

## Supporting information

### Experimental section

#### Preparation of LBL self-assembly of PAH/PAA multilayers coated Zn anode

500 mg PAH (Sigma-Aldrich, average  $M_w \sim 50,000$ ) was mixed in 10 mL distilled water to form PAH aqueous solution. PAA aqueous solution was prepared by 450 mg PAA (Sigma-Aldrich, average  $M_w \sim 450,000$ ) and 10 mL distilled water. Zn@PAH/PAA was coated by a 50  $\mu\text{m}$  doctor blade, where the PAH layer was coated on the Zn foil first and dried under UV light, after rinsing with water for 5-10 min, the PAA layer was then coated on the Zn foil. Repeat above steps to obtain the PAH/PAA multilayers coated Zn foil. According to GCD curves (Figure S1), three double layers coated Zn foil exhibits the best cycling performance, so three double PAH/PAA multilayer was used to prepare the Zn@PAH/PAA in this work.

#### Battery Assembly

For full cell assembly, commercial  $\text{MnO}_2$  (Sigma-Aldrich) was mixed and grounded with carbon black and PVDF at a 7:2:1 weight ratio in NMP solution. The mixture was evenly coated on a hydrophilic carbon paper with the areal loading mass around  $1.5\text{--}2\text{ mg cm}^{-2}$ , and dried in a vacuum oven at  $65\text{ }^\circ\text{C}$  overnight. Afterwards, the dried cathode was assembled with the PAH/PAA multilayers coated Zn anode in a CR2032-coin cell using 2 M  $\text{ZnSO}_4$  and 0.2 M  $\text{MnSO}_4$  as the electrolyte. For symmetrical cell assembly, the PAH/PAA multilayers coated Zn foil was assembled with 2 M  $\text{ZnSO}_4$  as the electrolyte.

#### Materials Characterisation

X-ray diffraction (XRD) patterns were obtained by a Bruker Vantec500 under the radiation source of Cu metal. Scanning electron microscopy (SEM) images were collected by a JEOL JSM-6701F Field Emission Scanning Electron Microscope (JEOL, Japan) at the acceleration voltage of 15 kV. The Energy-dispersive X-ray spectroscopy (EDX) images were collected by a Carl Zeiss EVO MA10 (Carl Zeiss AG, Germany) and Ultim Extreme Silicon Drift Detectors (Oxford Instrumental plc, UK). Transmission electron microscope (TEM) images were carried out by a JEOL JEM-2100 Electron Microscope. Fourier transform infrared spectroscopy (FTIR) was measured by a Shimadzu IRTracer-100 with the wavenumber from 400 to  $4000\text{ cm}^{-1}$ . The Raman data was obtained by a Thermo Scientific™ DXR3 Raman Microscope with a laser wavelength of 532 nm. The optical images and depth profile were collected by a Keyence VHX-7000N Digital Microscope, the HER reaction was observed on anode and Zn deposition was observed on cathode in the discharge process.

#### Electrochemical Characterisation

The long-term galvanostatic charge-discharge (GCD) test was operated by NEWARE battery testing systems. The cyclic voltammetry (CV) was measured by a VMP3 Biologic potentiostat. The electrochemical impedance spectroscopy (EIS) was tested by a Gamry Interface 1000E.

#### Computational Details

Density functional theory (DFT) calculations were performed using the Vienna ab initio Simulation Program (VASP). The generalized gradient approximation (GGA) method in Perdew-Burke-Ernzerhof (PBE) functional was applied to describe the exchange-correlation interaction. Conjugate gradient algorithm was employed for geometrical

optimization. The convergence criterion for the total energy and ionic force were  $10^{-4}$  eV and  $0.03$  eV/Å, respectively. The cut-off energy for the plane-wave basis set was 500 eV. Monkhorst-Pack scheme was used to sample the Brillouin zone with  $k$ -point of  $1 \times 1 \times 1$  for geometrical optimization. The van der Waals (vdW) interaction was considered through DFT-D3 correction. To avoid the interlayer interactions, the vacuum layer was larger than 20 Å. To obtain the diffusion energy barriers of Zn ions on electrode surface, the climbing image nudged elastic band (CI-NEB) method was adopted. A  $6 \times 6$  supercell of Zn (002) surface containing 2 atomic layers was constructed as the Zn electrode model.

The adsorption energy ( $E_{ads}$ ) is defined as

$$E_{ads} = E_{total} - E_{surface} - E_{adsorbent} \quad (1)$$

Where  $E_{total}$ ,  $E_{surface}$ , and  $E_{adsorbent}$  represent the total energies of the adsorption system, the substrate, and adsorbent, respectively. It means stronger adsorption with more negative adsorption energy.

The binding energy is calculated as

$$E_b = E_{total} - \sum_i n_i \mu_i \quad (2)$$

Where  $n_i$  is the number of atoms, and  $\mu_i$  is the corresponding chemical potential.

