Supporting information

# Densely packed spherical zinc deposition by cation buffer strategy enabled highrate alkaline zinc batteries with lean electrolyte

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# **Experimental Section**

### Materials.

Zinc (Zn) foil (0.08 mm and 0.5 mm in thickness), EPTFE film, and Zn-Air batteries (ZABs) were purchased from Changsha Sipulin Energy Technology Co., Ltd. KOH (Meryer, 99.99%), Poly-(dimethyl diallyl ammonium chloride) (PDDA) (Meryer, 35wt.%; Mw< 100000), RuO<sub>2</sub> (Macklin, 99.99%) and Diallyl dimethyl ammonium chloride (DDA) (Meryer, 60wt.%). Commercial Zn-Nickel (Ni) battery electrodes were purchased from CHILWEE Co., Ltd. Pt/C (Platinum, nominally 20% on carbon black) and Nafion solution (5.0wt.% in H<sub>2</sub>O) were obtained from Taobao's Scientific Materials Station. Deionized water was used to prepare all aqueous electrolytes.

#### **Electrolyte preparation.**

1.683 g KOH was dissolved into 5 mL of the deionized water to obtain the 6 M KOH electrolyte as the bare electrolyte (Denoted as 0 PDDA). 1.683 g KOH was separately added into 5 mL dilutions of 1%, 5%, and 10% PDDA dispersions as 6 M KOH-PDDA modified electrolytes (The remarks are 0 PDDA, 5 PDDA, and 10 PDDA). 1.683 g KOH added into 5 mL 5% DDA solution which remarks is 5 DDA.

### The air cathode preparation.

The air cathode was fabricated by compositing a hydrophobic gas diffusion layer and a hydrophilic catalyst layer. The electrocatalyst suspension was prepared by dispersing 18 mg electrocatalysts (the 9 mg Pt/C and 9 mg RuO<sub>2</sub>) and 90  $\mu$ L Nafion solution into 4.4 mL ethanol and ultrasonicating the mixture for 30 min. The suspension was cast on carbon paper to make an air cathode. The loading mass is 2 mg cm<sup>-2</sup>. For ZABs, the area of Zn anode (0.5 mm thickness), and air cathode in this study were 4 and 1 cm<sup>2</sup>, respectively.

#### Characterizations.

The micro-morphology of the samples was investigated by a Scanning Electron Microscope (SEM, Zeiss GeminiSEM 500) equipped with an Energy-Dispersive X-ray Spectroscopy (EDS) detector. The structure of the samples was conducted on X-ray Diffraction (XRD, Bruker D8 ADVANC) with Cu K $\alpha$  irradiation. X-ray Photoelectron Spectroscopy (XPS, Thermo Fisher ESCALAB Xi+) was used to analyze the chemical composition of the Zn electrode surface. The 3D dendritic growth was performed by Laser Confocal Microscopy (CLSM, Leica DCM8). Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS, ION-TOF M6) analysis was performed using a PHI nanoTOF||Time-of-Flight SIMS equipped with a 30 kV Bi-cluster liquid metal ion gun. Lorenz Transmission Electron Microscope (TEM, Thermo Fisher Talos F200X) was used to analyze the morphology of the deposited Zn, which was treated by the Ion Thinning Instrument (Fischione M1051). *In-situ* Differential Electrochemical Mass Spectrometry (DEMS) was performed on a commercial mass spectrometer (LingLu, Shanghai) with a Zn||Zn cell containing Zn electrodes ( $\Phi$  14 mm), glass fiber separator (GF/D,  $\Phi$  16 mm) and a stainless-steel spacer. The solutions tested at Small Angle X-ray Scattering (SAXS point 2.0) were 1M KOH electrolytes containing saturated

ZnO with/without PDDA. Atomic Force Microscope (AFM, SPM-9700HT), Rheometer (MCR 302), Raman (InVia Qontor), ICP-OES (ICAP 7400), and Zeta potential (Zetasizer Nano ZSE).

