# Supporting Information

# Zinc iso-plating/stripping: Toward a practical Zn powder anode with ultra-long life over

5600 h

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### EXPERIMENTAL

### **Part I: Methods**

# 1. Materials.

The chemicals and materials in this work are all commercially available. Zinc sulfate heptahydrate (ZnSO<sub>4</sub>·7H<sub>2</sub>O, AR), zinc powder (Zn powder, 5N) and sulfuric acid (0.5 M) were purchased from Sinopharm Chemical Reagent Co., Ltd. Manganese sulfate monohydrate (MnSO<sub>4</sub>·H<sub>2</sub>O, AR), Potassium Permanganate (KMnO<sub>4</sub>, AR) and ethylene glycol (EG, 99.5%) were purchased from Adamas-beta. Bismuth trinitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, 99.9%) was purchased from Macklin. Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, AR) and ethanol (EtOH, 99.5%) were purchased from Energy Chemical. The coin cells were obtained from Guangdong Canrd New Energy Technology Co., Ltd.

#### 2. Bare Zn powder anode Preparation.

Typically, the bare Zn powder anode was fabricated by simply mixing Zn powders with polyvinylidene fluoride (PVDF; Aladdin) binder in N-methyl pyrrolidone (NMP; AR grade, Aladdin) solvent according to a mass ratio of 98:2, followed by vigorous stirring for 12 h. After that, the wet mixture was cast on Ti foil via a scraper and dried at 80 °C overnight in a vacuum environment. The Zn powder mass loading is 5-20 mg cm<sup>-2</sup>.

### 3. Bi@Zn powder anode Preparation.

First, the mixed solution of 0.728g bismuth nitrate pentahydrate ( $Bi(NO_3)_3 \cdot 5H_2O$ ) and 10 mL ethylene glycol (EG) was magnetically stirred for 30 minutes. Following the addition of

20 mL ethanol (EtOH), the solution was kept under ultrasonic conditions for 30 minutes and then stirred for 30 minutes to obtain solution A. 10g Zn powder was then impregnated in the solution for 5 minutes to obtain a black coating layer. After that, the resulting Bi@Zn powder was collected by filtration, washed three times with ethanol, and dried using a vacuum oven at 50 °C.

Finally, the Bi@Zn powder anode was fabricated by simply mixing Bi@Zn powder s with polyvinylidene fluoride (PVDF; Aladdin) binder in N-methyl pyrrolidone (NMP; AR grade, Aladdin) solvent according to a mass ratio of 98:2, followed by vigorous stirring for 12 h. After that, the wet mixture was cast on Ti foil via a scraper and dried at 80 °C overnight in a vacuum environment. The Bi@Zn powder mass loading is 5-20 mg cm<sup>-2</sup>.

#### 4. The α-MnO<sub>2</sub> cathode Preparation.

 $\alpha$ -MnO<sub>2</sub> was synthesized according to the reported hydrothermal method.<sup>1</sup> Typically, 3 mmol of MnSO<sub>4</sub>·H<sub>2</sub>O and 2 mL of H<sub>2</sub>SO<sub>4</sub> (0.5 M) were dissolved in 90 mL of water. After sonicating for 10 min, 20 mL of KMnO<sub>4</sub> (0.1 M) was dropped into the solution and stirred for 2h at room temperature. The solution was then transferred to a Teflon-lined autoclave and heated at 120 °C for 12 h. After cooling naturally, the product was washed with pure water and finally dried at 80 °C for a whole night.

The  $\alpha$ -MnO<sub>2</sub> cathodes were prepared by a standard method:  $\alpha$ -MnO<sub>2</sub> was mixed with acetylene black and polyvinylidene fluoride (PVDF) in a mass ratio of 7:2:1 and ground for 0.5 h. Then, the mixture was mixed with an appropriate amount of N-methyl-2-pyrrolidone (NMP) solvent and stirred to form a slurry. After that, the slurry was evenly spread onto Titanium foil and dried overnight at 80 °C under vacuum. The  $\alpha$ -MnO<sub>2</sub> mass loading is 2 mg cm<sup>-2</sup>.

# 5. Characterization.

Materials characterization: The surficial chemical composition was detected using the Raman spectra (HORIBA Scientific LabRAM HR Evolution), X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha<sup>+</sup>), X-ray diffraction (XRD, Bruker D2 Phaser) with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) at a scan rate of 2° min<sup>-1</sup> between 5-90° under 40 KV voltage. The microstructures and morphologies of Bi@Zn powder were investigated by field emission scanning electron microscopy (FESEM, JEOL 7100F) and transmission electron microscopy (TEM, JEOL 2100F). The elemental distributions and line-scan profiles of Bi@Zn powder were analyzed by using energy dispersive spectroscopy (EDS) affiliated with the TEM (JEOL 2100F). The inductively coupled plasma mass spectrometry (ICP-MS, Aglient 7800) was adopted to determine the contents of Bi and Zn in Bi@Zn powder.