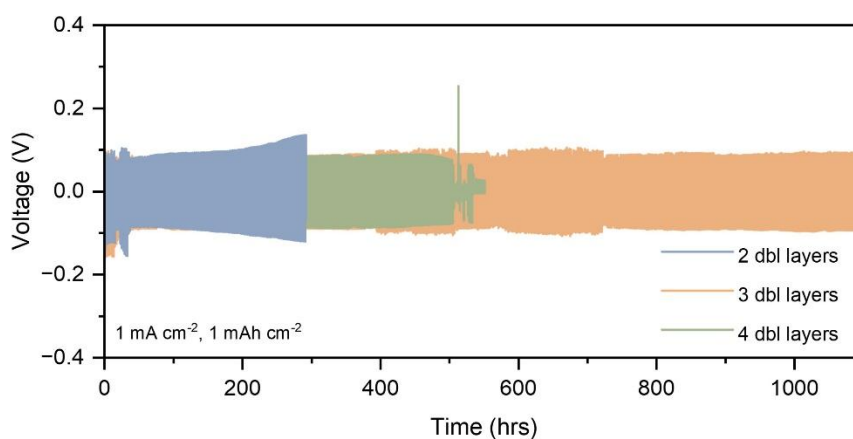
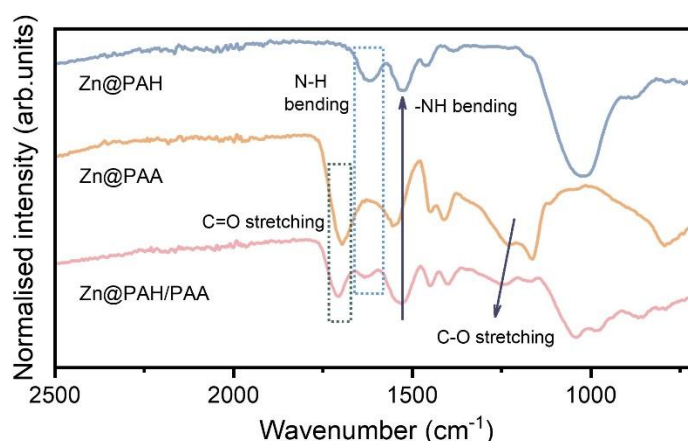


Figure S1. Galvanostatic charge-discharge (GCD) curves of the symmetric battery with different PAH/PAA layers at  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$ .



| Wavenumber (cm <sup>-1</sup> )   |        |        |            |
|----------------------------------|--------|--------|------------|
| Chemical composition             | Zn@PAH | Zn@PAA | Zn@PAH/PAA |
| C=O stretching (carboxylic acid) | N/A    | 1695   | 1710       |
| C-O stretching (carboxylic acid) | N/A    | 1232   | 1247       |
| N-H bending (amine)              | 1624   | N/A    | 1633       |
| -NH bending (amide)              | 1527   | N/A    | 1532       |

Figure S2. Fourier transform infrared (FTIR) spectra of Zn@PAH, Zn@PAA, and Zn@PAH/PAA.

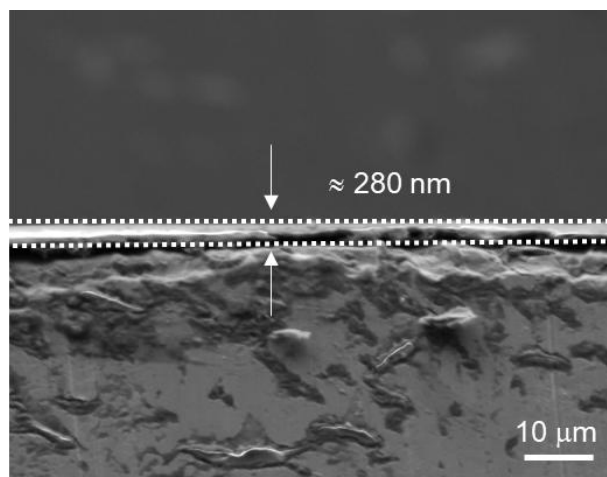


Figure S3. The cross-section SEM image of Zn@PAH/PAA before cycling.

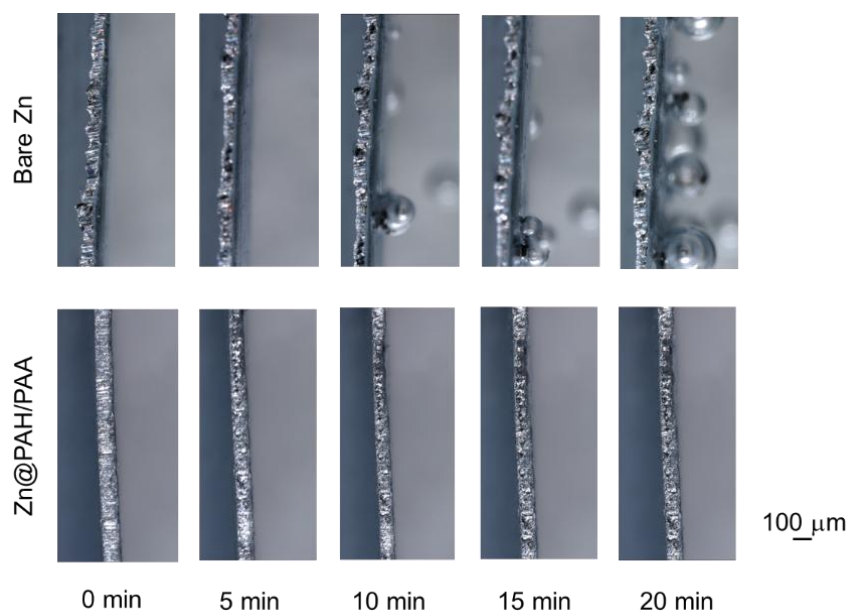
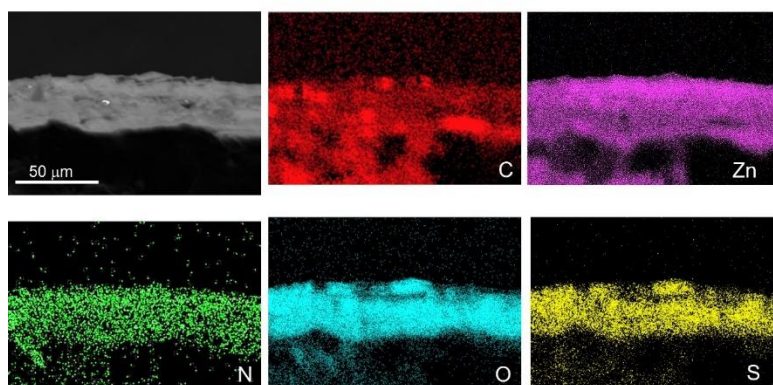