The Electrochemical Digital Holography (EDH) measurement was carried out in a cuvette with Zn electrodes. 0 PDDA and 5 PDDA were selected as electrolytes, respectively. A Mach-Zehnder interferometer optical setup was employed for electrochemical digital holography with a charge-coupled device camera to document the dynamic processes. During the Zn deposition process, the concentration of certain species in the solution can alter, which can be described as follows:

$$\Delta C = k\Delta n = k \left(\frac{\lambda_0}{2\pi d}\right) \Delta \phi \tag{1}$$

where  $\Delta C$  represents the change in the solution concentration. k refers to the concentrative refractivity.  $\Delta n$  is the change in the solution refractive index.  $\lambda_0$  refers to the wavelength of the laser light. d is the path length of the refractive index change.  $\Delta \phi$  refers to the phase difference. The relationship between  $\Delta C$ ,  $\Delta \phi$  and the colors in the phase diagram is described below:

If  $\Delta \phi < 0$ ,  $\Delta C < 0$ , the phase map turns purple, indicating the concentration decreases;

If  $\Delta \phi > 0$ ,  $\Delta C > 0$ , the phase map turns yellow, indicating the concentration increases.

### **Electrochemical tests.**

The Zn||Zn symmetric cell, Zn||Ti asymmetric cell, and Zn-Air coin cell were fabricated based on the CR2032 coin cell configuration. The volume of electrolyte was 50  $\mu$ L for each cell (except the Zn-Air coin cell, 150  $\mu$ L). All the foils were cut into circle discs with a diameter of 3 mm. The Zn-Ni battery was fabricated based on the Swagelok cell configuration. The cells were assembled at ambient conditions at room temperature. The electrodes were separated by glass fiber separators (GF/D, Whatman). The cells were galvanostatically charged/discharged on the Neware BTS4000 series.

The Zn foil was first sanded down to a thickness of 80  $\mu$ m with fine sandpaper ( $m_{\Phi_{12}mm}=64$  mg). The data and calculation process related to the DOD are acquired from the following equations:

$$DOD_{(\%)} = \frac{I \times t \times S}{m \times M_{theoretical}} \times 100\%$$
<sup>(2)</sup>

where I (mA cm<sup>-2</sup>) refers to the applied current, t (h) is the galvanostatic time, s (cm<sup>2</sup>) and m (g) are the actual area and mass of the electrode, and  $M_{theoretical}$  (~820 mAh g<sup>-1</sup>) the capacity of Zn.

$$DOD_{(20\%)} = \frac{9.87 \, mA \, cm^{-2} \times 1 \, h \times 1.1 \, cm^2}{0.06 \, g \times 820 \, mAh \, g^{-1}} \times 100\% \approx 20\%$$

*In-situ* optical microscopy test was carried out using two Zn foils as electrodes and a constant current of 3 mA cm<sup>-2</sup> to observe the changes in the Zn deposition over time.

The corrosion and hydrogen evolution behaviors of the Zn electrode were both performed under an electrochemical workstation (CHI660E). The corrosion Tafel plot was recorded with a potential range of  $-1.8 \sim -1.1$ V at a scan rate of 5 mV s<sup>-1</sup> vs. Hg/HgO with a three-electrode system (Pt as work electrode and Zn foil as counter electrode). To investigate the nucleation process of

zincate, chronoamperometry (AC) was performed with Zn foil electrodes. The hydrogen evolution was conducted by performing linear voltammetry scanning (LSV) at a scan rate of 10 mV s<sup>-1</sup> vs. Zn/ zincates ([Zn(OH)<sub>4</sub>]<sup>2-</sup>).

For ZABs, the LSV test was carried out at a scan rate of 5 mV s<sup>-1</sup>, which was carried out in O<sub>2</sub>-saturated (ensured via continuous O<sub>2</sub> flow). Based on the LSV profiles, the discharge power density (*P*) was calculated using the following equation:

$$P = U_d \times j_d \tag{3}$$

where  $U_d$  is the discharge voltage and  $j_d$  is the discharge current density.