In-situ characterization: The in-situ optical images were obtained on a dendrite observation microscope (YUESCOPE YM710R) by an electrochemical cell with an optical window. In-situ XRD measurements were characterized via Bruker D8 advance with Cu Ka radiation ( $\lambda = 1.5406$  Å) under 40 KV voltage. A homemade cell, with a glassy carbon window (which serves as the working electrode) and a Zn powder anode, was cycled at 1 mA cm<sup>-2</sup> and 0.5 mAh cm<sup>-2</sup> with a single XRD pattern (25-40°) collection time of 6 min. The insitu DEMS experiment was carried out through online electrochemical mass spectrometry

(QAS 100Li) and EC-DEMS cell (swagelok type). During the DEMS test, the Zn  $\parallel$  Zn symmetrical cell was continuously purged by Ar gas at a flow rate of 1.12ml/min. The evolved gases from the battery were pumped into the mass spectrometer, where they were bombarded to form different fragments with different m/e values for structural analysis. The galvanostatic charging and discharging processes were performed by Neware battery system at the current density of 0.5 mA cm<sup>-2</sup>.

#### 6. Electrochemical Measurements.

All coin-type batteries tested were assembled in CR2032 cells based on the electrolyte of 2 M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub> and glass fiber separators of 19 mm diameter (Whatman GF/D). Each coin-type symmetric battery consisted of two identical bare Zn powder or Bi@Zn powder electrodes (12 mm diameter and 20 mg cm<sup>-2</sup> mass loading). Each coin-type Zn//Ti half battery contained a bare Zn powder electrode or a Bi@Zn powder electrode of 12 mm diameter as the anode and a Ti foil of 12 mm diameter as the cathode. The coin-type Zn//MnO<sub>2</sub> full batteries were assembled from the  $\alpha$ -MnO<sub>2</sub> cathodes (12 mm diameter and 2 mg cm<sup>-2</sup> mass loading) and Zn anodes (12 mm diameter and 5 mg cm<sup>-2</sup> mass loading).

Each pouch-type Bi@Zn powder//MnO<sub>2</sub> full battery was assembled with a  $4\times8$  cm<sup>2</sup> Bi@Zn powder anode and a  $4\times8$  cm<sup>2</sup>  $\alpha$ -MnO<sub>2</sub> cathode. The shell of the pouch battery was an aluminum–plastic film and the separator is a  $4.5\times8.5$  cm<sup>2</sup> glass fiber.

Note that all the batteries were assembled in open air condition and aged for 3 h before the electrochemical measurements. All of the galvanostatic charge/discharge of symmetrical and asymmetrical batteries were carried out on a CT3001A cell testing system (Wuhan LAND Electronic Co.Ltd.). The full cell test was performed using a sequence of charging followed by discharging with cut-off voltages of 1.8 V and 1.0 V.

The linear polarization and linear sweep voltammetry (LSV) tests were carried on a CHI 660E electrochemical workstation. The LSV tests were analyzed by assembled CR2025 coin cells which stainless steel foil as working electrode, Zn plate as counter and reference electrode, a glass fiber membrane GF/D (Whatman) was used as the separator, the electrolyte was adopted to the 1 M Na<sub>2</sub>SO<sub>4</sub> solution. The linear polarization test was analyzed by three-electrode systems which Ti foil, Zn plate and Ag/AgCl adopted as working, counter and reference and reference electrode, 2 M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub> was used as electrolyte.

# 7. Calculation of negative/positive electrode capacity ratio (N/P ratio).

$$N/P \ ratio = \frac{Zn \ anode \ capacity}{MnO_2 \ capacity} = \frac{m_{Zn} \times Q_{g,Zn}}{m_{MnO_2} \times Q_{g,MnO_2}}$$
(1)

Where  $m_{Zn}$ ,  $Q_{g,Zn}$ ,  $m_{MnO_2}$ ,  $Q_{g,MnO_2}$  represent the mass of Zn (12 mm diameter and 5 mg cm<sup>-2</sup> mass loading), gravimetric capacity of Zn (820 mAh g<sup>-1</sup>), the mass of  $MnO_2$  (12 mm diameter and 2 mg cm<sup>-2</sup> mass loading), gravimetric capacity of  $MnO_2$  (308 mAh g<sup>-1</sup>).

According to equation (1), the  $\frac{N/P \, ratio}{2 \times 10^{-3} \times 308} = 6.65$ . Note that only the theoretical capacity provided by the cathode and anode active materials is considered in this work.

# 8. Calculation of Energy Density (ED) and Power Density (PD).

$$PD = I \times \Delta V_{cell} \tag{2}$$

$$ED = Q \times \Delta V_{cell} \tag{3}$$

Where I,  $\Delta V_{cell}$ , Q represent the electric current density (0.5 A g<sup>-1</sup>), the difference of the average operating potentials of the positive and the negative electrode (~1.4 V), the specific capacities of the active materials (99 mAh g<sup>-1</sup>). According to equation (2), the  $PD = I \times \Delta V_{cell} = 0.5 \times 1000 \times 1.4 = 700 W kg^{-1}$ . According to equation (3), the  $ED = Q \times \Delta V_{cell} = 99 \times 1.4 = 138.6 kW kg^{-1}$ .

