Supporting Information

Toward Stable Zinc Metal Anodes in Aqueous Zinc-Ion Batteries: A Green and Bifunctional Electrolyte Additive

Experimental section

Reagents: All reagents and materials used in this study were obtained commercially without further purification. Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, purity 99%), 4-chlorobenzenesulfonamide (purity 99%) and anhydrous ethanol (purity 99.5%) were purchased from Aladdin Reagent. Zn foil and Ti foil were purchased from Qingyuan Metal Materials. Glass fiber separator was purchased from Whatman.

Preparation of the electrolytes: The 2 M $ZnSO_4$ electrolyte (BE) was prepared by dissolving 17.32 g of $ZnSO_4 \cdot 7H_2O$ in 22.44 mL of deionized water under continuous stirring at room temperature until complete dissolution was achieved. The BE+CBS electrolyte was prepared by adding 4-chlorobenzenesulfonamide into $ZnSO_4$ solution.

Materials Characterization: Surface morphology and corresponding elemental analysis were obtained using a Tescan Mira scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were collected using a Rigaku SmartLab SE with Cu Kα (α=1.5406 Å) as the radiation source. Fourier transform infrared (FTIR) spectroscopy was performed using a Thermo Scientific iN10 instrument. X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific Kalpha spectrometer.

Electrochemical measurements: The electrochemical properties of symmetric cells and full cells were tested in CR2032 coin cells, which were assembled in air atmosphere. Bare Zn was used as the anode. BE and BE+CBS were used as the electrolyte. At the same time, α-MnO_2 was used as the cathode. Galvanostatic charge/discharge cycling tests were carried out on a LAND battery testing system at room temperature. Chronoamperometry (CA), Linear sweep voltametric (LSV), electrochemical impedance spectroscopy (EIS) and Tafel Curve were measured on a CHI760E electrochemical workstation (Chenhua, China).

DFT calculation:

The binding energy of the configuration (E_{bind}) was calculated by the following equation:

$$E_{bind}=E_{AB}-(E_A+E_B) \quad (1)$$

where E_A, E_B, and E_{AB} respectively represent the energies of A (Zn^{2+}) and B (single polymer) and the complex energy, a negative value of E_{bind} indicates that the process is an exothermic reaction and a high negative value corresponds to a stronger interaction, which indicates more heat release and a more stable product.

The adsorption energy (E_{ads}) of the CBS on Zn(002) surface was obtained by using the following equation:

$$E_{ads}=E_{CBS+Zn(002)}-E_{CBS}-E_{Zn(002)} \quad (2)$$

where $E_{CBS+Zn(002)}$ was the total energy of the adsorption systems. E_{CBS} was the energy of the optimized CBS configurations and $E_{Zn(002)}$ was the energy of the Zn(002) surface.

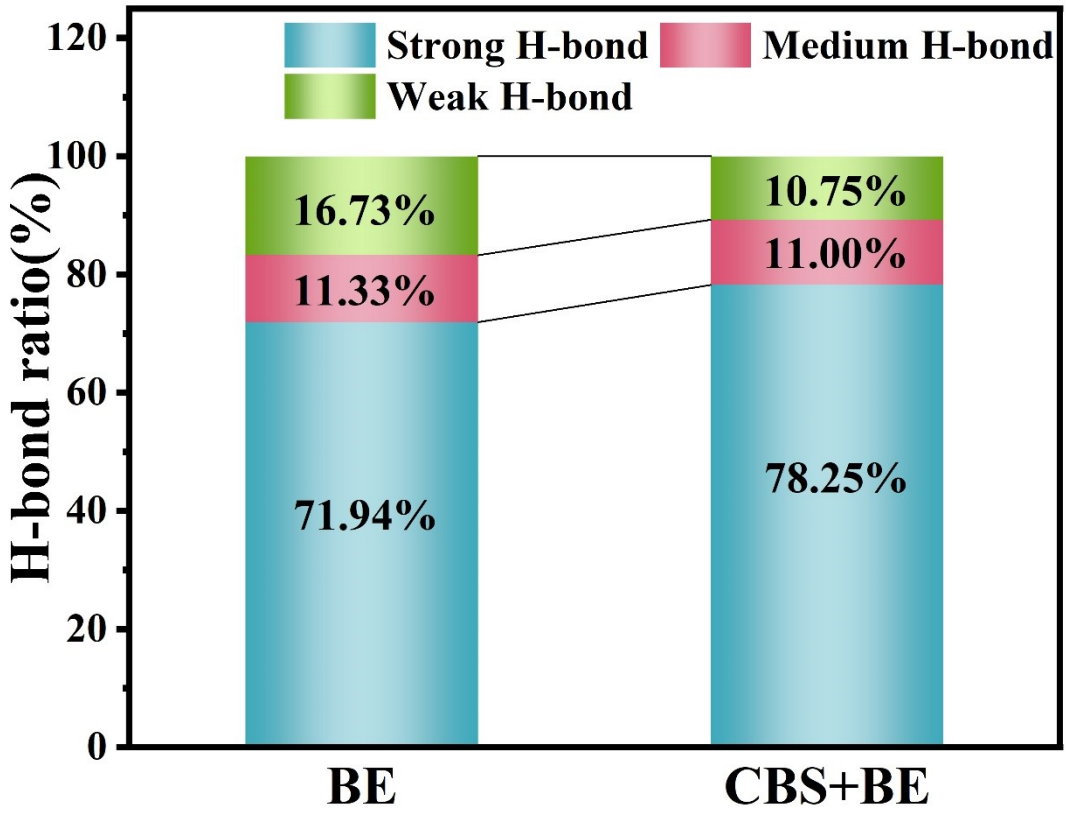

Figure S1 The proportions of strong, medium, and weak H-bond;

