

Supplementary Materials

Metal Organic Complexes as an Artificial Solid-Electrolyte Interface with Zn-ion Transfer Promotion for Long-life Zinc Metal Batteries

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1. Experimental

1.1 Materials

Zn, Cu and Ti foil with a thickness of 50 μm were purchased from Shenzhen Kejing Star Technology. The polished Zn electrode was obtained by removing the passivation layer using an abrasive paper. ZnSO₄·7H₂O (> 99.0%), V₂O₅ (> 99.0%) and LiNO₃ were purchased from Sigma-Aldrich Chemical Co. and Shanghai Macklin Biochemical Co., Ltd. THBA (2,3,4 trihydroxybenzaldehyde) was purchased from TCI (Shanghai) Development Co., Ltd. All other reagents were analytical grade and used directly without further purification. Deionized water was used to prepare all aqueous electrolytes.

1.2 The preparation of metal organic complex SEI layer

Zn-THBA@Zn was synthesized by a solvothermal reaction. Typically, 25.0 mg of THBA (2,3,4 trihydroxybenzaldehyde) was added into 100 mL of ethanol solution under stirring to form a clear and harmonious solution. Then, the solution with different concentration (x) of THBA were prepared as 0, 0.05, 0.25, 1.0 and 5.0 mg mL⁻¹ THBA-EtOH solution and the products were labelled as Zn-THBA@Zn-x, respectively. Then, 20 mL of the solution was transferred to a 50 mL Teflon autoclave liner, the polished Zn foil was immersed into the solution and kept at 25 °C, 120 °C,

and 200 °C for 12 h respectively and the products were labelled as Zn-THBA@Zn-25°C, Zn-THBA@Zn-120°C and Zn-THBA@Zn-200°C. The obtained Zn foils were washed by ethanol and dried at room temperature, and then cut into pieces as the electrodes (d =10 mm).

1.3 Characterization

The morphological and elemental analysis were done by scanning electron microscopy (SEM, Hitachi S-4800, Japan), operated at 10 kV and 10 mA, along with energy dispersive X-ray spectroscopy (EDS) mapping. The bare Zn foil and Zn-THBA@Zn foil with a thickness of about 50 µm were soaked into liquid nitrogen for several minutes before breakage for the formation of fresh cross-section. The crystalline structure was analyzed by X-ray diffraction (XRD, GBC MMA diffractometer) with Cu K α radiation at a voltage of 40kV and a scanning rate of 1° min⁻¹. X-ray photoemission spectroscopy (XPS) analysis was carried out on an Imaging Photoelectron Spectrometer (Kratos Analytical Ltd.) and the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. The FTIR spectra of all samples were obtained from Fourier transform infrared (Nicolet iS50). Pore structures of the samples were analyzed by N₂ adsorption/desorption isotherms on a Brunauer-Emmett-Teller surface area analyzer (BET, Tristar II 3020, Micromeritics Instrument Corporation, US). Atomic force microscopy (AFM) images were acquired in air under PeakForce QNM mode on Dimension FastScan Bio Atomic Force Microscope (Bruker, Billerica, CA) using silicon nitride tips with a spring constant of 200 N/m (RTESPA-525, Bruker, US). Before scanning, the AFM tips were cleaned via UV/ozone to ensure no contamination on the tips. ICP results were acquired in Argon on Agilent ICPOES730 with RF Power of 1.0 kW, plasma flow of 15 L min⁻¹, auxiliary gas flow of 1.5 L min⁻¹ and nebulizer gas flow of 0.75 L min⁻¹. The results of organic element analysis were acquired on vario El cube (German elemental element analyzer).

1.4 Electrochemical measurements

1.4.1 Preparation of V₂O₅ cathodes and electrolytes

The commercial V₂O₅ materials was treated by LiNO₃ according to the previous method.¹ The pre-treated V₂O₅ was used as cathode precursor, which is prepared by mixing V₂O₅ precursor, carbon black and polyvinylidene fluoride (PVDF) binder into slurry (dissolved in NMP) at a weight ratio of 8:1:1 and spreading on a piece of Ti foil and then the coated Ti foil was dried under vacuum at 90 °C for 12 h. The mass load of the active material (V₂O₅) is ~1.5 mg cm⁻², corresponding to a capacity of ~0.45 mA h cm⁻² as the cathode. All the aqueous electrolytes were prepared by deionized water.

1.4.2 Test Cells Assembling

The 2032-type coin cells were assembled under ambient atmosphere using glass fiber membrane and 2.0 M ZnSO₄ solution as separator and electrolyte, respectively. The Zn plating/stripping test were carried out in coin cells consisting of the Zn-THBA@Zn foils or bare Zn foils as both working and counter electrodes. The bare Zn || bare Zn symmetrical cells and Zn-THBA@Zn || Zn-THBA@Zn symmetrical cells were assembled with two Zn foil electrodes with or without Zn-THBA protective layer, respectively. The V₂O₅ cathode electrodes were assembled with Zn-THBA@Zn or bare Zn foil anodes as V₂O₅ full cells.

1.4.3 Electrochemical Tests

Electrochemical performance was evaluated on a battery testing system (Neware battery tester, ShenZhen, China). The M204 electrochemical workstation (Metrohm Autolab, Netherland) was employed for electrochemical measurement.

