Electronic Supplementary Information

Long-life Zinc Electrode Achieved by Oxygen Plasma Functionalization

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Experimental Part

Preparation of POZn foil

The POZn foil was prepared through SY-DT03S type coupled with a high-frequency plasma generator. In detail, a piece of Zn foil (thickness of 1 mm) was carefully cleaned with acetone and absolute ethyl alcohol and then dried in a vacuum oven at 40 °C. The cleaned Zn foil was treated on the glow discharge reactor at an output power of 200 W in an oxygen atmosphere for 2 min.

Fabrication of α-MnO_2 and α-MnO_2 cathode

α-MnO_2 was synthesized by a previously reported hydrothermal method[1]. In a typical synthesis process, 3 mmol $MnSO_4·H_2O$ and 2 mL 0.5 mol·L^{-1} H_2SO_4 were dissolved in 90 mL of deionized water under mechanical stirring for 30 min and then 20 mL 0.1 mol·L^{-1} $KMnO_4$ was slowly added into the above solution. After stirring for 2 h, the mixture was transferred into a Teflon-lined autoclave and aged at 120 °C for 12 h. Finally, α-MnO_2 was collected by filtration, washed with deionized water several times, and freeze-dried for 2 days. To prepare the α-MnO_2 cathode, α-MnO_2 power, black carbon, and PVDF at a mass ratio of 7:2:1 was stirred using 1-methyl-2-pyrrolidone (NMP) as the solvent. Then, the obtained slurry was scraped on stainlesssteel mesh and dried in a vacuum at 60 °C for 8 h.

Assembly of Zn/Zn Symmetric Cells and Zn/MnO$_2$ Batteries

CR2032-type coin symmetric cells were assembled in an open-air atmosphere using identical bare Zn or POZn as electrodes, glass fiber as a separator, and 2 M $ZnSO_4$ as electrolytes. For the fabrication of Zn/MnO_2 batteries, the α-MnO_2 cathode and anode (bare Zn or POZn) electrodes were separated by glass fiber separators. A mixed aqueous solution of 2 M $ZnSO_4$ and 0.2 M $MnSO_4$ is used as an electrolyte.

Materials Characterizations

The surface wettability of anodes was carried out on a contact angle measuring system (JC2000D1, Powereach). X-ray diffraction (XRD) patterns were recorded on a Bruker D2 Advanced diffractometer with a Cu Kα-radiation (λ= 0.15418 nm). X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo Scientific, USA) was used to characterize the element type and atomic configurations of POZn foil. Scanning electron microscope (SEM) images and the mapping of element were procured using a SU1510 (Hitachi) equipped with an energy dispersive spectrometer (EDS). Ultra-Depth Three-Dimensional Microscope (VHX-1000C) was carried out to observe the micromorphology of the initial electrode samples and the cycled electrode samples after the cycling test. The sheet resistance was tested by a four-point probe tester (ST2263, Suzhou Jingge Electronic Co., China).

Electrochemical Measurements

Cyclic voltammetry (CV) curves and Electrochemical impedance spectra (EIS) was conducted on the electrochemical workstation (CHI660E, China). Galvanostatic charge/discharge (GCD) measurements were performed on a battery test system (LAND, CT3001A, China). Coulombic efficiency (CE) measurements were carried out against the CC electrode by plating 1 mAh·cm^{-2} of Zn and then stripping it to 0.5 V.

Table S1. The sheet resistance in different regions for bare Zn and POZn plates

Sample	Sheet resistance (mΩ·sq^{-1})	Average surface electrical resistance (mΩ·sq^{-1})	Standard deviation
Zn	0.541,0.553,1.092,0.542,0.518,0.530,0.391, 0.553,1.046,0.518,0.578,0.553,0.518,0.542, 0.534	0.601	0.188
POZn	0.567,0.567,0.588,0.502,0.542,0.518,0.729, 0.518,0.521,0.530,0.490,0.542,0.545,0.634, 0.612	0.560	0.059

Table S2. Comparison of the electrochemical performance of the full Zn/MnO_2 batteries with different modified Zn anodes

Anode	Capacity (mAh·g^{-1})@Life span (h)@current density	Reference
MXene@Zn	205.5@500@1 A·g^{-1}	[2]
TiO_2/PVDF	234@300@5C	[3]
UIO-66	210@50@5C	[4]
$H_3Sb_3P_2O_{14}$	111.7@1000@1 A·g^{-1}	[5]
$CaCO_3$	177@1000@1 A·g^{-1}	[6]
Si_3N_4	201@400@0.6 A·g^{-1}	[7]
COF	172@300@2 A·g^{-1}	[8]
POZn	216@1000@1 A·g^{-1}.	This work