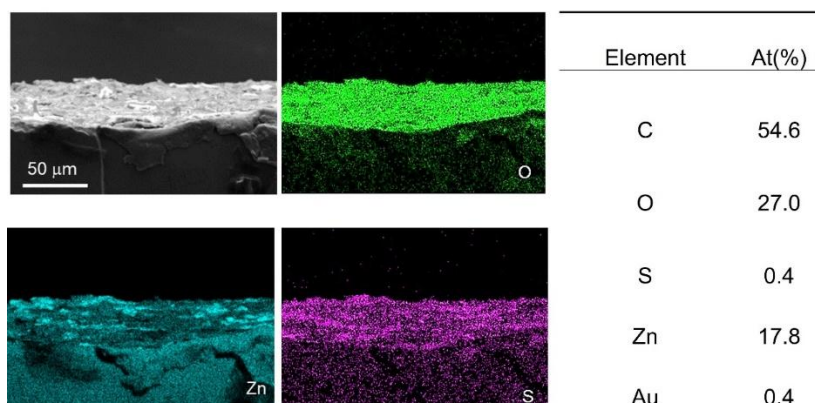
Figure S4. *In-situ* optical image of Zn stripping on Zn@PAH/PAA and Bare Zn at a current density of 30 mA cm<sup>-2</sup>.

### Zn@PAH/PAA electrode



| Element | At(%) |
|---------|-------|
| C       | 52.6  |
| O       | 27.9  |
| S       | 1.0   |
| N       | 0.3   |
| Cl      | 0.2   |
| Zn      | 18.0  |
| Au      | 0.1   |

### Bare Zn electrode



| Element | At(%) |
|---------|-------|
| C       | 54.6  |
| O       | 27.0  |
| S       | 0.4   |
| Zn      | 17.8  |
| Au      | 0.4   |

Figure S5. EDX images of Zn@PAH/PAA and Bare Zn after 50 cycles at  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mAh cm}^{-2}$ .

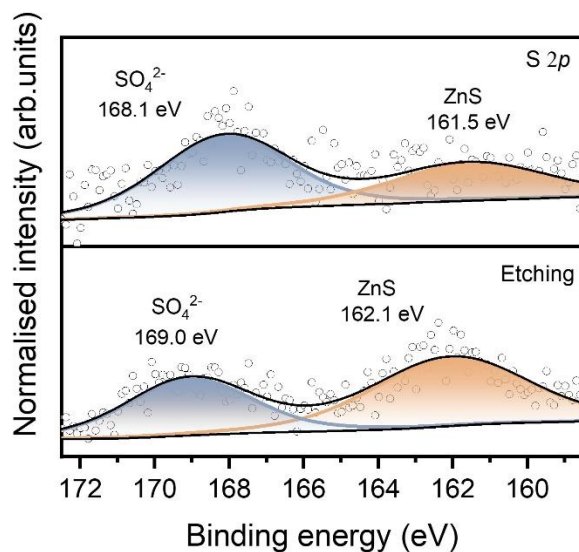


Figure S6. XPS spectra of S 2p for the cycled Zn@PAH/PAA electrode before and after  $\text{Ar}^+$  etching (etching depth was set to 50 nm ( $\text{TiO}_2$  reference)). (Cycling parameter: 50 cycles at  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mAh cm}^{-2}$ ).

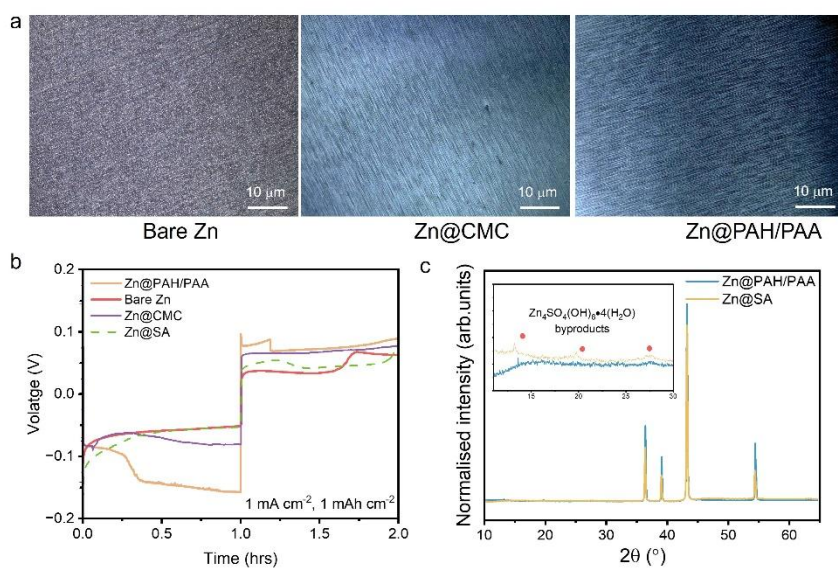


Figure S7. (a) Optical image after coating in mono and multilayers. (b) Zn||Zn performance at  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$ . (c) XRD comparisons after 50 cycles at  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$ .



Figure S8. Contact angle test of  $2\text{M ZnSO}_4$  on Zn@PAH/PAA and Bare Zn.

