Supporting Information

A hybrid-aqueous biphasic electrolyte for suppressed shuttle effects and self-discharge of zinc bromide battery

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1. Experimental section

1.1. Polybromide solution preparation.

A 6 mL 2 M HBr solution, a 6 mL 2 M KBr solution, and a 8 mL 0.1 M $NaBrO_3$ solution were mixed together and stirred for 10 minutes to obtain a 20 mL solution containing ~120 mM polybromides. The reactions to form polybromides are as follows:

$$NaBrO_3 + 5Br^- + 6H^+ \rightleftharpoons 3Br_2 + 3H_2O$$

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

$$Br_2 + Br_{(2n-1)}^- \rightleftharpoons Br_{(2n+1)}^- (n \geq 1)$$

1.2. Electrode and electrolyte preparation and cell fabrication.

The commercial graphite felt (Guangzhou Dingshenghua Glass Instrument Co., Ltd.) was first soaked in ethanol for 3 hours to remove the oil-soluble materials, and then repeatedly washed with deionized H_2O for 5 times. After boiled with deionized H_2O for 6 times, this graphite felt was dried in an oven at 120 ℃ for 5 h. The Zn foils (Guangzhou Kerong Biotechnology Co., Ltd.) were washed with ethanol and deionized H_2O to remove impurities.

The hybrid solutions were obtained by dissolving $ZnBr_2$ (Shanghai Aladdin Biochemical Technology Co., Ltd.) into a mixture of deionized H_2O and TEGDME (1:1 volume ration) with a concentration of 1 M. The aqueous solutions were obtained by dissolving $ZnSO_4$ (Shanghai Aladdin Biochemical Technology Co., Ltd.) into deionized H_2O with a concentration of 1 M. The biphasic electrolytes were obtained by mixing a 5 mL hybrid solution, a 5 mL aqueous solution, and required weights of $MgSO_4$ (Tianjin Chemical Three Plant Co., Ltd.).

The bip-ZBB cells were assembled in a beaker with graphite felt as the cathode host, Zn foil as the anode, and 10 mL biphasic electrolyte with 0.25 g $MgSO_4$. The amplified bip-ZBB cell used 20 mL biphasic electrolyte with 0.5 g $MgSO_4$. While the c-ZBB cells used 10 mL 1 M $ZnBr_2$ solution as the electrolyte.

1.3. Materials characterization.

The surface morphologies of Zn foils and graphite felt were analyzed by LIFM-Ultra-high-resolution field emission scanning electron microscope (SU8010), with energy dispersive X-ray spectroscopy (EDS) for the element determination. The surface element components of zinc foil were determined on X-ray photoelectron spectrometer (XPS, Nexsa) with monochromatic Al-Kα source (Mono AlKα, 1486.6eV, 12kV 720W). The X-ray diffraction (XRD) patterns of Zn foils were tested using an X-ray diffractometer (D-MAX 2200 VPC, RIGAKU) with a 2θ range of 5°

to 80°. The Raman spectra of the electrolytes were obtained using the Functional Inorganic-Laser Microscopy Raman spectrometer (inVia) at 4000-500cm^{-1}. The polybromides in the electrolytes were characterized using a UV-visible-near-infrared spectrophotometer (UV-3600).

1.4. Electrochemical measurements.

The cyclic voltammetry (CV) measurements were conducted using an electrochemical workstation (CHI660E, Shanghai, China). The galvanostatic charge/discharge (GCD) measurements were conducted using Neware Battery Measurement System (CT-ZWJ-4'S-T-1U, Shenzhen, China). The ionic conductivities were measured using a Conductivity Meter (DDS-11A, Shanghai Youke).

