

Supporting Information

**Dual-additives-based electrolyte design for aqueous zinc ion
batteries with high plating/stripping efficiency**

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Experimental Section

1.1 Preparation of electrolyte

0.1 mol zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, Sinopharm, $\geq 99.5\%$) was dissolved in deionized water in a beaker and transferred to a 50 mL volumetric flask to obtain the baseline electrolyte 2 M ZnSO_4 . The identical method was employed to prepare other electrolytes. The electrolyte containing a single additive was prepared by adding 0.025 M zinc acetate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, Sinopharm, $\geq 99.0\%$) and 0.5 mM tetramethylammonium acetate (TMAOAc, Aladdin, $\geq 98\%$) to 2 M ZnSO_4 , respectively. The electrolyte with double additives was prepared by combining the two mentioned additives.

1.2 Preparation of MnO_2 cathode

The hydrothermal method was employed to synthesize $\beta\text{-MnO}_2$ nanowires.¹ For a standard synthesis, 0.1 M KMnO_4 (Sinopharm, $\geq 99.5\%$) and 0.6 M $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Sinopharm, $\geq 99.0\%$) were dissolved in 30 mL deionized water and stirred at room temperature for 30 min, respectively. After complete dissolution, the two solutions were mixed and stirred for 30 min. The mixture was transferred to a 100 ml Teflon-lined autoclave and maintained at 140 °C for 12 h. The obtained products were washed and centrifuged three times in anhydrous ethanol and deionized water, respectively. The obtained product was centrifuged, washed thoroughly using water and absolute ethyl alcohol, and dried at 80 °C for 10 h. The final product was obtained by vacuum drying at 80 °C for 12 h in the oven. The MnO_2 cathode was prepared by rolling the membrane of MnO_2 , super-p and PTFE at a mass ratio of 7:2:1 with ethanol as solvent, and dried in an oven at 80 °C overnight. The prepared membrane was pressed on the titanium mesh for use, and the loading of MnO_2 was $3.5 \text{ mg cm}^{-2} \pm 0.1 \text{ mg cm}^{-2}$.

1.3 Materials characterizations

The X-ray diffraction (XRD) analysis of the Zn anode was conducted using a Bruker D-8 Advance diffractometer (Cu $\text{K}\alpha$ radiation, $\lambda = 0.154 \text{ nm}$) within 5~80 ° with a step size of 0.05 ° and a scan rate of 0.1 ° s^{-1} . The dynamic pH change of the electrolyte was measured using the PHS-3C pH meter (Shanghai INESA Scientific Instrument Co. Ltd). The deposition morphology of the surface and cross section of

the Zn anode was observed by S4800 scanning electron microscope (SEM, Hitachi) at 5 kV. In-situ optical microscope PSM-1000 (Motic) was used to observe the real-time Zn deposition morphology.

1.4 Electrochemical measurements

All batteries are assembled in the air with CR2032 type coin cell. Glass fiber as separator (Whatman GF/A). The battery performance is tested by the Neware battery test system (Shenzhen, China). The Zn//Cu asymmetric cell was assembled to measure the Zn plating/stripping efficiency, and the Zn//Zn symmetric cell was used to measure the cycle life of the cell. Both cyclic voltammetry (CV) and chronoamperometry (CA) were tested on the AUTOLAB (RGSTAT 302N) electrochemical workstation. The assembled Zn//MnO₂ was cycling tested within the voltage range of 0.8-1.8 V.