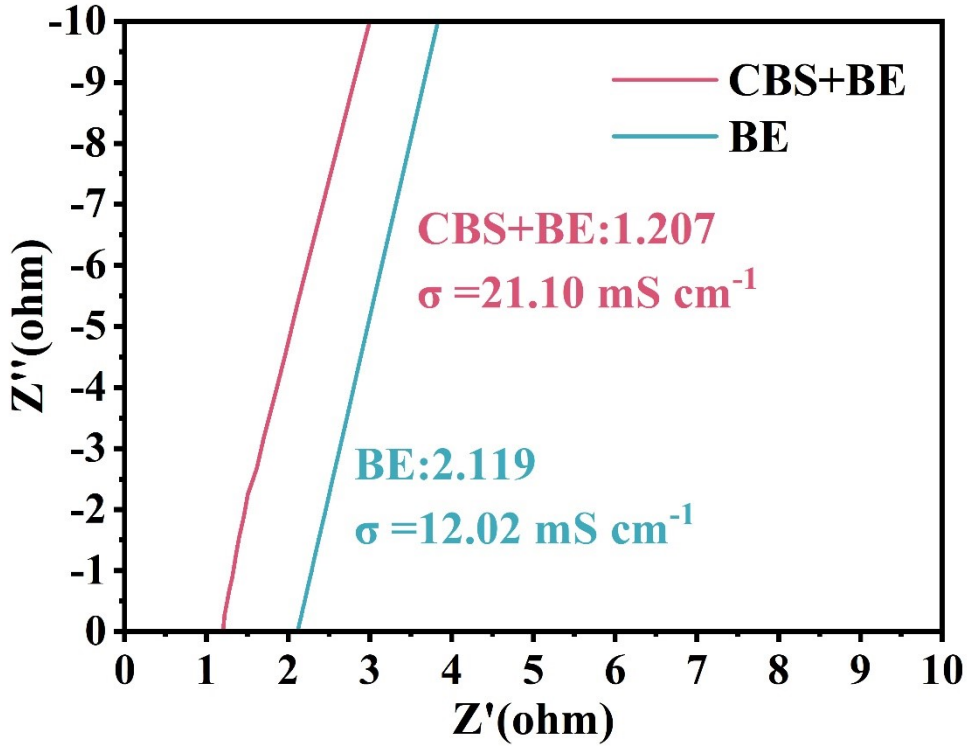

Figure S2 EIS spectra of blocked cells assembled with different electrolytes.

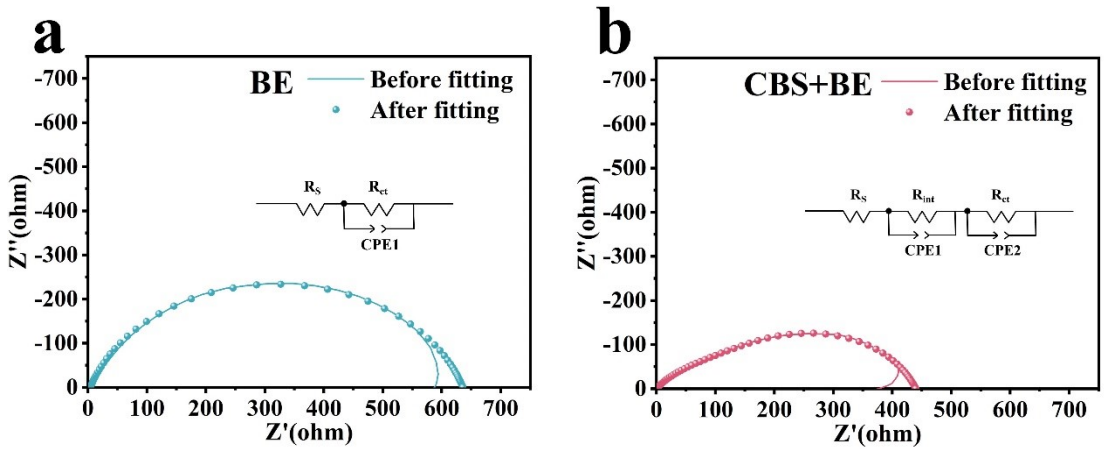

Figure S3. EIS spectra of the a) BE and b)CBS+BE electrolytes.