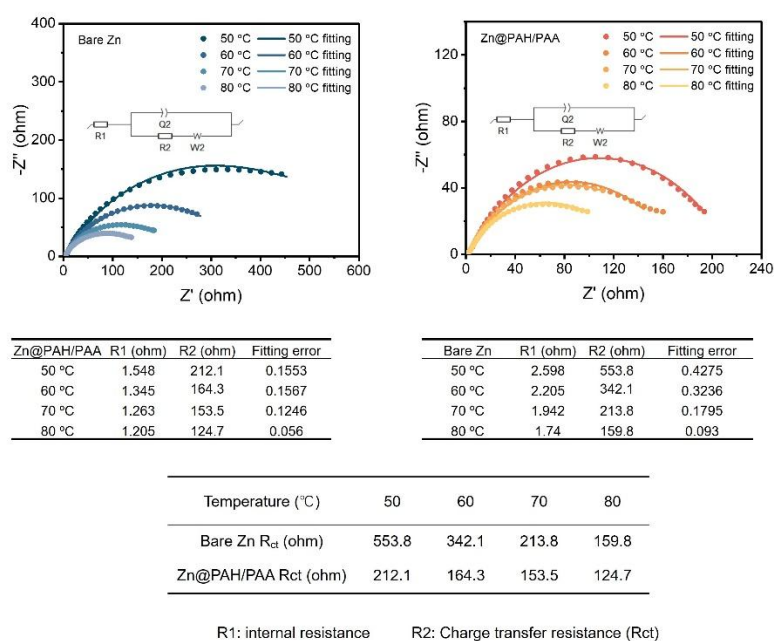


Figure S9. EIS test at different temperatures of Zn@PAH/PAA and Bare Zn.

Zn transference number was calculated by the equation as below, where the potentiation polarisation ( $\nabla V$ ) is 5 mV,  $R_o$  and  $R_{ss}$  are the initial and steady state resistances, and  $I_o$  and  $I_{ss}$  are initial and steady currents, respectively.

$$t_+ = \frac{(\nabla V/I_o - R_o)}{(\nabla V/I_{ss} - R_{ss})}$$

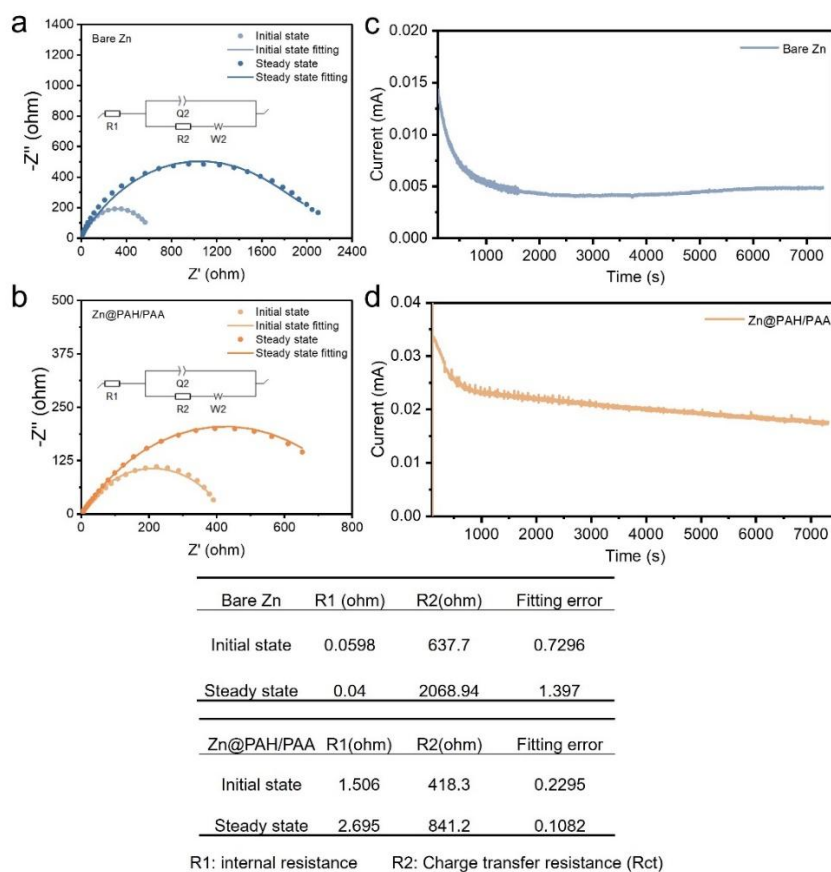


Figure S10. Zn transference number calculation. EIS test at before and after the potentiostatic polarisation for Bare Zn (a) and Zn@PAH/PAA (b). Current profile under the potentiostatic polarisation ( $\nabla V = 5$  mV) for Bare Zn (c) and Zn@PAH/PAA (d).

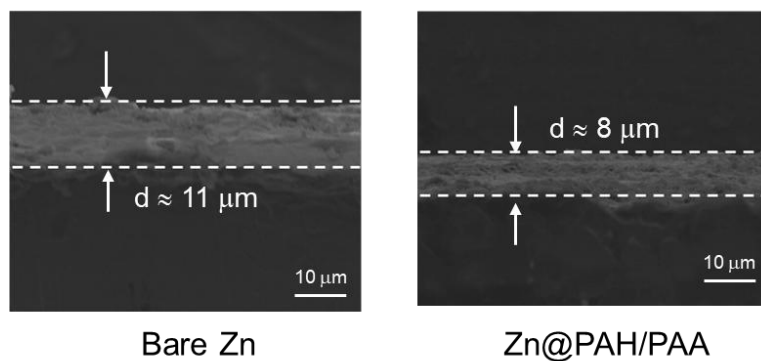


Figure S11. Cross-section SEM images after 50 cycles at  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mAh cm}^{-2}$ .

