Supporting Information

Solvation Structure Regulation of Deep Eutectic Solvents: Stabilize the Zinc Anode in Rechargeable Zinc-Air Batteries

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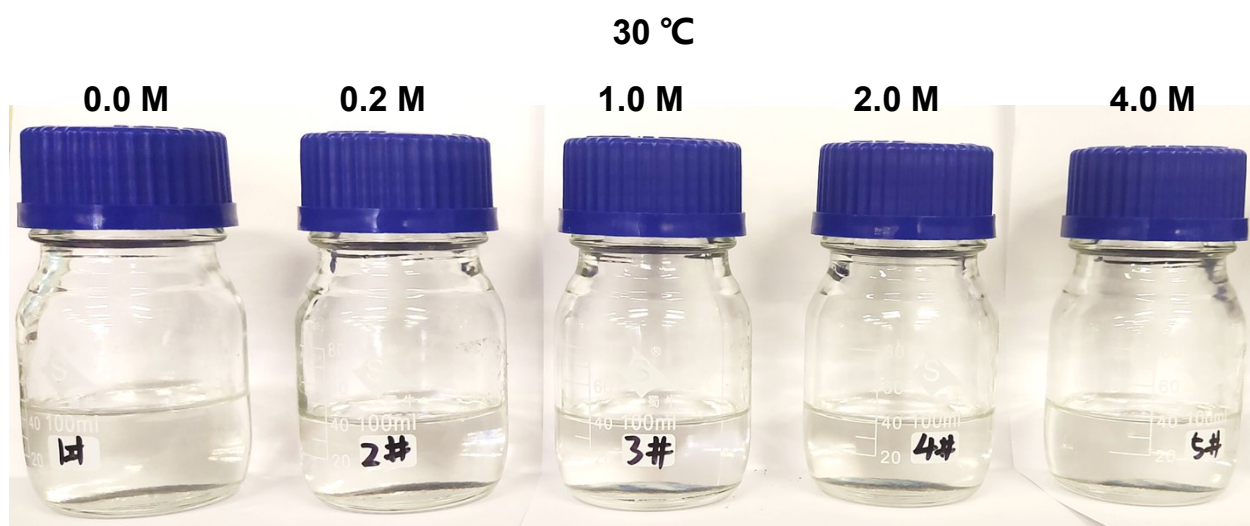
Results and Discussion

30 ℃

| 0.0 M | 0.2 M | 1.0 M | 2.0 M | 4.0 M |

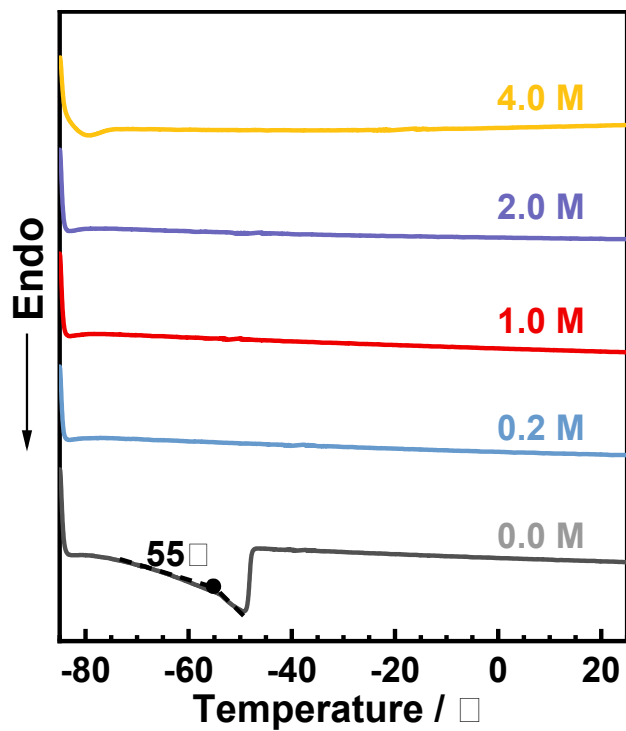**Fig. S1** The optical photographs of different C_{ZnCl_2} electrolyte at 30℃