The ionic conductivity of the electrolyte was obtained by using the blocking electrode method using two Zn foils as the electrodes. The electrochemical impedance spectroscopy (EIS) test was conducted by applying an AC impedance voltage with 5 mV amplitude in a frequency range from 10 kHz to 1 Hz. The ionic conductivity ( $\sigma$ ) was calculated by the following equation:

$$\sigma = \frac{L}{R_b \times A} \tag{4}$$

where *L* represents the thickness (cm),  $R_b$  represents the bulk resistance (U), and *A* represents the area (cm<sup>2</sup>) of the Zn electrode.

The activation energy  $(E_a)$  was calculated from the Arrhenius equation by performing EIS tests at different temperatures and by linear fitting of  $\ln(R_{ct}^{-1})$  versus 1/T plots. The Arrhenius equation is given below:

$$\frac{1}{R_{ct}} = A \times \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

The ion transfer number was estimated in Zn||Zn Swagelok cell by a combination measurement of Electrochemical impedance spectra EIS before and after the CA test, and calculated by the following equation:

$$t = \frac{I_s \left(\Delta V - R_0 I_0\right)}{I_0 \left(\Delta V - R_s I_s\right)} \tag{6}$$

 $\Delta V$  is the applied polarization potential (value 20 mV in this experiment),  $I_0$  and  $I_s$  are the initial and steady-state currents, respectively;  $R_0$  and  $R_s$  represent the initial and steady-state resistance, respectively.

#### **DFT calculations.**

The calculations related to the absorbed energy of H<sub>2</sub>O, KOH, or PDDA molecules on the Zn (002) surface were implemented by using the Vienna ab initio simulation package (VASP)<sup>[1]</sup>. The projector-augmented wave (PAW) method and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functions within the generalized gradient approximation (GGA) were used. A cutoff energy of 400 eV was used for the plane-wave basis set. The convergence criteria were set to  $10^{-4}$  eV and the residual force of atom relaxation was less than 0.05 eV/Å. To avoid the artificial interaction of periodic conditions, the vacuum layer of 15 Å was built for all slabs. On the Zn (002)

surface, calculations were performed with two layers of the  $5 \times 5$  supercell (50 Zn atoms with the bottom two layers fixed) to represent the absorbed surface.

The absorbed energy of the Zn slab and different species is defined as follows:

$$E_{abs.} = E_{total} - E_{species} - E_{Zn-slab} \tag{7}$$

where  $E_{total}$  is the total energy of the whole system,  $E_{species}$  is the energy of X (X=H<sub>2</sub>O, KOH or PDDA) molecule,  $E_{Zn-slab}$  is the energy of the Zn slab, respectively.

#### Molecular dynamic simulations.

Molecular dynamic (MD) simulations were applied to investigate the  $[Zn(OH)_4]^{2-}$  diffusion and concentration distribution of [Zn(OH)4]<sup>2-</sup> and PDDA on the Zn electrode surface. The solidliquid interface calculations were conducted with COMPASS ||| force field <sup>[2, 3]</sup> using the Forcite module in Materials Studio (MS) 2020. The dimensional lengths of the Zn electrode slab are 39.97 Å  $\times$  41.54 Å in the X-Y axis planes. The bare electrolyte contains 480 KOH, 80 [Zn(OH)<sub>4</sub>]<sup>2-</sup> (after dissolution of ZnO), and 2200 H<sub>2</sub>O molecules in a rectangular box with length scales of 39.97 Å  $\times$ 41.54 Å  $\times$  43.93 Å. By adding 4 PDDA (n=3) molecules in the bare electrolyte, we obtained a test sample electrolyte with PDDA. After geometry optimization, the two solutions were respectively placed on the optimized electrode surface. All MD calculations were performed under the NVT ensemble (T=298.0 K) with a time step of 1 fs and a total simulation time of 600 ps, during which simulation trajectories were recorded every 4000 steps. The running time was long enough for system energy and temperature to reach stable. The temperature was controlled by a Nose-Hoover thermostat. The Ewald scheme and atom-based cutoff method (i.e., a radius of 12.5 Å) were applied to treat electrostatic and van der Waals (vdW) interactions, respectively. The concentration profiles of [Zn(OH)<sub>4</sub>]<sup>2-</sup> and PDDA along perpendicular direction were analyzed. The solid-liquid interface snapshots were also displayed. The diffusion coefficient (D) of  $[Zn(OH)_4]^{2-}$  was estimated from the slope of the mean square displacement (MSD) curves by Einstein's formula<sup>[4]</sup>:

