**Supplementary Information** 

# Carbonized Polymer Dots as Electrolyte Additives for Suppressing Zn Dendrite Growth, Corrosion, and HER in Zn-Ion Batteries

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## **Experiment section**

#### Synthesis of CPDs

Firstly, 0.576 g (3 mmol) of citric acid was dissolved in 10 mL of DMF solution. Then, 0.601 g (10 mmol) of urea was added to the solution and stirred at room temperature. After stirring for 30 min, the resulting solution was transferred to a sealed polytetrafluoroethylene (PTFE) - lined autoclave for solvothermal reaction at 180°C for 12 h. After cooling to room temperature, excess ethyl acetate was added to the solution to induce precipitation. The product was washed several times with a mixture of ethyl acetate and methanol, then dried in a vacuum oven to obtain a black powder.

## Preparation of Electrolytes

Ultrapure water (Macklin) was used to prepare aqueous electrolytes. The 2M  $ZnSO_4$  electrolyte was formulated by dissolving  $ZnSO_4 \cdot 7H_2O$  into ultrapure water. The electrolyte with different CPDs was prepared by adding 1, 2, 4 and 6 mg of CPDs into 10 mL of 2M  $ZnSO_4$  solution, namely, 0.1, 0.2, 0.4, 0.6 g L<sup>-1</sup>.

#### Preparation of MnO<sub>2</sub> cathodes

In a typical synthesis process, 0.507 g of MnSO<sub>4</sub>·H<sub>2</sub>O and 2 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub> were dissolved in 60 mL deionized water under magnetic stirring for 30 min. Then, 20 mL of 0.1 M KMnO<sub>4</sub> was slowly added to the solution. The mixture was stirred for 1 h, followed by sonication for 1 h. Finally, the mixture was transferred to a Teflon-lined autoclave and heated at 120 °C for 12 h. After cooling to room temperature, MnO<sub>2</sub> was washed with deionized water and freeze-dried. The MnO<sub>2</sub> cathode was prepared using a blade-coating method. Briefly, MnO<sub>2</sub> powder, black carbon and PVDF with a weight

ratio of 7:2:1 were homogeneously mixed in N-methyl pyrrolidone (NMP). The slurry was then uniformly coated onto the surface of carbon paper collector and dried in a vacuum at 60 °C for 12 h. Finally, the as-prepared electrodes were obtained. Assembly of Zn||Zn Symmetrical Cells and  $Zn||MnO_2$  Cells

The CR2032 coin-type Zn||Zn symmetrical cells were composed of two Zn foil, 2 M ZnSO<sub>4</sub> and 2 M ZnSO<sub>4</sub> with CPDs electrolyte and a glass fiber separator (Whatman GF/D). For Zn||MnO<sub>2</sub> cells, the MnO<sub>2</sub> cathode and bare Zn were separated by a glass fiber separator using 2 M ZnSO<sub>4</sub> + 0.2 M MnSO<sub>4</sub> without and with CPDs as electrolyte. *Characterizations* 

Surface functional groups of CPDs were characterized by Fourier transform infrared (FTIR) spectrum using Agilent Technologies Cray 630 FTIR. The materials were characterized by Agilent Technologies Cray 630 FTIR, scanning electron microscopy (SEM, Hitachi), transmission electron microscopy (TEM, JEM-2010F), X-ray diffractometer (XRD, Rigaku Smart Lab X-ray diffractometer), liquid-state hydrogen nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS, monochromatic Al Ka radiation). The contact angles between the Zn foil and different electrolytes were tested on Contact Angle Goniometer (SDC-100 China, Dongguan). The fluorescence images of Zn metal anode with and without CPDs were carried out by a confocal laser scanning microscope (CLSM, Olympus FV3000).

