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Electronic Supplementary Information (ESI)

Superhydrophobic and robust hetero-metal-polymer hybrid interphase enables deepcycling zinc metal anodes

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Experimental Methods

Preparation of Pb-PVDF@Zn and Pb@Zn electrodes.

A facile and rapid chemical displacement reaction was developed to prepare the Pb-based interphase layers on Zn metal. Typically, 0.2 mg PVDF powder was dissolved in 20 mL ethylene glycol (EG) solvent and stirred for 10 h to obtain 0.1 mg mL⁻¹ PVDF-EG solution. Then, 10 mM PbCl₂ salt was dissolved in the PVDF-EG solution. Next, a piece of commercial Zn foil (20 μm in thickness, 5 × 6 cm in size) was immersed into the above solution under stirring for 5 min. Finally, the obtained Pb-PVDF@Zn was carefully rinsed with anhydrous ethanol. Note that the Zn foil was pre-treated in 0.1 M dilute H₂SO₄ solution for 3 min to remove the oxide layer of the Zn surface. Similar to the preparation of Pb-PVDF@Zn, the Pb@Zn was prepared in the 10 mM PbCl₂ containing EG solution without containing PVDF, and the PVDF@Zn was prepared in the 0.1 mg mL⁻¹ PVDF-EG solution without containing PbCl₂. For comparison, other preparation conditions involving the reaction time (from 2 to 10 min), Pb²⁺ concentration (from 5 to 20 mM), and PVDF concentration (from 0.05 to 0.2 mg mL⁻¹), solvent (e.g., water, ethanol, and EG) were systematically studied. The preparation method is scalable and the large size of Pb-PVDF@Zn can be easily obtained by changing the solution volume and Zn foil size.

Preparation of Bi@Zn, Sn@Zn, Bi-PVDF@Zn, and Sn-PVDF@Zn.

Similar to the protocol of Pb-PVDF@Zn and Pb@Zn, the Bi-PVDF@Zn and Bi@Zn can be prepared by immersing Zn foils in the 5 mM BiCl₃ with and without 0.1 mg mL⁻¹ PVDF containing EG solutions under stirring for 2 min, respectively. The Sn-PVDF@Zn and Sn@Zn can be prepared by immersing Zn foils in the 10 mM SnCl₄ with and without 0.1 mg mL⁻¹ PVDF containing EG solutions under stirring for 5 min, respectively. Other preparation conditions involving the reaction time and Bi³⁺/Sn⁴⁺ concentration were also systematically studied.

Preparation of zinc sulfate hydroxide hydrate (ZSOH).

Typically, 0.05 M NaOH aqueous solution (50 mL) was dropwise added into the 0.1 M ZnSO₄ aqueous solution (50 mL) under constant stirring for 10 h. After that, the white precipitate of ZSOH was collected and washed with deionized water, then dried at 50 °C for 10 h.

Preparation of cathode materials.

For V₂O₅·nH₂O cathode material (denoted as VOH), 3 mM V₂O₅ powder was dissolved into 60 mL H₂O, then 10 mL H₂O₂ (30 wt%) was dropwise added to the above solution under stirring. Next, the obtained orange-red solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. After reacting for 10 h at 190 °C, the resulting precipitation was collected and then freeze-dried for 24 h. After that, the collected powder was annealed at 200 °C for 6 h to obtain the final product. For MnO₂ cathode material, 0.1 M KMnO₄ (30 mL) was added to 0.6 M MnSO₄·H₂O (30 mL). After stirring for 30 min, the mixture was transferred into a Teflon-lined autoclave (100 mL) and kept at 140 °C for 12 h. Afterward, the obtained product was washed by centrifugation with a mixture of water and alcohol and then dried at 60 °C overnight.

Cathode preparation.