Electrochemical impedance spectroscopy (EIS) of the Zn || Zn symmetrical cells was conducted in the frequency range of 0.01 Hz to 100 kHz. The activation energy (E_a) was calculated through the Arrhenius equation.

The CV test was conducted by Zn || Ti half-cells at the scan rate of 5 mV s⁻¹.

The transference number of Zn²⁺ ($t_{Zn^{2+}}$) in a symmetrical Zn (or ZnF₂-Cu@Zn) battery was determined by the following equation based on EIS measurements:

$$t_{Zn^{2+}} = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)}$$

where ΔV , I_0 , R_0 , I_s and R_s are the applied voltage, the initial current and resistance, the steady-state current and resistance, respectively.

The ionic conductivities were conducted by SS plate with two electrode configuration and calculated according to the following equation:

$$\sigma = d/(R \times S)$$

where σ is the ionic conductivity, R is the resistance, S is the area of ionic conductor, and d is the thickness of the ionic conductor, respectively. The Zn-THBA solid electrolyte film for ionic conductivity measurement is fabricated by blade coating on Ti foil, followed by electrochemical activation in 2 M ZnSO₄ aqueous electrolyte. Electrochemical impedance spectroscopy (EIS) is used for electric conductivity test.

The Tafel curves for Zn foils in different electrolytes were tested in the three-electrode systems at room temperature at a scan rate of 10 mV s⁻¹, and Zn foil, Ti foil and Ag/AgCl (3.5 M KCl) acted as the working, counter and reference electrode, respectively.

The Zn || Zn symmetrical cells were tested at different current density. The Zn || V₂O₅ full-cells were galvanostatically charged/discharged in the voltage range of 0.2-1.6 V vs. Zn/Zn²⁺ at different current density.

	Electric conductivity (mS cm ⁻¹)
Zn ₄ SO ₄ (OH) ₆ ·5H ₂ O	1.20 × 10 ⁻⁶
Zn-THBA	1.58 × 10 ⁻⁷

Tab. S1 The electric conductivity of Zn₄SO₄(OH)₆·5H₂O and Zn-THBA.

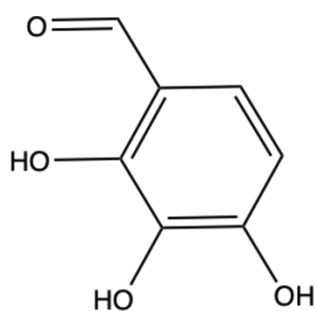


Fig. S1 The molecular structure of THBA.

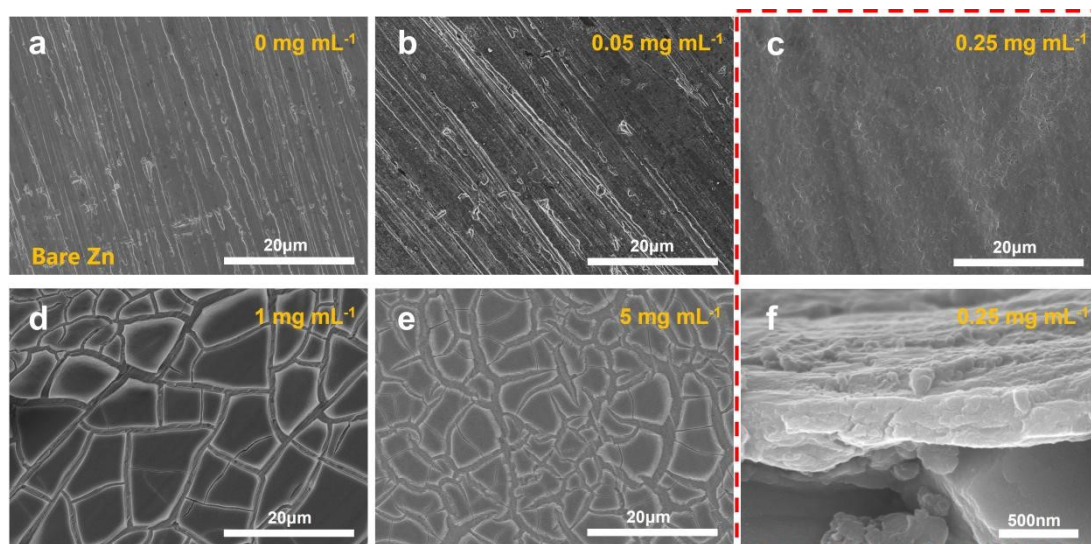


Fig. S2 The top-view SEM images of Zn metal surface after reacting with different concentrations of THBA solution at 25 °C. (a) 0 mg mL⁻¹, (b) 0.05 mg mL⁻¹, (c) 0.25 mg mL⁻¹, (d) 1 mg mL⁻¹, (e) 5 mg mL⁻¹. (f) The cross-sectional SEM image of Zn-THBA-0.25 at 25 °C.