1.5. Computational methods.

The theoretical structure of the biphasic electrolyte was investigated through Molecular dynamic (MD) simulations. In this system, the x, y and z dimensions were periodic boundary conditions. The optimized potentials for liquid simulations (OPLS) force field were used to optimize sample structures for preliminary structural optimization. Atomic charges of ions were multiplied by scale factor 0.73 to correct the polarization effect of anion and cation. First, the conjugate gradient algorithm and energy minimization were performed to obtain a stable structure before using dynamic simulations. Each sample was then equilibrated under the constant-pressure–constant-temperature (NPT) ensemble at a constant temperature of 400 K to achieve an equilibrium state with zero pressure for 5 ns. Subsequently, the system temperature was reduced from 400 K to 298 K for annealing 5 ns under the NPT ensemble (under 1 atmosphere). The Andersen feedback thermostat and Berendsen barostat algorithm were applied in the system with temperature and pressure conversion. Next, MD simulations were further carried out for 100 ns with a time step of 1 fs per integration step under the ensemble conditions of NVT (298 K). System energy can be obtained through structural optimization using the energy minimization.

The relative binding energies (E_b) were calculated as $E_b = E_{total} - E_1 - E_2$, where E_{total}, E_1, and E_2 are the total energy of the 1 and 2 complex, 1 component, and 2 component, respectively.

In the hybrid phase,

$$E_b(Br_3^-–H_2O) = E_{total} - E(Br_3^-) - E(H_2O)$$

$$E_b((Br_3^-–TEGDME) = E_{total} - E(Br_3^-) - E(TEGDME)$$

In the aqueous phase,

$$E_b(H_2O–SO_4^{2-}) = E_{total} - E(H_2O) - E(SO_4^{2-})$$

$$E_b\ (H_2O\text{–}TEGDME) = E_{total} - E(H_2O) - E(TEGDME)$$

2. Supplementary Figures

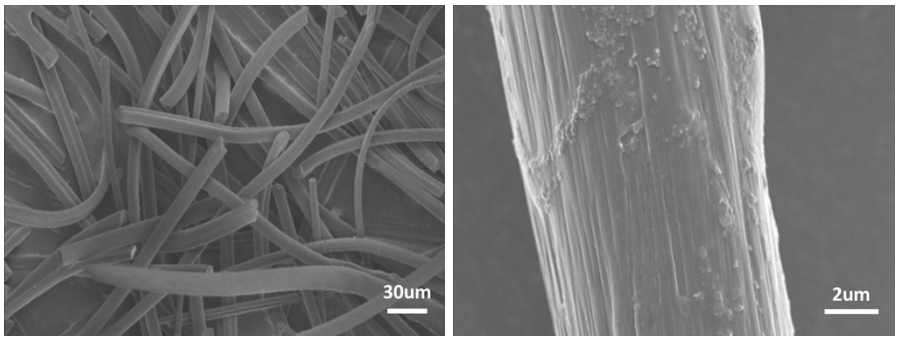

Figure S1. SEM images of the graphite felt.