The VOH or MnO₂ cathode was prepared by blending the slurry mixture of active material, super P carbon, and polyvinylidene difluoride in a mass ratio of 7:2:1 using N-methyl-2-pyrrolidine as the solvent onto a Ti foil, then it was dried at 60 °C for 10 h under vacuum. The typical mass loading of the as-prepared cathode is 2~3 mg cm⁻² for cointype cell assembly. The high-mass loading VOH cathode (10.8 mg cm⁻²) was also prepared for pouch-type cell assembly.

Material characterizations.

X-ray diffraction (XRD) patterns were obtained on a Rigaku MiniFlex600 (Cu K α radiation) at a scanning rate of 4° min⁻¹. Scanning electron microscopy (SEM) images were captured on a field-emission scanning electron microscope (JEOL, JSM-7500F). Raman spectra and corresponding Raman mapping images were collected on a Horiba HR-Evolution Raman microscope (532 nm excitation). FTIR spectra were measured by a Nicolet iS10 spectrometer (Thermo-Fisher Scientific). In-situ pH tests were conducted in a Zn//Zn cell that was assembled within an H-type cell, where two Zn electrodes (2 × 2 cm) were put in each half cell with 30 mL electrolyte and a pH meter (pH700, Eutech) was located at one side of the H-type electrolytic cell as close as possible to the Zn electrode. The testing current was set to 5 mA cm⁻². Contact angle measurement was performed on a Dataphysics OCA15 optical contact angle system. The in-situ characterization of Zn plating/stripping behavior on different Zn electrodes in 2 M ZnSO₄ aqueous electrolyte was recorded on an optical microscope (Shanghai Fenye, ZLD200-4XC) equipped with a digital camera, where a pressure-free Zn//Zn electrolytic cell was used and the current density was 10 mA cm⁻². For better observation, the thicker Zn foils with 50 µm thickness were used to prepare Pb@Zn and Pb-PVDF@Zn electrodes.

Electrochemical Measurements.

Electrochemical performances of half and full batteries with different Zn electrodes were mainly evaluated using CR-2032 coin-type cells. Glass fiber was used as the separator, and 2 M ZnSO₄ aqueous solution was used as the electrolyte. The Zn²⁺ plating/stripping Coulombic efficiencies were measured using asymmetric Zn//Cu cells with a cut-off charging potential of 0.5 V. The cycling stability of Zn electrodes was measured by symmetric Zn//Zn cells. Charge/discharge of battery was tested on a battery-testing instrument (LANHE-CT3002A). The linear polarization curve (LSV), cyclic voltammetry (CV) profiles, potentiostatic current-time transient curves, and electrochemical impedance spectroscopy (EIS with a frequency range from 100 mHz to 100 kHz) were performed on a Solartron 1470E electrochemical workstation. LSV was conducted in a three-electrode configuration in 2 M Na₂SO₄ aqueous electrolyte at 5 mV s⁻¹, where bare Zn, PVDF@Zn, Pb@Zn or Pb-PVDF@Zn serves as the working electrode, Pt foil serves as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. Tafel tests are performed in a three-electrode configuration, in which bare Zn, PVDF@Zn, Pb@Zn or Pb-PVDF@Zn serves as the working electrode, SCE as the reference electrode, and Ti foil as the counter electrode in 2 M $ZnSO_4$ electrolyte. The activation energy (E_{a}) of different Zn electrodes can be measured by the Nyquist plots of symmetric Zn cells with temperaturedependent charge transfer resistance (R_{ct}). The E_a can be obtained from the slope by linearly fitting ln(1/ R_{ct}) versus 1000/T. To compensate for the capacity loss of MnO_2 during cycling, 0.1 M MnSO₄ was used as the electrolyte additive for the $Zn//MnO_2$ battery assembly. 3 M ZnSO₄ aqueous solution was used as the electrolyte for Zn//VOH full battery assembly. The applied current density and specific capacity in the full battery were calculated based on the cathode mass.

Theoretical Calculations.