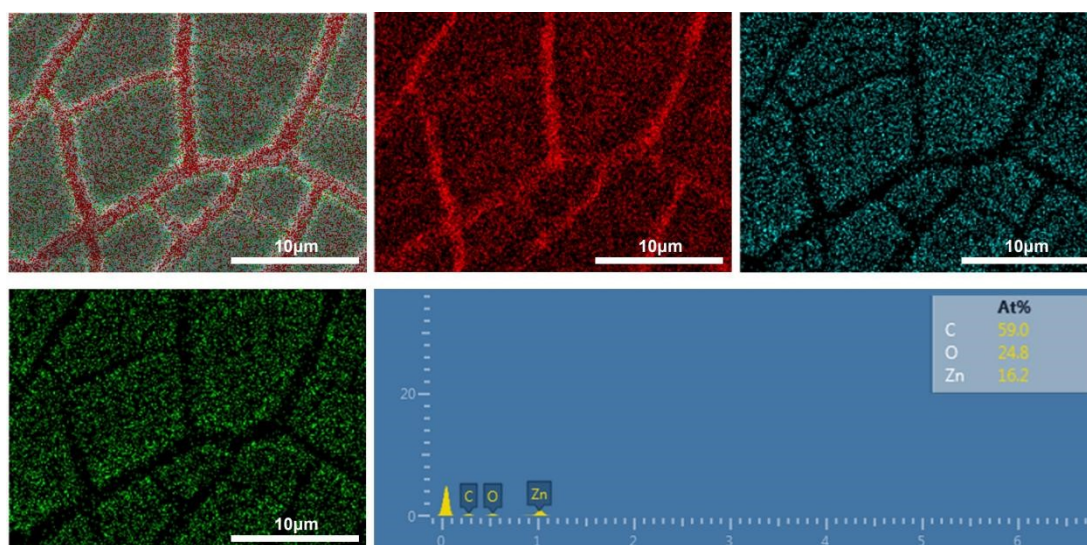


Fig. S3 The corresponding EDS data of Zn-THBA SEI layer with high concentration of THBA solution at 25 °C.

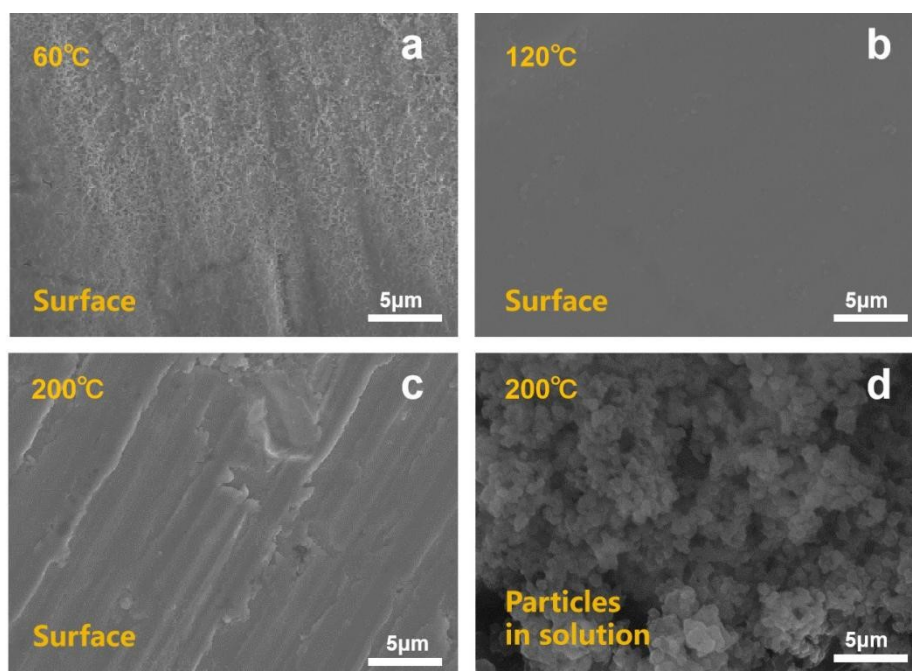


Fig. S4 The Zn-THBA (concentration: 0.25 mg mL⁻¹) SEI layers formed at 60°C, 120 °C and 200 °C respectively.