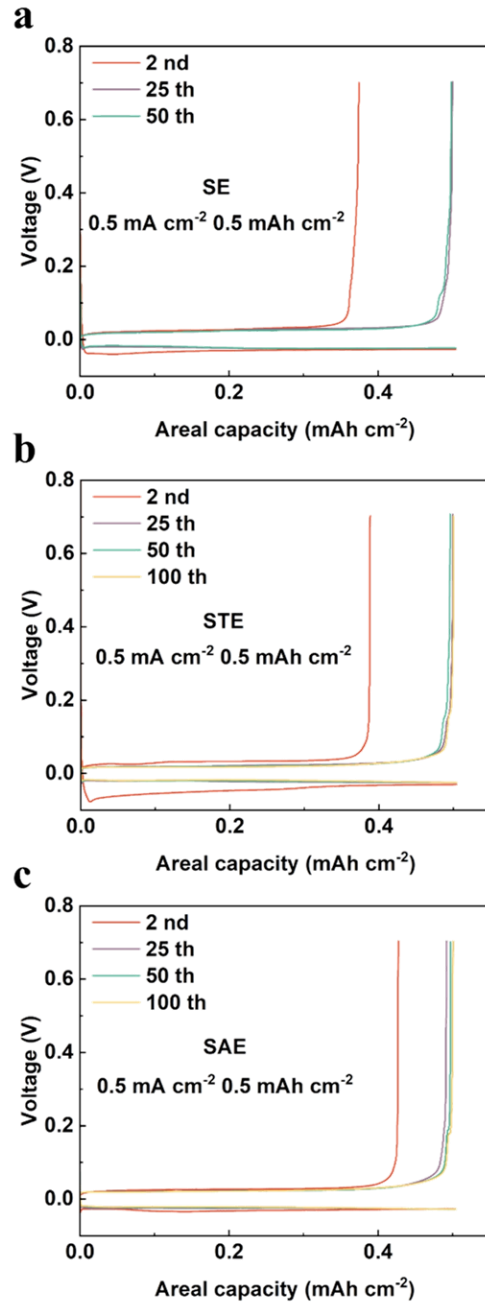


Fig. S1 Charge/discharge profiles of asymmetric Zn//Cu cells in the (a) SE group, (b) SAE group and (c) STE group at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2} during different cycles.

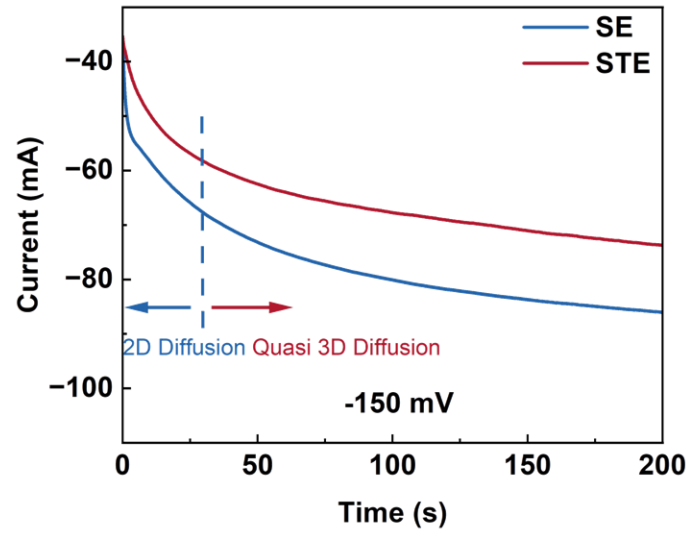


Fig. S2 Chronoamperometry (CA) curves of Zn anodes at -150 mV.