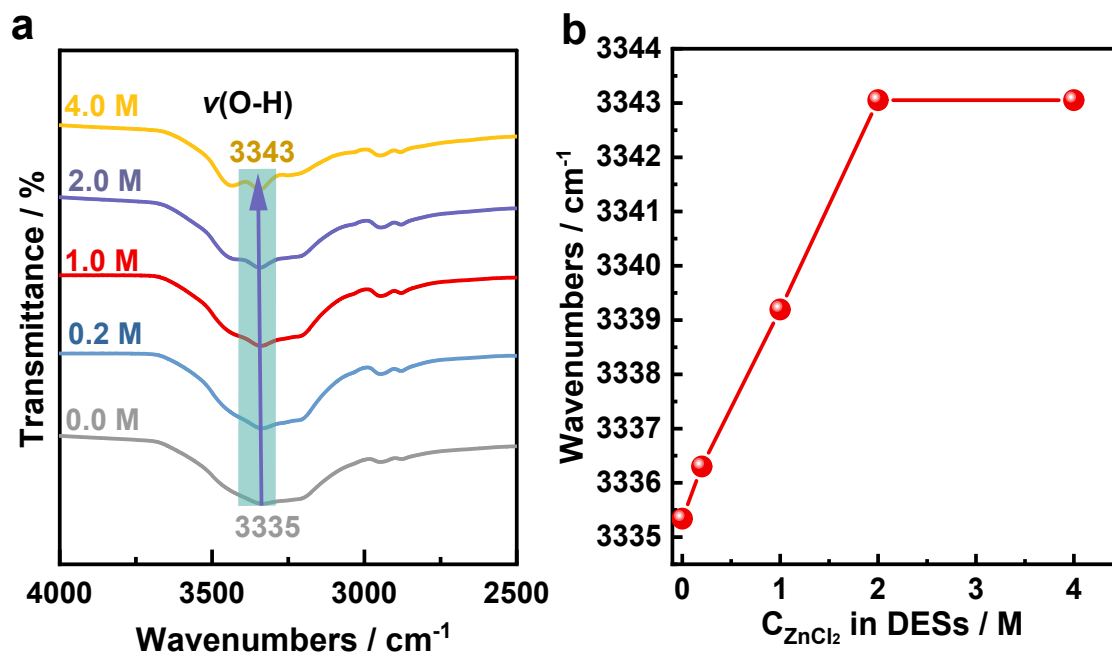**Fig. S2** DSC test from -85 to 25 °C at a scan rate of 2 °C/min;

Fig. S3 a) FTIR spectra and b) peak position of O-H stretch vibration band as a function of the C_{ZnCl_2}
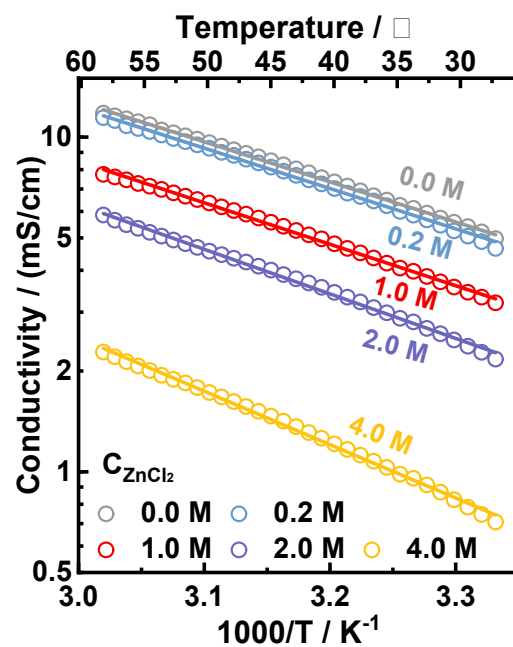
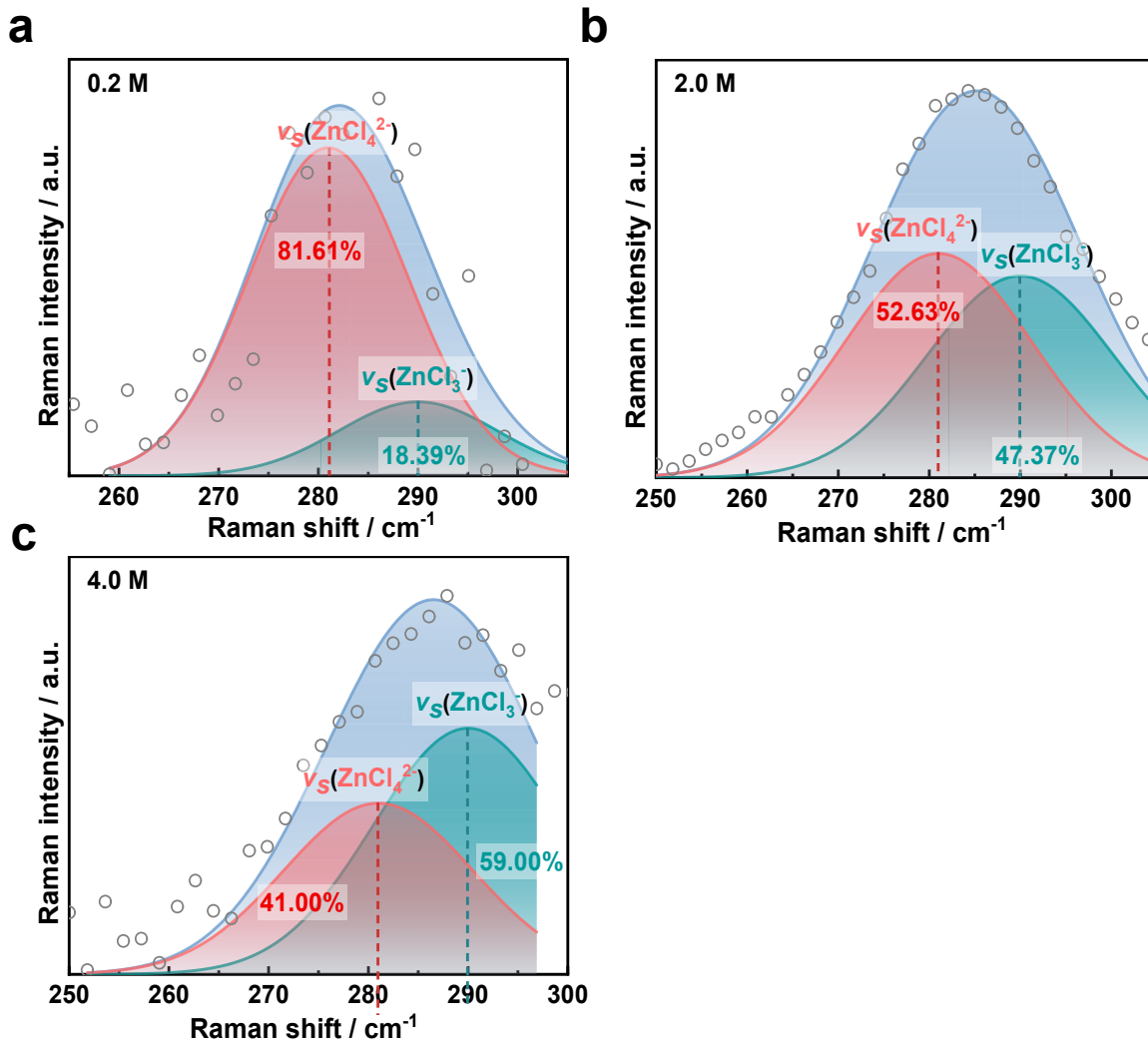**Fig. S4** Temperature (T) dependence of ionic conductivity of various C_{ZnCl_2};