$$\langle r^2(t) \rangle = 6Dt \tag{8}$$

where  $< r^2 >$  is the value of MSD, t is the time.

#### **COMSOL** simulations.

To simulate the dynamic Zn deposition on Zn electrodes in 0 PDDA and 5 PDDA electrolytes, a finite element analysis (FEA) model was developed using COMSOL Multiphysics 5.6 software, "cubic current distribution" and deformable geometric interface model. The simulation area size is set to  $66 \times 64 \mu m$ . The electrode reaction for the electrode surface follows the Butler-Volmer kinetic expression <sup>[5, 6]</sup>.

$$i_{loc} = -(C' - k\theta) \exp\left(\frac{-(\alpha - k'\theta)F\eta}{RT}\right)$$
(9)

where  $i_{loc}$  is the local current density, C' is the coefficient of ionic concentration, k is the coefficient of PDDA concentration,  $\theta$  is the coverage of adsorbed inhibiting additive and cannot exceed unity,  $\alpha$  is the transfer coefficient of the cathode, k' is the inhibiting transfer coefficient of

the TX, F is the Faraday constant, R is the molar gas constant, T is the ambient temperature,  $\eta$  is the overpotential and  $i_0$  is the exchange current density.



Figure S1. (a) Conductivity, and (b) viscosity ( $\eta$ ) of electrolytes with different PDDA additions.



Figure S2. Time-voltage curves of the Zn||Zn symmetric cells at 1 mA cm<sup>-2</sup> in different electrolytes.



**Figure S3.** Addition of PDDA versus voltage curves at 1 mA cm<sup>-2</sup>. Inset images are the optical images of different electrolytes.



Figure S4. Zeta potential of 1M KOH electrolytes with different PDDA additions.



**Figure S5.** Optical images of (a) aqueous solutions and (b) 6M KOH electrolytes containing 5% of different types of polyelectrolytes (PSS, PVP, and PVA).



**Figure S6.** Spatial distribution of charge density difference between Zn slab and H<sub>2</sub>O, and KOH molecules, respectively. The yellow and cyanine semi-transparent clusters represent an increase and decrease in electron density.



Figure S7. Adsorption energies of different bound forms of (a)  $H_2O$ , and (b) KOH molecules on Zn slab.



**Figure S8.** Raman spectra of PDDA powder, 5 PDDA electrolyte, and Zn foil in contact with 5 PDDA electrolyte.



**Figure S9.** XPS spectra of Zn foils dipped in the 0 PDDA and 5 PDDA electrolytes. The samples were then cleaned with deionized water before characterization.



Figure S10. Curves of contact angle of different electrolytes on Zn foils over time.



**Figure S11.** (a) Particle size distribution curves and (b) effective size of 0 PDDA and 5 PDDA electrolytes.



**Figure S12.** Ion transport properties of different electrolytes. Time-current curves of (a) 0 PDDA and (b) 5 PDDA electrolytes. The inset shows AC impedance spectra.



Figure S13. Nyquist plots at various temperatures in (a) 0 PDDA and (b) 5 PDDA electrolytes.



**Figure S14.** 3D snapshots of the bare electrolyte and Zn electrode system obtained from MD simulation.



**Figure S15.** Relative concentration distribution of PDDA molecules distance from the Zn electrode surface in the test electrolyte with PDDA.