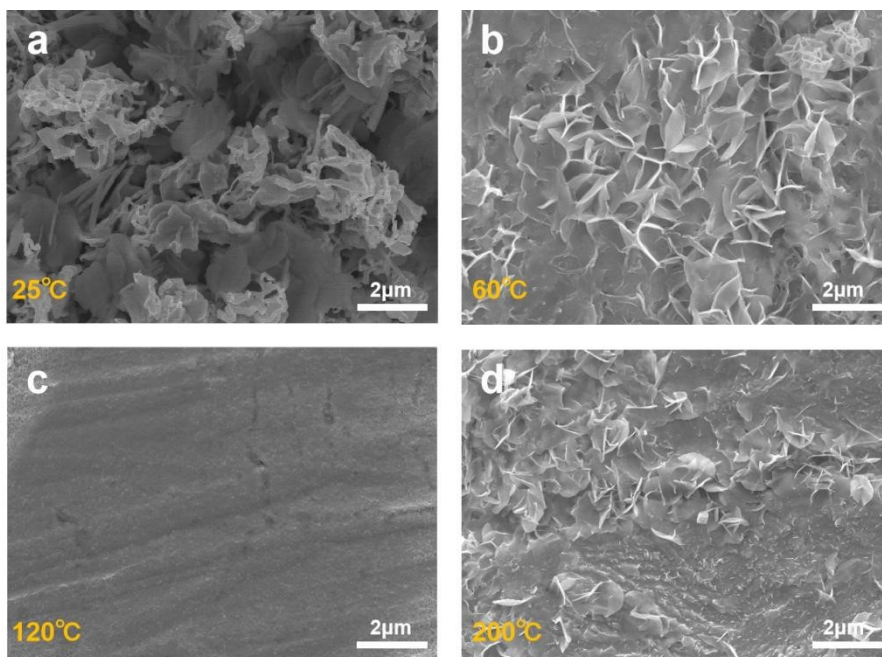


Fig. S5 SEM images for the surface of Zn-THBA@Zn foils (concentration: 0.25 mg mL⁻¹, formed at 25°C, 60°C, 120 °C and 200 °C, respectively) immersed in 2 M ZnSO₄ electrolyte for 5 days.

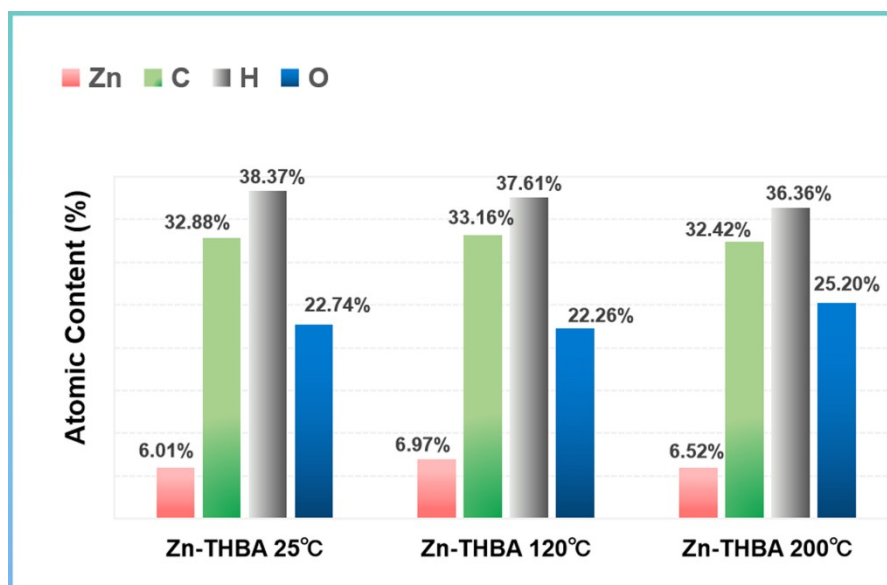


Fig. S6 The atomic contents of Zn, C, H and O element of Zn-THBA synthesized at different temperatures by ICP-OES and organic element analysis.

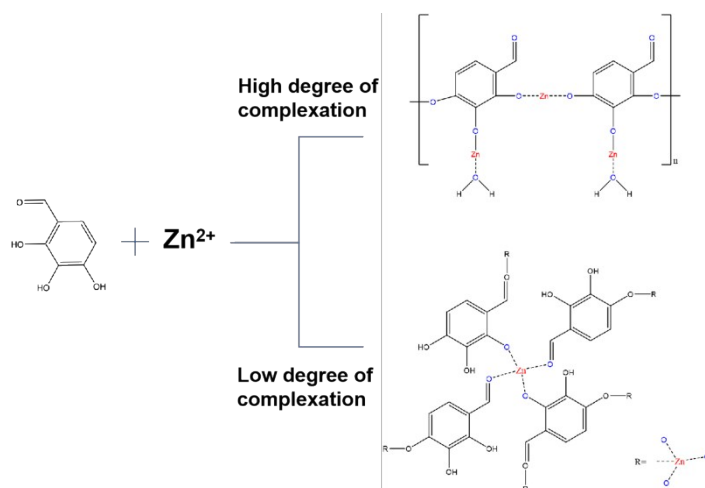


Fig. S7 The formation mechanism of Zn-THBA layer on Zn anode surface.