The adsorption energies were obtained using Vienna Ab-initio Simulation Package (VASP).^[51,52] The Perdew-Burke-Ernzerhof (PBE) functional described the exchange-correlation energy based on the generalized gradient approximation (GGA).^[53] The cutoff energy was set to 400 eV. The convergence criteria for the energy and force were set to 10⁻⁵ eV and 0.02 eV Å⁻¹, respectively. The long-range dispersion correction for the van der Waals interaction was implemented through the DFT-D2 method in all calculations.^[54] The Zn and Pb metal surfaces were modeled by

the four-layer slabs with 5 × 5 and 4 × 4 supercells, respectively. A vacuum layer of about 20 Å was applied to avoid the interaction between adjacent slabs. To counteract the positive charge of Zn^{2+} ions, Cl^{-} ions were inserted in boxes and fixed away from surfaces. The adsorption energies (E_{ads}) were calculated as follows:

$$E_{ads} = E(Zn^{2+}-sub) - E(Zn^{2+}) - E(sub)$$

where $E(Zn^{2+}-sub)$, $E(Zn^{2+})$ and E(sub) were the energies of substrate with adsorbed Zn^{2+} ion, Zn^{2+} ion, and clean substrate.

The Gibbs free energies of metal surfaces with adsorbed H were carried out based on the computational hydrogen electrode (CHE) model. The reaction energies were obtained as follows:

$\Delta \mathbf{G} = \Delta \mathbf{E} + \Delta \mathbf{E}_{\mathsf{ZPE}} - \mathsf{T} \Delta \mathsf{S}$

where ΔE , ΔE_{ZPE} , and ΔS were the electronic energy change, zero-point energy change, and entropy change, respectively.

Finite-element simulations.

The electric field distribution at the electrode-electrolyte interface was simulated by COMSOL Multiphysics software. The ion concentration followed Fick's First Law for diffusion, the electromigration followed the Nernst-Planck relationship, and the reaction on the electrode surface followed the Butler-Volmer equation. In the simplified 2D model cell, the length of the model was set to 3 μ m, and the distance between the working and counter electrodes was set to 4 μ m. Some protrusions and holes were plotted on the bare Zn anode to indicate its surface irregularity during the plating process based on the SEM results. The Pb nanoparticles and PVDF matrix on Pb-PVDF@Zn were represented by semi-ellipses and circles, respectively. For the aqueous electrolyte, the initial concentration was set to 2 M with an ionic conductivity of 57 mS cm⁻¹. The current density applied on the cathode was set to 5 mA cm⁻², and the anodic potential was set to 0 V.



Fig. S1 XRD patterns of Zn foils with different reaction times in the 10 mM PbCl₂ containing EG solution.



Fig. S2 SEM images of Zn foils after reacting for (a,b) 1 min, (c,d) 2 min, (e,f) 5 min, and (g,h) 10 min in the 10 mM PbCl₂ containing EG solution. The Pb interphase layer cannot fully cover the Zn surface at a shorter reaction time (e.g., 1 and 2 min). A longer reaction time of 10 min will induce the excess growth of Pb with some dendrites emerging.



Fig. S3 Galvanostatic cycling performances of Zn//Zn symmetric cells at 10 mA cm⁻² and 5 mAh cm⁻² with bare Zn and Pb@Zn electrodes obtained by Zn foils after reacting for 2, 5, and 10 min in the 10 mM PbCl₂ containing EG solution. The Pb@Zn electrode obtained by Zn foils after reacting for 5 min in the 10 mM PbCl₂ containing EG solution exhibits better cycling stability.



Fig. S4 XRD patterns of Zn foils after reacting in 5, 10, and 20 mM PbCl₂ containing EG solutions with a constant reaction time of 5 min.



Fig. S5 SEM images of Zn foils after reacting in (a,b) 5 mM PbCl₂, (c,d) 10 mM PbCl₂, and (e,f) 20 mM PbCl₂ containing EG solutions with the constant reaction time of 5 min. The relatively lower concentration of PbCl₂ (5 mM) cannot enable the full coverage of Pb interphase on the Zn surface. A larger concentration of PbCl₂ (20 mM) induces the massive and uneven growth of Pb.