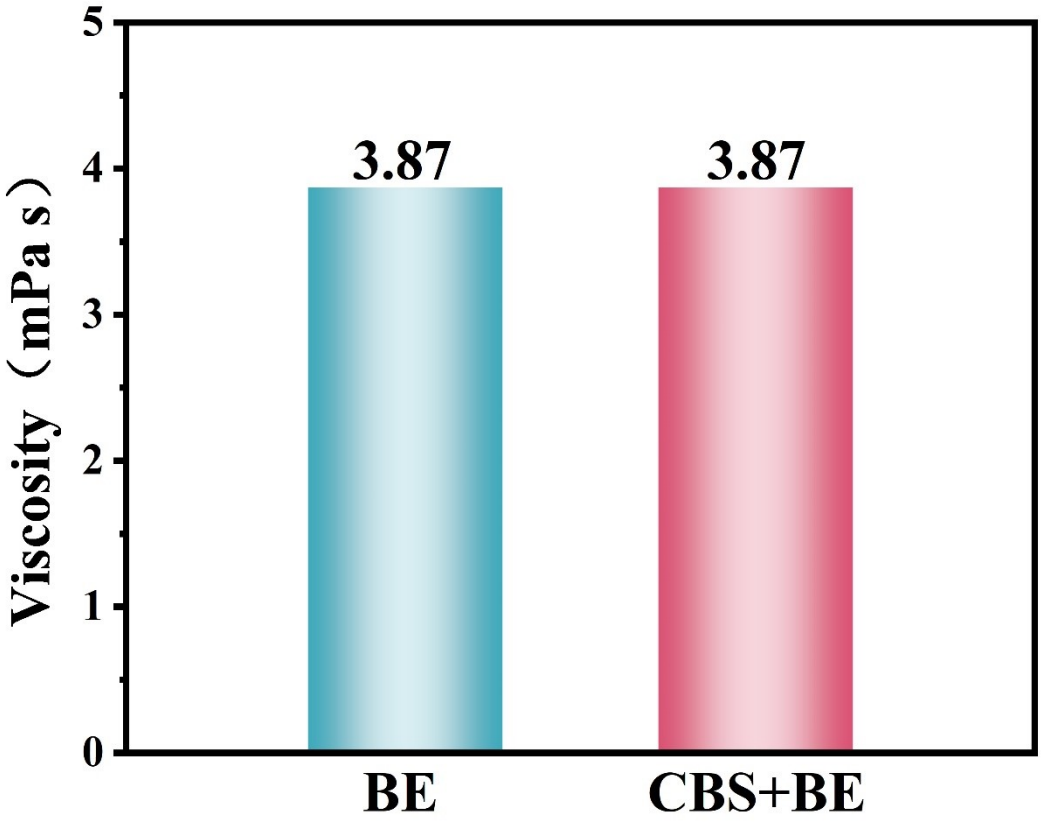

Figure S4. The viscosity of different electrolytes.

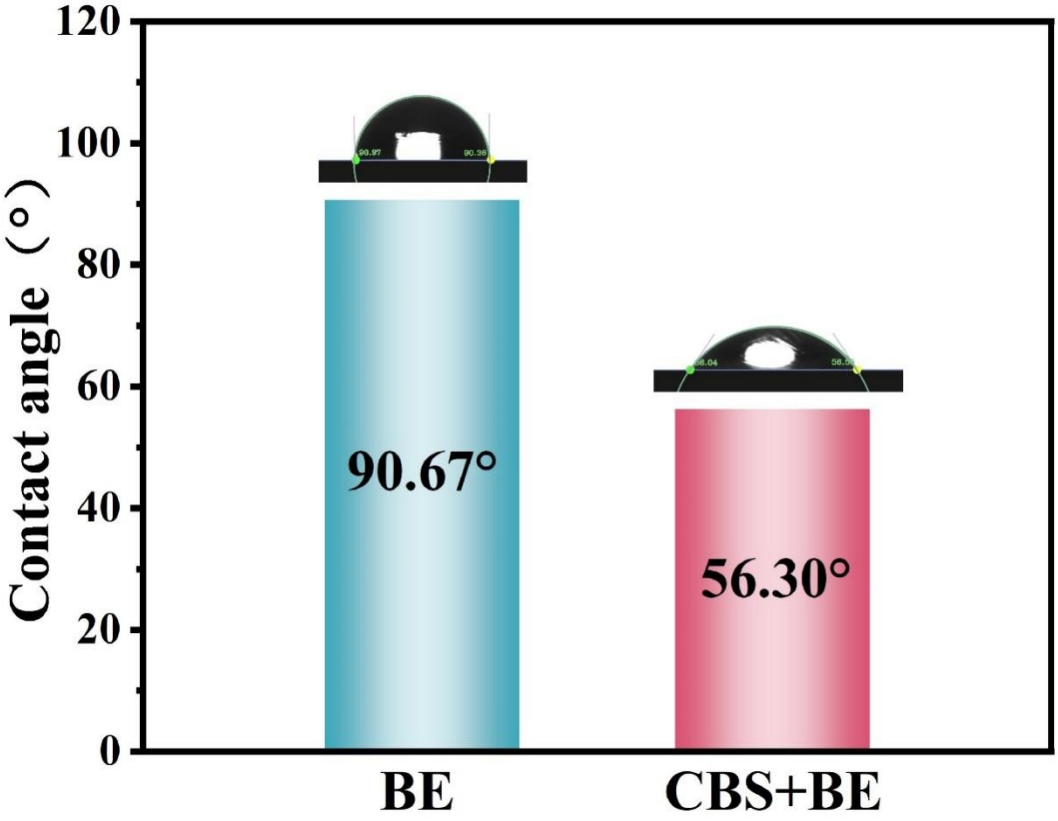

Figure S5. Contact angles of the BE and CBS+BE electrolytes on zinc foil.

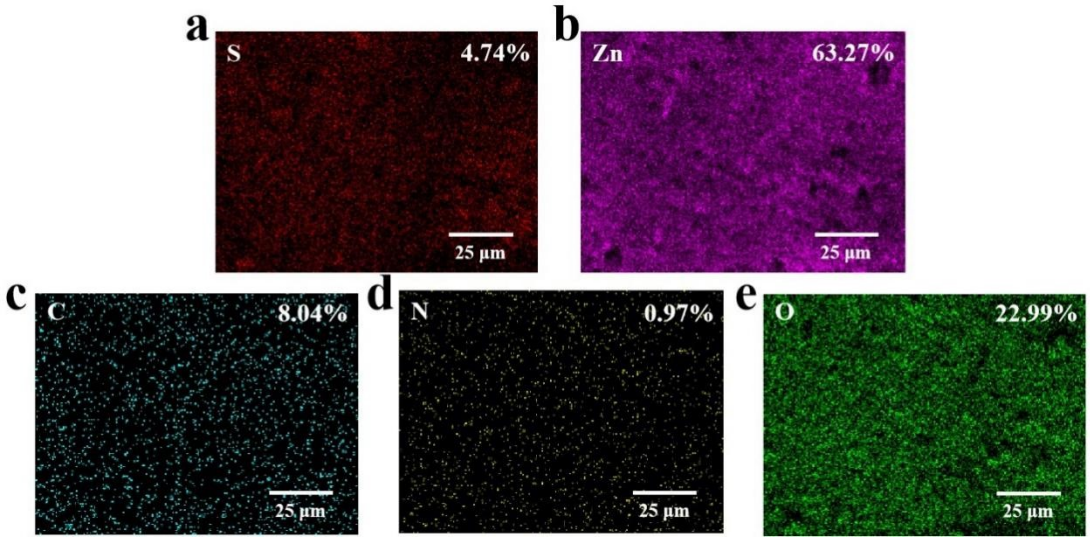

Figure S6. SEM elemental mapping of the zinc anode after immersion in the BE electrolyte for 7 days.