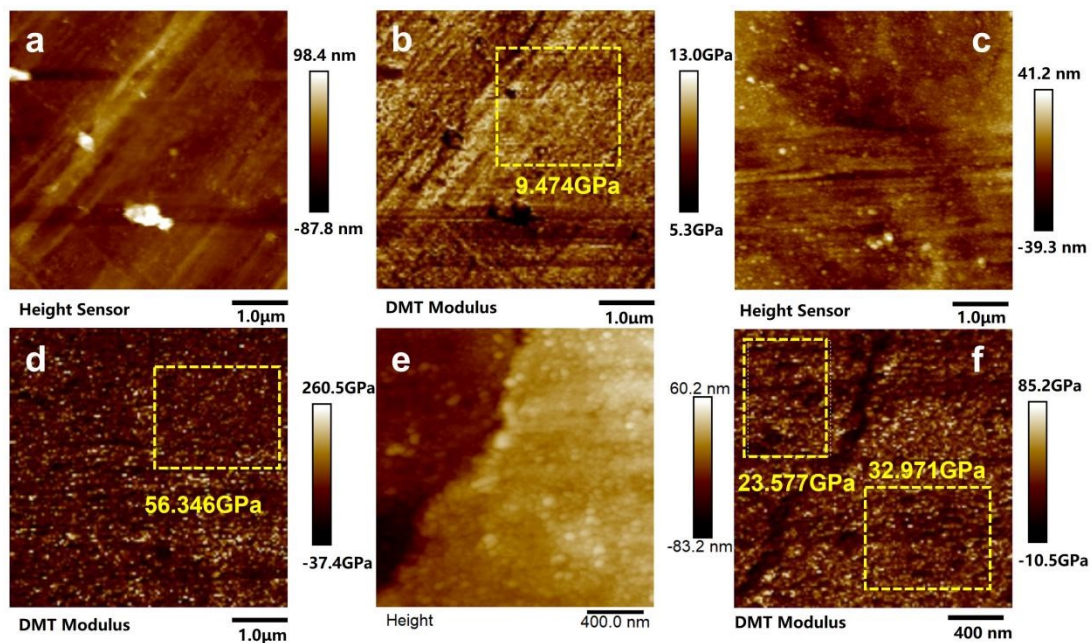


Fig. S8. AFM images of Zn-THBA@Zn anode and its corresponding mechanical property, Young's modulus mapping. (a-b) Zn-THBA-25°C. (c-d) Zn-THBA-120°C. (e-f) Zn-THBA-200°C.

	Stretching vibration of C- H in aldehyde group	Stretching vibration of C = O in aldehyde group	O-H deformation vibration on benzene ring	O-H deformation vibration on benzene ring	O-H deformation vibration on benzene ring
THBA	2736.80 cm ⁻¹	1674.94 cm ⁻¹	1379.05 cm ⁻¹	1341.78 cm ⁻¹	1312.35 cm ⁻¹
Zn-THBA	—	1655.06 cm ⁻¹	1318.47 cm ⁻¹	1318.47 cm ⁻¹	1280.25 cm ⁻¹

Tab. S2 FTIR peaks of THBA and Zn-THBA.

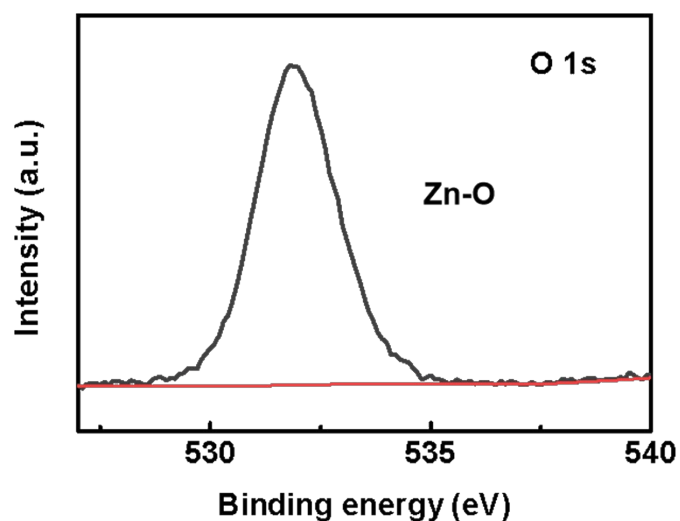


Fig. S9 XPS profiles of O 1s for the surface of Zn-THBA@Zn anode before cycling.