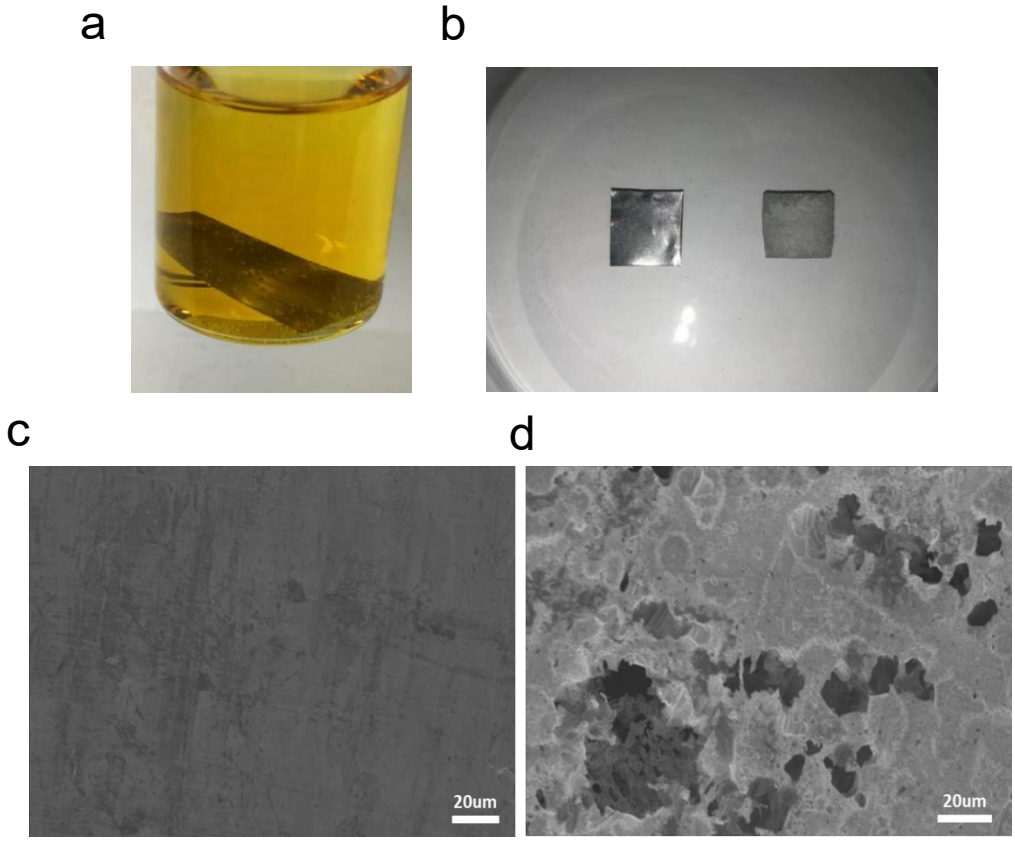

Figure S2. Photographs showing (a) the Zn foil immersed in a solution containing polybromides, (b) the pristine Zn foil and the polybromide-corroded Zn foil. SEM images of (c) the pristine Zn foil and (d) the polybromide-corroded Zn foil.

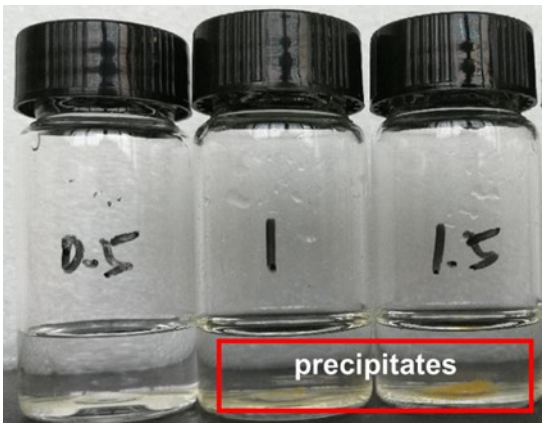

Figure S3. Photographs showing the biphasic electrolytes with $MgSO_4$ weights of 0.5 g, 1 g, and 1.5 g after 1 day of storage.

