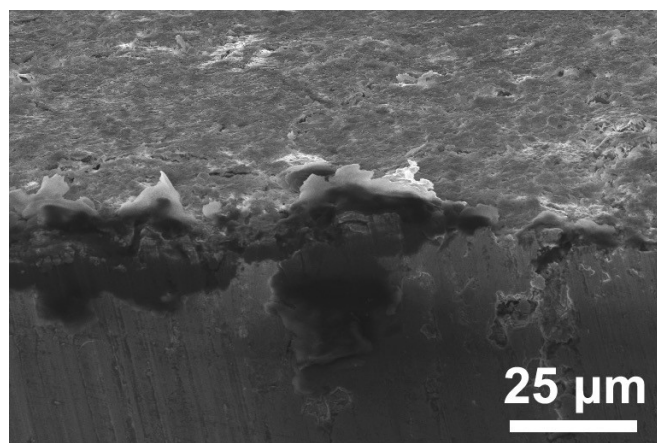


**Fig. S15** Digital photos of the (a, c) pristine Zn, (b, d) pitted Zn after deposition at  $1.0 \text{ mA cm}^{-2}$  for (a, b) 5 h and (c, d) 10 h, respectively.

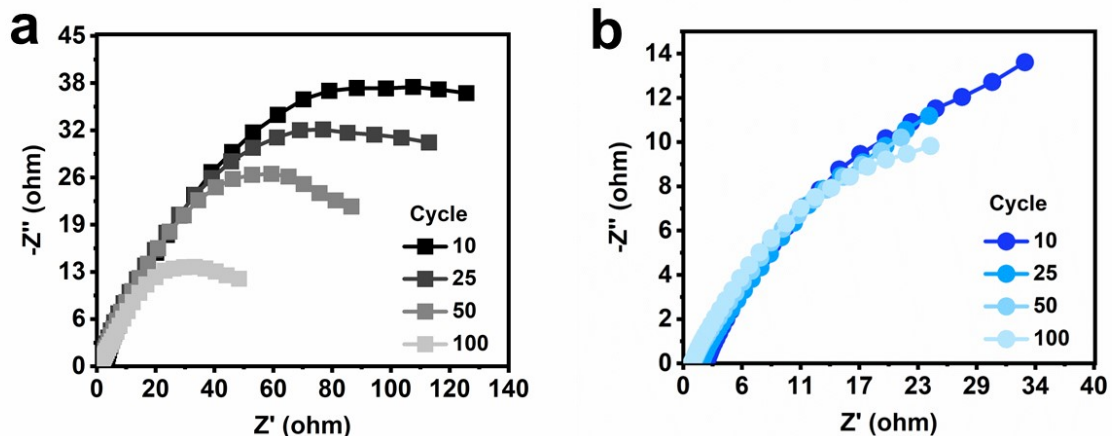




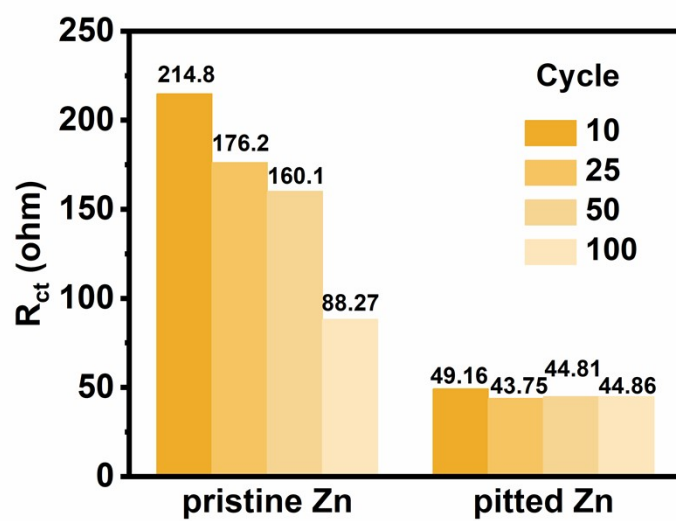
**Fig. S16** CP curve of the pristine Zn and pitted Zn electrodes during a plating-stripping process.