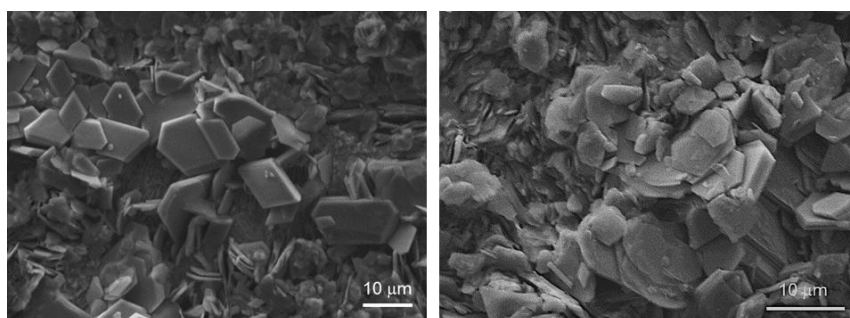


Figure S12. SEM images of Bare Zn after 50 cycles at  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mAh cm}^{-2}$ .

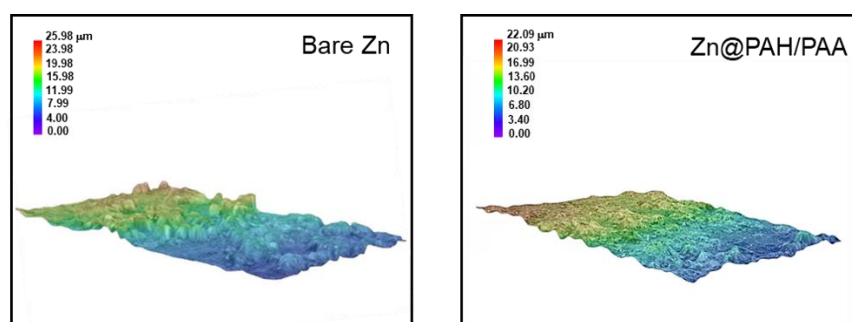


Figure S13. 3D depth profiles of Zn@PAH/PAA and Bare Zn after 50 cycles at  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mAh cm}^{-2}$ .

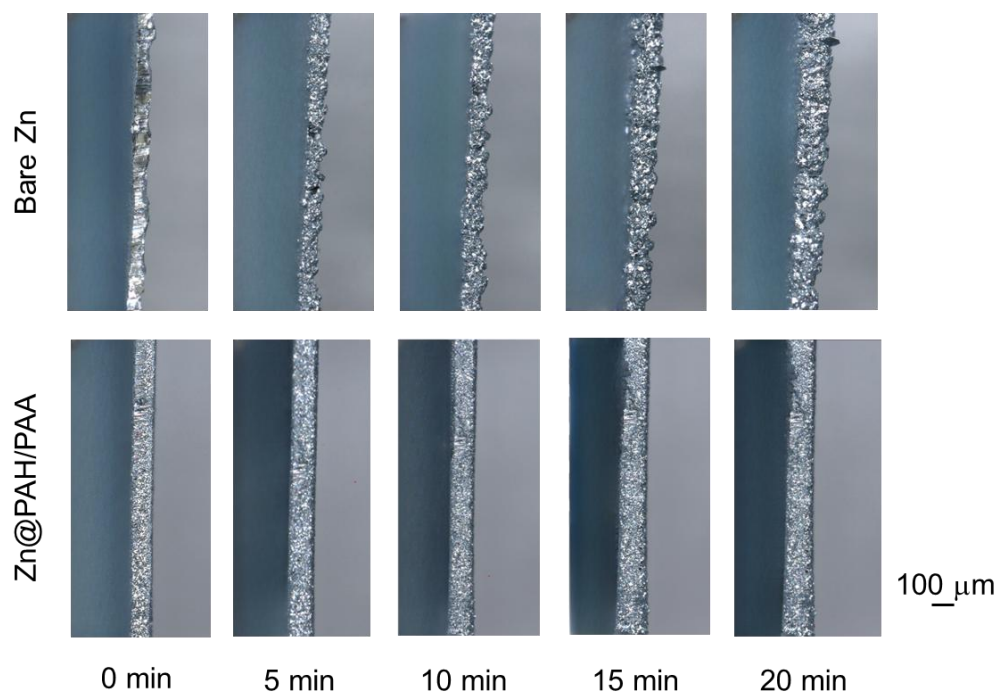


Figure S14. *In-situ* optical image of Zn plating on Zn@PAH/PAA and Bare Zn at a current density of  $30 \text{ mA cm}^{-2}$ .

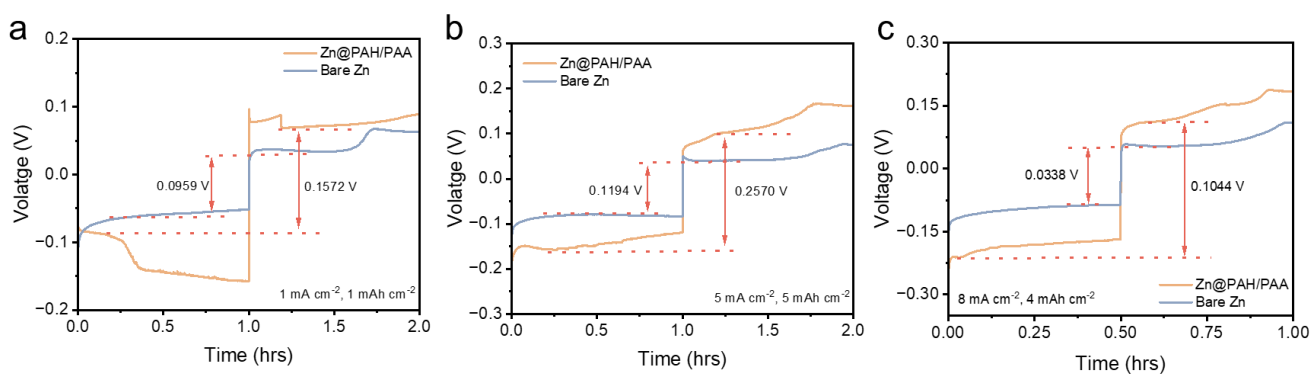


Figure S15. The voltage profile of the symmetric Zn cell at  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$  (a),  $5 \text{ mA cm}^{-2}$  and  $5 \text{ mAh cm}^{-2}$  (b), and  $8 \text{ mA cm}^{-2}$  and  $4 \text{ mAh cm}^{-2}$  (c).

