

A biocompatible and fully erodible conducting polymer enables implanted rechargeable Zn battery

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Experimental

Materials synthesis

EDOT-COOCH₃ Synthesis: EDOT-OH (2.0 g, 11.6 mmol) was added to dry tetrahydrofuran (50 mL) under a N₂ atmosphere and cooled down in an ice bath. Potassium iodide (0.38 g, 22.8 mmol) and sodium hydride (0.556 g, 23.2 mmol) were subsequently added, followed by the dropwise addition of methyl 3-bromopyruvate (1.52 mL). After reacting for 48 h under a N₂ atmosphere, deionized water was used to quench the reaction, followed by the removal of the tetrahydrofuran under reduced pressure. Then, the aqueous mixture was extracted with ethyl acetate, dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (hexane: EtOAc = 5:1) to give a clear, viscous liquid (2.52 g, 9.76 mmol, 84.2% yield). ¹H NMR (400 MHz, CDCl₃): δ 6.32 (2H, s), 4.26-4.33 (1H, m), 4.22 (1H, dd, J = 11.6, 2.3 Hz), 4.03 (1H, dd, J = 11.6, 7.5 Hz), 3.79 (2H, t, J = 6.3 Hz), 3.67 (3H, s), 3.62-3.76 (2H, m), 2.62 (2H, t, J = 6.3 Hz) (Fig. S2a, S2b).

EDOT-COOH Synthesis: EDOT-COOCH₃ (0.5 g) was reacted with 2 M NaOH (50 mL) for 4 h at 80 °C and then filtered to remove the insoluble powder. Then the obtained purple solution was treated with 10% HCl to afford a precipitate. The black powder was washed with water and dried under a vacuum (~300 mg). ¹H NMR (400 MHz, DMSO) δ 12.21 (s, 1H), 6.62-6.50 (m, 2H), 4.31-4.26 (m, 1H), 4.23 (dd, J = 11.7, 2.2 Hz, 1H), 3.96 (dd, J = 11.7, 7.7 Hz, 1H), 3.66 (t, J = 6.3 Hz, 2H), 3.63-3.60 (m, 2H), 2.46 (d, J = 6.2 Hz, 2H) (Fig. S2c).

PEDOT-COOH Synthesis: EDOT-COOCH₃ (0.64 g, 2.48 mmol) was dissolved in anhydrous chloroform (6 mL), dropwise added to the FeCl₃ (1.45 g, 8.94 mmol) chloroform mixture and then left stirring for 24 h at room temperature under N₂ atmosphere. The mixture was poured into methanol (~300 mL) and centrifuged to collect the polymer. To remove the methyl group on the side chain, PEDOT-COOCH₃ was treated with 2 M NaOH at 80 °C for 4 h, followed by precipitating the polymer with 10% HCl.

The PEDOT-COOH was also electropolymerized onto ITO glass or PVA-Au leaf using a CV method from a solution containing 0.01 M EDOT-COOH and 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile at 0 °C. The electrodeposition was performed by cycling the potential between -0.6 and 1.8 V vs. Ag/Ag⁺ at a scan rate of 100 mV s⁻¹ for 20 cycles. The polymer film was washed with deionized water to remove the loosely bound particles or other residues and dried under a vacuum at 50 °C for 24 h.

Materials characterizations

The ¹H nuclear magnetic resonance (NMR) was performed on a 400 MHz NMR spectrometer (Bruker AMX 400 system) to confirm the chemical structures of EDOT-COOH and EDOT-COOCH₃ monomer. *Ex-situ* Raman spectra (Renishaw's InVia Raman Microscopes) and XPS (Thermo ECSALAB 250) were also used to clarify the reaction mechanism of the cathode, accompanied by C1s peak calibration (284.8 eV). Crystal structures of PEDOT-COOH and anode were characterized using Rigaku wide-angle X-ray diffractometer (XRD, D/max rA, using Cu K α radiation, $\lambda=1.5406$ Å). Morphology of the Zn anode was observed using field-emission SEM (FEI Nova Nano SEM 450) before and after long-term cycles.