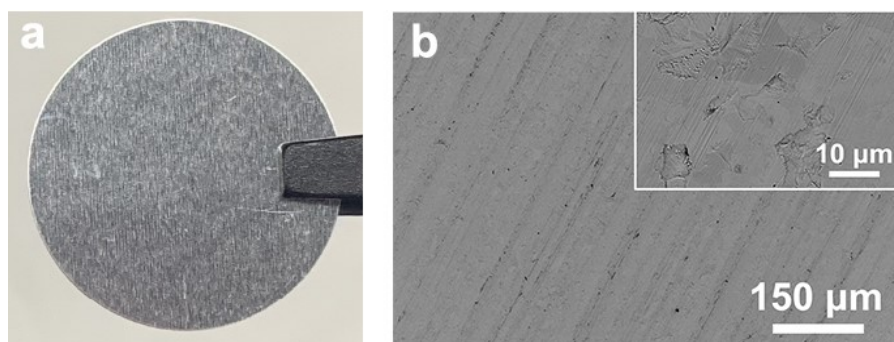
**Fig. S17** Cross-sectional SEM image of the pitted Zn after a plating-stripping process.



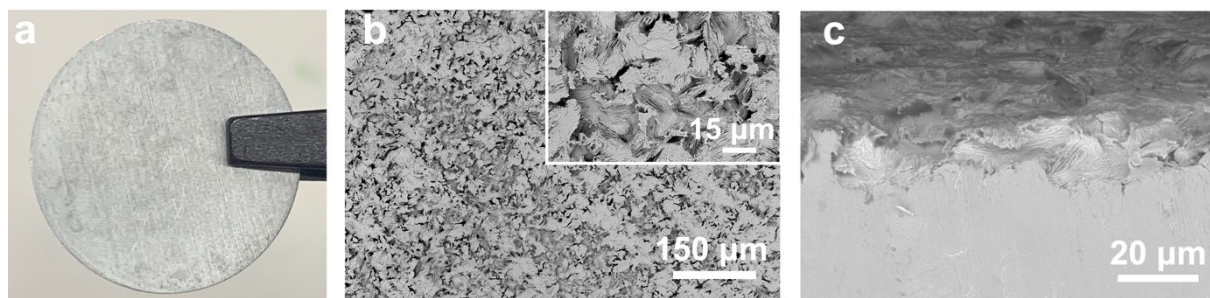
**Fig. S18** Nyquist plots of the (a) pristine Zn and (b) pitted Zn symmetric cells at different cycles under  $1.0 \text{ mA cm}^{-2}/1.0 \text{ mAh cm}^{-2}$ .



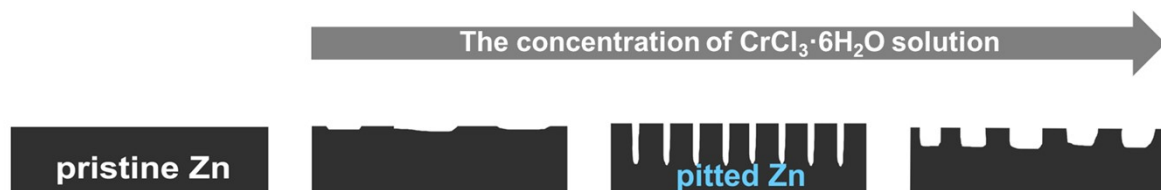
**Fig. S19**  $R_{ct}$  of the pristine Zn and pitted Zn symmetric cells at different cycles at  $1.0 \text{ mA cm}^{-2}/1.0 \text{ mAh cm}^{-2}$ .



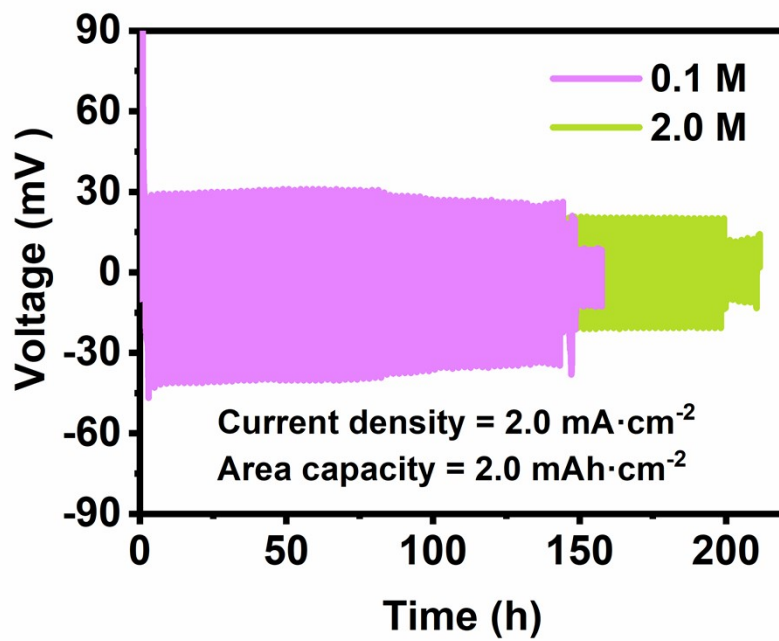
**Fig. S20** (a) Digital photo and (b) SEM image of the electrode etched by 0.1 M  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  for 5 minutes.