**Figure S16.** Time-potential curves at constant current (2 mA cm<sup>-2</sup>) in 0 PDDA and 5 PDDA electrolytes.

Chazalviel proposed a space charge theory to interpret the metal nucleation and growth behavior <sup>[7]</sup>. This model is presented in the dilute electrolytes in which the transport of ions just considers the mobility and diffusion coefficient without the electrolyte convection. According to this theory, the concentration gradient within a symmetric cell model with a small electrode distance can be described  $\frac{\partial c}{\partial x}$  <sup>[8]</sup>. If  $dC/dX > 2C_0/L$  (Potential-time curve of the 0 PDDA electrolyte above), the initial average concentration, where *L* is the electrode distance and  $C_0$  is the initial concentration of the electrolyte. The metal ion concentration on the negative electrode surface will decrease to zero within Sand time  $\tau$ . The depletion of ions at the interface leads to the formation of a space charge layer and a space electric field, which accelerates local ion deposition rates at the electrolyte electrolyte interface. On the tip of the electrode surface, a local current density is generated, which causes the aggregation of metal ion fluxes, finally resulting in the 'tip effect' and metal dendrite growth <sup>[9, 10]</sup>.

$$\tau = \pi D \left(\frac{eC_0}{2Jt_a}\right)^2 \tag{10}$$

J represents the effective current density of the electrode. D represents the bipolar diffusion coefficient  $t_a$  denotes the anions migration numbers. On the contrary, if  $dC/dX < 2C_0/L$  (Potential-time curve of the 5 PDDA electrolyte above), the ion concentration distribution between electrodes is linear and can be regarded as a steady state.



**Figure S17.** The number of Zn nuclei on the Zn anode deposited for 30 min using different concentrations of KOH electrolytes.



Figure S18. Time-current curves of different concentrations of KOH electrolytes. The inset shows AC impedance spectra.



Figure S19. SEM images of Zn deposition at 1 mA cm<sup>-2</sup> for 1, 5, 10, and 20 h, respectively, inset white scale 10  $\mu$ m.



**Figure S20.** SEM images on the cross-sectional morphology of Zn deposition at 1 mA cm<sup>-2</sup> for 1, 5, 10, and 20 h, respectively.



**Figure S21.** SEM images of morphological features of Zn deposition at 1 mA cm<sup>-2</sup> for predeposition, 30 and 60 min, respectively.



Figure S22. AFM images of Zn deposition for 1h.



**Figure S23.** Chronoamperometric test. The curves of Zn electrodes in (a) 0 PDDA and (b) 5 PDDA electrolytes at different overpotentials. Comparison of the theoretical dimensionless plots for instantaneous and progressive nucleation with the experimental nucleation process in (c) 0 PDDA and (d) 5 PDDA electrolytes.

Scharifker proposed the theory of the potentiostat current transient for three-dimensional multiple nucleation with diffusion-controlled growth <sup>[11]</sup>. According to the Scharifker model of electrochemical nucleation, nucleation can be instantaneous or progressive. Theoretically, instantaneous nucleation means that all nuclei appear simultaneously at all possible growth sites in the initial step and then grow at a similar rate. Nucleation sites are gradually activated in progressive nucleation, and the nucleation process is accompanied by nuclear growth <sup>[12]</sup>. Instantaneous nucleation and progressive nucleation can be described by:

Instantaneous:

$$\left(\frac{j}{j_m}\right)^2 = 1.9542 \left(\frac{t}{t_m}\right)^{-1} \{1 - exp \left[-1.2564 \left(\frac{t}{t_m}\right)\right]\}^2$$
(12)

Progressive:

$$\left(\frac{j}{j_m}\right)^2 = 1.2254 \left(\frac{t}{t_m}\right)^{-1} \{1 - exp[-2.3367 \left(\frac{t}{t_m}\right)^2]\}^2$$
(13)

The nucleation pattern can be obtained by comparing dimensionless  $(\frac{j}{j_m})^2 vs. (\frac{t}{t_m})$  plots with theoretical models from Equation (12) and Equation (13) <sup>[13,14]</sup>.