Bioerosion study

Pressed pellets from chemically polymerized PEDOT-COOH were incubated in different PBS solutions (15 mL, pH: 4, 7.4, and 10) at 37 °C on an orbital shaker. Culture media was changed every 12 h and subsequently analyzed with UV-Vis spectroscopy. The mass retention was analyzed by removing the incubation media, washing the pellet with deionized water, and drying them under a vacuum. The erosion rate was illustrated as the weight ratio after incubation to the original weight. All experiments were performed in triplicate. The chemical structure of the eroded solution was determined by FTIR (BRUKER VECTOR 22 Spectrometer). The pellet morphology change at various incubation stages was observed using SEM (FEI Nova Nano SEM 450).

Electrochemical measurements

Erosion effect on the electrical properties: The electrical conductivity was monitored during the incubation in PBS with a four-probe resistance tester (RTS-2, Guangzhou four-probe). The electrical conductivity was calculated according to equation 1:

$$\sigma = \frac{1}{Rd} \quad (1)$$

where σ is the electrical conductivity (S cm^{-1}), R is the bulk resistance (Ω), d represents the sample thickness (cm), respectively.

CV of PEDOT-COOH film on ITO glass was monitored during the incubation period in a three-electrode system, with a Pt wire counter electrode, an Ag/AgCl reference electrode, and PBS as the culture medium and electrolyte. The copper tape was attached to films before incubation in the PBS solution as an electrical contact. EIS

was tested in the frequency range of 100 kHz to 0.01 Hz on a CHI660e electrochemical workstation. Due to the continuous change in the mass of PEDOT-COOH during the incubation, the areal-specific capacitance of electrodes was calculated according to the following equation from the CV curves:

$$C = \frac{A}{2 \times S \times v \times \Delta V} \quad (2)$$

where C is the specific capacitance (F cm^{-2}), A is the area of the CV loop, S was the electrode area (cm^2), v is the scan rate (V s^{-1}), and ΔV is the voltage window (V).

Fabrication of Zn battery: Gelatin (15 g) was dissolved in 1 M ZnSO_4 (100 mL) at 80 °C for 3 h. The solution was cooled to room temperature before being transferred to a Teflon mold. Gelatin- ZnSO_4 gel electrolytes were obtained after 3 freeze-thaw cycles, i.e. frozen at -20 °C for 6 h and thawed at room temperature.

To fabricate a biodegradable substrate, gold leaf (0.15 μm thickness) was placed onto non-stick paper on a flat surface and then transferred to a PVA film (100 μm thickness) followed by slight pressing. PEDOT-COOH was electrochemically polymerized to the PVA-Au substrate. The compact battery was assembled by stacking PEDOT-COOH film (10 \times 10 mm) cathode, gelatin- ZnSO_4 gel electrolyte (10 \times 10 mm), and Zn foil (5 \times 10 mm) anode. The crystallinity of the outermost PVA encapsulation layer (400 μm thickness) was controlled by baking at 130 °C on a hot plate for 30 min. The edges were adhered with PVA solution as the binder and further laminated using a thermal-press process.

Electrochemical tests of Zn battery: CV and EIS were performed on a CHI660E

workstation using a two-electrode setup. A galvanostatic charge/discharge profile was carried on a Neware battery tester. They were sealed in bags to prevent water evaporation from the gel electrolyte. *Ex-situ* XPS (Thermo ECSALAB 250) was used to clarify the reaction mechanism of the cathode, using C1s peak (284.8 eV) as the calibration.

The theoretical capacity of the cathode was calculated using equation 3:

$$Q_s = \frac{n \times F}{3.6 \times M} \quad (3)$$

where Q_s is the theoretical specific capacity (mAh g⁻¹), n is the theoretical electron-transfer numbers of active materials, F is the Faraday constant (96485 C mol⁻¹), and M is the corresponding molecular mass of polymer fragments.