## Electrochemical Measurements

Electrochemical impedance spectroscopy (EIS) was measured with an amplitude of 5 mV from 0.01 Hz to 1000000 Hz. Chronoamperometry (CA) was performed by using Zn||Zn cells at a constant overpotential of -150 mV for 400 s. The hydrogen evolution reaction (HER) was tested by using linear sweep voltammetry (LSV) method at a scan rate of 1 mV s<sup>-1</sup> from 0 to -0.9 V. Tafel plots was tested between -0.7 and -1.5 V (versus saturated calomel electrode) at 1 mV s<sup>-1</sup>. The transference number was calculated by a current-time plots under potentiostatic polarization at 25 mV for 4000 s. Furthermore, the transparent symmetric cells of Zn electrodes in the different electrolytes were assembled to observe the surface morphology evolution by in-situ optical microscope.



**Fig. S1.** Optical images of electrolyte with different CPDs concentration at (a) initial state, (b) after standing more than six months, (c) under UV light, (d) after standing more than six months under UV light.



Fig. S2. (a, b) SEM images of unpolished Zn foils before cycling at different magnification.



Fig. S3. (a, b) SEM images of polished Zn foils before cycling at different magnification.



Fig. S4. Cycling performance of symmetric cells with different CPDs concentration at  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$  and (b) the corresponding voltage profile.



**Fig. S5.** (a) Cycling performance of symmetric cells with different CPDs concentration at 2 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>.

The addition of CPDs severely impacts electrochemical cycling stability. The insufficient CPDs have little impact on the cycling life, because there are not enough CPDs to bind to  $Zn^{2+}$  to guide the uniform deposition of  $Zn^{2+}$ . Inversely, excessive CPDs will hinder the migration of  $Zn^{2+}$  and reduce ionic conductivity, resulting in increasing polarization voltage and lower cycle life. Therefore, choosing the suitable amount to add is important. According to the above cycling performance, the 0.2 g L<sup>-1</sup> is the optimal CPDs concentration.



Fig. S6. (a) Cycling performance of symmetric cells with and without CPDs at 10 mA

 $\rm cm^{-2}$  - 1 mAh  $\rm cm^{-2}$  and (b) the corresponding voltage profiles.



Fig. S7. The corresponding voltage profiles at certain cycles of  $Zn \|Cu$  asymmetric cells in electrolyte with and without CPDs at 5 mA cm<sup>-2</sup> - 1 mAh cm<sup>-2</sup>.



Fig. S8. CE of Zn||Cu half cells in electrolyte with and without CPDs at 1 mA cm<sup>-2</sup> - 1 mAh cm<sup>-2</sup>.



**Fig. S9.** SEM images of (a, b) Zn foil and (c, d) Cu foil for Zn||Cu cells assembled in electrolyte without CPDs after 50 cycles at 5 mA cm<sup>-2</sup> - 1 mAh cm<sup>-2</sup>. SEM images of (e, f) Zn foil and (g, h) Cu foil for Zn||Cu cells assembled in electrolyte with CPDs after 50 cycles at 5 mA cm<sup>-2</sup> - 1 mAh cm<sup>-2</sup>.



**Fig. S10.** SEM images of Zn foils after soaking in electrolyte (a, b) without CPDs and (c, d) with CPDs for 7 days.



Fig. S11. XRD pattern of Zn foils after soaking in different electrolytes for 7 days.



**Fig. S12.** Current-time plots of Zn||Zn symmetric cells in electrolyte (a) without CPDs and (b) with CPDs after polarization at a constant potential (25 mV) for 4000 s. The insets present the impedance spectra before and after polarization.

The transference number of  $(t_{Zn}^{2+})$  was calculated by the following equation:

$$t_{Zn}^{2+} = \frac{Is(\Delta V - I0R0)}{I0(\Delta V - IsRs)}$$

Where  $\Delta V$  is the applied polarization voltage (25 mV),  $I_0$  and  $R_0$  are the initial current and resistance, and  $I_s$  and  $R_s$  are the steady-state current and resistance, respectively.



Fig. S13. Contact angles of electrolyte on Zn foil (a) without CPDs and (b) with CPDs.



Fig. S14. Optical images of Zn||Zn transparent cells after depositing 30 minutes at current of 10 mA cm<sup>-2</sup>.