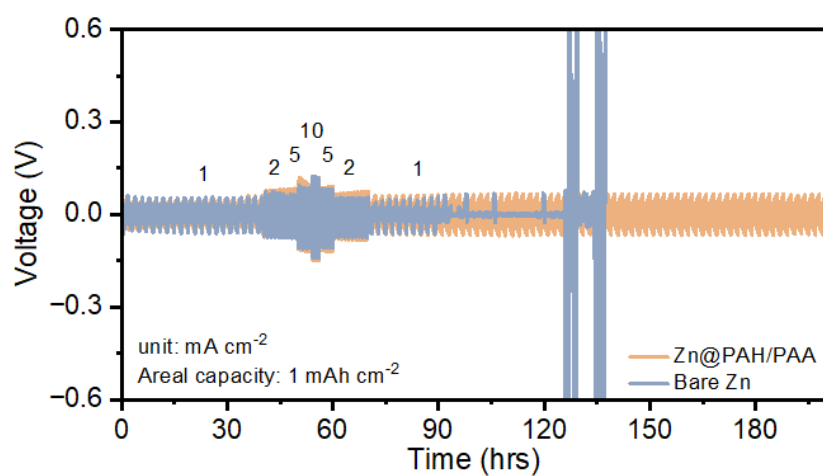


Figure S16. The rate performance of the symmetric Zn cell.

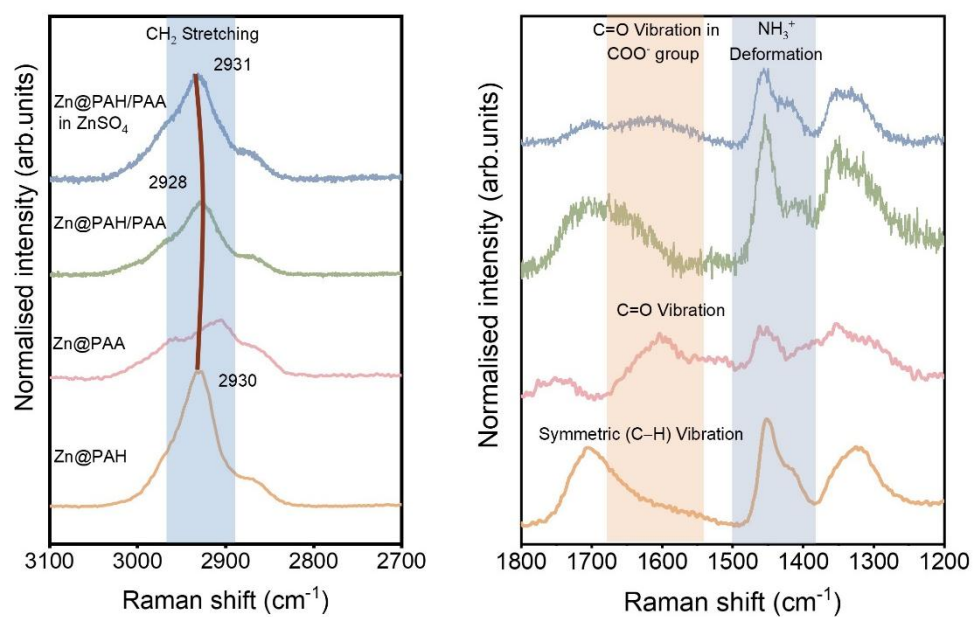


Figure S17. *In-situ* Raman spectra of different substrates.

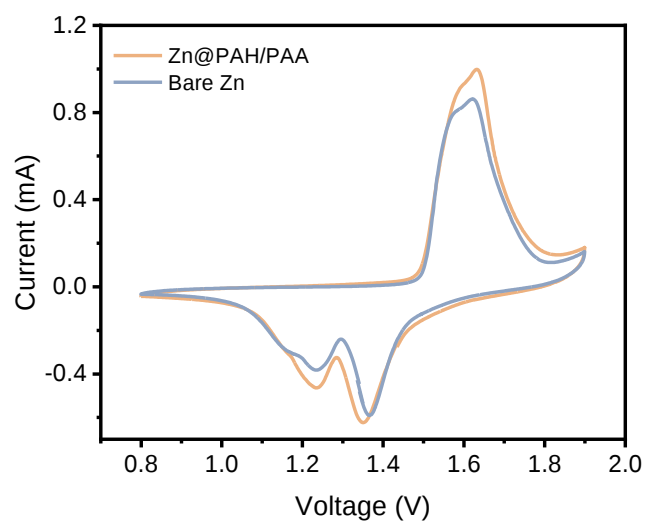


Figure S18. CV curves at a scan rate of  $0.1 \text{ mV s}^{-1}$  for the Zn-MnO<sub>2</sub> full cell.