The capacitive contribution (CC) can be calculated by the following equations 4 and 5:

$$i = k_1 \times v + k_2 \times v^{1/2} \quad (4)$$

$$CC = \frac{k_1 \times v}{i} * 100\% \quad (5)$$

where i is current (mA) at different potentials, $k_1 v$ is the capacitive contribution and $k_2 v^{1/2}$ is the ionic diffusion contribution.

The potential of the electrode ($E_{1/2}$, V) and V_{cell} (V) were calculated according to Equations 6 and 7:

$$E_{1/2} = (E_{ox} + E_{re})/2 \quad (6)$$

$$V_{cell} = E_{1/2, cathode} - E_{1/2, anode} \quad (7)$$

where E_{ox} and E_{re} were the potentials of the oxidation peak and reduction peak, respectively.

The energy density (mWh g⁻¹) and power density (mW g⁻¹) were calculated by equations 8 and 9:

$$E = \frac{\int QdV}{m} \quad (8)$$

$$P = \frac{E}{t} \quad (9)$$

where E and P represented the energy density (Wh kg⁻¹) and power density (W kg⁻¹), Q and V represented the discharging specific capacity and voltage, respectively. m was the mass of the cathode and t was the discharging time.

Cell culture and proliferation assay

Cell culture with the eroded products: The eroded solution was obtained by incubation of the PEDOT-COOH pellet in PBS for 72 h and then diluted to various concentrations. hADSCs cells were seeded in a 96-well plate at a density of 5×10³ cells per well with different concentrations of eroded solution. Cells were cultured in Gibco Dulbecco's Modified Eagle's Medium media supplemented with 10% Fetal bovine serum. The cell viability in 96-well plates was examined by the MTT assay. At specific time intervals of cultivation, 10 μL of MTT was added to the culture medium, and the resulting solution was incubated at 37 °C for 4 h. The enzyme-labeled instrument was then used to measure the optical density at 490 nm (Bio-Tek Instruments).

Cell culture on the polymer surface: PVA-Au and PEDOT-COOH polymerized onto PVA-Au substrate were treated by being soaked in sterile PBS supplemented with 500 Unit mL⁻¹ penicillin-streptomycin for 20 h. They were placed into 24-well polystyrene cell culture plates and soaked overnight with a culture medium, followed by rinsing

with PBS twice. hADSCs cells were seeded on the samples at a density of 2×10^4 cells cm^{-2} and cultured for three days. Then, cells were visualized using live/dead staining with 2 μM calcein acetomethoxy (calcein AM) and 4 μM propidium iodide (PI) in PBS. Images were obtained using a Zeiss Axio Imager microscope (Carl Zeiss).

Implantation of Zn battery

All *in vivo* experiments were approved by the Institutional Animal Care and Use Committee (IACUC) of Jilin University (Approval No. 2022-0599). The feeding conditions strictly followed the GB14925 protocol. The encapsulated batteries and all surgical instruments were sterilized by Gamma-ray irradiation and autoclaving methods for 1 h. The SD rats (5 weeks) were anesthetized with the inhalation of mixed isopentane gas (1-3%) before implantation. The Zn battery ($1 \times 20 \times 20$ mm) was inserted into the subcutaneous tissue of the dorsal region under anesthesia. To observe the *in vivo* degradation, the SD rats were sacrificed and dissected two and four weeks after implantation. After the Zn battery entirely disappeared, the subcutaneous tissues with and without implantation and organs were excised and stored in the tissue fixative at 4 °C. Tissue skin and organs were stained with H&E for histopathological analysis.

Table S1. Electrochemical performance and biodegradation comparison of Zn-polymer battery with biodegradable/implantable rechargeable batteries.

