# **Supplementary Information**

# Intelligent ion-sieving bridge enabled by zinc-rich artificial SEI layer with high Zn<sup>2+</sup>-conductivity for reversible zinc metal anode

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### **Experimental Section/Methods**

## Preparation of ZnTiO<sub>3</sub>

First, 160 ml ethylene glycol, 2.19 g Zn(CH<sub>3</sub>COO)<sub>2</sub> and 3.4 g C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti were added to the beaker with vigorous stirring, then 2.0 g PVP was added to the above solution with vigorous stirring for 24 h. The mixed solution was put into the reaction kettle and heated at 60 °C for 24 h. After the reaction, the obtained product precursor was washed by centrifugal precipitation, and then dried at 80 °C for 10 h in vacuum. After a calcination at 600 °C for 6 h in air (at a warming rate of 5 ° C per minute, the temperature drops naturally), ZnTiO<sub>3</sub> (ZTO) powder was obtained.

### Preparation of VO<sub>2</sub>

All chemicals and materials were used without further purification. In a typical synthesis process of VO<sub>2</sub> (B), a mixture of V<sub>2</sub>O<sub>5</sub> (1.2 g, Aladdin, 99%) and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1.8 g, RHAWN, 99.5%) was initially dissolved in deionized water (40 mL). The resulting solution was then heated to 75°C with continuous magnetic stirring for 60 min to form a dark blue dispersion. Subsequently, this dispersion was transferred into a 50 mL Teflon-lined autoclave and maintained at 180°C for 180 min. The product was then collected, washed sequentially with ethanol and deionized water. The desired VO<sub>2</sub> (B) was obtained after frozen-drying for 12 h.

#### **Preparation of protected electrode**

The ZTO powders and PVDF with a weight ratio of ZTO to PVDF of 9:1 were dispersed in N-methyl-2-pyrrolidinone (NMP, Aladdin, >99.5%, GC) to form a slurry.

This slurry was applied onto Zn foil or Cu foil using the doctor blading technique, and then dried under vacuum at 60 °C to eliminate the solvent. The final products were labeled as ZTO@Zn and ZTO@Cu, respectively.

### Material characterization

The electrode morphology was analyzed using a scanning electron microscope (SEM, ZEISS sigma500) at a voltage of 5 kV, a current of 10  $\mu$ A, and energy-dispersive X-ray spectroscopy (EDX, BRUKER XFlash 6130) mapping performed using an OXFORD XPLORE300 instrument. X-ray diffraction (XRD) spectra were obtained using a D/MAX2500 instrument, covering a scanning range of 10° to 80°. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific) were used to analyze the elemental and surface chemistry of the samples. The in-situ optical microscope was conducted on YueScope (YM710TR). The surface wettability of anodes was performed by OCA25 contact angle measuring system (Dataphysics, Germany). Oxygen defects in the material are detected by EPR technology (Bruker EMXplus-6/1).

#### **Electrochemical measurements**

The ZTO@Zn//ZTO@Zn symmetric, ZTO@Cu//Zn asymmetric cell and VO<sub>2</sub>//ZTO@Zn battery were both assembled based on CR2016 coin-cell. Before use, the Zn foil (thickness ~0.1 mm) was polished by softback sanding sponges and then wiped with ethanol. The symmetric batteries were constructed by two bare Zn (or ZTO@Zn) electrodes with a diameter of 16 mm, a glass fiber separator (Whatman GF/A 1823-070) and 3 m Zn(OTf)<sub>2</sub> aqueous electrolyte. As for asymmetric batteries,