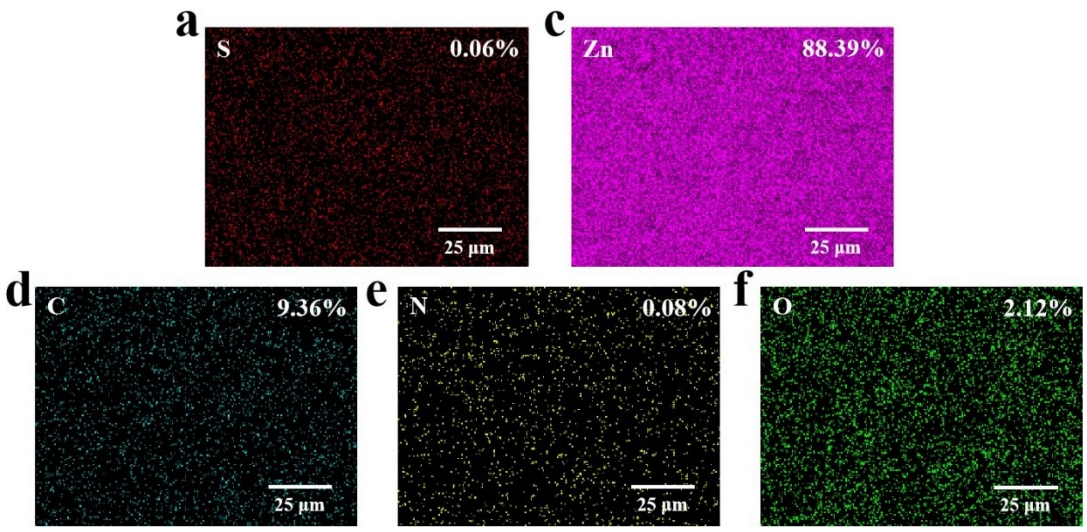

Figure S7. SEM elemental mapping of the zinc anode after immersion in the CBS+BE electrolyte for 7 days.

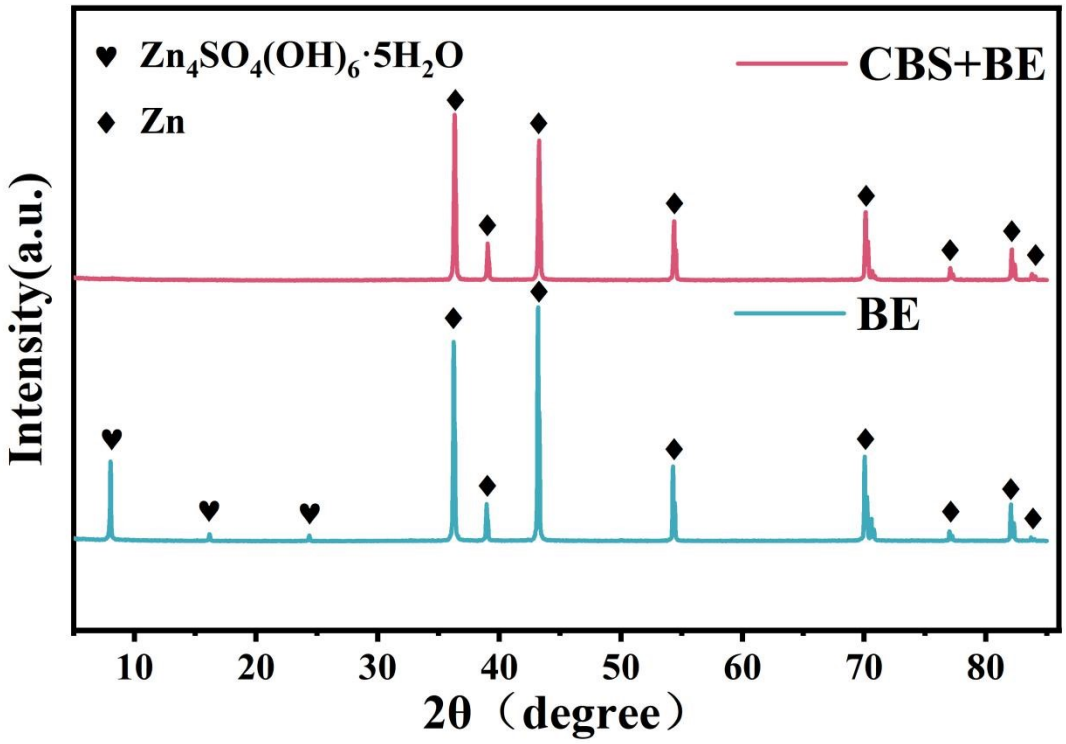

Figure S8. XRD patterns of zinc anodes after immersion in different electrolytes for 7 days.