# **Part II: Calculations**

## 1. Method of DFT calculations.

All the theoretical calculations were carried out with the density functional theory (DFT) method as implemented in the Vienna Ab Initio Simulation Package (VASP).<sup>2</sup> The electronion interaction was described with the projector augmented wave (PAW) method,<sup>3</sup> while the electron exchange and correlation energy were solved within the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.<sup>4, 5</sup> The kinetic energy cutoff of the plane wave was set to be 400 eV and the convergence criterion for the residual forces and total energies were set to be 0.05 eV Å<sup>-1</sup> and 10<sup>-5</sup> eV, respectively. A vacuum layer of at least 15 Å along the z direction was set between the periodically repeated slabs to avoid strong interactions and a  $3\times3\times1$  Monkhorst-Pack k-point grids was used to sample the Brillouin zone. The empirical correction in Grimme's method (DFT+D3) was used to describe van der Waals interaction,<sup>6</sup>

The Gibbs free energy change ( $\Delta G$ ) was calculated by using the computational hydrogen electrode (CHE) model proposed by Nørskov et al.<sup>7</sup> In this model, the chemical potential of the proton-electron pair in aqueous solution is related to that of one-half of the chemical potential of an isolated hydrogen molecule. The  $\Delta G$  value can be obtained by the formula:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \tag{4}$$

where  $\Delta E$  is the reaction energy of reactant and product species adsorbed on the catalyst directly obtained from DFT calculations;  $\Delta ZPE$  and  $\Delta S$  are the changes between the adsorbed species and the gas phase molecules in zero-point energies and entropy at 298.15 K, which can be calculated from the vibrational frequencies.

The adsorption energy  $(E_{ads})$  was calculated based on the equation:

$$E_{ads} = E_{total} - E_{substrate} - E_{adsorbate}$$
(5)

where  $E_{total}$ ,  $E_{substrate}$  and  $E_{adsorbate}$  represent the total energies with potential dependence of the systems containing the substrate and adsorbate, the substrate, and the adsorbate, respectively. According to this definition, a more negative adsorption energy indicates a stronger interaction.

#### 2. COMSOL simulations.

In order to simulate the dynamic Zn deposition/dissolution on different electrodes, a Finite Element Analysis (FEA) model was performed using COMSOL Multiphysics 6.1 software with the "Tertiary Current Distribution" and "Phase Field" module. The size of the entire two-dimensional model for electric field distribution analysis was set to  $240 \times 120 \mu m$ . The simplified physical structure of the bare Zn powder anode is a stack of multiple circles with a radius of 10  $\mu m$  (Figure S8b). Since Bi-metal nanosheets are protrusions on the surface of Bi@Zn powder, the structure is modeled as a 10  $\mu m$  radius circle with six 1  $\mu m$  radius circles (Figure S8c). A transient simulation of the process was carried out in an area filled with electrolyte. The current density was set to 1 mA cm<sup>-2</sup> and the plating/stripping process was simulated using the phase field method.

The  $Zn^{2+}$  transfers by the concentration diffusion in model follow the Fick's law as shown in equation (6) and (7):

$$N_i = J_i = -D_i \nabla c_i \tag{6}$$

$$\frac{\partial c_i}{\partial t} + \nabla J_i = R_{i,tot} \tag{7}$$

where  $J_i$  is the ion flux,  $D_i$  is the diffusion coefficient of electrolytes (  $D_{Zn} = 2.0 \times 10^{-9} m^2 s^{-1}$  for ZnSO<sub>4</sub> electrolyte),  $c_i$  is the ion concentration of electrolytes (  $c_i = 2.0 M_{i}$ ,  $\nabla c_i$  is concentration gradient.

The relation between the diffusion coefficient and electric mobility follows the Nernst-Einstein relation as shown in equation (8):

$$N_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l + u c_i = J_i + u c_i$$
(8)

where  $z_i$  is the transfer number ( $z_{Zn} = 2$ ),  $u_{m,i}$  is the electric mobility coefficient, F is the Faraday constant (96485 C mol<sup>-1</sup>),  $\phi$  is the electrolyte potential.

The equilibrium potential of the electrode surface follows the Nernst equation as shown in equation (9) and (10):

$$E_{eq} = -\frac{\Delta G}{nF} \tag{9}$$

$$E_{eq} = E_{eq,ref} - \frac{RT}{nF} ln \prod_{i} \left( \frac{\alpha_i}{\alpha_{i,ref}} \right)^{\nu_i}$$
(10)

where  $E_{eq}$  is the electrode potential,  $E_{eq,ref}$  is the standard electrode potential,  $\Delta G$  is the Gibbs free energy, R is the ideal gas constant, T is the temperature (T = 298 K), n is the transfer electron number of the reaction,  $\alpha_i$  is the electrode reactive ion concentration,  $\alpha_{i,ref}$  is the standard electrode reactive ion concentration,  $v_i$  is the reaction stoichiometric number.