the bare Cu or ZTO@Cu was used as one electrode and the bare Zn or ZTO@Zn was applied as the counter electrode. The VO<sub>2</sub> electrode was prepared by coating the slurry (a mixture of VO<sub>2</sub>, PVDF, and Super B at a weight ratio of 7:2:1) on stainless steel mesh and then dried at 60 °C under vacuum for 10 h. The Zn//VO2 full batteries were assembled using  $VO_2$  as the cathode and bare Zn or ZTO@Zn as the anode with 3 m Zn(OTf)<sub>2</sub> aqueous electrolyte. The cathode loading mass of assembled Zn//VO<sub>2</sub> coin cells is around 2.5~3.5 mg. Cyclic voltammetry (CV), electrochemical impedance spectra (EIS), Linear sweep voltammetry (LSV), Tafel curves, chronoamperometry measurement (CA) and i-t curves were conducted on a CHI 760E electrochemical workstation (Chenhua, Shanghai). Linear sweep voltammetry (LSV) was conducted utilizing three-electrode system, employing Zn foil and ZTO@Zn as working electrodes, Pt plate as counter electrodes, and Ag/AgCl as reference electrodes. EIS was performed over a frequency range of  $10^5$  to  $10^{-2}$  Hz. CV curves of the Zn//VO<sub>2</sub> battery were obtained between 0.2 and 1.5 V. Galvanostatic charge-discharge tests, Coulombic efficiency (CE), self-discharge tests and cyclic performance of battery were carried out using the LAND battery test system (CT3002A) and the Neware battery test system (CT-3008, China).

The calculation of activation energy  $(E_a)$  based on electrochemical impedance spectrum (EIS) analysis at different temperatures. The  $E_a$  can be quantitatively calculated by the following Arrhenius equation:

$$\frac{1}{R_{ct=}}A \exp(\frac{-E_a}{RT})$$

where the  $R_{ct}$ ,  $E_a$ , A, R, and T stand for the charge-transfer resistance, the activation energy, the frequency factor, the ideal gas constant, and the temperature in Kelvin.

The ionic conductivity was calculated by following equation:

$$\sigma = \frac{l}{R_b S}$$

where l was the thickness of the ZTO membrane,  $R_b$  was the resistance according to EIS, and S was the contact area between ZTO and block electrode. During the ionic conductivity measurement, a drop of 3 m Zn(OTf)<sub>2</sub> electrolyte was employed for ZTO and glass fiber membranes to reflect the apparent ionic conductivity under the battery working station.

The Zn<sup>2+</sup> transference number  $(t_{Zn}^{2+})$  was calculated using the following equation:

$$t_{Zn^{2+}} = \frac{Is(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)}$$

where  $\Delta V$  represents the applied voltage (10 mV),  $I_0$  and  $R_0$  are the initial current and resistance, respectively, and  $I_s$  and  $R_s$  are the steady-state current and resistance, respectively.

EDLC was calculated by the equation of  $C = i_c/v$ , where C is the capacitance,  $i_c$  is the double layer current, v is the scan rate. The capacitance (C) can be obtained from the slope of the  $i_c$ , versus v. Here, we define  $i_c$  as the half value of the current difference during the forward scan and negative scan at 0 V, that is  $(i_{ov}^+ - i_{ov}^-)/2$ .

### Calculation

Adsorption energy on the Zn surface, free energies and binding energies were carried out using the DFT as implemented in the DMOL3 program <sup>[1]</sup>, applying the Perdew-Burke-Ernzerhof (PBE) exchange-correction functional within the Generalized Gradient Approximation (GGA) <sup>[2, 3]</sup> flavor of DFT and the projector augmented wave method. Valence electrons were modeled with plane-wave basis sets, employing a plane-wave cut-off energy of 450 eV. A Zn (002) surface with four layers and a 20 Å vacuum layer was used, where only the top two layers were fully relaxed while the bottom two layers remained fixed during geometry optimization. The convergence criteria were set to energy differences of  $1 \times 10^{-5}$  eV for solving electronic wavefunctions, and all geometries (atomic coordinates) were optimized until the maximum force components were less than  $1 \times 10^{-2}$  eV·Å<sup>-1</sup>. The formula for calculating adsorption energy (Eads) is as follows:

$$E_{ads} = E_{total} - E_{substrate} - E_{adsorbate}$$
(3)

The energies of the adsorption structure, substrate, and adsorbate (Zn atoms) are denoted as *Etotal*, *Esubstrate* and *Eadsorbate*, respectively.



Fig. S1 Mechanism and characterization of ZTO@Zn anode.



Fig. S2 Top-view SEM image of ZTO materials.