Fig. S6 Galvanostatic cycling performances of Zn//Zn symmetric cells at 10 mA cm⁻² and 5 mAh cm⁻² with bare Zn and Pb@Zn electrodes obtained by Zn foils after reacting in 5 mM, 10 mM, and 20 mM PbCl₂ containing EG solutions under a constant reaction time of 5 min. The Pb@Zn electrode obtained by Zn foils after reacting in 10 mM PbCl₂ containing EG solution exhibits better cycling stability.



Fig. S7 XRD patterns of Zn foils after reacting in 0.05, 0.1, and 0.2 mg mL⁻¹ PVDF containing EG solutions with 10 mM PbCl₂ under a constant reaction time of 5 min.



Fig. S8 SEM images of Zn foils after reacting in (a,b) 0.05, (c,d) 0.1, and (e,f) 0.2 mg mL⁻¹ PVDF containing EG solutions with 10 mM $PbCl_2$ under a constant reaction time of 5 min.



Fig. S9 Galvanostatic cycling performances of Zn//Zn symmetric cells at 10 mA cm⁻² and 5 mAh cm⁻² with bare Zn and Pb-PVDF@Zn electrodes obtained by Zn foils after reacting in 0.05, 0.1, and 0.2 mg mL⁻¹ PVDF containing EG solutions with 10 mM PbCl₂ under a constant reaction time of 5 min. The Pb-PVDF@Zn electrode obtained by Zn foil after reacting in 0.1 mg mL⁻¹ PVDF containing EG solution exhibits better cycling stability.



Fig. S10 (a) Low and (b) high magnification SEM images of Zn foils after reacting in the water-based solution with 10 mM PbCl₂ under a constant reaction time of 5 min (without containing PVDF).

The preparation of Pb@Zn was used to screen the solvent. In the water solvent, the displacement reaction is violent due to the high reactivity of water, which induces the massive and dendrite-like Pb on Zn. For comparison, in the EG solvent, uniform Pb nanoparticles can be obtained on the Zn surface (Fig. S5c,d).



Fig. S11 (a) A photo of 3 mM $PbCl_2$ in ethanol solvent with some undissolved salt. (b) XRD pattern of Zn foil after reacting for 30 min in the ethanol-based solution.

In the conventional ethanol solvent, the PbCl₂ shows a very small solubility (< 3 mM), which renders the sluggish displacement reaction between Pb and Zn as confirmed by a very weak Pb signal on Zn even after reacting for 30 min. For comparison, in the EG solvent, uniform Pb nanoparticles can be obtained on the Zn surface after a rapid reaction for 5 min (Fig. S5c,d).



Fig. S12 FTIR spectra of Pb@Zn and Pb-PVDF@Zn compared with the spectra of EG solvent and PVDF powder.



Fig. S13 Low magnification SEM image of Zn foil after reacting in the EG-based solution with 10 mM $PbCl_2$ and 0.1 mg mL⁻¹ PVDF under a reaction time of 5 min.



Fig. S14 SEM images of (a) bare Zn and (b) PVDF-Zn. (c) FTIR spectra of PVDF powder and PVDF@Zn electrode. Note that the preparation method of PVDF-Zn remains the same as the Pb-PVDF@Zn except that the precursor EG solution does not contain PbCl₂. The low concentration of PVDF in EG (0.1 mg mL⁻¹) and the short reacting time (5 min) co-render the insufficient coating of PVDF on Zn as shown in the SEM image.



Fig. S15 Contact angle measurements of an aqueous electrolyte droplet on the surface of (a) PVDF@Zn and (b) Pb@Zn.



Fig. S16 Contact angle comparison of this work with the currently reported metal/alloy-based interphase layers on Zn.



Fig. S17 Digital photos of (a) Bi-PVDF@Zn and (b) Sn-PVDF@Zn.