The electrode reaction for the electrode surface follows the Butler-Volmer kinetics expression, as shown in equation (11):

$$i_{loc} = i_0 \left( exp\left(\frac{\alpha_a F \eta}{RT}\right) - exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right)$$
(11)

where  $i_{loc}$  is the local current density at the electrode/electrolyte interface,  $i_0$  is the

exchange current density ( $i_0 = 1 \ mA \ cm^{-2}$ ), and is the cathodic and anodic charge transfer coefficients ( $\alpha_a = 0.5$ ,  $\alpha_c = 1.5$ ),  $\eta$  is the activation overpotential.

# Part III: Supporting Figures



Figure S1. (a-b) In-situ optical observation of Zn plating on the bare Zn powder anode at 5

mA cm<sup>-2</sup>.



Figure S2. (a-b) In-situ optical observation of Zn stripping on the bare Zn powder anode at 5 mA cm<sup>-2</sup>. COMSOL simulation of (c-d) current density distribution, (e-f) Zn<sup>2+</sup> concentration distribution and morphology evolution of the bare Zn powder anode during stripping.



Figure S3. Long-term galvanostatic cycling performance of symmetric batteries with the bare Zn powder anode tested at 0.2 mA cm<sup>-2</sup> and 0.2 mAh cm<sup>-2</sup>.



**Figure S4.** Morphology evolution of (a-c) bare Zn powder anodes after different cycles at 1 mA cm<sup>-2</sup> and 0.5 mAh cm<sup>-2</sup>. (d) Digital image of the membrane after cycling.



Figure S5. COMSOL simulation of current density distribution and morphology evolution of

the Zn foil anode during plating.



Figure S6. Long-term galvanostatic cycling performance of symmetric batteries with the Zn

foil anode tested at 0.2 mA cm<sup>-2</sup> and 0.2 mAh cm<sup>-2</sup>.



Figure S7. Digital images of (a) the in-situ optical microscope (YM710R), top view (b) and

(c) front view of the combined in-situ optical cell.



Figure S8. COMSOL simulation of physical model: (a) Zn foil, (b) bare Zn powder anode,

and (c) Bi@Zn powder anode.



Figure S9. The price of metals with high hydrogen evolution overpotential.

The price of metals with high hydrogen evolution overpotential. (Metal prices were referenced from the following links: https://www.dailymetalprice.com/metalpricecharts.php; https://www.recyclingmonster.com/price/bi-metal-crv-cans/352.)

Zincophilic metal Bi<sup>8-11</sup> has the advantages of low cost, non-toxic and suitable voltage, which can significantly improve the corrosion resistance due to its chemical inertness. Most importantly, Bi metal can effectively inhibit HER because of the weak binding energy to H<sup>\*</sup> intermediates. These characteristics indicate that it is very promising to construct Bi metal on zinc powder surface as nucleating agent and inhibitor.



Figure S10. The synthetic route of Bi@Zn powder.

Zn powders are decorated with zincophilic metal Bi nanosheets by a spontaneous galvanic replacement reaction  $(3Zn + 2Bi^{3+} \rightarrow 3Zn^{2+} + 2Bi)$  through dipping bare Zn powders into 0.05 M Bi(NO<sub>3</sub>)<sub>3</sub> solution (ethylene glycol: ethanol=1:2, volume ratio) for 5 minutes (Figure S10-13). Since the redox potential of Zn (-0.76 V vs. SHE) is lower than that of Bi (0.32 V vs. SHE), the in-situ growth of Bi-metal on the surface of Zn powders can occur by the reaction process of  $3Zn + 2Bi^{3+} \rightarrow 3Zn^{2+} + 2Bi$ . Such in-situ formed protective layer can not only guarantee uniform surface coating of Bi-metal but also enable good adhesion between Zn powders and Bi-metal.



Figure S11. (a) Commercial zinc powder. (b-c) SEM of commercial Zn powder (d) Particle size distribution of commercial Zn powder.

Commercial Zn powder appeared a gray pile in macroscopic view (Figure S11a), which is composed of smooth spherical particles (Figure S11c) with a size ranging from 3.18 to 37.5  $\mu$ m and the mean diameter of 13.68  $\mu$ m 6.3 to 27.5  $\mu$ m (Figure S11d). Zn powder particle size can be accepted as normal distribution basically.



Figure S12. (a) The surface morphology and EDS mappings of Bi@Zn powder.

(b) Energy dispersive X-ray spectrum of the species scraped from Bi@Zn powder.



Figure S13. The transmission electron microscopy (TEM) image of the Bi@Zn powder.

The transmission electron microscopy (TEM) image also revealed the nanosheets of the Bi@Zn powder.



**Figure S14.** The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding elemental mapping images of the Bi@Zn powder.