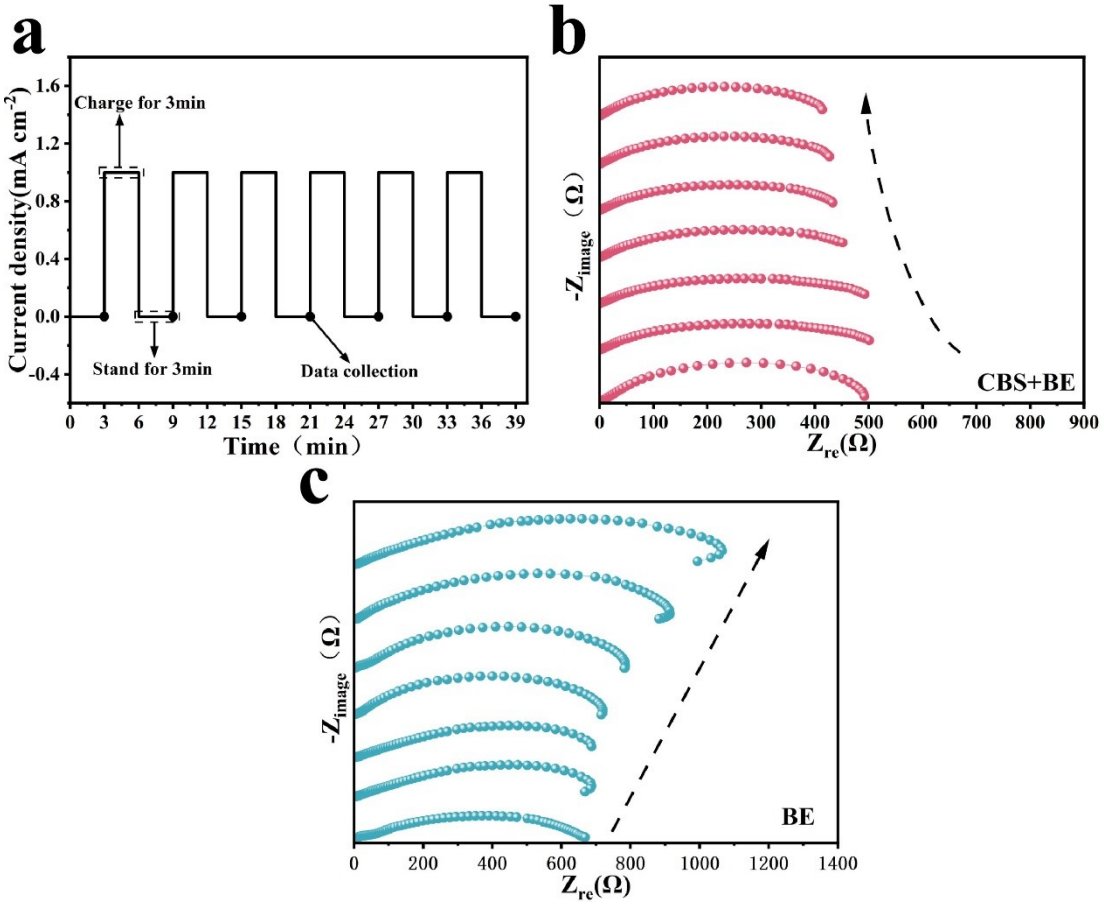

Figure S9. a) Schematic of the experimental protocol for the continuous deposition process. b) EIS curves of the CBS+BE electrolyte after different Zn deposition times. c) EIS curves of the $ZnSO_4$ (BE) electrolyte after different Zn deposition times.

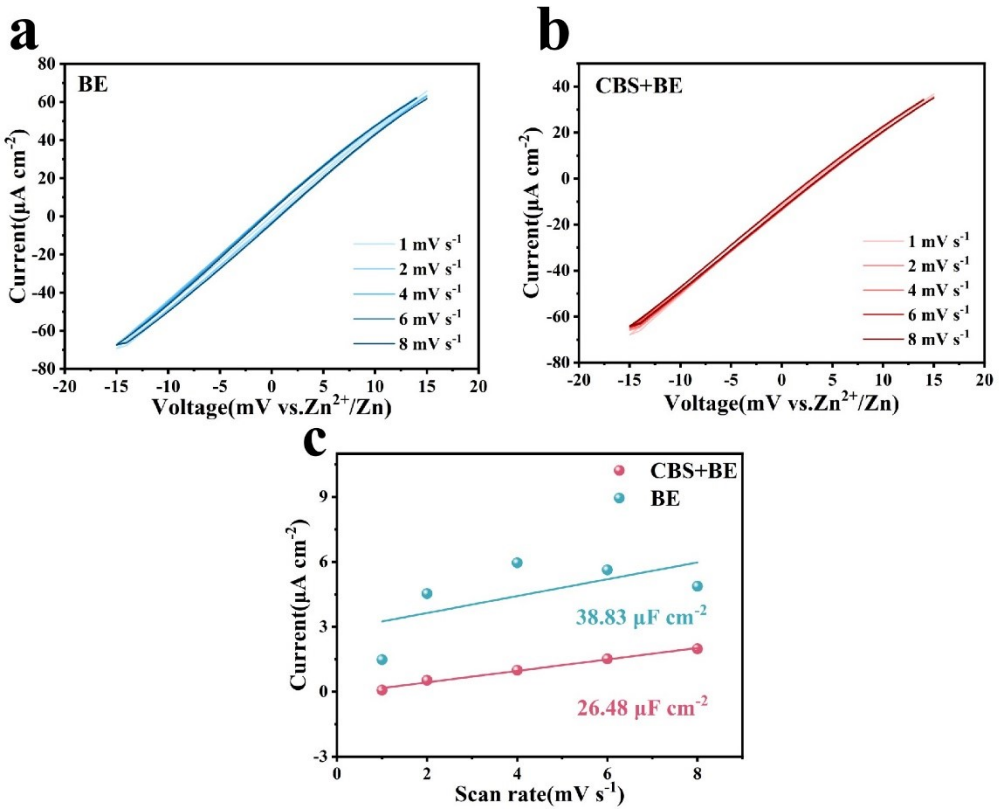

Figure S10. CV curves of Zn||Zn symmetric cells at various scan rates (-15 mV to 15 mV) for a) BE and b) CBS+BE electrolytes. c) Plot of capacitive current versus scan rate for cells using CBS+BE and BE electrolytes.