**Fig. S21** (a) Digital photo and (b, c) SEM image of the electrode etched by 2.0 M  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  for 5 minutes.



**Fig. S22** Schematic diagrams of the electrode surfaces etched by different concentrations of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  solution.



**Fig. S23** Cycling performance of the electrode etched by 0.1 M and 2.0 M  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$  solution.



**Table S1.** Resistance results of pristine Zn and pitted Zn symmetric cells fitting by the equivalent circuit.

Symmetric Cells	pristine Zn	pitted Zn
$R_s$ ( $\Omega$ )	0.43	0.75
$R_{ct}$ ( $\Omega$ )	991.1	270.0

**Table S2.** The intensity obtained from as-measured XRD patterns of the electrodes ( $I_{(hkl)}$ ) and the standard intensity ( $I_{0(hkl)}$ ).

Intensity		(002)	(100)	(101)	(102)	(103)	(110)	(004)
Zn	$I_0$	53.0	40	100	28	25.0	21.0	2.0
pristine Zn	$I$	264601	52431	226190	75801	97227	20655	15915
pitted Zn	$I$	157946	57176	239278	85791	109835	21235	7169

**Table S3.** Comparison in cycling performance of the pitted Zn electrode with that of Zn metal electrodes in recent publications under the same conditions ( $1.0 \text{ mA cm}^{-2}/1.0 \text{ mAh cm}^{-2}$ ).

Electrode	Lifespan (h)	Voltage hysteresis (mV)	Ref.
<b>pitted Zn</b>	<b>1000</b>	<b>41</b>	<b>This work</b>
Indium-based Zn	300	55	1
Zn In	500	240	2
Zn@ZnF <sub>2</sub>	800	71.5	3
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> MXene@Zn	300	75	4
Zn (002)	500	76	5
CNT scaffold-stabilized Zn	400	100	6
TiO <sub>2</sub> @Zn	150	114.2	7

**Table S4.**  $R_{ct}$  of pristine Zn and pitted Zn symmetric cells at different cycles fitting by the equivalent circuit.

$R_{ct}$ ( $\Omega$ )	pristine Zn	pitted Zn
Cycle 10	214.8	49.16
Cycle 25	176.2	43.75
Cycle 50	160.1	44.81
Cycle 100	88.27	44.86

## References

- 1 K. Hu, X. Guan, R. Lv, G. Li, Z. Hu, L. Ren, A. Wang, X. Liu, J. Luo, *Chem. Eng. J.* 2020, **396**, 125363.
- 2 D. Han, S. Wu, S. Zhang, Y. Deng, C. Cui, L. Zhang, Y. Long, H. Li, Y. Tao, Z. Weng, Q.-H. Yang, F. Kang, *Small* 2020, **16**, 2001736.
- 3 Y. Yang, C. Liu, Z. Lv, H. Yang, Y. Zhang, M. Ye, L. Chen, J. Zhao, C. C. Li, *Adv. Mater.* 2021, **33**, 2007388.
- 4 Y. Tian, Y. An, C. Wei, B. Xi, S. Xiong, J. Feng, Y. Qian, *ACS Nano* **2019**, 13, 11676.
- 5 M. Zhou, S. Guo, J. Li, X. Luo, Z. Liu, T. Zhang, X. Cao, M. Long, B. Lu, A. Pan, G. Fang, J. Zhou, S. Liang, *Adv. Mater.* 2021, **33**, 2100187.
- 6 L. Dong, W. Yang, W. Yang, H. Tian, Y. Huang, X. Wang, C. Xu, C. Wang, F. Kang, G. Wang, *Chem. Eng. J.* 2020, **384**, 123355.
- 7 K. Zhao, C. Wang, Y. Yu, M. Yan, Q. Wei, P. He, Y. Dong, Z. Zhang, X. Wang, L. Mai, *Adv. Mater. Interfaces* 2018, **5**, 1800848.