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding elemental mapping images of the Bi@Zn powder also confirm that nanosheets are mainly composed of element Bi.



Figure S15. The Inductive Coupled Plasma Emission Spectrometer (ICP) of the bare Zn powder and Bi@Zn powder.

The content of Bi element Bi@Zn powder is 1.58% measured by Inductive Coupled Plasma Emission Spectrometer (ICP).



Figure S16. The high-resolution transmission electron microscopy (HRTEM) image and the contrast line profiles of Bi@Zn powder.

The high-resolution TEM (HRTEM) image of the nanosheets structure on the surface of the Bi@Zn powder depicted that the lattice spacings are 0.328 and 0.237 nm, respectively, well indexed to (012) and (104) planes of metallic Bi.



Figure S17. The X-ray diffraction (XRD) pattern of the bare Zn powder and Bi@Zn powder.

Besides the peaks of Zn- metal (JCPDS No. 87-0713), the two diffractions peaks located at 27.16° and 37.95° can be assigned to the (012) planes and the (104) planes of Bi (JCPDS No. 85-1329), respectively, which is consistent with the results of HRTEM.



Figure S18. The Raman spectroscopy of the bare Zn powder and Bi@ Zn powder.

Compared with the bare Zn powder, the Bi@Zn powder shows a strong Raman peak centered on 91.2 cm<sup>-1</sup> and a weak Raman peak centered on 309.0 cm<sup>-1</sup>, which assign to the Bi-Bi and Bi-O bonds, accordingly.



Figure S19. The X-ray photoelectron spectroscopy (XPS) spectra of the bare Zn powder and Bi@ Zn powder. (a) Full spectra, (b) high-resolution Bi 4f spectra of Bi@Zn-p, and (c) high resolution Zn 2p spectra.

XPS analysis confirms the similar composition of Zn, O and C elements in the bare Zn powder and Bi@Zn powder, indicating their inevitable presence of Zn-O and/or Bi-O bonds (Figure S19a). In the Bi 4*f* spectrum, signals at 164.2/158.9 eV and 162.1/156.8 eV are attributed to Bi-O bonds and metallic Bi, respectively (Figure S19b).<sup>12, 13</sup> These are consistent with the results of Raman spectroscopy, which may be related to the inevitable oxidation of Bi metal particles in the air.<sup>14</sup> In addition, the Zn 2p XPS spectrum of the bare Zn powder (Figure S19c) shows two typical peaks, Zn 2p<sub>3/2</sub> (1021.4 eV) and Zn 2p<sub>1/2</sub> (1044.5 eV), showing spin energy separation of 23.1 eV, consistent with the value of Zn<sup>2+.15</sup> In contrast, the characteristic peaks of Zn 2p in Bi@Zn powder shift to the lower binding energy, indicating a decrease in the valence state for Zn.<sup>10</sup>



Figure S20. Optical photograph of Zn powder@Ti.

Zn powder, well-known as the anode materials of dry battery, can be directly used in existing electrode preparation techniques, such as electrode paste-casting method. The use of zinc powder allows for large-scale preparation of electrodes and better control of mass loading.



Figure S21. Optical photographs and SEM of (a-b) the bare Zn powder anode and (c-d) the

Bi@Zn powder anode.



**Figure S22.** The voltage profiles of the Zn symmetric cell are tested using the bare Zn powder anode and the Bi@Zn powder anode at the current density of 0.2 mA cm<sup>-2</sup> with the capacity of 0.1 mAh cm<sup>-2</sup>.

Zn//Zn symmetric batteries are assembled using the anode prepared by the different samples, and the constant current charge-discharge tests are carried out to study the influence of Bi hetero-metallic interface layer on the cycle performance.

As presented in Figure S22, the deterioration of overpotential (take 0.2 mA cm<sup>-2</sup>, 0.1 mAh cm<sup>-2</sup> as the criterion) of bare Zn powder anode is earlier than 25 h, while the Bi@Zn powder enabled better cycling durability over 600 h. The results show that the Bi heterometallic interface layer has positive effects on zinc powder anode.



Figure S23. The voltage profiles of the Zn symmetric cell are tested using 0.05 M Bi@Zn powder, 0.01 M Bi@Zn powder, and 0.1 M Bi@Zn powder anode at the current density of 0.2 mA cm<sup>-2</sup> with the capacity of 0.1 mAh cm<sup>-2</sup>.

The Zn powders are soaked in Bi (NO<sub>3</sub>)<sub>3</sub> solution of 0.01 M, 0.05 M and 0.1 M for 5 min, and recorded as 0.01 M Bi@Zn powder, 0.05 M Bi@Zn powder and 0.1 M Bi@Zn powder, respectively.

We use Bi@Zn powder obtained in different concentrations of solution or reaction time as examples to investigate the impact on the performance of the Zn powder anode in Zn//Zn symmetric batteries. Among the different concentrations explored, 0.05 M Bi@Zn powder anode displays the best cycling performance, with a longer lifespan than those of 0.01 M Bi@Zn powder (104 h) and 0.1 M Bi@Zn powder (173 h).