Anode//Cathode	Electrolyte	Degradation	Voltage (V) ¹	Capacity (mAh/g @A/g)	Cycling ² (retention @cycles)	Rate ³ (retention @A/g)	Energy density (mWh/g)	Ref.
Zn//PEDOT-COOH	Gelatin-ZnSO ₄	Full degradation after 30 days in PBS or 56 days <i>in vivo</i>	1.2	31.8 @0.25	78%, 4000	51.5% 0.25-10	37.8	This work
Zn//MnO ₂	Cellulose-ZnSO ₄	Partial degradation after 45 days <i>in vivo</i>	1.4	221 @0.06	77%, 100	51% 0.2C-2C	309	[1]
MoO ₃ -PPy//Na _{0.44} MnO ₂	0.9% NaCl	-	0.7	43 @1.0	72%, 100	67% 0.5-1.5	30.1	[2]
PDA-PPy//MnO ₂	Body fluid	Biodegradation after 84 days in PBS	0.6	25.6 @1.0	69%, 200	71.7% 0.5-1.5	15.3	[3]
Pyroprotein-based carbon//Na ₄ Fe ₃ (PO ₄) ₂	NaClO ₄	Environmental degradation after 120 days in soil	3.0	50 @0.026	80%, 50	-	150	[4]
Polypeptide radical battery	LiCF ₃ SO ₃	Full degradation in 1 M HCl at 110 °C	1.3	37.8 @1C	20%, 250	68% 1C-20C	49.1	[5]
NTP//melanin	Na ₂ SO ₄	-	0.5	78 @0.05	-	-	39	[6]
Melanin//MnO ₂	Na ₂ SO ₄	-	0.5	16 @0.01	-	-	8	[7]
Melanin vs. SCE (half-cell)	Mg(NO ₃) ₂	-	0.4	61.6 @0.10	98%, 500	20% 0.1-5	-	[8]
PDHA vs. Ag/AgCl (half-cell)	PBS	-	0.85	130 @10	-	-	-	[9]

Notes:

1. Voltage was the potential difference between the cathode and anode.
2. Cycles stability was evaluated after GCD cycles.

3. Rate performance is the capacity retention ratio.

-: data not provided, PDA: polydopamine, NTP: sodium-titanium phosphate, SCE: saturated calomel electrode, PDHA: polydopamine-hyaluronic acid.