![](_page_8_Figure_0.jpeg)

Fig. S3 XPS survey spectrum of ZTO@Zn.

![](_page_9_Figure_0.jpeg)

Fig. S4 The fitting XPS spectra of O 1s.

![](_page_10_Picture_0.jpeg)

Fig. S5 (a) and (b) Top-view and (c) and (d) cross-sectional SEM of bare Zn electrode.

![](_page_12_Figure_0.jpeg)

**Fig. S6** The performance of Zn//Zn and ZTO@Zn//ZTO@Zn symmetrical cells at 10 mA cm<sup>-2</sup> and 1 mA h cm<sup>-2</sup>.

![](_page_13_Figure_0.jpeg)

Fig. S7 The performance of symmetrical Zn batteries at 2 mA cm<sup>-2</sup> and 5 mA h cm<sup>-2</sup>.

![](_page_14_Figure_0.jpeg)

**Fig. S8** The asymmetric cells of bare Cu//Zn and ZTO@Cu//Zn at 2 and 1 mAh cm<sup>-2</sup> in different cycles.

![](_page_15_Figure_0.jpeg)

**Fig. S9** CV curves showing Zn plating/stripping behaviors on Cu foil when combined with bare Zn and ZTO@Zn, respectively.

![](_page_16_Figure_0.jpeg)

Fig. S10 Hydrogen evolution potentials were measured by three-electrode in 1 m  $Na_2SO_4$  with a scan rate of 1 mV·s<sup>-1</sup>.

![](_page_17_Figure_0.jpeg)

Fig. S11 EDL capacitance of Zn and ZTO@Zn symmetric cells.

![](_page_18_Figure_0.jpeg)

Fig. S12 The impendence at different temperature for bare Zn and ZTO@Zn electrodes.

![](_page_19_Figure_0.jpeg)

Fig. S13 Arrhenius curves of ZTO@Zn and bare Zn anodes.

![](_page_20_Figure_0.jpeg)

Fig. S14 EIS curves of Bare Zn and ZTO@Zn layers to determine the ionic conductivity.

![](_page_21_Figure_0.jpeg)

Fig. S15 The i-t curves and corresponding EIS plots of (a) bare Zn and (b) ZTO@Zn.

![](_page_22_Figure_0.jpeg)

![](_page_23_Figure_0.jpeg)

Fig. S17 EIS of symmetrical cells assembled with bare zinc and ZTO@Zn before and after resting 48 h.

![](_page_24_Figure_0.jpeg)

Fig. S18 Nyquist plots of  $Zn//VO_2$  using bare Zn or ZTO@Zn as the anode after 50 cycles.

Anode	Current Density (mA cm <sup>-2</sup> )	Plating/stripping capacity (mAh cm <sup>-2</sup> )	Cycling life (h)	Ref
ZTO@Zn	5	5	2400	Our
	1	1	4500	work
	2	2	1154	
	10	10	360	
TCNQ@Zn	1	1	500	[4]
Zn@ZnPO	1	1	469	[5]
Zn-LT@Zn	1	1	650	[6]
Zn@ZSO	1	1	1600	[7]
TCCF@Zn	10	10	180	[8]
PVDF-	1	1	1600	[9]
SBA15@Zn				
ZnTA@Zn	10	2	1500	[10]
Tar-Zn	1	1	1600	[11]
Zn-ND	1	1	3600	[12]
gradient	1	1	2000	[13]
fluorinated				
alloy coated				
Zn anode				
Gradient	1	1	1200	[14]
PVDF/Sn/Zn				
anode				

Table S1. Comparison of the cycling performance of Zn//Zn symmetrical batteries with

different interface layers.

Table S2. The ionic conductivity of bare Zn and ZTO@Zn for 3 m  $Zn(OTf)_2$ 

electrolyte-infiltrated glass fiber separator (GF)

Anode	Electrolyte	Ionic conductivity (mS cm <sup>-1</sup> )
Bare Zn with GF	$3 \text{ m Zn}(\text{OTf})_2$	15.4
ZTO@Zn with GF	3 m Zn(OTf) <sub>2</sub>	35.3

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