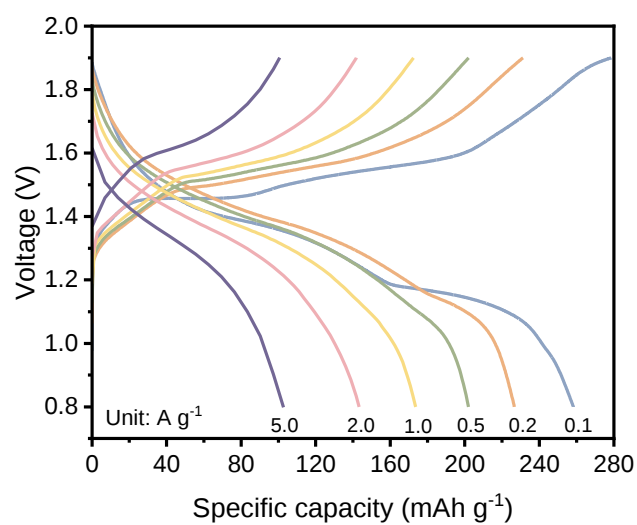


Figure S19. The correspond voltage-capacity profile at different current density.

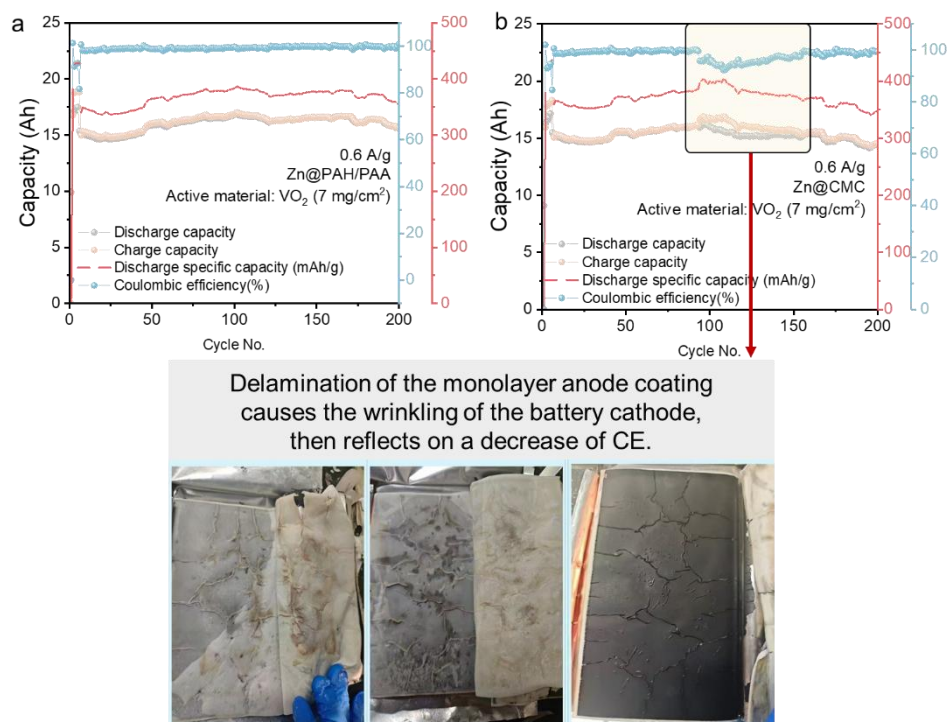


Figure S20. (a) Pouch cell of Zn@PAH/PAA in 15Ah; (b) Pouch cell of Zn@CMC in 15Ah (Anode coating layer delamination).

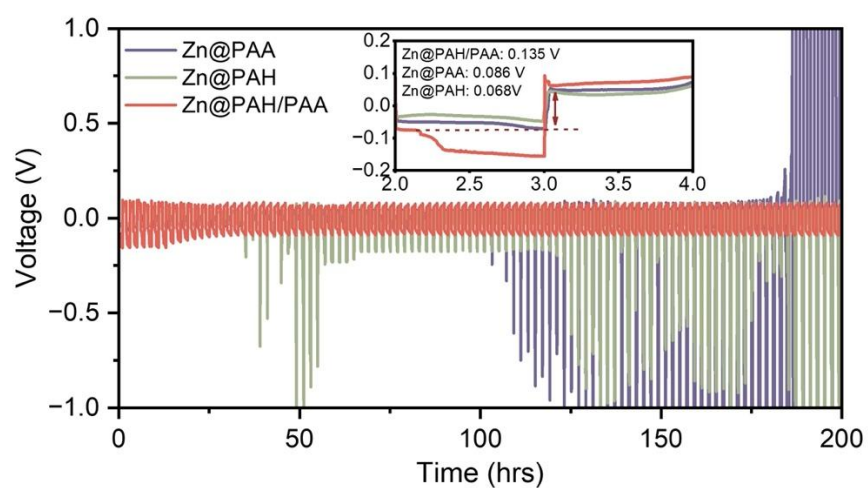


Figure S21 The galvanostatic cycling performances of Zn symmetric cells at  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$  with coatings of PAH/PAA multilayers, PAA monolayer, and PAH monolayer, respectively.