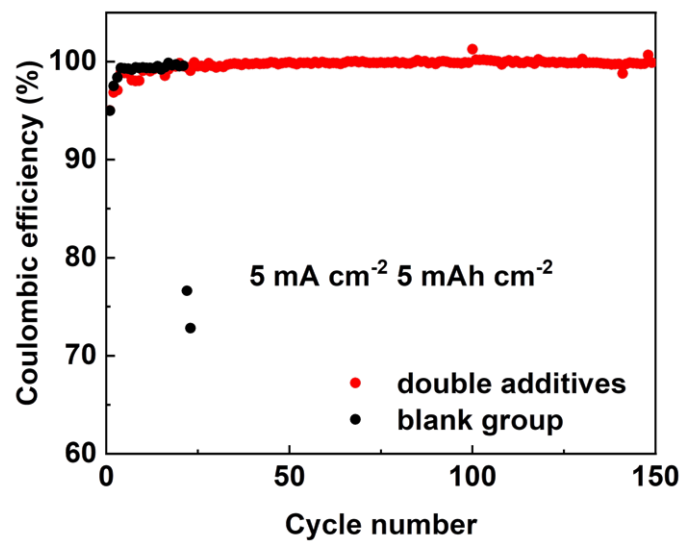


Fig. S3 CE of Zn//Cu asymmetric cells at 5 mA cm⁻² and 5 mAh cm⁻² in different electrolytes.

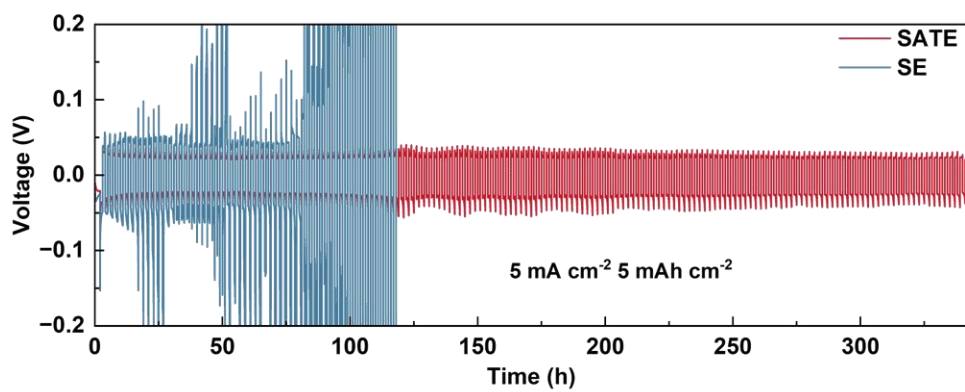


Fig. S4 Cycling performance of Zn//Zn symmetric cells in the SE group and SATE group at 5 mA cm^{-2} , 5 mAh cm^{-2} .

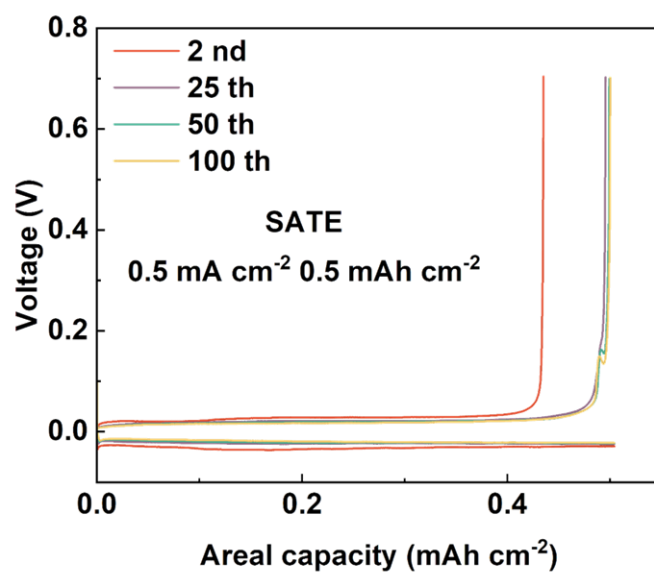


Fig. S5 Charge/discharge profiles of asymmetric Zn//Cu cells in the SATE group at 0.5 mA cm⁻² and 0.5 mAh cm⁻² during different cycles.