Figure S24. The voltage profiles of the Zn symmetric cell are tested using Bi@Zn powder (5min), Bi@Zn powder (1min), and Bi@Zn powder (20min)anode at the current density of 0.2 mA cm<sup>-2</sup> with the capacity of 0.1 mAh cm<sup>-2</sup>.

The Zn powders are soaked in 0.05 M Bi (NO<sub>3</sub>)<sub>3</sub> solution for 1 min, 5 min and 20 min, and the prepared samples are denoted as Bi@Zn powder (1 min), Bi@Zn powder (5 min) and Bi@Zn powder (20 min), respectively.

The Bi@Zn powder (5 min) has the best cycle life among different reaction times. Therefore, it is concluded that the optimal concentration of Bi  $(NO_3)_3$  is 0.05 M and the optimal reaction time is 5 minutes, which is applied in the follow-up experiment.


Figure S25. Morphology evolution of Bi@Zn powder anodes after different cycles at the current density of 1 mA cm<sup>-2</sup>.

As shown in Figure S4, the bare zinc powder anode exhibited structural collapse and powders fall-off after cycling. In sharp contrast, Bi@Zn powder anode showed tight 3D build-up structure at both high and low magnification, where  $Zn^{2+}$  could be deposited uniformly across the electrode (Fig. 2b-e and Figure S25).



Figure S26. The SEM image and the corresponding mapping of Bi@Zn powder anode after

5000 cycles at the current density of 1 mA cm<sup>-2</sup>.



Figure S27. The XRD pattern after cycling 10 cycles.



**Figure S28.** The voltage profiles of the Zn symmetric cell are tested using the bare Zn powder anode and the Bi@Zn powder anode at the current density of 5 mA cm<sup>-2</sup> with the

capacity of 2.5 mAh cm<sup>-2</sup>.



**Figure S29.** The voltage profiles of the Zn symmetric cell for bare Zn powder at the current density of 15 mA cm<sup>-2</sup> with the capacity of 7.5 mAh cm<sup>-2</sup>.



**Figure S30.** Cycling performance of the symmetric batteries for (a) bare Zn powder anode and (b) Bi@Zn powder anode at a current density of 40 mA cm<sup>-2</sup> for a capacity of 10 mAh

 $\mathrm{cm}^{-2}$ .



Figure S31. Digital images of P(AMPS-AN) hydrogel at (a) room temperature and (b) -20 °C.
(c) Cycling performance of the symmetric batteries using Bi@Zn powder anode at a low temperature of -20 °C at a current density of 0.5 mA cm<sup>-2</sup> for a capacity of 0.5 mAh cm<sup>-2</sup>.



Figure S32. The first Zn deposition voltage profiles of the bare Zn powder anode and Bi@Zn powder anode at 1 mA cm<sup>-2</sup>.

In the main text, the nucleation overpotential is the voltage difference between the lowest voltage when sharp voltage drops happen and the plateau overpotential, was used to demonstrate that Bi metal favors the nucleation of Zn (Fig. 3a). This definition of nucleation overpotential is widely used in aqueous Zn-ion batteries and lithium batteries.<sup>16-19</sup>

According to Cui's work, the nucleation overpotential is the magnitude of the voltage spike at the onset of Zn deposition, i.e., 62.9 mV for Bi@Zn powder anode and 74.7 mV for bare Zn powder anode (Figure S32).<sup>20</sup> It is also demonstrated that Bi@Zn powder exhibit a smaller nucleation overpotential than that of bare Zn powder, indicating that the Bi-metal benefits the nucleation of Zn.



Figure S33. SEM images of (a) bare Zn powder anode and (b) Bi@Zn powder anode with a plating capacity of 5 mAh cm<sup>-2</sup>.



Figure S34. The atomic structures of a Zn atom adsorbed on the (a) Zn and (b) Bi material.



**Figure S35.** COMSOL simulation of (a) current density distribution and, (b) Zn-ion concentration and morphology evolution of the Bi@Zn powder anode during plating.



**Figure S36.** COMSOL simulation of (a) current density distribution and, (b) Zn-ion concentration and morphology evolution of the bare Zn powder anode during plating.



Figure S37. SEM of (a) bare Zn powder anode and (b) Bi@Zn powder anode with a plating

capacity of 10 mAh cm<sup>-2</sup>.



Figure S38. A homemade cell for in-situ XRD



Figure S39. The XRD pattern of the (a) bare Zn powder and (b) Bi@Zn powder before the formal in-situ test.

We first performed three cycles after the device was assembled. The XRD at cycles of 0.5, 1, 1.5, and 3 were tested, confirming that there was a relatively noticeable change in peak intensity. Only then did we start the formal in-situ test. Thus, it has been cycled three times before the in-situ XRD test.

In-situ XRD measurements were characterized via Bruker D8 advance with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) under 40 KV voltage (Fig. 5g-h and Figure S39).



