Electronic Supplementary Information

Porous PEDOT:PSS network over Cu foil for highly reversible dendrite-free zinc deposition

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1. Experimental section

1.1 Preparation of 3D porous PEDOT:PSS

The polystyrene (PS) microspheres was prepared by emulsion polymerization at 75°C with $K_2S_2O_8$ as the initiator. The obtained PS microspheres were dispersed in ethanol to achieve 2 wt% suspension. For the fabrication of 3D porous PEDOT:PSS host, about 5 mL of commercial PH1000 (PEDOT:PSS suspension) was mixed with 10 mL 2 wt% PS suspension. After sonication for 30 min and vigorous stirring for 10 min, a homogeneous dispersion was obtained. Then, about 70 µL of the mixed dispersion was drop-cast on the Cu foil with 10 mm in diameter. After water evaporations at room temperature, the PEDOT:PSS/PS composite over the Cu foil was obtained. Finally, the PEDOT:PSS/PS composites was immersed in tetrahydrofuran for 6 h to remove the PS microspheres. In a controlled experiment, nonporous PEDOT:PSS film over Cu foil was prepared by the similar procedure except that PS microspheres were not added.

1.2. Deposition of Zn over various hosts

The deposition of metallic Zn over various hosts was conducted in a CR2032 cells configured with the 3D PEDOT:PSS over Cu foil, nonporous PEDOT:PSS film over Cu foil or the bare Cu foil as the working electrode. The Zn foil was employed as the counter electrode and mixed solution composed of 2 M ZnSO₄, 1 M Na₂SO₄ and 0.4 M H₃BO₃ was used as aqueous electrolyte. The deposition of metallic Zn over three hosts was conducted at 1 mA cm⁻² for various durations. The obtained samples were denoted as 3D PEDOT:PSS@Zn, nonporous PEDOT:PSS@Zn and bare Cu@Zn.

1.3 Preparation of NaV₃O₈ and cathode fabrication

The NaV₃O₈ (NVO) was prepared by the hydrothermal method.¹ Specifically, 0.36 g commercial V₂O₅ powder and 0.80 g NaOH were dissolved in 85 mL deionized water under magnetically stirring for 1 h at room temperature. The above solution was then transferred into a Teflon-lined autoclave (100 mL) for hydrothermal reaction at 180 °C for 48 h. After cooling down naturally and rinsed thoroughly with deionized water and ethanol, the NVO nanowires were obtained. The cathode was prepared by mixing NaV₃O₈ nanowires, Ketjen Black, and PVDF with a mass ratio of 7:2:1 in NMP solvent.

Then the slurry was coated on the Ti foil and vacuum-drying at 80 °C for 6h. The average mass loading of NaV_3O_8 per electrode was about 1.2 mg cm⁻².

1.4 Cell fabrication

In the fabrication of symmetrical Zn||Zn cells, two identical 3D PEDOT:PSS@Zn, PEDOT:PSS@Zn or bare Cu@Zn were used as both anode and cathode. The Zn||Cu asymmetrical cells were assembled using Cu foil as cathode, 3D PEDOT:PSS@Zn, PEDOT:PSS@Zn or bare Cu@Zn as the anode and 2 M ZnSO₄ as the electrolyte. In the assembly of Zn||NVO full cells, 3D PEDOT:PSS@Zn or bare Zn was used as the anode and NaV₃O₈ nanowires were used as cathode. All the electrodes were cut into round disks of 10 mm diameter and assembled into CR2032-type coin cells, in which 90 μ L of mixed electrolyte composed of 2 M ZnSO₄ and 0.2 M Na₂SO₄ was added and glass fiber (GF/D) as separator was used. Taking the deposited Zn over 3D PEDOT:PSS (10 mAh cm⁻²), the mass loading of NaV₃O₈ (1.2 mg cm⁻²) and the theoretical capacity of NaV₃O₈ (530 mAh cm⁻²) into consideration, the actual N/P ratio in the full cell was 15.

The discharge capacities (C_m) of the full cell at different current densities were based on the mass of cathode and calculated according to following equation:²

$$C_m = \frac{I \times t}{3.6 \times m} \tag{S1}$$

Where $C_{\rm m}$ is the specific capacity (mAh g⁻¹), *I* is discharge current (mA), *t* is discharge time (h), *m* is mass of cathode (g) and the coefficient of 3.6 referred to the unit conversion factor. The Coulombic Efficiency in full cells were calculated according to following equation:³

$$CE(\%) = \frac{C_C}{C_{Dis}} \tag{S2}$$

Where $C_{\rm C}$ is the charge specific capacity, $C_{\rm Dis}$ is the discharge specific capacity.

