Supporting Information

Enabling rapid Zn^{2+} ions diffusion and anionic repulsion toward high-performance aqueous zinc-ion batteries

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Experimental Procedures

Synthesis of Carboxymethylated polyvinyl alcohol：

A 10%wt aqueous solution of polyvinyl alcohol (PVA) was configured at 80 °C. At room temperature, 30 g of aqueous PVA solution was weighed and 4.5 g of NaOH was dissolved in 20 mL of DI. water and added dropwise to the PVA solution. The solution was placed in a water bath at 70 °C for 10 min, and 6.5 g of chloroacetic acid (dissolved in 5 mL of DI. water) was added dropwise to the solution during stirring. After 4 hours, the reaction was terminated and the product was precipitated using ethanol, with repeated filtration using ethanol. Vacuum drying was carried out at 50 °C for 24 hours to obtain the white colored target product.

Synthesis of Zn-CP：

A 10%wt solution was configured by dissolving 5 g of carboxymethyl polyvinyl alcohol in 45 g of DI. water. Then, the Zn foil (4 cm * 4 cm, thickness: 100 μm) was connected to the negative terminal and the graphite paper (4 cm * 4 cm), was connected to the positive terminal of the DC power supply, and immersed in the above solution. During the electrodeposition process, a constant current of 10 mA was applied for a certain time and get the Zn foil with artificial interface layer. The Zn-CP was rinsed several times using DI. water and dried to obtain Zn-CP.

Preparation of Zn-CP||I_2/AC full cells:

The Zn-I_2 battery was prepared as in that of our previous work.[1] The solution-adsorption method was used for the preparation of cathodes. In brief, 300 mg of I_2 was mixed with 300 mg active carbon (AC), followed by adding 20 mL of deionized water. The Iodine ratio in the I_2/AC composite was about 15~20wt%, as calculated by deducting the mass of AC from the final weighted composite. The I_2/AC, sodium carboxymethyl cellulose (CMC) and super P were mixed in deionized water with a mass ratio of 8:1:1. Then the slurry was cast on a carbon cloth followed by drying for 12 h in the air at 60 °C. The average areal loading of I_2/AC composite was about 4-6 mg cm^{-2} in the electrode. For the fabrication of Zn||I_2/AC full cell, 2 M aqueous ZnSO4 solution was used as the electrolyte.

Characterization Methods：

Scanning electron microscopy (SEM): The SEM images were achieved on Hitachi SU8220 after freeze-dried.
X-ray diffraction (XRD): The samples were performed by Rigaku SmartLab, Cu-Kα radiation, λ = 1.5406 Å) system at a range of 2θ = 5~80° (20° min^{-1}).
Atomic force microscope (AFM): The AFM images and the corresponding roughness were acquired under tapping mode on a Dimension FastScan (Bruker).
Fourier Transform Infrared Spectrometer (FT-IR): The FT-IR Spectrometer was achieved on THEMOR-FILSHER iS50R.

Electrochemical testing:

The CR2032 coin cell was chosen to measure the full cell test, symmetry cell test, electrochemical impedance measurement and Tafel slope test. The Neware electrochemical testing system (CT-4008-5V6A-S1-F, Shenzhen, China) was used to measure the electrochemical performance of these

cells. Electrochemical impedance spectroscopy (EIS) analysis at the frequency ranges from 0.01 to 10^6 Hz and an applied amplitude of 10 mV. The cyclic voltammetry (CV) and chronoamperometry (CA) measurements were carried out on Gamry multi-channel electrochemical workstation. The CV measurement of other samples was measured by Gamry Potentiostat.

The Zn^{2+} transference number was investigated by measuring EIS of Zn||Zn and Zn-CP||Zn-CP symmetric cells with the resting time of 5 h before and after chronoamperometry (CA) test, and calculated by the following equation:

$$t_{Zn^{2+}} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (1)$$

Where I_0 and R_0 are the initial current and resistance, respectively. ΔV is the voltage polarization applied (20 mV), I_s and R_s are the steady state current and resistance, respectively.