Fig. S5 The Raman spectra fitted peaks of various C_{ZnCl_2} electrolyte: a) 0.2 M; b) 2.0 M; c) 4.0 M;
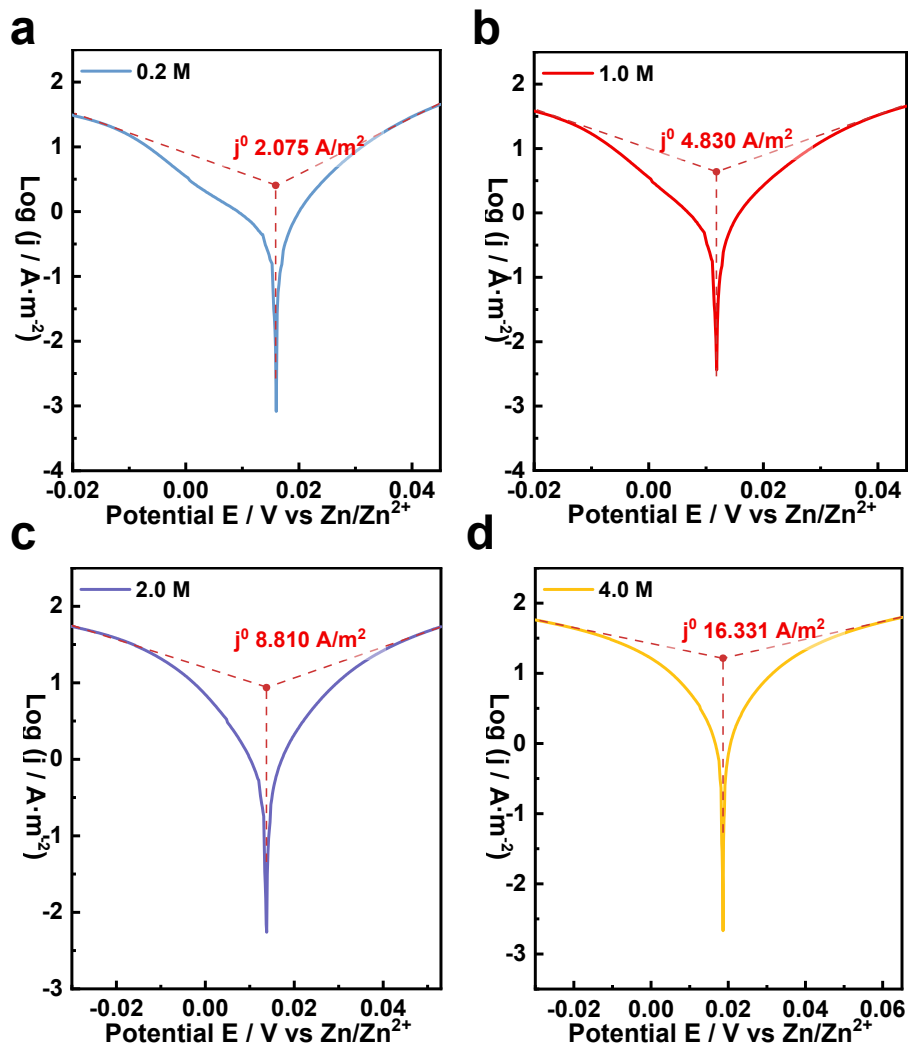
Fig. S6 The tafel curves for Zn electrode in various C_{ZnCl_2} electrolytes, a) 0.2 M; b) 1.0 M; c) 2.0 M; d) 4.0 M
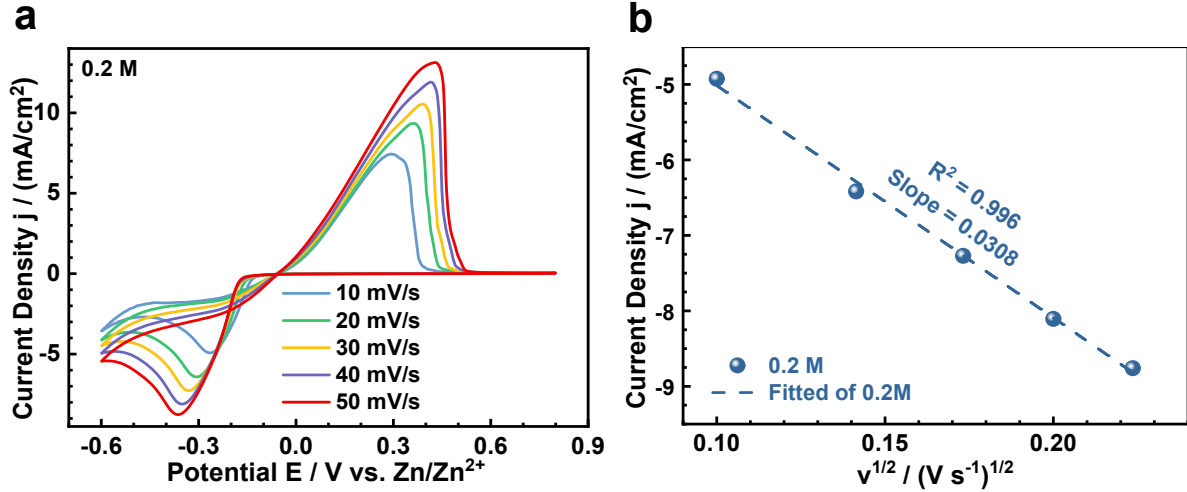
Fig. S7 a)The CV curves of W wire electrode in 0.2 M ZnCl$_2$ with different scan rates; b) Relationships between cathodic peak current density (j$_{pc}$) and square root of scan rate(v$^{1/2}$) calculated from a)