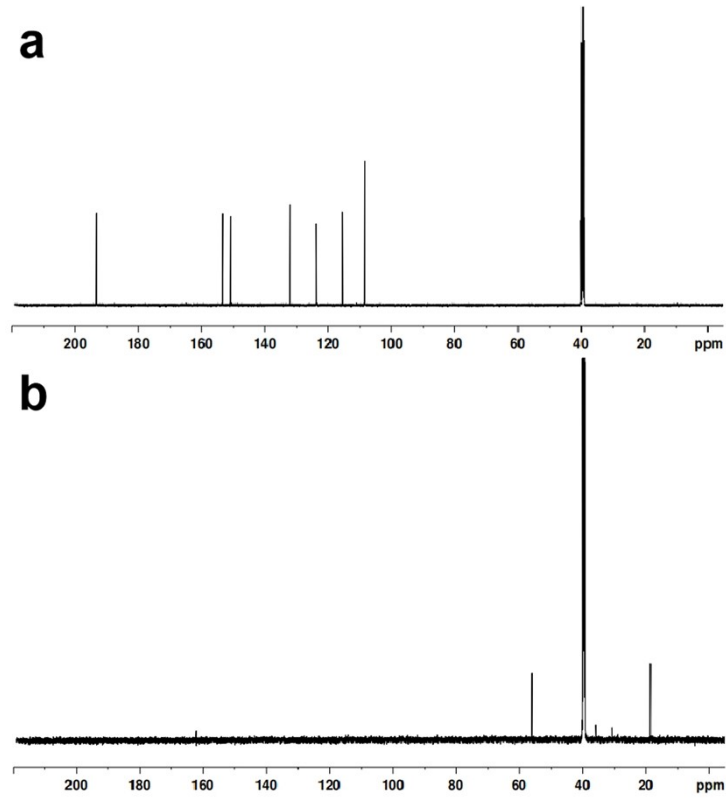
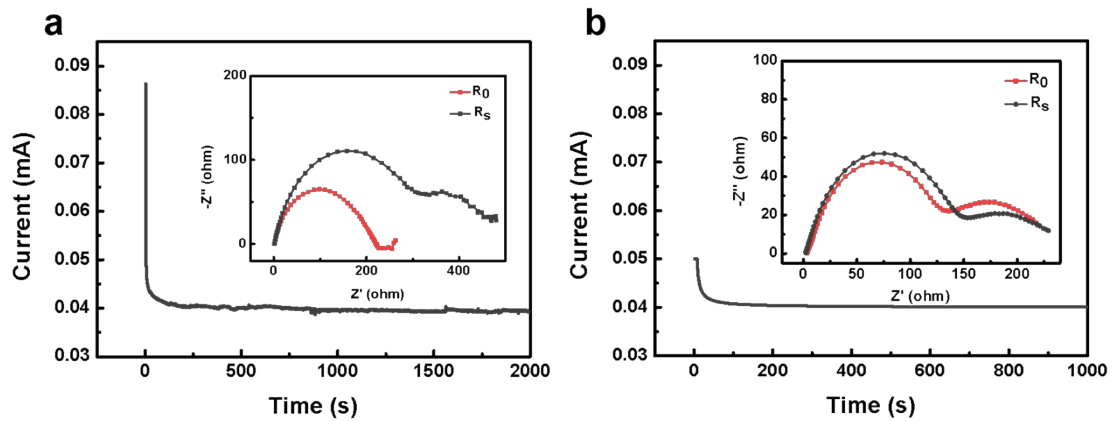


Fig. S10 The ^{13}C NMR spectra of (a) pure THBA and (b) Zn-THBA complexes.



Bare Zn: $I_0 = 0.0863$ mA, $I_s = 0.0398$ mA, $R_0 = 208.9035$ ohm, $R_s = 387.0644$ ohm

$$\tau_{\text{Zn}^{2+}} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} = \mathbf{0.3351}$$

Zn-THBA: $I_0 = 0.0497$ mA, $I_s = 0.0401$ mA, $R_0 = 138.5906$ ohm, $R_s = 154.3177$ ohm

$$\tau_{\text{Zn}^{2+}} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} = \mathbf{0.7678}$$

Fig. S11 The transference number of Zn^{2+} was tested by EIS measurements in a symmetrical cell with (a) bare Zn anode and (b) Zn-THBA anode.

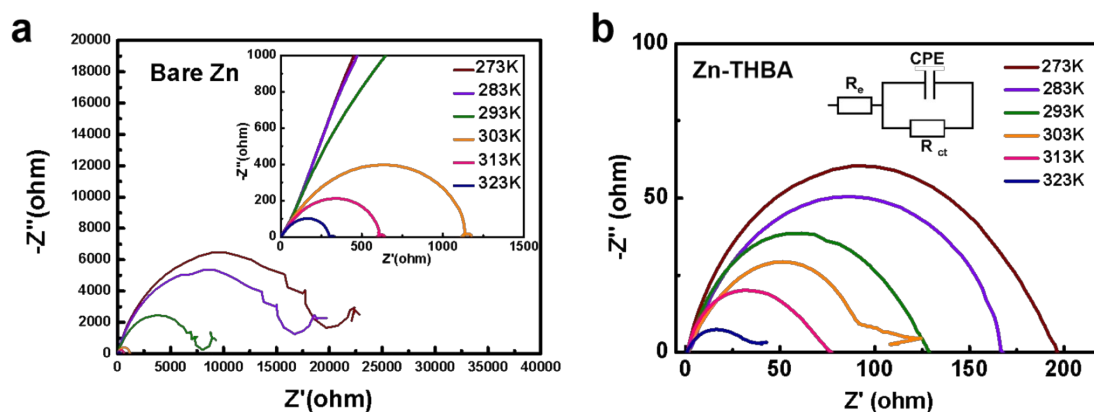


Fig. S12 The EIS data for Zn || Zn symmetrical cell using Zn anode without or with Zn-THBA layer at different temperatures.