**Figure S24.** The number of Zn nuclei on the Zn anode deposited for 30 min using 1 PDDA, 5 PDDA, and 10 PDDA electrolytes, respectively.



**Figure S25.** Time-current curves of (a) 1 PDDA and (b) 10 PDDA electrolytes. The inset shows AC impedance spectra.



Figure S26. Schematic illustration of the mechanism of Zn nucleation and spherical growth.



Figure S27. The TEM image of dendrites on the cycled Zn electrode with 0 PDDA electrolyte.



**Figure S28.** SEM images of morphological features of Zn deposition at 10 mA cm<sup>-2</sup> for 1, 5, 10, and 20 h, respectively.



**Figure S29.** SEM images on the cross-sectional morphology of Zn deposition at 10 mA cm<sup>-2</sup> for 1, 5, 10, and 20 h, respectively.



Figure S30. SEM images of Zn deposition at 10 mA cm<sup>-2</sup> for 1, 5, 10, and 20 h, respectively, inset white scale 10  $\mu$ m.



**Figure S31.** SEM images on the cross-sectional morphology of Zn deposition at 10 mA cm<sup>-2</sup> for 1, 5, 10, and 20 h, respectively.



**Figure S32.** SEM images showing morphological features of Zn deposition with 5 DDA electrolyte at 10 mA cm<sup>-2</sup> for 1, 5, 10, and 20 h, respectively, inset white scale 10  $\mu$ m.



Figure S33. Overall optical images of Zn deposition at  $10 \text{ mA cm}^{-2}$  for 20 h.



Figure S34. SEM images and EDS of Zn foil after 5 days of soaking.



Figure S35. LSV curves.



Figure S36. The SEM image of pristine Zn foil.



**Figure S37.** SEM images of discharged Zn electrode after 50 cycles at 2 mA cm<sup>-2</sup> and 2 mAh cm<sup>-2</sup> under 5 PDDA electrolyte.



Figure S38. Raman spectra of 0 PDDA and 5 PDDA electrolytes.



**Figure S39.** Cycling stability of the Zn||Zn coin cells at 9.87 mA cm<sup>-2</sup>, 9.87 mAh cm<sup>-2</sup> in the 1 PDDA and 10 PDDA electrolytes.



**Figure S40.** Cycling stability of the Zn||Zn coin cells using 5 DDA electrolyte at (a) 1 mA cm<sup>-2</sup>, 0.5 mAh cm<sup>-2</sup>, (b) 5 mA cm<sup>-2</sup>, 1 mAh cm<sup>-2</sup>.



**Figure S41.** (a) Zn plating/stripping profiles of Zn||Ti coin cells cycled at 1 mA cm<sup>-2</sup>, 0.5 mAh cm<sup>-2</sup>. (b) Corresponding voltage profiles at different cycles.



Figure S42. The 3D image of pristine Zn foil.



**Figure S43.** (a) SEM images, (b) XRD, and (c) EDS mapping of the element distributions (Pt, C, O, and Ru) of the air cathode.



Figure S44. The open-circuit voltage (OCV) curves of ZABs in 0 PDDA and 5 PDDA electrolytes.



Figure S45. Photographs of the Zn-Air coin cell of (a) device and (b) composition.



**Figure S46.** Galvanostatic cycling curves of Zn-Air coin cells at 2 mA cm<sup>-2</sup> with a charge/discharge time of 15 min at different temperatures.



**Figure S47.** Galvanostatic cycling curves of Zn-Air coin cells with 5 DDA electrolyte at (a) 2 mA cm<sup>-2</sup>, 30 min for each cycle, and (b) 10 mA cm<sup>-2</sup>, 6 min for each cycle.



Figure S48. (a) Schematic illustration and (b) photograph of a Zn-Air block cell device.