Theoretical calculation detail:

Gaussian09 E.01[2] software was used to perform density functional theory (DFT) calculations. The B3LYP-D3[3] functional and def2-TZVP [4] basis set was used to optimize the geometries of molecules. The vibration analysis was performed at the same theoretical level to ensure that all structures are energy minima (0 imaginary frequency). The electrostatic potential (ESP) were calculated by Multiwfn[5] software.

Results and Discussion

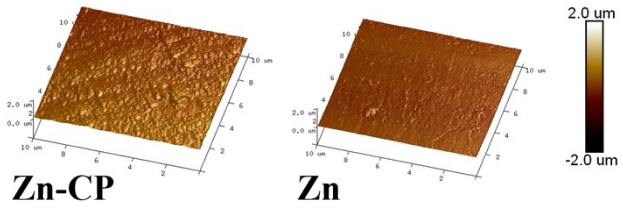

Figure S1. The AFM mapping of Zn-CP and Zn before cycle.

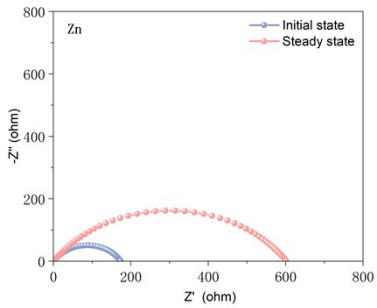

Figure S2. The EIS Curves of the Zn||Zn cell for calculating Zn^{2+} transference number.

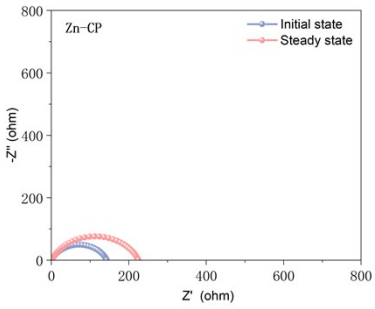

Figure S3. The EIS Curves of the Zn-CP||Zn-CP cell for calculating Zn^{2+} transference number.

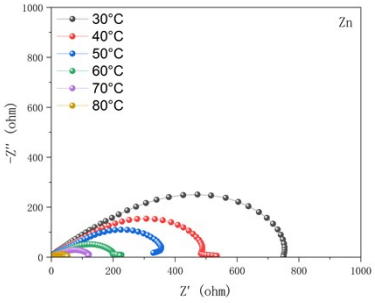

Figure S4. The EIS curves of Zn||Zn cell in different temperature (form 30°C to 80°C).

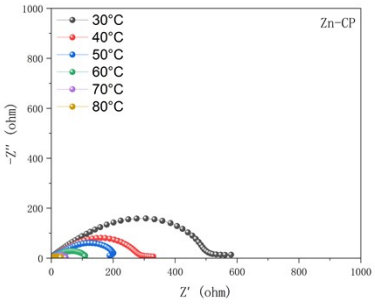

Figure S5. The EIS curves of Zn-CP||Zn-CP cell in different temperature (form 30°C to 80°C).

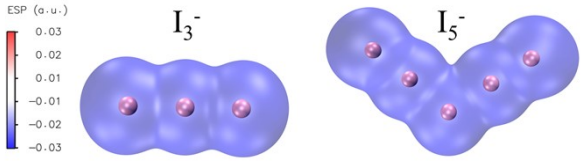

Figure S6. The ESP diagram of I_3^- and I_5^-.

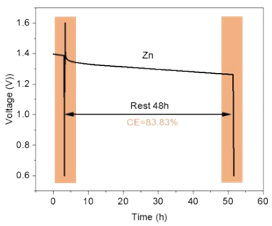

Figure S7. The self-discharge curve of the Zn||I_2 full cell.

Reference

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