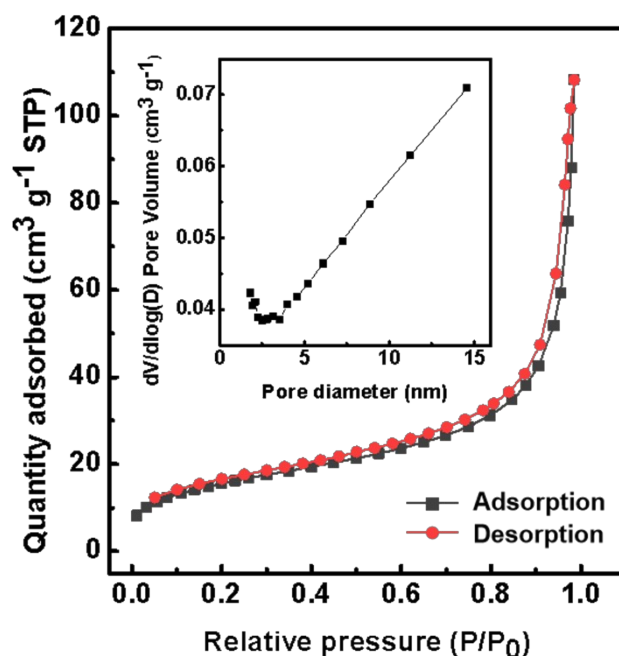


Fig. S13 Nitrogen adsorption/desorption isotherm of Zn-THBA layer and the corresponding size distribution of pores. The BET surface area is $56.26 \text{ m}^2 \text{ g}^{-1}$ and the pore volume is $0.1674 \text{ cm}^3 \text{ g}^{-1}$.

	1 mA cm^{-2}	2 mA cm^{-2}	5 mA cm^{-2}	10 mA cm^{-2}	20 mA cm^{-2}
Zn-THBA (mV)	12	20	25	35	45
Bare Zn (mV)	45	70	120	shortcut	shortcut

Tab. S3 The over-potential at different current density for Zn || Zn symmetrical cell using Zn anode without or with Zn-THBA layer.

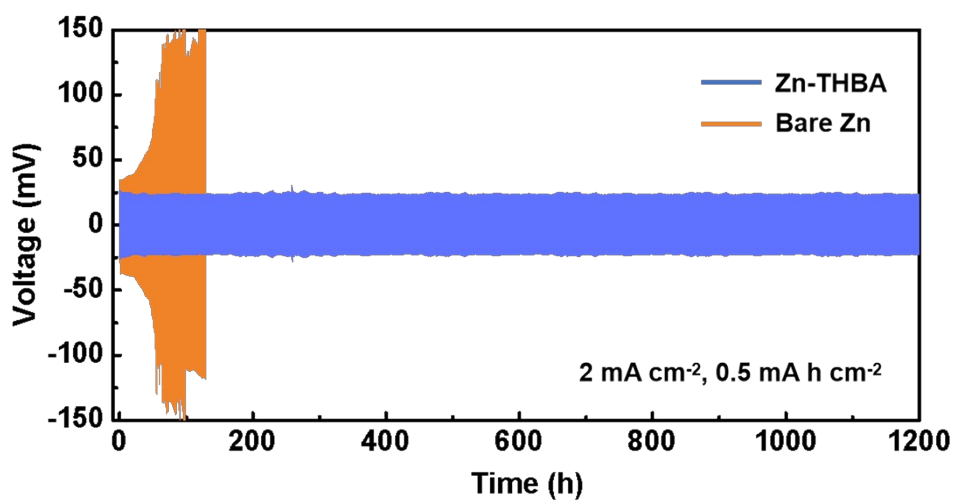


Fig. S14 The cycling performance of Zn || Zn symmetrical cells at 2 mA cm⁻² with capacity of 0.5 mA h cm⁻².

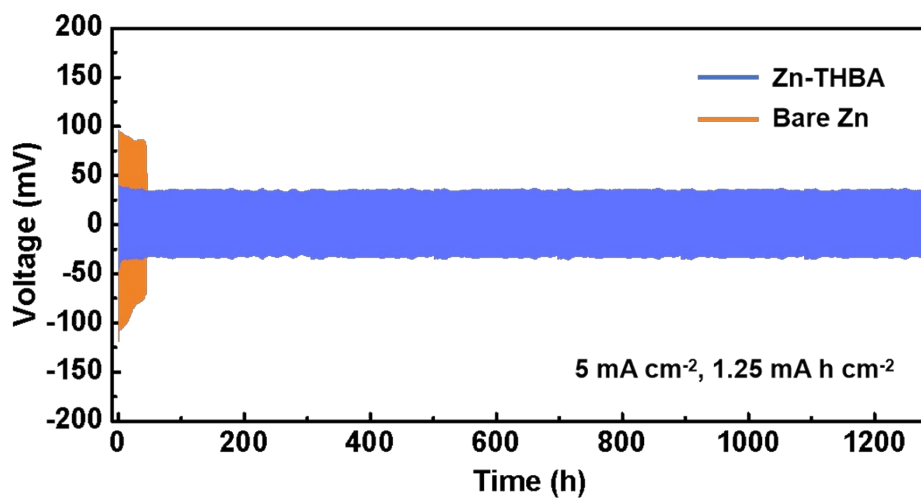


Fig. S15 The cycling performance of Zn || Zn symmetrical cells at 5 mA cm⁻² with capacity of 1.25 mA h cm⁻².