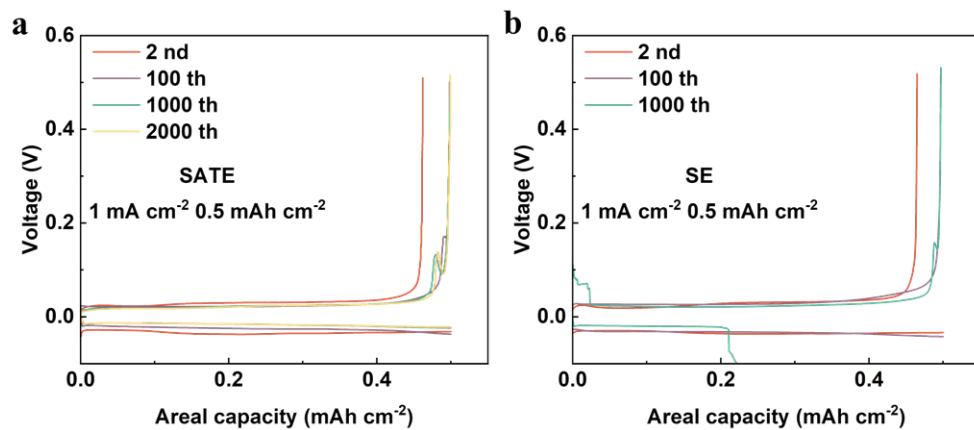


Fig. S6 Charge/discharge profiles of asymmetric Zn//Cu cells in the (a) SE group and (b) SATE group at 1 mA cm⁻² and 0.5 mAh cm⁻² during different cycles.

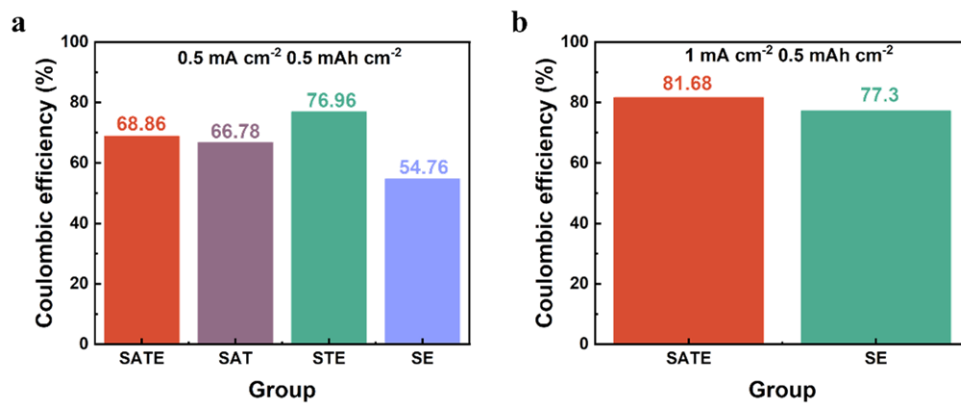


Fig. S7 Initial coulombic efficiency comparison between different electrolytes (a) at 0.5 mA cm⁻², 0.5 mAh cm⁻² and (b) at 1 mA cm⁻², 0.5 mAh cm⁻².

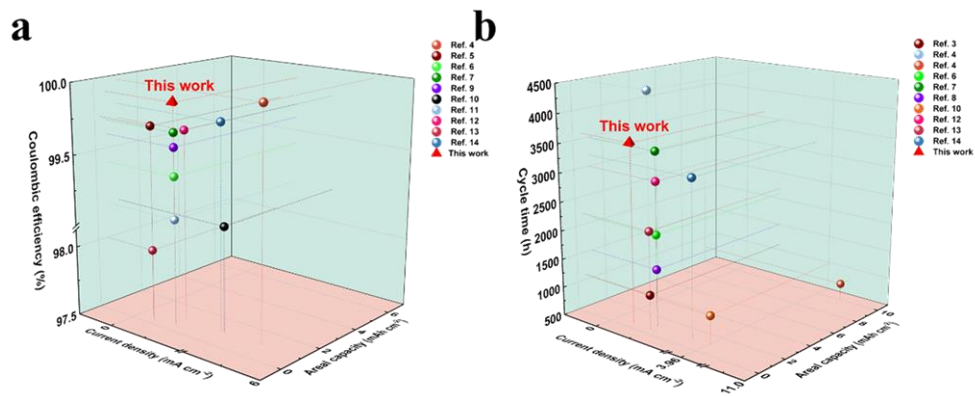


Fig. S8 Comparison of (a) CE and (b) cycle life at different current densities and areal capacities with recent reports²⁻¹⁴.