Fig. S18 SEM images of Zn foils after reacting for (a,b) 1 min, (c,d) 2 min, and (e,f) 5 min in the 5 mM BiCl₃-containing solutions.



Fig. S19 (a) H_2 evolution polarization curves in 2 M Na_2SO_4 aqueous electrolyte at 5 mV s⁻¹ of different Bi@Zn electrodes after reacting for 1, 2, and 5 min in the 5 mM BiCl₃-containing EG solutions. (b) Corresponding Tafel slopes. The Bi@Zn electrode obtained by Zn foils after reacting for 2 min exhibits stronger resistance for H_2 evolution.



Fig. S20 SEM images of Zn foils after reacting in (a,b) 2 mM BiCl₃, (c,d) 5 mM BiCl₃, and (e,f) 10 mM BiCl₃ containing EG solutions under a reaction time of 2 min.



Fig. S21 (a) H_2 evolution polarization curves in 2 M Na_2SO_4 aqueous electrolyte at 5 mV s⁻¹ of different Bi@Zn electrodes obtained by Zn foils after reacting in 2, 5, and 10 mM BiCl₃ containing EG solutions under a reaction time of 2 min. (b) Corresponding Tafel slopes. The Bi@Zn electrode obtained by Zn foils after reacting in 5 mM BiCl₃-containing solution exhibits stronger resistance for H_2 evolution.



Fig. S22 SEM images of Zn foils after reacting for (a,b) 2 min, (c,d) 5 min, and (e,f) 10 min in the 10 mM SnCl₄ containing EG solutions.



Fig. S23 (a) H_2 evolution polarization curves in 2 M Na_2SO_4 aqueous electrolyte at 5 mV s⁻¹ of different Sn@Zn electrodes obtained by Zn foils after reacting for 2, 5, and 10 min in the 10 mM SnCl₄ containing EG solutions. (b) Corresponding Tafel slopes. The Sn@Zn electrode obtained by Zn foils after reacting for 5min exhibits stronger resistance for H_2 evolution.



Fig. S24 SEM images of Zn foils after reacting in (a,b) 5 mM SnCl₄, (c,d) 10 mM SnCl₄, and (e,f) 20 mM SnCl₄ containing EG solutions under a reaction time of 5 min.



Fig. S25 (a) H_2 evolution polarization curves in 2 M Na_2SO_4 aqueous electrolyte at 5 mV s⁻¹ of different Sn@Zn electrodes obtained by Zn foils after reacting in 5,10, and 20 mM SnCl₄ containing EG solutions under a reaction time of 5 min. (b) Corresponding Tafel slopes. The Sn@Zn electrode obtained by Zn foils after reacting in 10 mM SnCl₄-containing solution exhibits stronger resistance for H_2 evolution.



Fig. S26 FTIR spectra of Bi@Zn, Sn@Zn, Bi-PVDF@Zn, and Sn-PVDF@Zn electrodes compared with the spectra of bare Zn and PVDF powder.



Fig. S27 Low-magnification SEM images of (a) Bi-PVDF@Zn and (b) Sn-PVDF@Zn electrodes.

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Fig. S28 Contact angle measurements of an aqueous electrolyte (2 M ZnSO₄) droplet on the surface of (a) Bi@Zn, (b) Bi-PVDF@Zn, (c) Sn@Zn, and (d) Sn-PVDF@Zn electrodes.



Fig. S29 XRD patterns of (a) bare Zn, (b) Pb@Zn, and (c) Pb-PVDF@Zn electrodes soaked in 2 M ZnSO₄ electrolyte after different days.

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Fig. S30 (a) XRD patterns of Bi@Zn and Bi-PVDF@Zn electrodes after soaking in 2 M ZnSO₄ electrolyte with different days. SEM images of (b,c) Bi-PVDF@Zn after soaking for 14 days. SEM images of Bi@Zn after soaking for (d,e) 7 days and (f,g) 8 days.