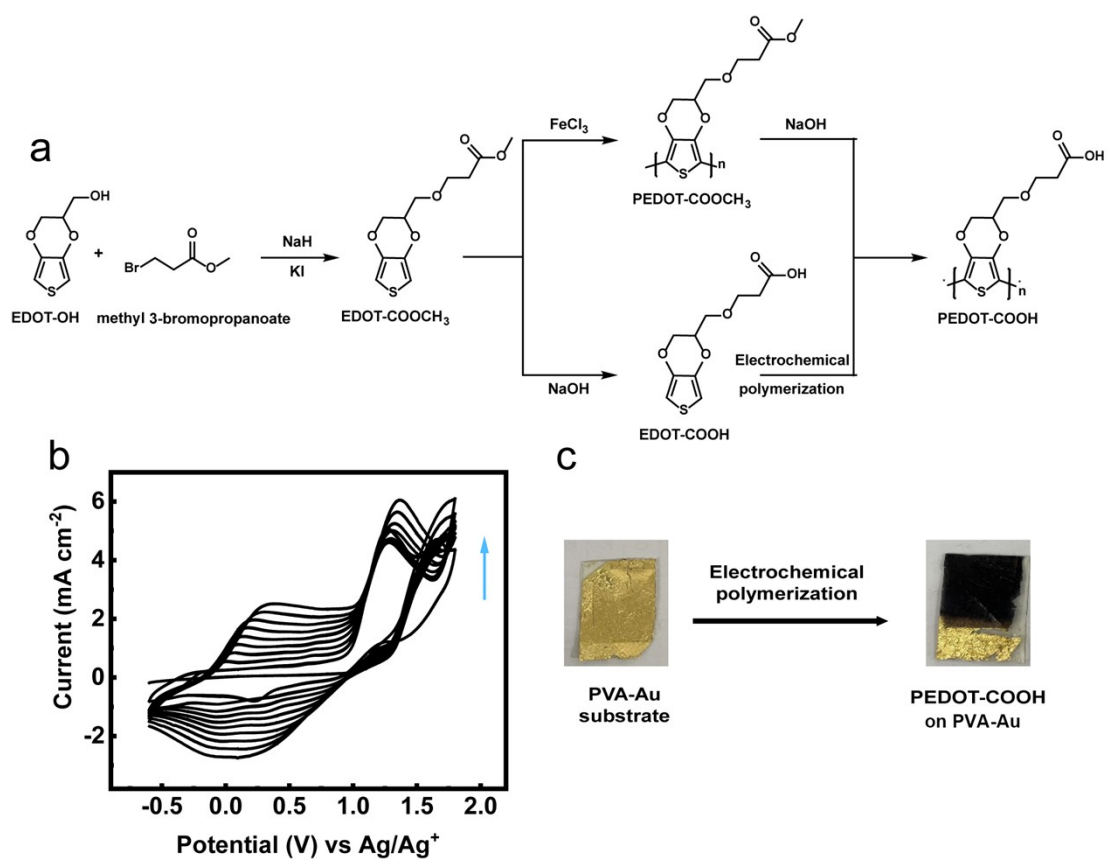
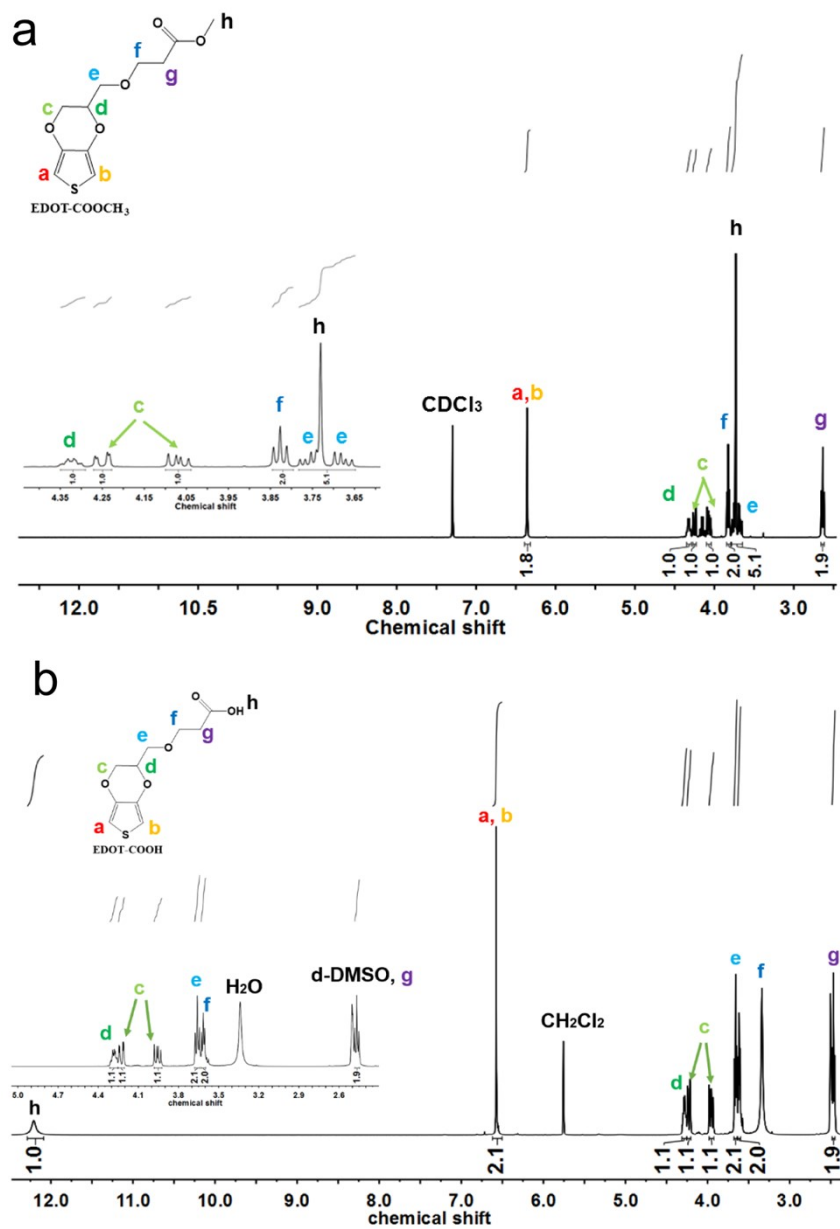