Table S1 XRD Intensity.

| Plane | Pristine | 15 cycles | 30 cycles | 50 cycles |
|-------|----------|-----------|-----------|-----------|
| 002   | 46.94    | 69.96     | 126.92    | 190.96    |
| 100   | 81.66    | 107.3     | 78.44     | 106.26    |
| 101   | 768      | 638.78    | 552.14    | 642.14    |

Table S2 Comparison of recent anode performance on CPC, cycle number and average CE.

| Reference | Sample (coating layer)                                                                         | Test condition                                       | Cycle number | Cumulative plated capacity (mAh cm <sup>-2</sup> ) | Average CE (%) |
|-----------|------------------------------------------------------------------------------------------------|------------------------------------------------------|--------------|----------------------------------------------------|----------------|
| 43        | CCF (cerium based conversion film)                                                             | 1.13 mA cm <sup>-1</sup> ; 0.57 mAh cm <sup>-2</sup> | 120          | 68.4                                               | 99.1           |
| 44        | ZCS (Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> and ZnF <sub>2</sub> composite SEI layer) | 4 mA cm <sup>-2</sup> ; 2 mAh cm <sup>-2</sup>       | 90           | 180                                                | 99.54          |
| 45        | PVA@SR-ZnMoO <sub>4</sub>                                                                      | 0.5 mA cm <sup>-2</sup> ; 0.5 mAh cm <sup>-2</sup>   | ~500         | ~250                                               | 99.42          |
| 46        | ZnS                                                                                            | 2 mA cm <sup>-2</sup> ; 1 mAh cm <sup>-2</sup>       | 200          | 200                                                | 99.2           |
| 47        | ZnO(3D)                                                                                        | 2 mA cm <sup>-2</sup> ; 0.5 mAh cm <sup>-2</sup>     | 300          | 150                                                | 99.55          |
| 48        | PVB(poly(vinyl butyral))                                                                       | 4 mA cm <sup>-2</sup> ; 2 mAh cm <sup>-2</sup>       | 110          | 220                                                | 99.4           |
| This work | PAH/PAA                                                                                        | 0.5 mA cm <sup>-2</sup> ; 0.25 mAh cm <sup>-2</sup>  | 1585         | 396                                                | 99.7           |

Table S3 The periodic band changes at -CH<sub>2</sub> and C=O groups.

| CH <sub>2</sub> stretching      |         |          |         |         |         |         |
|---------------------------------|---------|----------|---------|---------|---------|---------|
| Cycle                           | 1st Dis | 1 st Chr | 2nd Dis | 2nd Chr | 3rd Dis | 3rd Chr |
| Raman shift (cm <sup>-1</sup> ) | 2925.8  | 2929.1   | 2926.4  | 2929.9  | 2924.4  | 2928.2  |
| C=O vibration                   |         |          |         |         |         |         |
| Cycle                           | 1st Dis | 1 st Chr | 2nd Dis | 2nd Chr | 3rd Dis | 3rd Chr |
| Raman shift (cm <sup>-1</sup> ) | 1609.9  | 1616.7   | 1594.5  | 1604.7  | 1599.6  | 1604.2  |

Table S4 The binding energy of different coordination structure of PAH<sup>+</sup>.

| Coordination                                                         | Binding energy (eV) |
|----------------------------------------------------------------------|---------------------|
| ZnSO <sub>4</sub>                                                    | -3.785              |
| [Zn(SO <sub>4</sub> ) <sub>2</sub> ] <sup>2-</sup>                   | -10.069             |
| [(PAH) <sub>3</sub> SO <sub>4</sub> ] <sup>+</sup>                   | -18.766             |
| [(PAH) <sub>3</sub> Zn(SO <sub>4</sub> ) <sub>2</sub> ] <sup>+</sup> | -26.33              |
| [(PAA) <sub>1</sub> SO <sub>4</sub> ] <sup>3+</sup>                  | -7.384              |

Table S5 Comparison of anode performance regarding Zn metal pouch cells on capacity, cycle number and C-rate.

| Reference | Material                                                            | Capacity (Ah) | Specific current (A g <sup>-1</sup> ) | Cycle number |
|-----------|---------------------------------------------------------------------|---------------|---------------------------------------|--------------|
| 55        | VO <sub>2</sub>                                                     | 0.8           | 0.1                                   | 200          |
| 56        | Zn <sub>0.25</sub> V <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O | 2.3           | 0.044                                 | 160          |
| 57        | Zn <sub>x</sub> V <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O    | 0.9           | 0.2                                   | 200          |
| 58        | Commercial VOX                                                      | 2.7           | 0.05                                  | 220          |
| 59        | V <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O                    | 1.32          | 0.1                                   | 65           |
| This work | VO <sub>2</sub>                                                     | 17.36         | 0.43                                  | 250          |

Table S6 Cost breakdown for the LbL self-assembled PAH/PAA multilayers strategy.

| Item                                 | Unit Price              | Quantity Required              | Total Cost               | Notes                                                        |
|--------------------------------------|-------------------------|--------------------------------|--------------------------|--------------------------------------------------------------|
| Poly(allylamine hydrochloride) (PAH) | \$6.1 / g               | 2 g per m <sup>2</sup> coating | \$12.20 / m <sup>2</sup> | Based on ¥218.0 / 5 g; molecular weight ~50,000.             |
| Poly(acrylic acid) (PAA)             | \$0.98 / kg             | 5 g per m <sup>2</sup> coating | \$0.001 / m <sup>2</sup> | Economical, bulk industrial price of PAA at ¥7,000 per ton.  |
| Deionized Water (Solvent)            | \$0.007 / L             | 2 L per m <sup>2</sup> coating | \$0.014 / m <sup>2</sup> | Environmentally friendly solvent used for LbL assembly.      |
| Processing (Roll-to-Roll Coating)    | \$0.56 / m <sup>2</sup> | 1 m <sup>2</sup> coating area  | \$0.56 / m <sup>2</sup>  | Estimated using industrial roll-to-roll coating costs.       |
| Energy Costs (Drying)                | \$0.11 / m <sup>2</sup> | 1 m <sup>2</sup> coating area  | \$0.11 / m <sup>2</sup>  | Includes heating and drying during the LbL assembly process. |
| Total (Lab scale)                    | \$12.87/ m <sup>2</sup> |                                |                          |                                                              |
| Total (Industrial Scale)             | \$4-6.40/m <sup>2</sup> |                                |                          | 50-70% price reduction                                       |