Sn-PVDF@Zn-11 days

Sn-PVDF@Zn-10 days Sn@Zn-6 days

Sn@Zn-5 days

Journal Name

а



Fig. S31 (a) XRD patterns of bare Zn, Sn@Zn and Sn-PVDF@Zn electrodes after soaking in 2 M ZnSO₄ electrolyte. SEM images of (b,c) Sn-PVDF@Zn after soaking for 11 days. SEM images of Sn@Zn after soaking for (d,e) 5 days, and (f,g) 6 days.





Fig. S32 H₂ evolution polarization curves of Pb-PVDF@Zn, Bi-PVDF@Zn, and Sn-PVDF@Zn electrodes in 2 M Na₂SO₄ aqueous electrolyte at 5 mV s⁻¹. The Pb-PVDF@Zn electrode exhibits higher HER resistance as revealed by a much reduced HER potential of -1.97 V (at 2 mA cm⁻²), compared with the Sn-PVDF@Zn (-1.84 V) and Bi-PVDF@Zn (-1.87 V).



Fig. S33 Tafel slopes of bare Zn, Pb@Zn, and Pb-PVDF@Zn electrodes in 2 M Na₂SO₄ aqueous electrolyte at 5 mV s⁻¹.



Fig. S34 Tafel plots of bare Zn, Pb@Zn, and Pb-PVDF-@Zn electrodes at 5 mV s⁻¹. Tafel tests are performed in a three-electrode configuration, in which bare Zn/Pb@Zn/Pb-PVDF@Zn serves as the working electrode, SCE as the reference electrode, and Ti foil as the counter electrode in 2 M ZnSO₄ electrolyte. The corrosion current densities for bare Zn, Pb@Zn, and Pb-PVDF@Zn electrodes are 17.4, 5.8, and 4.2 mA cm⁻², respectively, demonstrating the effectiveness of the Pb-PVDF interphase layer to alleviate Zn corrosion.



Fig. S35 (a) H_2 evolution polarization curves of bare Zn and PVDF@Zn electrodes at 5 mV s⁻¹. (b) Tafel plots of bare Zn and PVDF@Zn electrodes at 5 mV s⁻¹.



Fig. S36 Digital photos of the *in situ* pH measurements of (a) bare Zn, (b) Pb@Zn, and (c) Pb-PVDF@Zn during discharge at 5 mA cm⁻².



Fig. S37 Nyquist plots of (a) Pb@Zn and (b) bare Zn electrodes at different temperatures. Insets are the equivalent circuit models. The activation energy (E_a) of different Zn electrodes can be measured by the Nyquist plots of symmetric Zn cells with temperature-dependent charge transfer resistance (R_{ct}). By linearly fitting ln(1/ R_{ct}) versus 1000/T, the E_a can be obtained from the slope.^[S19]



Fig. S38 (a) XRD patterns of electrodeposited Zn with 10 mAh cm⁻² on bare Zn, PVDF@Zn, Pb@Zn, and Pb-PVDF@Zn. (b) XRD pattern of Pb nanoparticles collected by carefully scraping them from the Pb@Zn surface. (c) The lattice mismatch between the Pb-(111) plane and Zn-(101) plane.