1.5 Electrochemical Measurements

The galvanostatic charge-discharge and cycling stability of the cell were tested on LAND-CT3002A battery-testing systems. The Coulombic efficiencies of Zn plating/stripping were measured by assembling Zn||Cu asymmetric cell using 3D

PEDOT:PSS@Zn (Zn deposit of 10 mAh cm⁻²) as anode and Cu foil as cathode. The plating/stripping behaviors were investigated at a current density of 1 mA cm⁻² with a constant capacity of 0.5 mAh cm⁻² and a charging cutoff voltage of 0.5 V. The Coulombic efficiency (CE) of Zn||Cu asymmetrical cells were calculated according to following equation:⁴

$$CE(\%) = \frac{1}{N} \sum_{1}^{N} \frac{Q_S}{Q_P}$$
(S3)

Where Q_S and Q_P are stripping and plating capacity, N is cycle numbers.

The linear polarization curve (LSV), Tafel curve, current-time curve (CA) and electrochemical impedance spectroscopy (EIS) were recorded on a CHI760E electrochemical workstation. The LSV was conducted in a three-electrode system in 2 M Na₂SO₄ aqueous electrolyte with a scan rate of 5 mV s⁻¹, where 3D PEDOT:PSS@Zn was used as the working electrode, Pt foil as the counter electrode, and Ag/AgCl electrode as the reference electrode. The Tafel plots were recorded at a scan rate of 1 mV s ⁻¹ in 2 M ZnSO₄ aqueous solution. The CA curves were tested in Zn||Zn symmetric cells by the chronoamperometry method at an overpotential of -150 mV. The CV curves were collected on an Autolab electrochemical workstation (PGSTAT302N). The EIS of cells was obtained in the frequency range from 0.01 to 105 Hz using a 5 mV sinusoidal signal perturbation.

1.6 Materials characterizations

The X-ray diffraction (XRD) patterns of the electrodes were collected on a Rigaku Miniflex 600-type X-ray diffractometer with a Cu-K α (λ = 0.154 nm) source (scan rate of 10 min⁻¹ and scan range of 10–80°). The micromorphology of the samples was observed by field-emission scanning electron microscopy (FESEM, SU8020) equipped with corresponding energy dispersive spectroscopy elemental mapping (EDS). XPS spectra (AXIS ULTRA spectrometer, Escalab Xi+) was used to characterize the elemental composition of a material surface. Raman and FT-IR spectra were recorded on a Renishaw Via Raman spectrometer (using 532 nm excitation) and Bruker EQUINX55 infrared spectrometer.

2. Supplied Figures



Fig. S1 Top-view SEM images of the nonporous PEDOT:PSS film (a-d) and Bare Cu (e-h) after plating metallic Zn with various capacities: (a, e) 1 mAh cm⁻², (b, f) 3 mAh cm⁻², (c, g) 6 mAh cm⁻² and (d, h) 10 mAh cm⁻².



Fig. S2 XRD patterns of metallic Zn deposited over nonporous PEDOT:PSS host (a) and bare Cu foil (b) with different plating capacities.



Fig. S3 FT-IR spectra of 3D PEDOT:PSS host before and after Zn deposition with a capacity of 10 mAh cm⁻².



Fig. S4 CA curves (a) at a potential of -150 mV and Tafel plots (b) of different electrodes.



Fig. S5 Nyquist plots of Zn||Zn symmetric cells built with different electrodes.



Fig. S6 Voltage-time profiles at 10 mA cm⁻² and 1 mAh cm⁻² of Zn||Zn symmetric cells built with different electrodes.



Fig. S7 The surface SEM images (a, b) and powder XRD (c) of the 3D PEDOT:PSS@Zn electrode after cycle for 100 h (a) and 200 h (b) at 1 mA cm⁻² and 2 mAh cm⁻².

Host	Current density (mA cm ⁻²)	Depth of discharge (%)	Life span (h)	Ref.
CNF-Zn	2	25	260	5
Sn@NHCF	1	8.3	360	6
	3	50	100	
TiOx/Zn-NC	1	12.5	450	7
	4	50	200	/
3DP-NC	1	10	380	8
At-Sn@HCN	1	50	120	9
Zn-Sn/CF	1	7	400	10
rHGP-N	1	25	180	11
Zn@Zn/P-S	1	40	100	12
3D PEDOT:PSS	1	20	400	This work
		50	270	

Table S1. Comparison of our results with recent publications of anode hosts in term of DOD, current density and life span in aqueous ZIBs.



Fig. S8 The XRD pattern (a) and SEM image (b) of NVO nanowires.



Fig. S9 XRD patterns of the Zn anodes of cycled Zn||NVO and 3D PEDOT:PSS||NVO full cells at 1 A g⁻¹ for 1000 cycles.

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