Figure S40. Digital images of the battery using the bare Zn powder anode after cycling.

Hydrogen evolution reaction in the process of charge and discharge also brings safety risks such as battery shell popping.

The much-enlarged contact area of Zn powder poses a higher risk of side reactions including hydrogen evolution reaction (HER) and corrosion. The chemical oxidation (reaction 1) and hydrogen evolution (reaction 2) take place wherever the active Zn metal is accessible to aqueous electrolyte, regardless of whether the battery is in cycling or resting state. The hydrogen production causes high OH<sup>-</sup> ions concentration in electrode vicinity, resulting in a corrosion reaction (reaction 3) and the formation of a solid by-product called zinc sulfate hydroxide hydrate (ZSH, (Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>·nH<sub>2</sub>O)).

$$Zn - 2e^{-} \rightarrow Zn^{2+}$$
(1)  

$$2H_{2}O + 2e^{-} \rightarrow H_{2}\uparrow + 2OH^{-}$$
(2)  

$$4Zn^{2+} + 6OH^{-} + SO_{4}^{2-} + xH_{2}O \rightarrow Zn_{4}SO_{4}(OH)_{6} \cdot xH_{2}O$$
(3)



Figure S41. (a) Thickness change of (b) the bare Zn powder and (c) Bi@Zn powder symmetric batteries before and after cycling at 1.0 mA cm<sup>-2</sup>.

The thickness of the coin cell increases significantly by 34% after symmetric batteries cycling of the bare Zn powder anode, while that of the Bi@Zn powder anode is negligible, suggesting that the presence of the Bi-metal can inhibit gas formation.



**Figure S42.** Digital images of in-situ DEMS test device, which mainly include the (a) online electrochemical mass spectrometry (QAS 100Li), (b) EC-DEMS cell (SWAGLOK TYPE),

and (c) Neware battery test system.



Figure S43. The pH of (a) 1 M  $Na_2SO_4$  and (b) 2 M  $ZnSO_4 + 0.1$  M  $MnSO_4$ .

In order to avoid the interference of  $Zn^{2+}$  reduction and ensure the conductivity of the electrolyte, we use 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte (pH=3.50, Figure S43a) for the LSV test. <sup>21</sup>



Figure S44. The atomic structures of a H atom adsorbed on the (a) Zn and (b) Bi material.

To elucidate the origin of inhibiting HER, the free energy of  $\Delta G_{H^*}$  is calculated to predict and evaluate the HER activity (Fig. 6e and Figure S44). According to the Sabatier principle, the greater the absolute value of  $\Delta G_{H^*}$ , the weaker HER activity and the more difficult H<sub>2</sub> generation. The Bi (1.00 eV) metal shows greater absolute value of  $\Delta G_{H^*}$  than Zn (0.27 eV), indicating that its HER inert feature.



Figure S45. The Tafel curves of bare Zn powder anode and Bi@Zn powder anode (b) before cycling, and (c) after 10 cycles

The corrosion potential of the Bi@Zn powder anode remains the highest even after the cycle, indicating that it continues to inhibit corrosion during charging and discharging (Figure S45). Furthermore, the corrosion current after the cycle is still small, meaning that the rate of corrosion is always suppressed



Figure S46. SEM images of (a) bare Zn powder anode and (b) Bi@Zn powder anode after immersing 5 days in the aqueous 2 M  $ZnSO_4 + 0.1$  M  $MnSO_4$  electrolyte.



Figure S47. SEM images of (a) bare Zn powder and (b) Bi@Zn powder after immersing in

water.



Figure S48. The charging and discharging curves of (a) bare Zn powder//Ti and (b) Bi@Zn powder//Ti asymmetric batteries in different cycles.

This additional peak at the end (around 0.1 V) of the stripping voltage profile for the bare Zn powder//Ti may be related to side reactions and electrode structure defects. The much-enlarged surface area of Zn powder poses a higher risk of side reactions, as evidenced by Fig. 6. In addition, the formation process of half batteries cycling twice at a small current  $(0.2 \text{ mA cm}^{-2})$  in the voltage range of 0.02-0.5 V, which may have produced structural defects.



Figure S49. XRD pattern of  $\alpha$ -MnO<sub>2</sub>.

The XRD pattern in Figure S49 confirms the crystal structure of  $\alpha$ -MnO<sub>2</sub> (JCPDS No. 72-1984).



Figure S50. (a-b) SEM images and (c-d) corresponding mapping of  $\alpha$ -MnO<sub>2</sub>.

SEM images also show its typical rod-like morphology (Figure S50).



Figure S51. The charging and discharging curves of the bare Zn powder//MnO<sub>2</sub> and Bi@Zn powder//MnO<sub>2</sub> full batteries at the activation region.

We used 2 M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub> as the electrolyte, which corresponds to the introduction of the  $Mn^{2+}$  additive. Regarding the role of  $Mn^{2+}$  additives, in addition to inhibiting the dissolution of manganese oxides, they also contribute to the capacity of the battery.