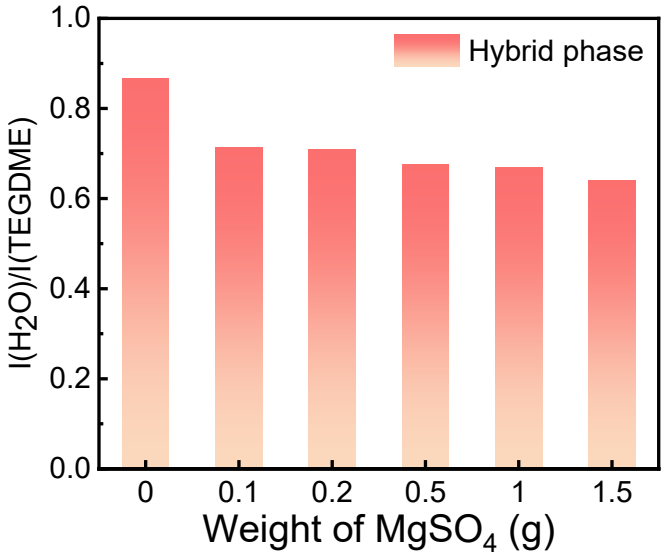

Figure S4. The relative Raman band intensities of H_2O molecules to TEGDME molecules in the hybrid phases of biphasic electrolytes with $MgSO_4$ weights of 0, 0.1, 0.2, 0.5, 1.0, and 1.5 g.