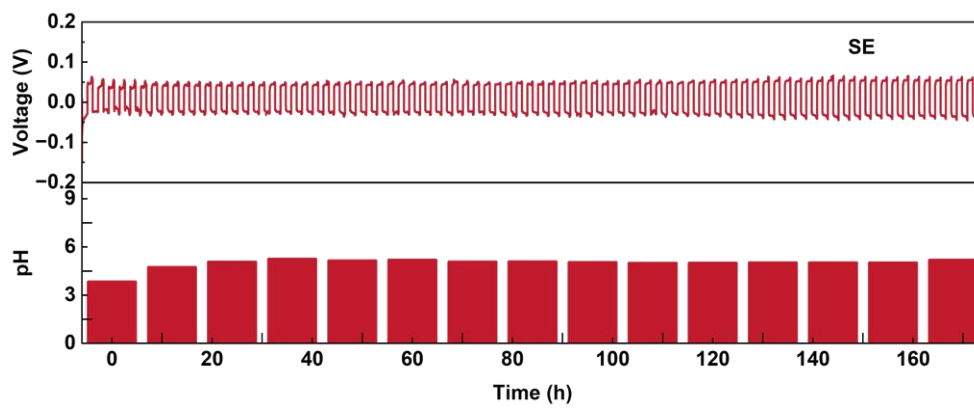


Fig. S9 The dynamic pH shift and cycle curve of the electrolyte during the cycle process.

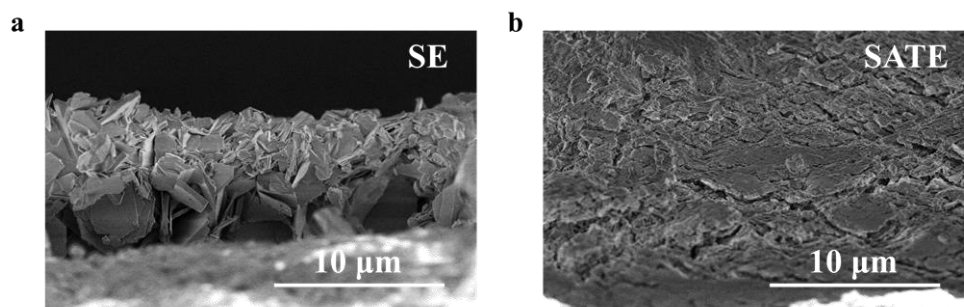


Fig. S10 SEM images of Zn anode with magnification of 5000 times in different electrolytes.