The intensity ratio of (101) to (002) peak ($I_{(101)}/I_{(002)}$) can reflect the electrodeposited Zn texture. The $I_{(101)}/I_{(002)}$ value of electrodeposited Zn with 10 mAh cm⁻² on PVDF-Zn (2.7) is similar to that on bare Zn (2.1), suggesting that the PVDF layer has a weak effect on regulating the epitaxial Zn electrodeposition. For the Pb@Zn and Pb-PVDF@Zn, the $I_{(101)}/I_{(002)}$ values reach 8.2 and 12.5, respectively, demonstrating the Pb interphase can induce the epitaxial Zn electrodeposition with a (101) plane-dominated texture. Compared with Pb@Zn, the Pb-PVDF@Zn exhibits a higher $I_{(101)}/I_{(002)}$ value, mainly because the hybrid interphase has a stronger capability to induce uniform Zn electrodeposition (Fig. 4m,r) and suppress H₂ evolution during Zn electrodeposition (Fig. 3a-j). Previous works have demonstrated that a low lattice mismatch ($\delta < 0.25$) between the preferred crystal plane of the interphase layer (or substrate) and the specific crystal plane of Zn can induce an interfacial lattice-locking effect to enable the epitaxial electrodeposition of Zn.^[58,520] The lattice mismatch can be calculated by the following formula: $\delta = |d_1 - d_2|/d_2$, where d_1 is the lattice constant of the Zn deposit and d_2 is the lattice constant of the interphase layer (or substrate). In the present work, the Pb-based interphase on Zn exhibits a preferred (111) orientation (Fig. 1c). Note that the (200) plane of Pb is overlapping with the (002) plane of Zn (at 36.4°, 2 theta degree). To further confirm the orientation of the Pb interphase, the Pb nanoparticles are collected by carefully scraping them from the Pb@Zn surface. XRD result shows that the Pb nanoparticles indeed have a preferred (111) orientation, as shown in Fig. S38b. Accordingly, the δ between the Pb-(111) plane

and the Zn-(101) plane is calculated to be 0.16, indicating that the as-prepared Pb-based interphase can induce the epitaxial electrodeposition of Zn with a (101) plane-dominated texture (Fig. S38c).



Fig. S39 Cycling performance of PVDF@Zn and bare Zn symmetric cells at 5 mA cm⁻² and 2.5 mAh cm⁻².



Fig. S40 (a) Cycling performance of Pb-PVDF@Zn, Pb@Zn, and bare Zn symmetric cells at 10 mA cm⁻² and 5 mAh cm⁻². (b) Corresponding enlarged voltage profiles.



Fig. S41 Cycling performance of the Pb-PVDF@Zn symmetric cell at 1 mA cm⁻² and 0.5 mAh cm⁻².



Fig. S42 The selected voltage profiles of (a) bare Zn//Cu cell, (b) Pb@Zn//Cu cell, and (c) Pb-PVDF@Zn//Cu cell at 2 mA cm⁻² and 1 mAh cm⁻².



Fig. S43 Low-magnification SEM images of the cycled (a) bare Zn, (b) Pb@Zn, and (c) Pb-PVDF@Zn electrodes under the plating state.



Fig. S44 Raman spectra of the cycled Pb-PVDF@Zn, Pb@Zn, and bare Zn electrodes compared with the Raman signals of the as-prepared ZSOH powder.



Fig. S45 SEM images of (a) bare Zn, (b) Pb@Zn, and (c) Pb-PVDF@Zn under the stripping state after 50 cycles.



Fig. S46 XRD pattern and SEM image (inset) of the as-prepared VOH material.

The XRD pattern of the as-prepared VOH is very similar to the experimental and calculated results of previously reported bilayered $V_2O_5 \cdot nH_2O$ material,^[521] demonstrating that the as-prepared VOH has a typical bilayered structure and high purity.



Fig. S47 XRD pattern and SEM image (inset) of the as-prepared MnO₂ nanorods.

The XRD pattern of the as-prepared MnO_2 is well consistent with the standard XRD pattern of β -MnO₂ (JCPDS no. 24-0735), demonstrating that the as-prepared MnO_2 has a typical tunnel-type structure and high purity.



Fig. S48 Typical charge/discharge profiles of (a) Pb-PVDF@Zn//VOH and (b) bare Zn//VOH batteries at 2 A g⁻¹.



Fig. S49 Cycling performance of Pb-PVDF@Zn//MnO₂ battery at 0.2 A g^{-1} .



Fig. S50 Voltage profiles of the pouch-type Pb-PVDF@Zn//VOH battery.

Table S1. Comparison of electrochemical performances in this work with previously reported Zn electrodes with various protective layers.