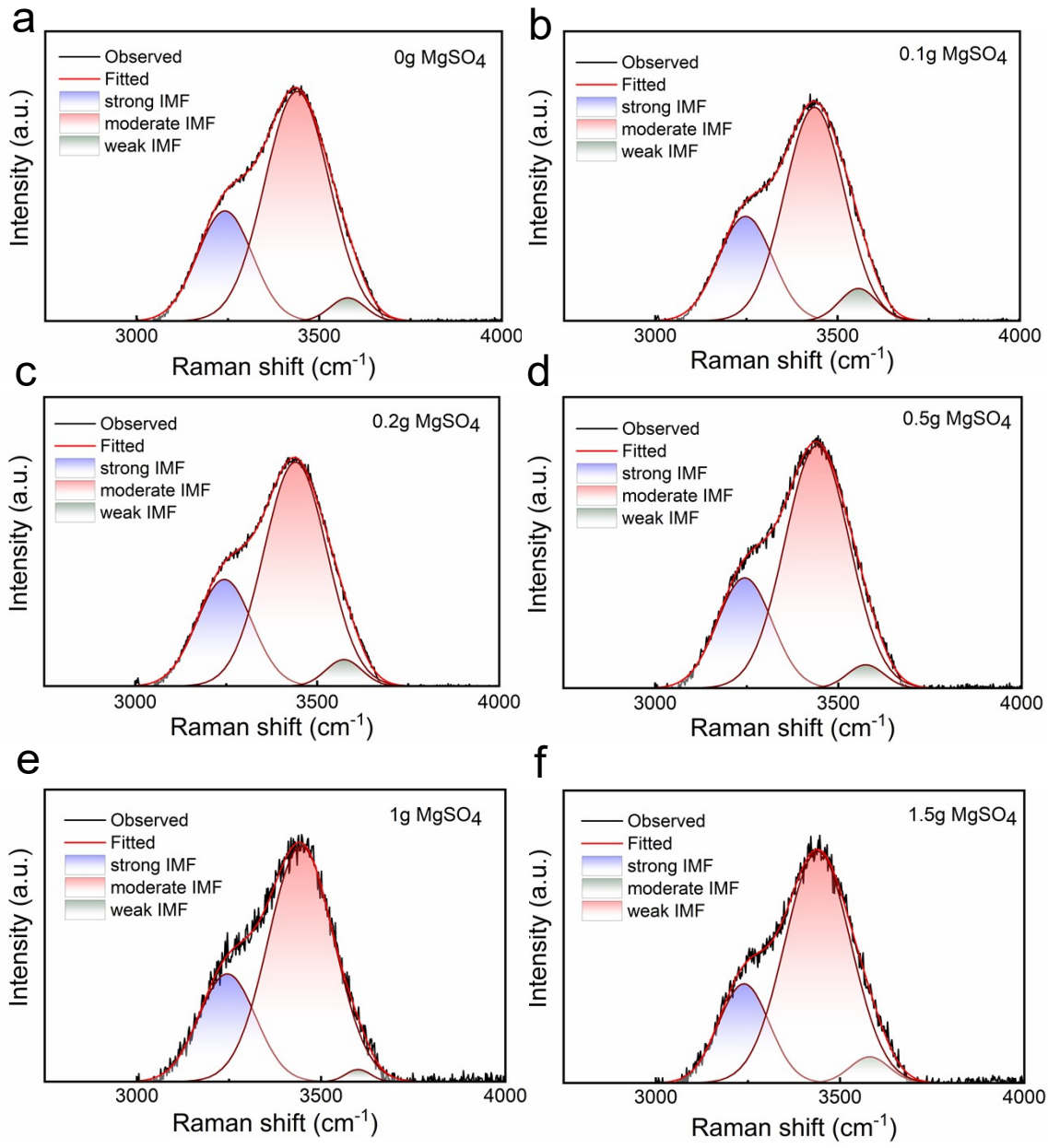

Figure S5. Deconvolution of the O–H stretching bands for the hybrid phases of biphasic electrolytes with $MgSO_4$ weights of (a) 0 g, (b) 0.1 g, (c) 0.2 g, (d) 0.5 g, (e) 1.0 g, and (f) 1.5 g.