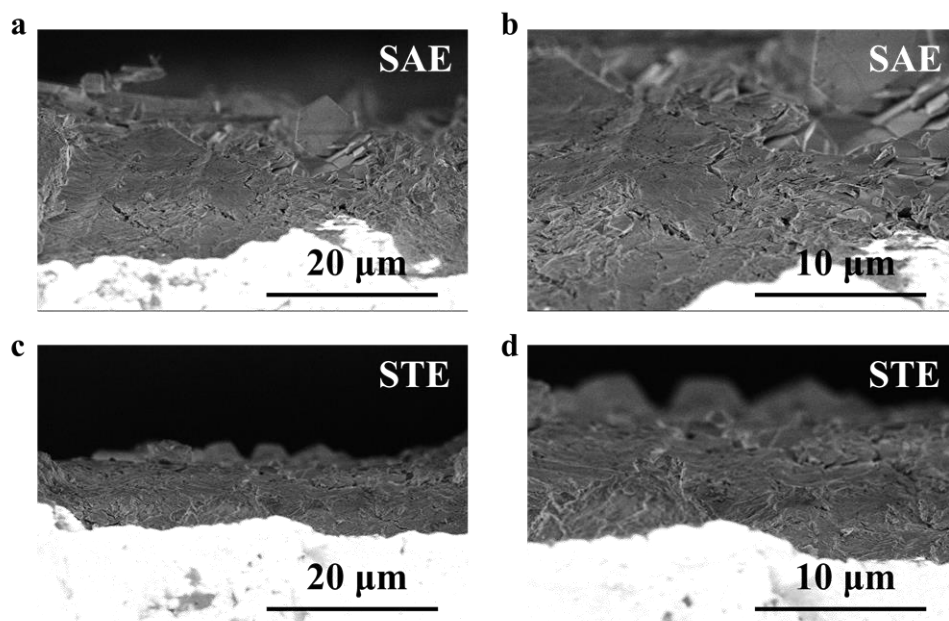


Fig. S11 SEM images of Zn anode in different electrolytes.

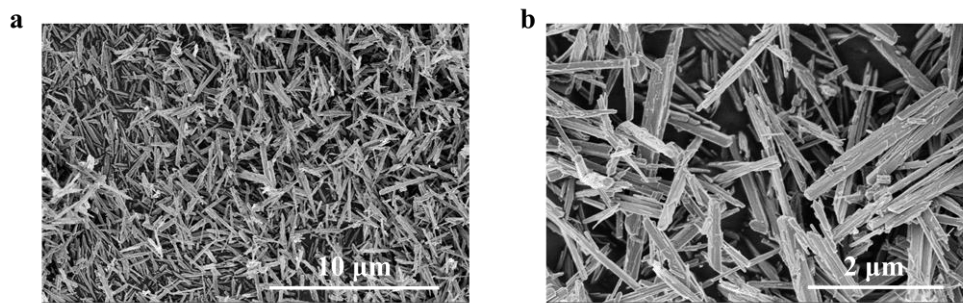


Fig. S12 SEM images of MnO₂ cathode at different magnifications.

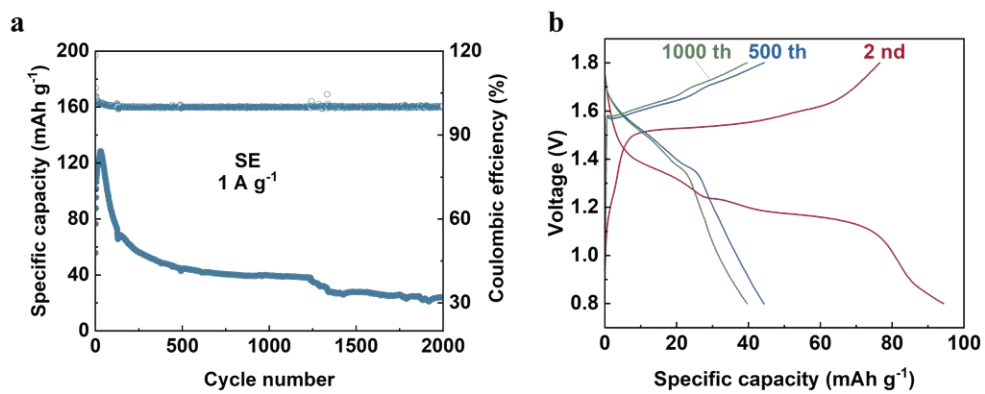


Fig. S13 (a) Cycling performance of the Zn//MnO₂ full cells at 1 A g⁻¹ in the SE group and (b) corresponding charge/discharge profiles.