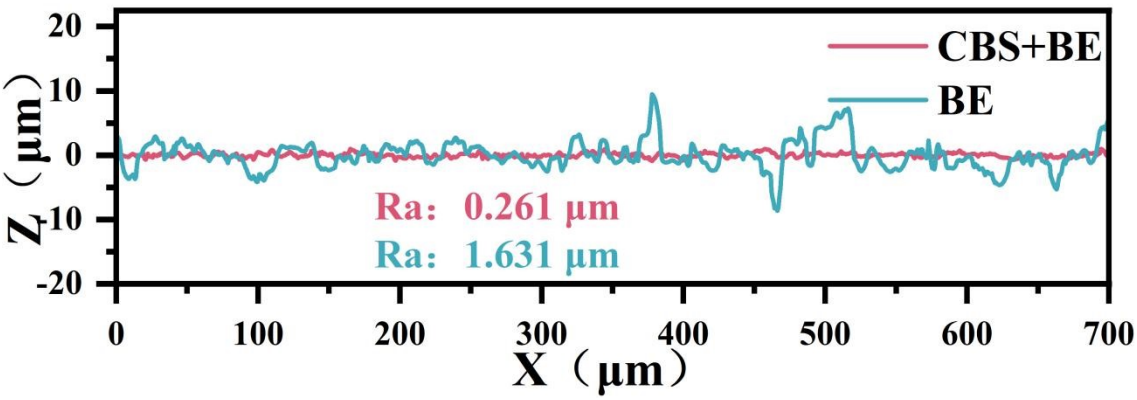

Figure S11. Surface roughness of zinc anodes after cycling in different electrolytes.

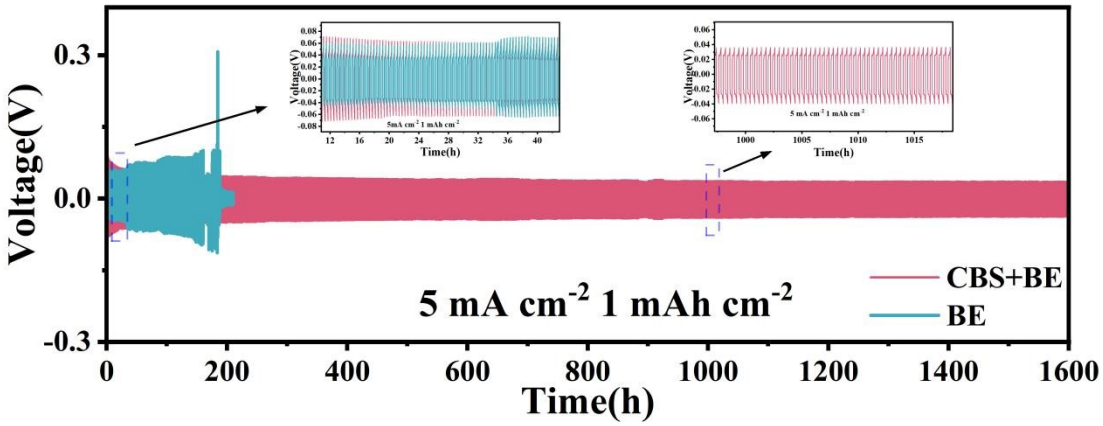

Figure S12. Cycling performance of Zn||Zn symmetric cells with different electrolytes at 5 mA cm^{-2} and 1 mAh cm^{-2}.

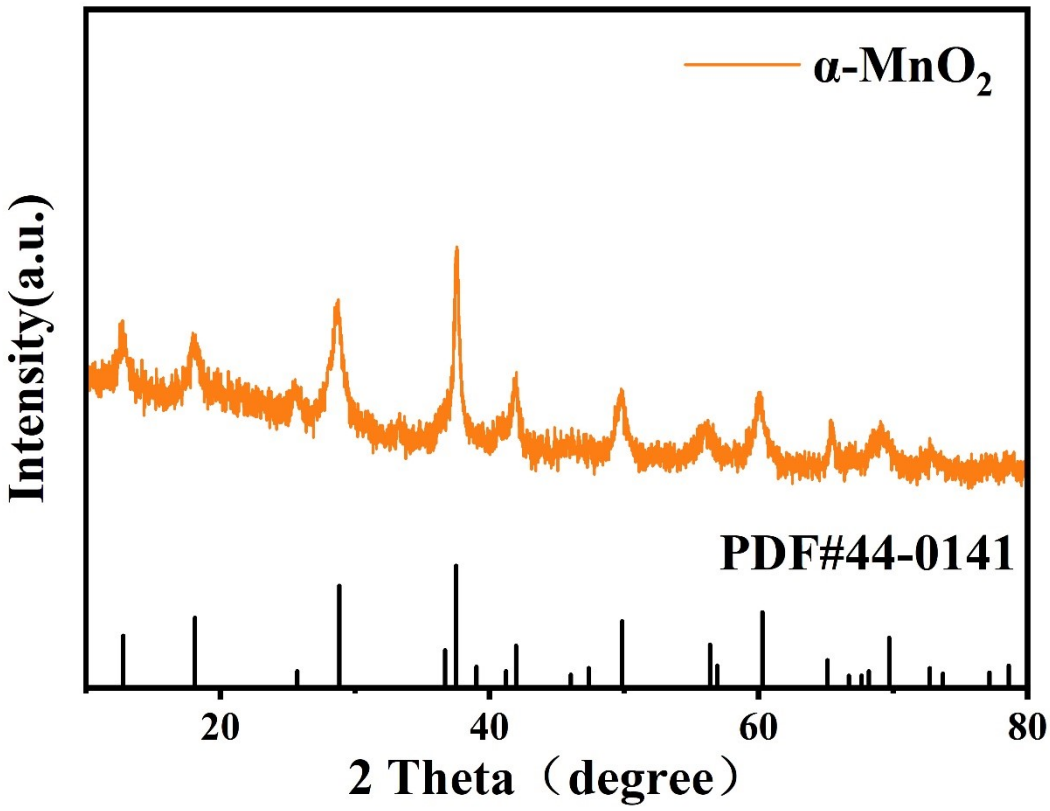

Figure S13. XRD pattern of the MnO_2 cathode material.