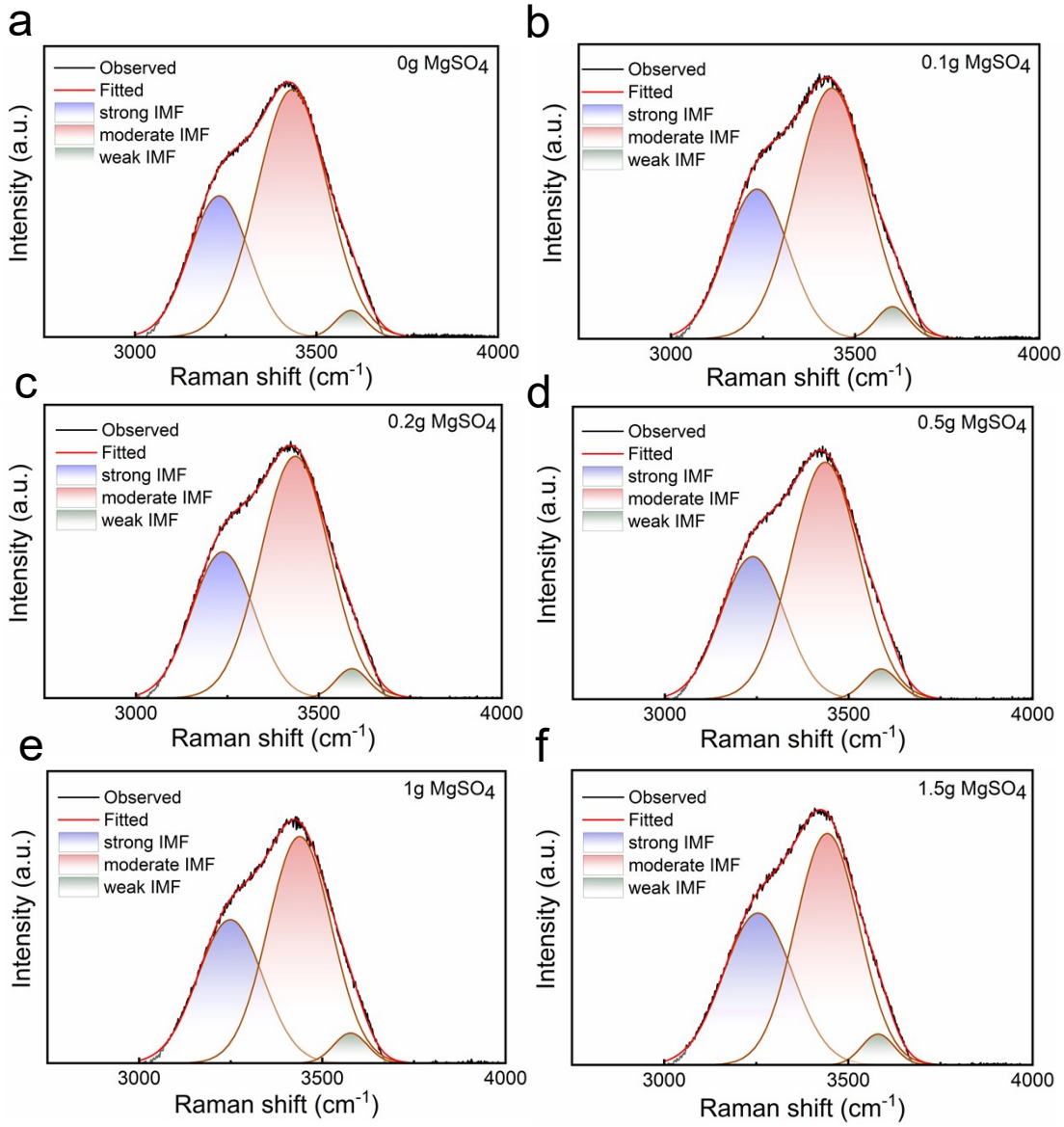

Figure S6. Deconvolution of the O–H stretching bands for the aqueous phases of biphasic electrolytes with $MgSO_4$ weights of (a) 0 g, (b) 0.1 g, (c) 0.2 g, (d) 0.5 g, (e) 1.0 g, and (f) 1.5 g.

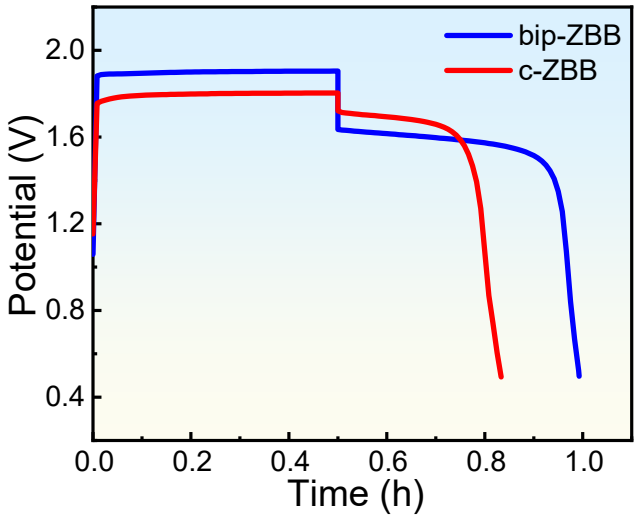

Figure S7. Voltage profiles of the bip-ZBB and c-ZBB without rest.

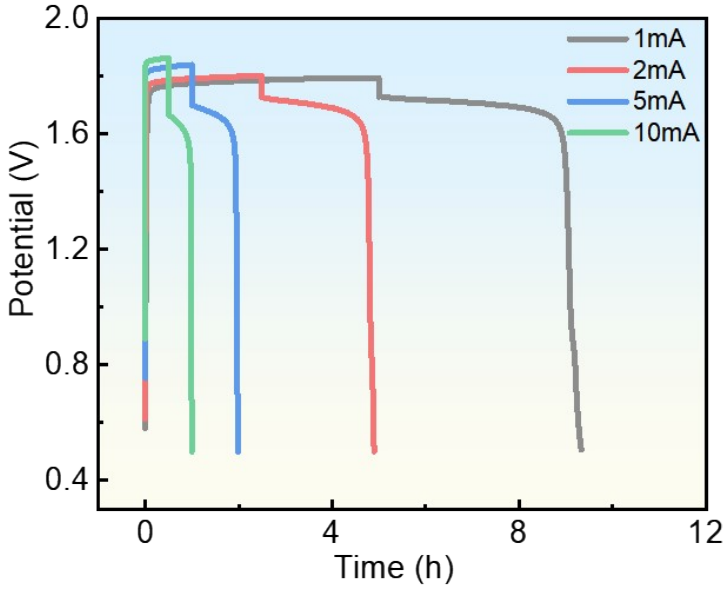

Figure S8. Charge discharge curves with different current densities.