Electrode (thickness)	Electrolyte	Current density/Capacity (mA cm ⁻² /mAh cm ⁻²)	Lifespan (hour)	Cumulative plating capacity (mAh cm ⁻²)	DOD%	Ref.
Pb-PVDF@Zn (20 μm)	2 M ZnSO_4	5/2.5 10/5 20/10	2000 1500 800	5000 7500 8000	21.4 42.7 85.4	This work
Bi@Zn (100 μm)	2 M ZnSO ₄	10/1	2000	10000	1.7	S9
Sn@Zn (100 μm)	$1{ m MZnSO_4}$	0.5/1 1/1 2/1	500 500 300	125 250 300	1.7 1.7 1.7	S7
Sb@Zn (100 μm)	2 M ZnSO₄	1/1 3/1	800 1000	400 1500	1.7 1.7	S13
Ag@Zn (30 μm)	2 M ZnSO₄	0.5/0.5 5/5	600 110	150 275	2.9 28.5	S22
ln@Zn (100 μm)	2 M ZnSO ₄	0.25/0.05 1/1 4/1	1400 300 400	175 150 800	0.1 1.7 1.7	S23
Zn-Sn-Bi@Zn (200 μm)	2 M ZnSO_4	1/0.25 5/5 20/6	3000 100 100	1500 250 1000	0.2 4.3 5.1	S16
ZnSe@Zn (100 μm)	2 M ZnSO ₄	1/1 30/10	1500 172	750 2580	1.7 17.1	S8
ZnTe@Zn (10 μm)	1 M ZnSO₄	1/0.5 30/1	3300 760	1650 11400	8.5 17.1	S6
Cu-Zn@Zn (50 μm)	3 M Zn(CF ₃ SO ₃) ₂	1/1 5/1 10/10	5496 450 450	2748 1125 2250	3.4 3.4 34.2	S14

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SA-Cu@Zn (30 μm)	2 M ZnSO_4	1/1	2000	1000	5.6	S24
Zn@ZnF₂ (100 μm)	2 M ZnSO₄	0.5/1 10/1 1/1	500 500 800	125 2500 400	1.7 1.7 1.7	S25
Zn@ZnSiO₃ (100 μm)	$2 \text{ M} \text{ZnSO}_4$	1/1 5/1	1600 1520	800 3800	1.7 1.7	S26
C _{flower} @Zn (250 μm)	3 M ZnSO ₄	0.5/0.25 2/1 5/2.5	2000 1050 150	500 1050 375	0.2 0.7 1.7	S27
TiO₂@Zn (30 μm)	$2 \text{ M} \text{ZnSO}_4$	1/1 2/2	460 280	230 280	5.7 11.4	S28
PAM@Zn (80 μm)	ZnSO₄	1/1 1/20 40/40	5100 1200 240	2550 600 4800	2.1 42.7 85.4	S29
P2VP@Zn (50 μm)	2 M ZnSO₄	1/1 5/5	600 300	300 750	3.4 17.1	S30
ZnCo@Zn (150 μm)	3 M ZnSO₄	5/2	620	1550	2.3	S31
PAgZn (80 μm)	2 M ZnSO₄	4/2 10/5 20/5	800 550 200	1600 2750 2000	4.3 10.7 10.7	S5
Zn@PAQ (100 μm)	2 M ZnSO ₄	1/1 0.5/1	1750 1500	875 375	1.7 1.7	S32
3D Zn@P (50 μm)	3 M ZnSO ₄	1/1 5/5	5000 970	2500 2425	3.4 17.1	S33
Au@Zn ()	2 M ZnSO₄	5/1	490	1225		S17

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ZnTCF@Sn ()	2 M ZnSO ₄	2/1 20/3	2000 1200	2000 12000	 S12
lnSn@Zn ()	2 M ZnSO₄	1/0.5 1/1	2400 1800	1200 900	 S11
Zn/Sn-20 nm ()	2 M ZnSO₄	1/1 10/10	2000 300	1000 1500	 S34
Zn In ()	2 M ZnSO₄	0.2/0.2 1/1	1500 510	150 255	 S35

Supplementary References

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