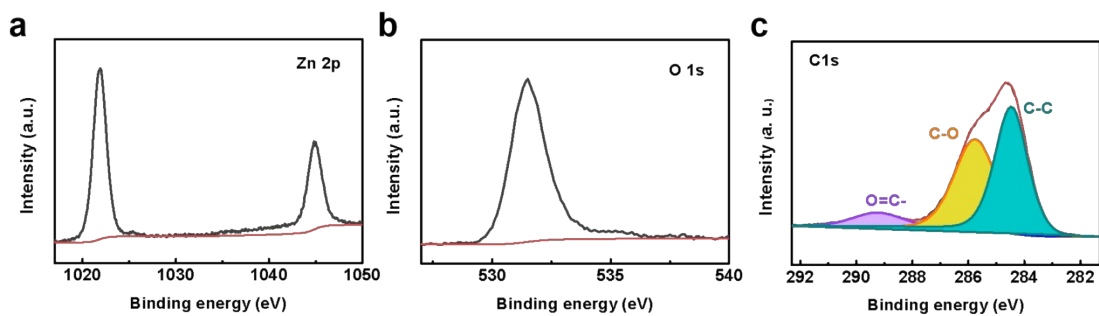


Fig. S16 XPS profiles for the surface of Zn-THBA@Zn anode after cycling at 2 mA cm^{-2} with capacity of 2 mA h cm^{-2} for 20 cycles. **(a)** Zn 2p, **(b)** O 1s and **(c)** C 1s.

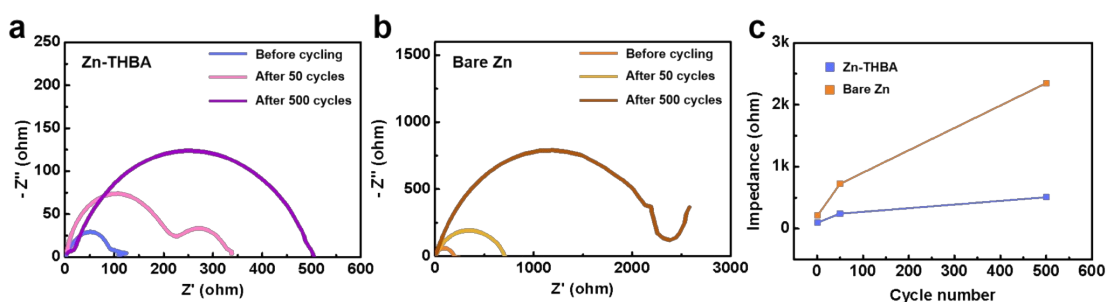


Fig. S17 The EIS data for Zn || Zn symmetrical cell using Zn anode without or with Zn-THBA layer after cycling for different cycles.

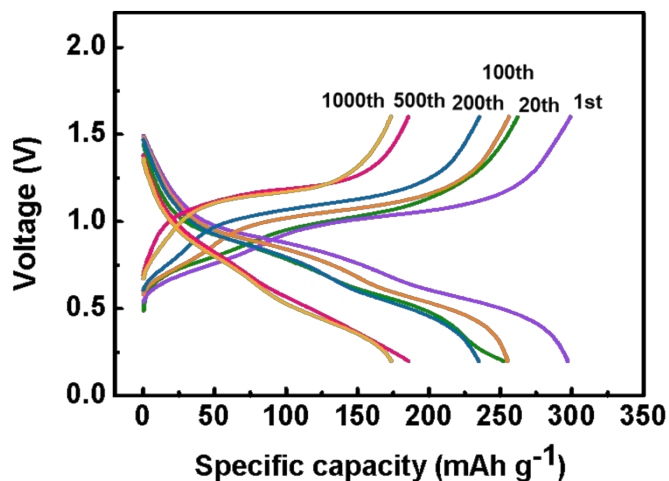


Fig. S18 Representative galvanostatic charge-discharge (GCD) curves at 10 A g^{-1} of Zn || V_2O_5 full-cells using bare Zn and Zn-THBA@Zn anodes.

Ref.	Coatings	Effects	Current Density (mA cm ⁻²)	Areal capacity (mAh cm ⁻²)	Cycling Time
			2 mA cm ⁻²	2 mAh cm ⁻²	1450 h
[2]	HfO ₂	Guides uniform deposition of Zn ²⁺	0.4 mA cm ⁻²	0.1 mAh cm ⁻²	150 h
[3]	polyacrylonitrile	Improves the hydrophilicity of the zinc anode	1 mA cm ⁻²	1 mAh cm ⁻²	1145 h
[4]	ZnSe	Enables lower nucleation energy barrier	2 mA cm ⁻²	1 mAh cm ⁻²	1500 h
[5]	Zn ₄ SO ₄ (OH) ₆ ·5H ₂ O/Cu ₂ O	alters the nucleation and deposition behavior of zinc ions	10 mA cm ⁻²	2 mAh cm ⁻²	700 h
[6]	Ag	Guide uniform zinc deposition	10 cm ⁻²	1 mAh cm ⁻²	100 h
[7]	BaTiO ₃	regulate the interfacial electric field at anode/electrolyte interface	5 mA cm ⁻²	0.5mAh cm ⁻²	1500 h
[8]	Au	Guide the Morphology evolution of plated Zn	10 mA cm ⁻²	5 mAh cm ⁻²	16 h
[9]	ZrO ₂	Contributes to the controllable nucleation sites for Zn ²⁺	5 mA cm ⁻²	1 mAh cm ⁻²	2100 h
[10]	ZnO	Alleviates of side reactions	5 mA cm ⁻²	2.5 mAh cm ⁻²	100 h

Tab. S4 The comparison of the cycling lifespan between our work and other coatings.

Notes and references

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