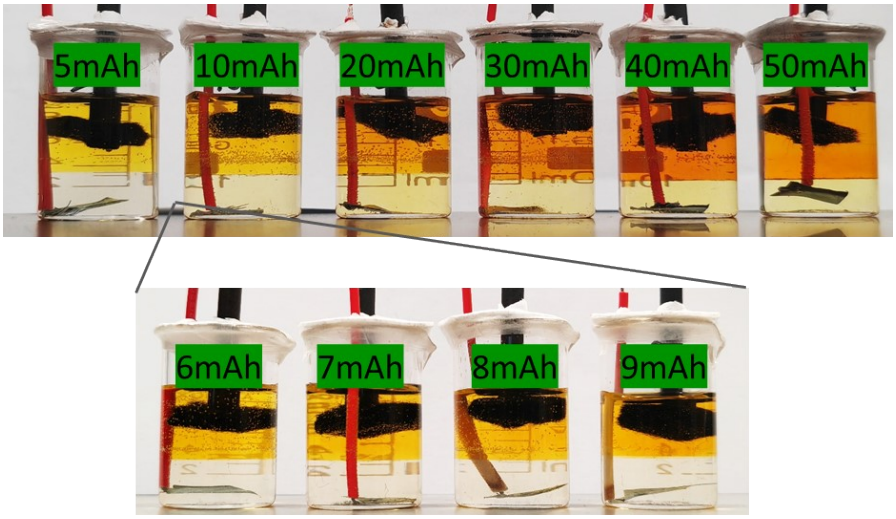

Figure S9. Photographs showing the diffusion of polybrominides in the biphasic ZBBs at different charge capacities.

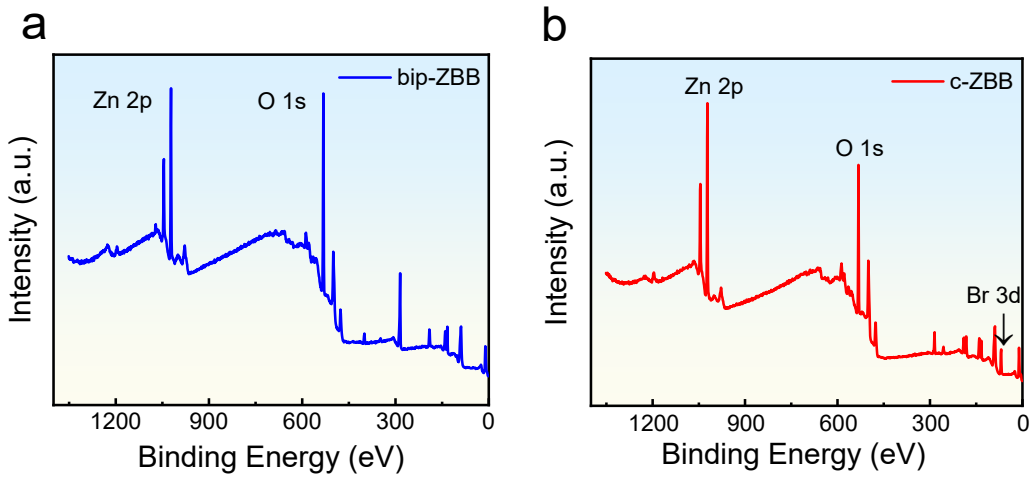

Figure S10. XPS spectra of cycled Zn anodes in (a) bip-ZBB and (b) c-ZBB.