Figure S49. (a, b) SEM images of the Ni(OH)<sub>2</sub> cathode and (c, d) the ZnO anode.



Figure S50. Long-term cycling performances of the commercial Zn-Ni batteries.



**Figure S51.** SEM images of the ZnO anode after 40 cycles with (a, b) 0 PDDA, and (c, d) 5 PDDA electrolytes.

**Table S1.** Nucleation density for Zn anodes and migration rate of  $[Zn(OH)_4]^{2-}$  using different electrolytes. Where the number of Zn nuclei in a fixed area indicates the nucleation density and the migration rate is the conductivity multiplied by the transfer number.

Electrolyte	Number of nuclei (N)	Conductivity (mS cm <sup>-1</sup> )	Transfer number	Rate of migration (mS cm <sup>-1</sup> )	
0.1M KOH	0	4.6	0.04	0.19	
0.5M KOH	1	7.5 0.59		4.42	
1М КОН	3	96.2	0.41	39.42	
ЗМ КОН	4	146.5	0.49	71.81	
6M KOH (0 PDDA)	7	231.9	0.56	129.86	
1 PDDA	11	165.8	0.58	96.17	
5 PDDA	19	135.2	0.65	87.88	
10 PDDA	20	83.8	0.32	26.82	

**Table S2.** Comparison of the cycling performance of Zn electrodes in the recent literature. The current density, lifespan, and cumulative capacity applied to the Zn electrode during the galvanostatic cycling can be considered indicators for evaluating strategies to optimize alkaline aqueous Zn batteries.

No.	Electrolyte	Type of Zn anode	Type of cell	J (mA cm <sup>-2</sup> )	C (mAh cm <sup>-2</sup> )	Lifespan (h)	Cumulative capacity (mAh cm <sup>-2</sup> )	Ref.
1 6M KOH	Zn powder	Swagclok cell (glass fiber)	1	0.5	900	900	Adv. Funct. Mater. 2022, 2207397, 1-8	
1 + 2M KBr			(≈30 mg cm <sup>2</sup> )	2	2	200		
2	6M KOH + 0.2M ZnO (0.4T)	Zn plate	homemade cell (non-woven fabric)	1	0.25	260	260	J. Mater. Chem. A.
				10	2	40	400	<b>2022</b> , 10, 11971-11979
2 IM I	1M KOH	Zn plate	coin cell (non-woven fabric)	1	0.5	750	750	Angew. Chem. Int. Ed.
5	+ 0.3M DMSO			5	1	100	500	<b>2022</b> , e202212767
4	PAM-SC gel (6M KOH)	Zn plate	flexible cell	1	/	50	50	Angew. Chem. Int. Ed. <b>2023</b> , e202301114
5	nano-SFQ gel (6M KOH+ ZnO)	Zn plate (0.3 mm)	flexible cell	1	0.5	800	800	<i>Adv. Mater.</i> <b>2023</b> , 35, 2209290
6	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	Zn plate (0.5 mm)	coin cell (CR 2025, GF/A)	10	5	30	300	Angew. Chem. Int. Ed. 2021, 60, 15281-15285
7	6M KOH + 1M Zn(OAc) <sub>2</sub>	Zn plate (50 µm)	homemade cell (GF/A)	0.8	0.8	17	13.6	Angew. Chem. Int. Ed. 2022, 61, e202207353
8	6М КОН	CBL@Zn plate	coin cell (CR 2016, filter paper)	0.5	0.5	200	100	<i>Small</i> <b>2022</b> , 18, 2106604
				2.5	0.5	40	100	
9	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	Ti <sub>3</sub> C <sub>2</sub> T <sub>X</sub> @Zn plate	coin cell (CR 2032, GF/D)	5	0.5	80	400	ACS Appl. Mater. Inter. 2023, 15, 10651-10659
				5	20	48.4	241.7	
10	6M KOH + 0.2M ZnO	ZG@Zn plate	coin cell (CR 2032, GF/A)	20	10	105.5	2111	J. Am. Chem. Soc. 2022, 144, 42, 19344–19352
11	4M KOH + 0.2M ZnO	Zn plate	homemade cell	20	10	130	2600	Adv. Mater. 2024, 2404834
12	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	2DV 7n0@7n	homemade cell	5	5	1100	5500	<i>Adv. Mater.</i> <b>2024,</b> 36, 2307819
		0.2M Zn(OAc) <sub>2</sub> SDK-ZnO@Zn		20	45	390	7800	
Our work	6M KOH + 5% PDDA	Zn plate 6M KOH + 5% PDDA	coin cell (CR 2032, GF/A)	1	0.5	550	550	
				9.87	9.87	70	690.9	
				5	1	390	1950	-
		Zn plate (0.5 mm)	homemade cell	20	10	455	9100	