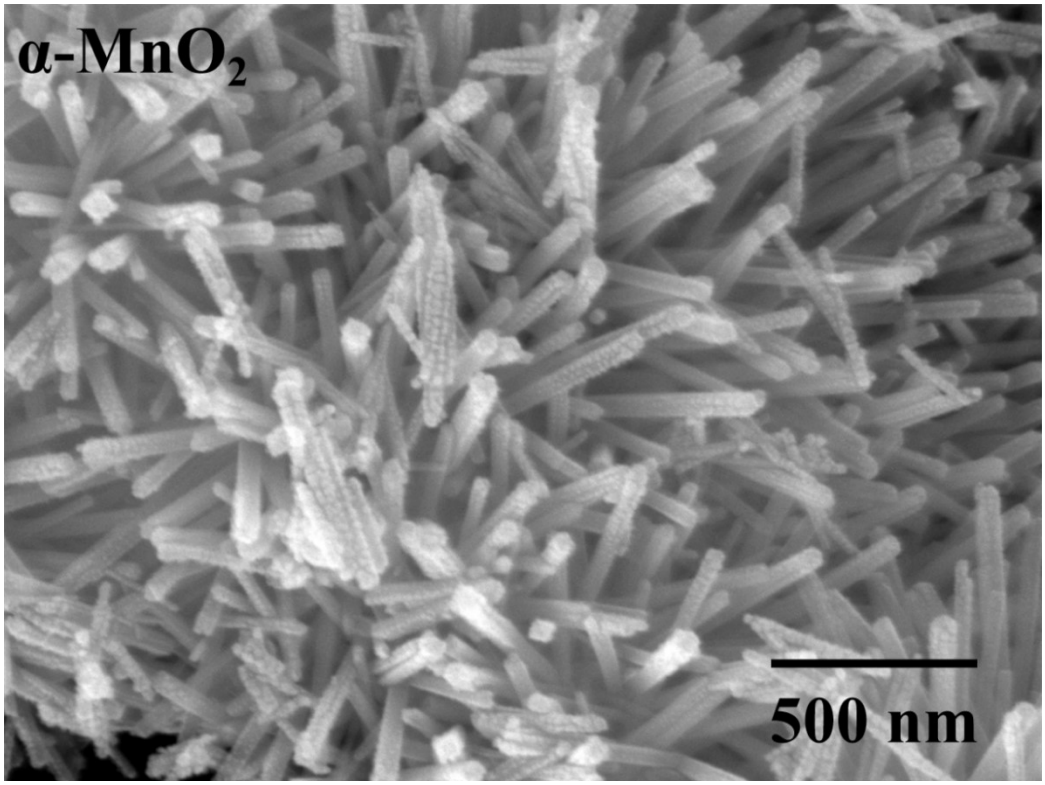

Figure S14. SEM image of the α-MnO_2 cathode material.