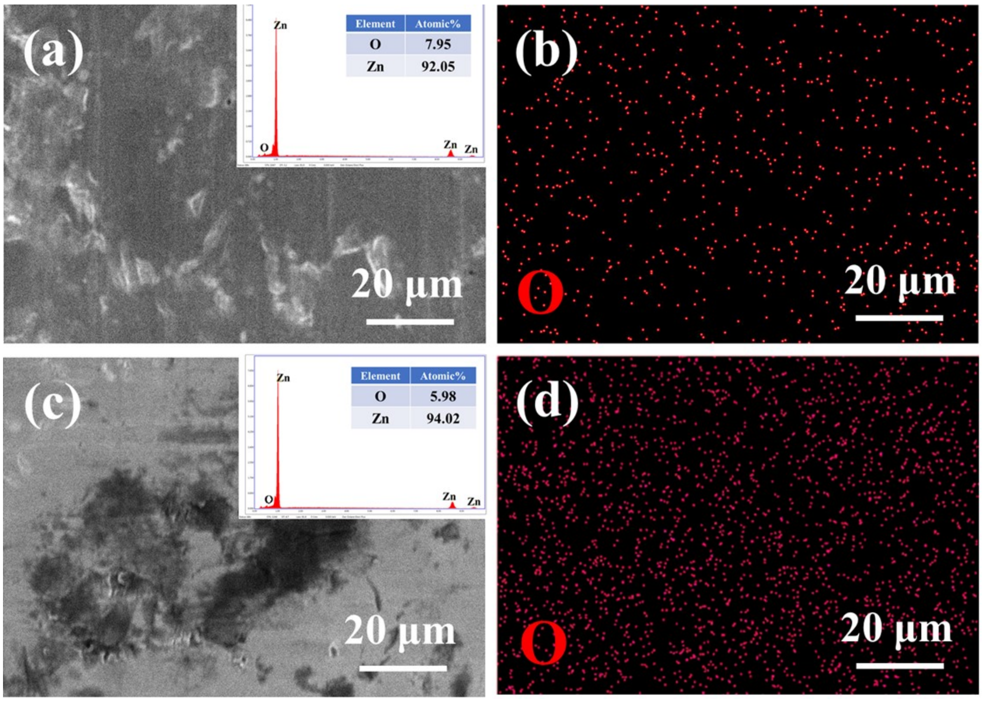

Fig. S1 SEM images with EDS pattern and oxygen element mapping for (a, b) bare Zn and (c, d) POZn plates.

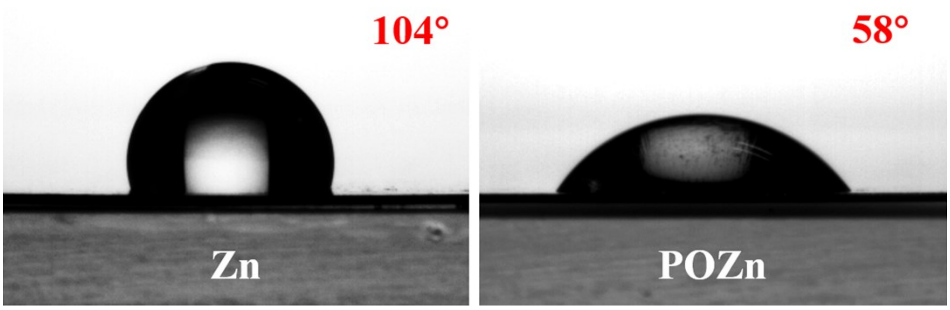

Fig. S2 Contact angles of the 2M $ZnSO_4$ electrolyte on bare Zn and POZn plates.

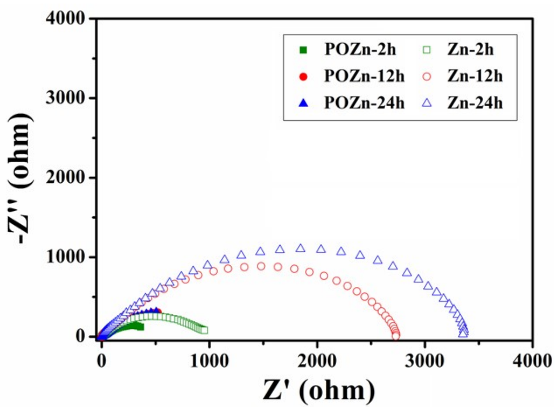

Fig. S3 Nyquist plots of bare Zn and POZn anodes after specific standing time.