When the battery is charged first, a complex chemical transformation process ( $Mn^{2+}$  oxidized to  $MnO_2$ ) occurs at the cathode.<sup>22</sup> The original  $MnO_2$  is discharged at the same time as the newly formed  $MnO_2$ , which produces a higher capacity than the charging capacity in the first two cycles (Figure S51). Furthermore,  $Zn//MnO_2$  full batteries have the activation region where  $MnO_2$  undergoes complex changes and capacity fluctuations.<sup>23</sup>

Therefore, all of our full batteries were activated to include 3 hours of aging and two charge/discharge cycles at 0.1 A  $g^{-1}$  before performing electrochemical tests (except for 5-10 mA  $g^{-1}$ ).



Figure S52. GCD curves of the bare Zn powder//MnO<sub>2</sub> and Bi@Zn powder//MnO<sub>2</sub> full batteries at 0.2 A  $g^{-1}$ .

The distinct comparison of charge-discharge curves in different cycles reflects the superior cycle performance of Bi@Zn powder anode in  $Zn//MnO_2$  full batteries at such a low N/P of 6.65 (Figure S52-54).



Figure S53. GCD curves of the bare Zn powder//MnO<sub>2</sub> full batteries at 0.2 A  $g^{-1}$ .



Figure S54. GCD curves of the Bi@Zn powder//MnO<sub>2</sub> full cells at 0.2 A  $g^{-1}$ .



Figure S55. The electrochemical performance of bare Zn powder// MnO<sub>2</sub> full batteries at lower rates: (a) 10 mA g<sup>-1</sup>; (b) 5 mA g<sup>-1</sup>.

Under ultra-low current (5-10 mA g<sup>-1</sup>) conditions, there is sufficient time for irreversible hydrogen evolution and corrosion reactions to occur on the Zn surface, which is regarded as one of the bottlenecks for the practical applications of AZIBs.<sup>24, 25</sup> The much-enlarged surface area of Zn powder poses a higher risk of side reactions, resulting in an unstable voltage profile in the initial charging stage and almost no discharge capacity of the bare Zn powder anode (Figure S55). In contrast, the voltage profile of the Bi@Zn powder anode increases steadily during the initial charging stage, indicating that the side reactions are significantly suppressed (Figure S56).



Figure S56. The electrochemical performance of  $Bi@Zn powder//MnO_2$  full batteries at

lower rates: (a) 10 mA  $g^{-1}$ ; (b) 5 mA  $g^{-1}$ .



Figure S57. (a) Self-discharge tests of the Zn//MnO<sub>2</sub> full batteries using the bare Zn powder anode after a rest of 120 h. (b) Cycling performance, and CE of the Zn//MnO<sub>2</sub> full batteries using the bare Zn powder anode after two stands for 120 h.

The newly assembled battery is charged to 1.8 V and its voltage drops to 1 V after the 45h rest, indicating serious self-discharge (Figure S57a). After the 120h rest, it is charged to 1.8 V. The voltage dropped rapidly, when standing again, which also prove that almost all the active substances in the Zn powder anode are lost, and the side reaction affects the storage process. Further storage tests via capacity examination for every 120h rest are implemented. The considerable capacity loss is detected after every rest substantiating the instability during storage (Figure S57b).

## Part IV: Supporting Tables

work						
Zn powder anodes	Current density	Areal capacity	Lifespan			
	(mA cm <sup>-2</sup> )	(mAh cm <sup>-2</sup> )	( <b>h</b> )	Ref.		
MXene@Zn	1	0.5	200	[26]		
Zn powder/PG	1	1	400	[18]		
	5	0.5	360			
Zn powder-MIEC	0.25	0.05	1270			
	1	1	400			
	2	2	220	[27]		
	5	2	180			
	10	1	100			
3DP-ZA	1	1	330	[ <sup>28</sup> ]		
	4	2	180			
3D ZnP/CF	1	1	3000	[29]		
	5	5	700			
Zn-Sn-PAM	1	0.5	300	[ <sup>30</sup> ]		
Zn powder/PEG	5	1	1000	[31]		
Zn_G	1	1	580	[ <sup>32</sup> ]		
	5	2	182			
ZP-Grad	1	1	1250	[33]		
	5	5	130	L J		

Table S1. The lifespan of symmetrical batteries based on Zn powder anodes in the previous

ss-ZnP	1	1	400	[ <sup>34</sup> ]
2DCED Marga/Za D	0.25	0.1	1400	Г <u>3</u> 51
	1	0.5	670	_ [55]
	2	2	480	<u>г361</u>
SLA	5	2	450	_ [50]
	1	0.5	1000	<b>F</b> 371
Zn-P(@In _	2	4	500	_ [3']
M3DP-MXene/Cu-	2	1	1800	[ <sup>38</sup> ]
THBQ/Zn-P	2	1	1000	LJ
	1	0.5	5600	
	5	2.5	650	- 
ы <i>@L</i> n powder	15	7.5	585	_ 1 nis work
_	40	10	32	_

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