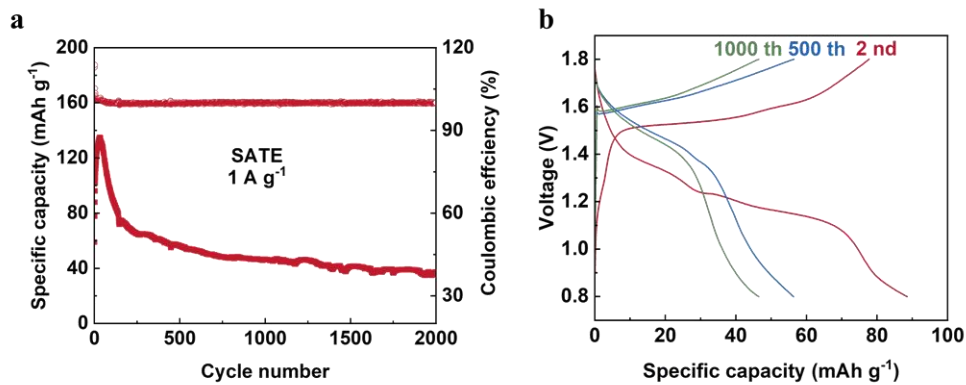


Fig. S14 (a) Cycling performance of the Zn//MnO₂ full cells at 1 A g⁻¹ in the SATE group and (b) corresponding charge/discharge profiles.

Table S1. The summary of performance applied to Zn in the recent reports using aqueous electrolytes.

Electrolyte	j/mA cm ⁻²	C/mAh cm ⁻²	CE/%	j/mA cm ⁻²	C/mAh cm ⁻²	Lifespan/h
1 M ZnSO₄+0.5 mM TMAOAc+0.025 M Zn(OAc)₂	1	0.5	99.90	0.5	0.5	3600 (This work)
2 M ZnSO ₄ +40 μL mL ⁻¹ DETA	0.5	0.5	98.31	0.5	0.5	2000 ²
2 M ZnSO ₄ +10 % sorbitol	2	0.67	99.76	1	0.5	2000 ³
1 M Zn(CF ₃ SO ₃) ₂ +50 mg mL ⁻¹ dextran	5	1	99.97	10	10	800 ⁴
2 M ZnSO ₄ +10 % TG	0.5	0.25	99.73	1	0.5	1100 ⁵
1 M ZnSO ₄ +25 mM NH ₄ H ₂ PO ₄	1	0.5	99.40	1	1	2100 ⁶
2 M ZnSO ₄ +50 mM NH ₄ OAc	1	0.5	99.70	1	1	3500 ⁷
2 M ZnSO ₄ +1 mM NH ₄ OH	/	/	/	1	1	1500 ⁸
2 M ZnSO ₄ +10 % DMA	1	0.5	99.60	1	0.5	4500 ⁹
2 M ZnSO ₄ +1 % FEC	4	1	99.10	4	1	1000 ¹⁰
2 M ZnSO ₄ +0.05 M SG	1	0.5	99.10	/	/	/ ¹¹
2 M ZnSO ₄ +5 mg mL ⁻¹ silk peptide	1	1	99.70	1	1	3000 ¹²
3 M ZnSO ₄ +0.25 mM PFOA	0.4	0.4	98	1	0.5	2200 ¹³
2 M ZnSO ₄ +0.02 M BMIm ⁺	2	1	99.80	2	1	3200 ¹⁴

Where j is the applied current density, C is the areal capacity per cycle and CE is the Coulombic efficiency.

*Note: Tetramethylammonium acetate (TMAOAc); Diethylenetriamine (DETA); Tripropylene glycol (TG); N, N-dimethyl acetamide (DMA); Fluoroethylene carbonate (FEC); Sodium glycerophosphate (C₃H₇Na₂O₆P, SG); Perfluorooctanoic acid (PFOA); 1-butyl-3-methylimidazolium cation (BMIm⁺ ion)

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