Fig. S1. (a) Synthesis of bio-erodible PEDOT-COOH. (b) CV curves of electrochemical polymerization of EDOT-COOH. (c) Photographs of PVA-Au before and after electrochemical polymerization of EDOT-COOH.



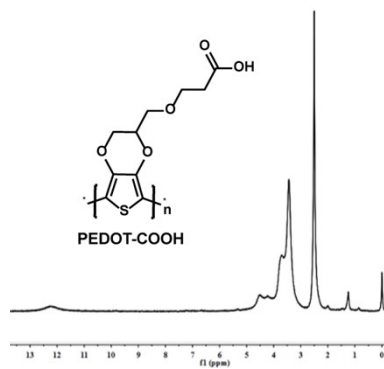


Fig. S3. ¹H NMR of PEDOT-COOH.

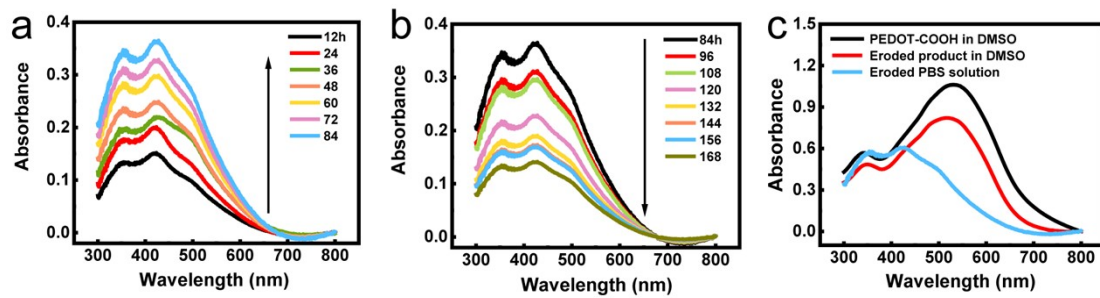


Fig. S4. (a, b) Absorption profiles of eroded PBS solution every 12 h during 7 days of incubation. (c) UV-Vis spectra of PEDOT-COOH pellet in DMSO before and after erosion, and eroded PBS solution.

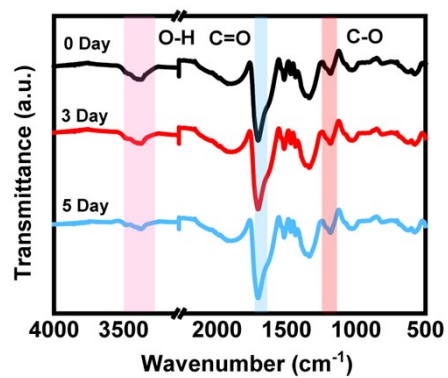


Fig. S5. FTIR of the pristine PEDOT-COOH pellet and eroded solution after 3 and 5 days.