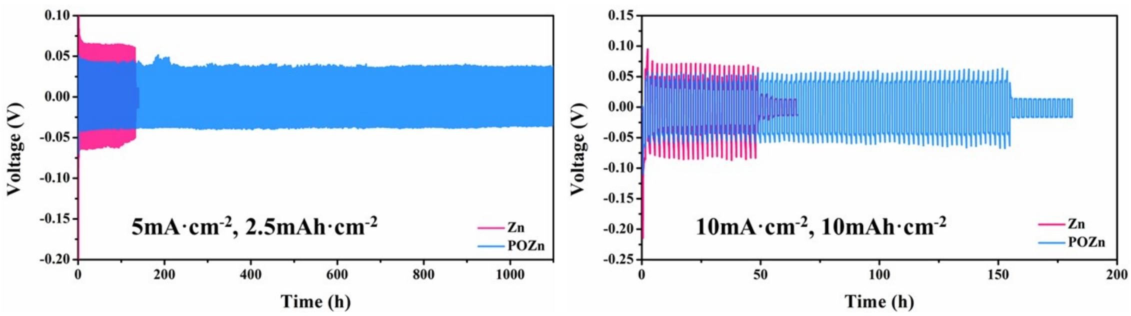

Fig. S4 The long-term galvanostatic cycling performance of symmetrical Zn and POZn cells at current densities of (d) 5 mA·cm^{-2} and (e) 10 mA·cm^{-2}.

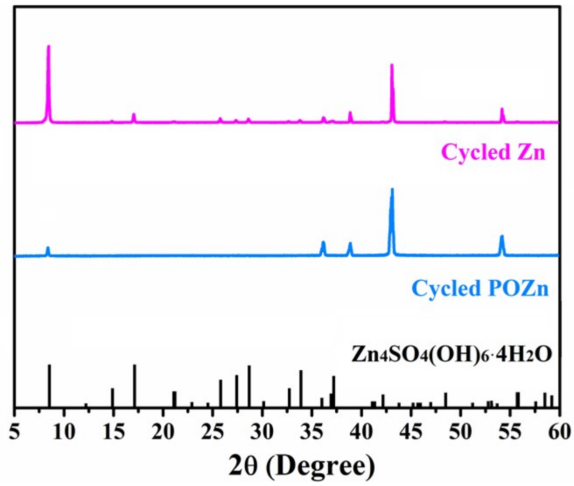

Fig. S5 XRD patterns of bare Zn and POZn electrodes after 20 cycles.

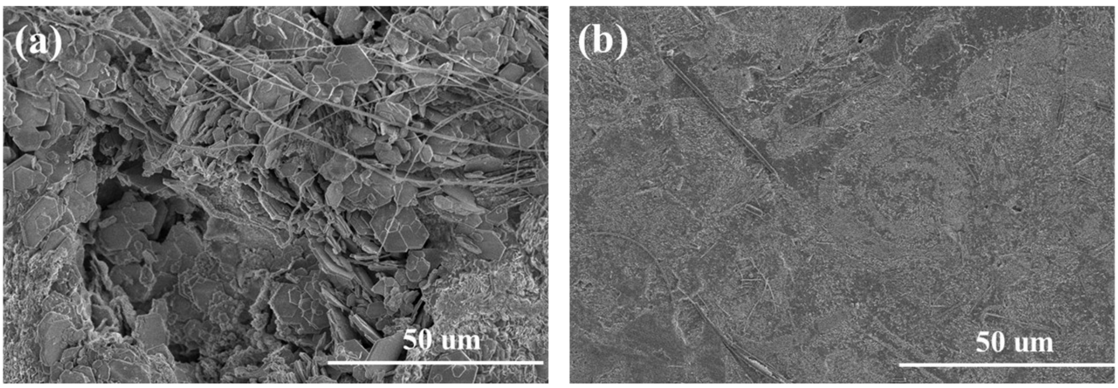

Fig. S6 Top SEM images of (a) Zn electrode and (b) POZn electrode after 100 cycles at 200 mA·g^{-1}.

Reference

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