**Table S3.** Comparison of the cycling performance of ZABs in the recent literature. The selected battery anodes are all full Zn foils and the air cathodes are commercial catalysts (e.g. Pt/C,  $Co_3O_4$ ,  $RuO_2$ , or  $IrO_2$ ) and were tested in ambient air. The cumulative capacity was chosen as a reference value for the E/C ratio to assess the practicality of long-term cycling of electrolytes in a semi-open system.

No.	Electrolyte	Type of cell	Electrolyte volume	J (mA cm <sup>-2</sup> )	Cycle number	Lifespan (h)	Cumulative capacity (mAh cm <sup>-2</sup> )	E/C ratio ( µL mAh <sup>-1</sup> )	Ref.
1	CNF-FHE gel (6M KOH+0.2M C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> Zn)	flexible cell	600 mm <sup>3</sup>	1	510	85	85	7.06	J. Mater. Chem. A. 2022, 10, 22730-22741
2	nano-SFQ gel (6M KOH+ ZnO)	flexible cell	600 mm <sup>3</sup>	1	450	450	450	1.33	<i>Adv. Mater.</i> <b>2023</b> , 35, 2209290
3	PAM-SC gel (6M KOH)	flexible cell	/	0.5	420	84	42	/	Angew. Chem. Int. Ed. 2023, e202301114
4	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	homemade cell	1600 μL	0.5	136	136	68	23.53	<i>Joule.</i> <b>2022</b> , 6, 1617-1631
5	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	homemade cell	flow electrolyte (>5000 $\mu$ L)	10	165	55	550	>9.09	<i>Chem. Eng. J.</i> <b>2021</b> , 418, 129321
6	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	homemade cell	flow electrolyte (>5000 $\mu$ L)	5	300	100	500	>10.00	<i>Adv. Funct. Mater.</i> <b>2021</b> , 31, 2010472
7	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	homemade cell	/	10	60	60	600	/	<i>Adv. Mater.</i> <b>2024</b> , 36, 2307819
8	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	homemade cell	/	5	210	35	175	/	ACS Appl. Mater. Inter. 2022, 14, 15176-15186
9	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	coin cell (CR 2032, GF/D)	200 μL	10	40	13.33	133.3	1.50	ACS Appl. Mater. Inter. 2023, 15, 10651-10659
10	6M KOH + 0.2M ZnO	coin cell (CR 2032, GF/A)	/	10	150	15	150	/	J. Am. Chem. Soc. 2022, 144, 19344-19352
11	6M KOH + 0.2M Zn(OAc) <sub>2</sub>	coin cell (CR 2032, GF)	/	5	30	30	150	/	Adv. Energy Mater. 2018, 8, 1800480
12	1M KOH + 0.2M Zn(OAc) <sub>2</sub>	coin cell (CR 2032, GF/D)	/	5	120	20	100	/	<i>Catalysts</i> <b>2023</b> , 13, 1332
Our work	6M KOH + 5% PDDA	homemade cell	2600 μL	10	1200	120	1200	2.17	
		coin cell (CR 2032, GF/D)	150 μL	10	250	25	250	0.60	-

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