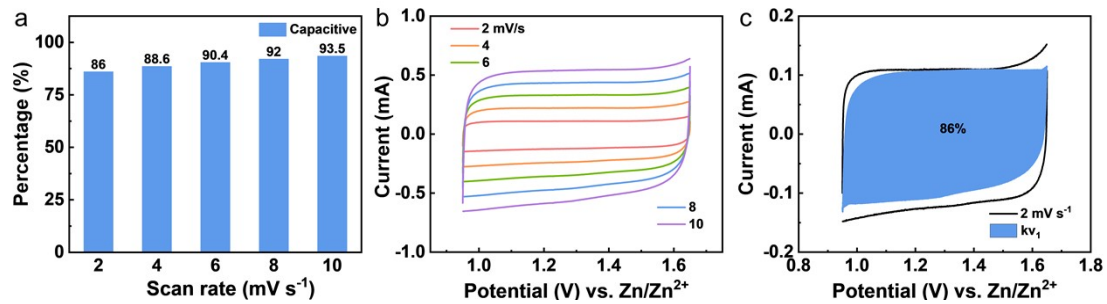


Fig. S6. (a) CV and (b) capacitive contribution of PEDOT-COOH electrode in ZnSO₄ electrolyte at various scan rates. (c) Fitting capacitive curve and pristine CV curves of PEDOT-COOH electrode at 2 mV s⁻¹

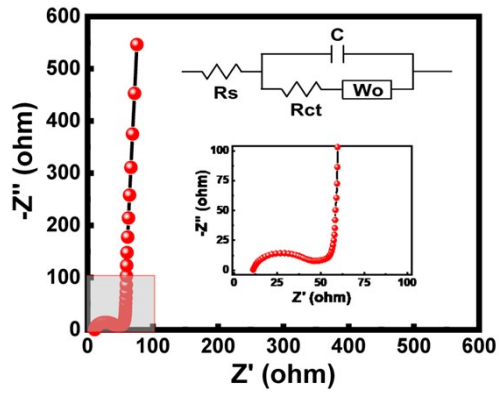


Fig. S7. Nyquist plot of PEDOT-COOH electrode in PBS electrolyte; inset shows the electrical equivalent circuit.

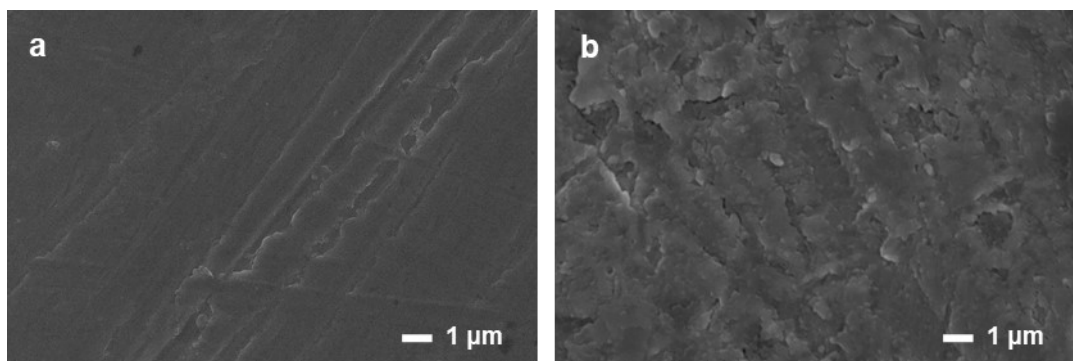


Fig. S8. SEM images of the Zn anode before (a) and after 4,000 cycles (b) at 0.5 A g^{-1} .

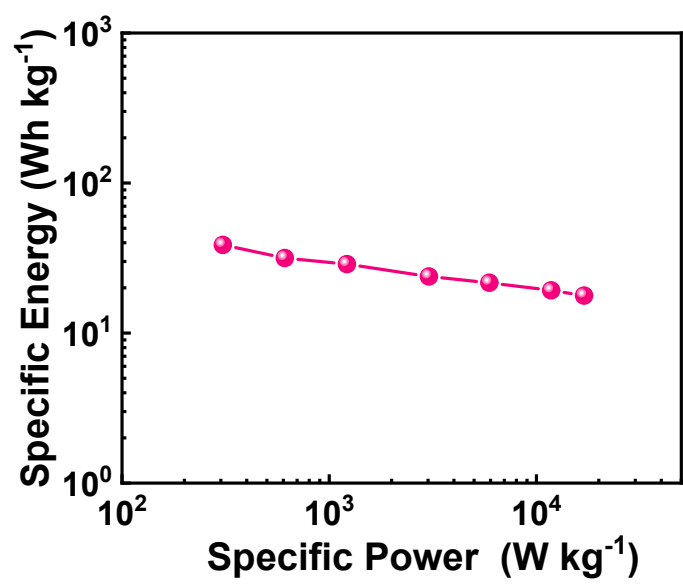


Fig. S9. Ragone plot of the compact Zn battery.