**Fig. S15.** Confocal luminescence images of Zn anode in electrolyte with CPDs after depositing (a-c) 1 mAh cm<sup>-2</sup> and (d-f) 2 mAh cm<sup>-2</sup> in (a, d) dark field, (b, e) bright field and (c, f) composite field, respectively.



Fig. S16. (a) SEM image and (b) XRD pattern of as-prepared MnO<sub>2</sub>.



**Fig. S17.** The equivalent circuit of fresh Zn||MnO<sub>2</sub> full cells using the electrolyte (a) with CPDs and (b) without CPDs.



Fig. S18. Galvanostatic charge-discharge curves of full cells at different current density

in electrolyte (a) without CPDs and (b) with CPDs.



Fig. S19. Charge-discharge curves of  $Zn||MnO_2$  full cells with different cycle numbers at a current density of 1 A g<sup>-1</sup> in electrolyte (a) without CPDs and (b) with CPDs.



**Fig. S20.** SEM images of zinc anode in  $Zn||MnO_2$  full cells at 1 A g<sup>-1</sup> after 50 cycles in electrolyte (a) without CPDs and (b) with CPDs.



Fig. S21. Optical image of the  $Zn||MnO_2$  pouch cell.



Fig. S22. Cycling performance of the  $Zn||MnO_2$  pouch cells in electrolyte with and without CPDs.

different additives.				
Electrolytes	Current density (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	Lifespan (h)	References
2 M ZnSO <sub>4</sub> +0.2 g L <sup>-1</sup> CPDs	1	1	1350	This work
1 M Zn(OTf) <sub>2</sub> - EmimFSI/H <sub>2</sub> O	1	1	680	[1]
1 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> + Dextran	1	1	850	[2]
2 M ZnSO <sub>4</sub> +0.004 M NiSO <sub>4</sub>	1	1	900	[3]
2 M ZnSO <sub>4</sub> +0.05 g L <sup>-1</sup> Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> MXene	1	1	1000	[4]
1 M Zn(ClO <sub>4</sub> ) <sub>2</sub> +10 mM β-CD	1	1	1000	[5]
1 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> + 25 mM Zn(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	1	1	1200	[6]
1 M ZnSO <sub>4</sub> +5 mM Thiourea	1	1	1200	[7]

Table S1. Comparison in electrochemical performance of Zn||Zn symmetric cells with

#### References

- [1] Yu Z, Yan L, Jun J, et al. Electrolyte Design for Lithium-Ion Batteries for Extreme Temperature Applications [J]. Adv. Mater., 2023, 2308484.
- [2] Li J, Guo Z, Wu J, et al. Dextran: A Multifunctional and Universal Electrolyte Additive for Aqueous Zn Ion Batteries [J]. Adv. Energy Mater., 2023, 13: 2301743.
- [3] Dai Y, Zhang C, Zhang W, et al. Reversible Zn Metal Anodes Enabled by Trace Amounts of Underpotential Deposition Initiators [J]. Angew. Chem. Int. Ed., 2023, 62: 202001192.
- [4] Sun C, Wu C, Gu X, et al. Interface Engineering via Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene Electrolyte
   Additive toward Dendrite-Free Zinc Deposition [J]. Nano-Micro Lett., 2021, 13:
   89.
- [5] Qiu M, Sun P, Wang Y, et al. Anion-Trap Engineering toward Remarkable Crystallographic Reorientation and Efficient Cation Migration of Zn Ion Batteries
   [J]. Angew. Chem. Int. Ed., 2022, 61: 202210979.
- [6] Zeng X, Mao J, Hao J, et al. Electrolyte Design for In Situ Construction of Highly Zn<sup>2+</sup>-Conductive Solid Electrolyte Interphase to Enable High-Performance Aqueous Zn-Ion Batteries under Practical Conditions [J]. Adv. Mater., 2021, 33: 2007416.
- [7] Qin H, Kuang W, Hu N, et al. Building Metal-Molecule Interface towards Stable and Reversible Zn Metal Anodes for Aqueous Rechargeable Zinc Batteries [J]. Adv. Funct. Mater., 2022, 32: 2206695.