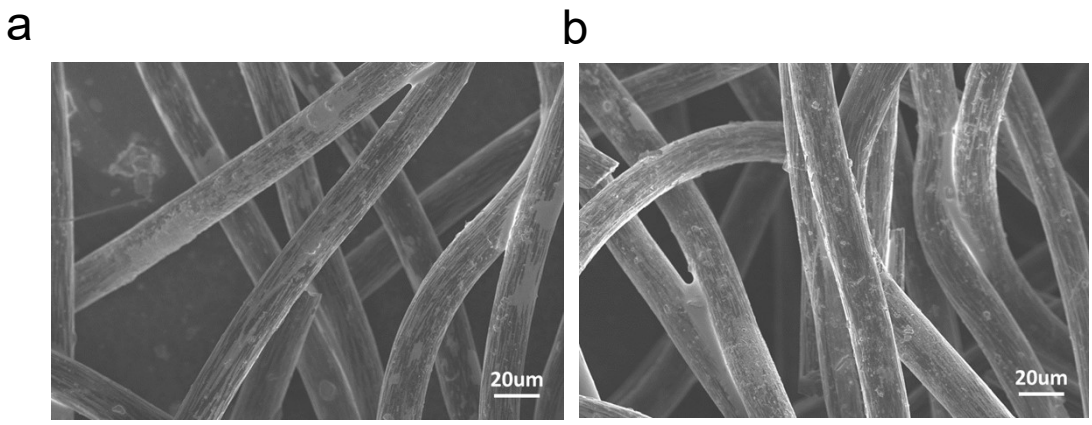

Figure S11. SEM images of the graphite felt cathode hosts cycled in (a) the bip-ZBB and (b) the c-ZBB.

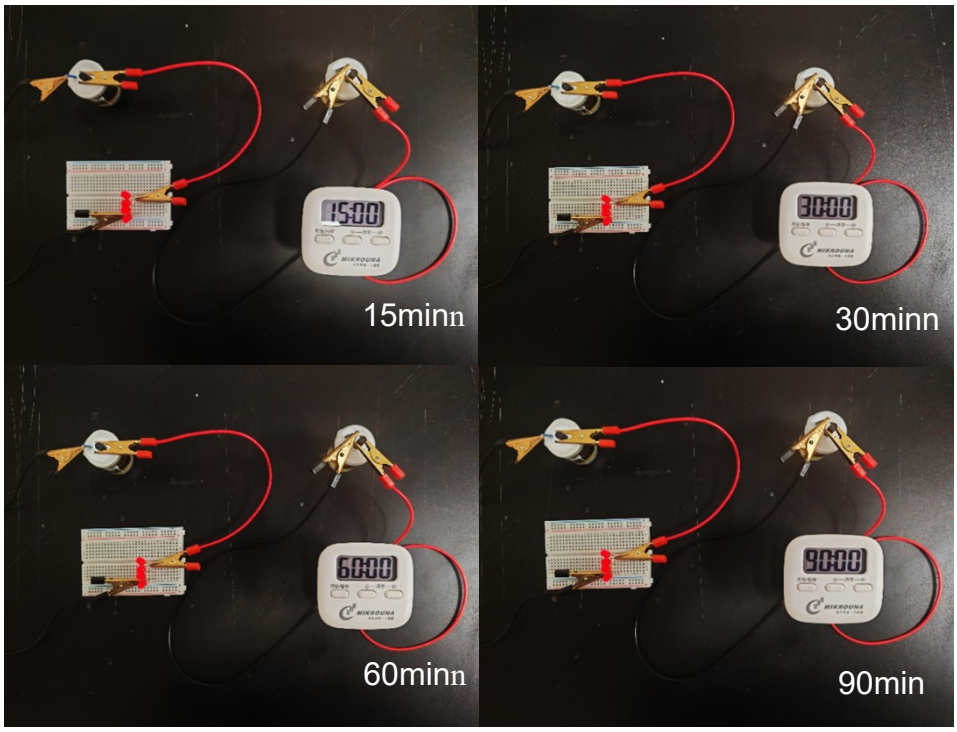

Figure S12. Photographs showing the bip-ZBB powering an electronic watch.