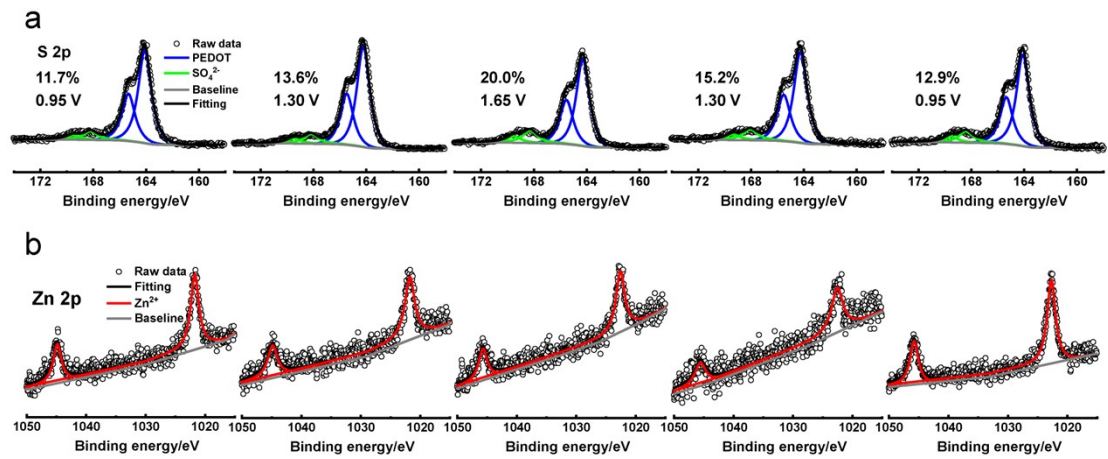


Fig. S10. *Ex-situ* XPS spectra of S 2p (inset shows the doping level), Zn 2p elements for PEDOT-COOH electrode at different voltages.

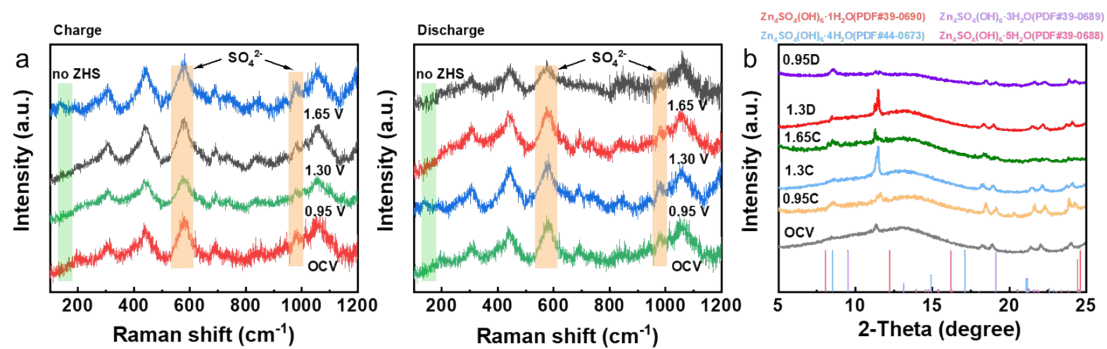


Fig. S11. The *ex-situ* Raman (a) and XRD spectra (b; Inset shows JCPDS cards of $\text{Zn}_4\text{SO}_4(\text{OH})_6$ with different crystallized water) of PEDOT-COOH electrodes at different potentials.

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