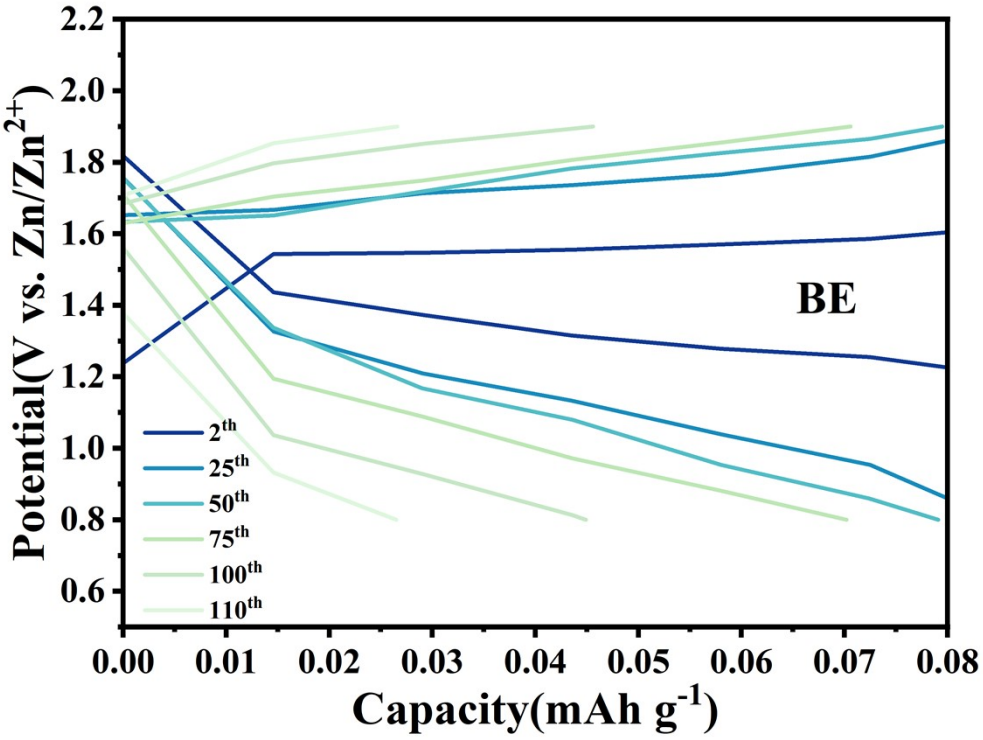

Figure S15. Charge-discharge profiles of the cell with BE electroly

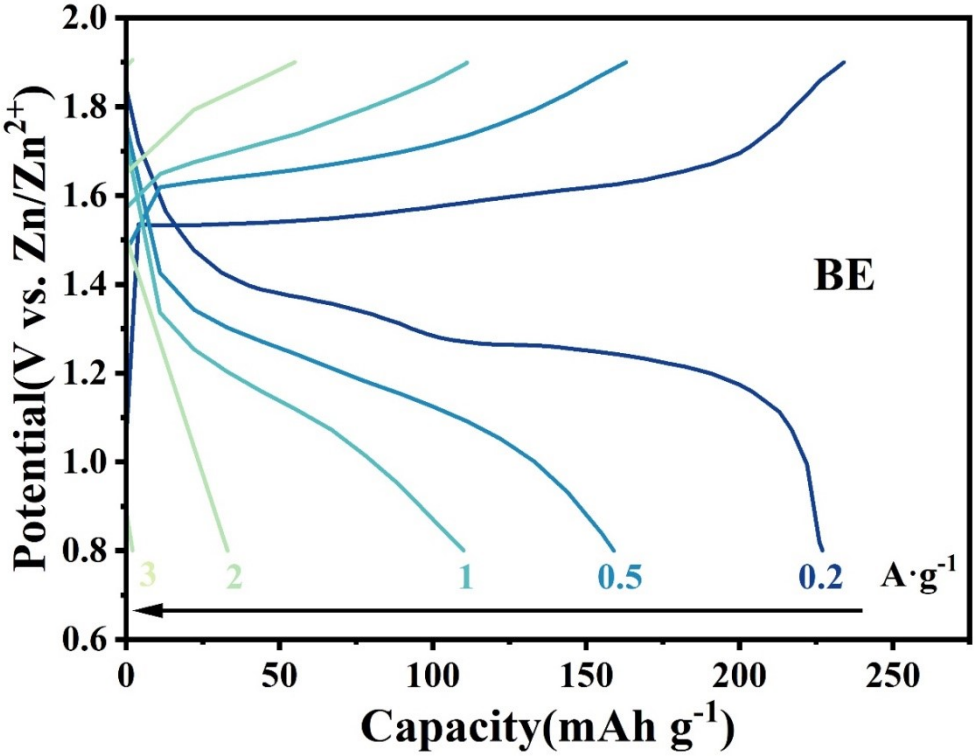

Figure S16. Rate performance: capacity-voltage profiles of the Zn||MnO_2 full cell with BE electrolyte at various current densities.

Table S1. Performance comparison of CBS with representative electrolyte additives for stabilizing Zn anodes in AZIBs.

Strategy / Additive	**Typical Concentration**	**Current density (mA cm^{-2})**	**Area capacity (mAh cm^{-2})**	**Zn // Zn Cycling** (h)	**Reference**
CBS	5mM (1mg/ml)	0.25	0.25	3000	This work
DOL	$Zn(OAc)_2·2H_2O$/ $ZnCl_2$/ H_2O/1,3-dioxolane	0.5	0.25	400	[1]
DMSO	1.3 m $ZnCl_2/H_2O$−DMSO (volume ratio of H_2O/DMSO = 4.3:1)	0.5	0.5	1000	[2]
PEG	1 m $Zn(TFSI)_2$ + 4 m LiTFSI in 70:30 wt% PEG/H_2O	0.25	0.4	850	[3]
FA	1 mol L^{-1} $Zn(OAc)_2$ in H_2O/FA (50 vol% H_2O + 50 vol% FA）	0.5	0.25	850	[4]
ZTEs	Zn(ClO4)2·6H2O/ niacinamide/dimethyl sulfone（molar ratio of 1:3:0.5）	0.5	0.5	2000	[5]
FDMA	1 M $Zn(TFSI)_2$+FDMA	0.2	0.2	2500	[6]

Table S2. CBS vs. sustainability metrics for reported “Green” additives.

Strategy / Additive	Type	Price (￥/100 g)	Environmental toxicity	System-level Green Benefits	Reference
CBS	Small molecules containing S, N, Cl	24	Contains chlorine (requires consideration for end-of-life management);Biologically non-toxic.	By significantly extending battery lifespan, it reduces battery replacements and material consumption per unit of energy storage duration, thereby contributing to system sustainability.	This work
EDS+water	Mixed solvent system (deep eutectic solvent + water).	1000	The ingredients are inexpensive, but they require large quantities for use;biodegradability.	Adjustable water content to avoid high-salt usage.	[7]
DMM	Organic ether solvents.	35	The addition of relatively high concentrations increases costs;;moderately priced;Low toxicity；Harmful to aquatic organisms.	Hydrophobic design reduces water activity, but requires a larger dosage.	[8]
APT	Polymetallic oxides, requiring synthesis.	60	Contains tungsten and phosphorus, with complex synthesis and high cost; poses environmental risks from heavy metals.	Developing LHCE reduces salt usage and conserves resources; Enhancing low-temperature performance enables application in wide-temperature-range energy storage systems.	[9]
DMA	High-Density Solvent Molecules (DN)	25	Large addition volume (by volume ratio) increases costs; Ionic conductivity decreases while polarization increases; Possesses a certain degree of volatility;environmental risks of heavy metals.	Extend service life, but high-concentration additives may increase the carbon footprint of production processes.	[10]
TG	Dual-functional ether molecules	30	Low cost;harmful to aquatic organisms, low toxicity.	Extend service life, but high-concentration additives may increase the carbon footprint of production processes.	[11]

Strategy / Additive	Type	Price (￥/100 g)	Environmental toxicity	System-level Green Benefits	Reference
	modulate overpotential.				
CTAB+ SDBS	Industrial surfactants	40	High concentration increases electrolyte viscosity and cost; environmental risks associated with bromine content.	Improve low-temperature adaptability and cyclic stability.	[12]

References

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