For a quasi-reversible charge transfer process, the diffusion coefficient of Zn(II) can be determined by the irreversible Randles-Sevick Eq-1[1], which is also applicable to the quasi-reversible systems[2, 3],

$$j_p = 0.4958 nFAC_{Zn(II)}D_{Zn(II)}^{1/2}\left(\frac{\alpha n_\alpha Fv}{RT}\right)^{1/2}$$

where j$_p$ is the cathodic peak current, n is the number of exchanged electrons, F is the Faraday constant, A is the electrode area, C$_{ZnCl_2}$ is the ZnCl$_2$ concentration, D$_{ZnCl_2}$ is the diffusion coefficient of Zn species, α is the transfer coefficient, n$_\alpha$ is the electron transfer number in the rate-determining step, v is the scan rate, R is the gas constant, T is the absolute temperature. The average transfer coefficient can be calculated as 0.34.[4]

Subsequently, the diffusion coefficients were calculated for other C$_{ZnCl_2}$ using the Nernst-Einstein equation.[5]

$$\kappa = \frac{C_i D_i Z_i F^2}{t_i RT}$$

C_i the concentration of active ion, mol·L^{-1}; D_i diffusion coefficient of active ion, cm^2·s^{-1}; Z_i the charge number of active ion, F the Faraday constant, 96485 C·mol^{-1}; t$_i$ ion mobility number;

Table S1 Physicochemical properties of different C_{ZnCl_2} electrolytes.

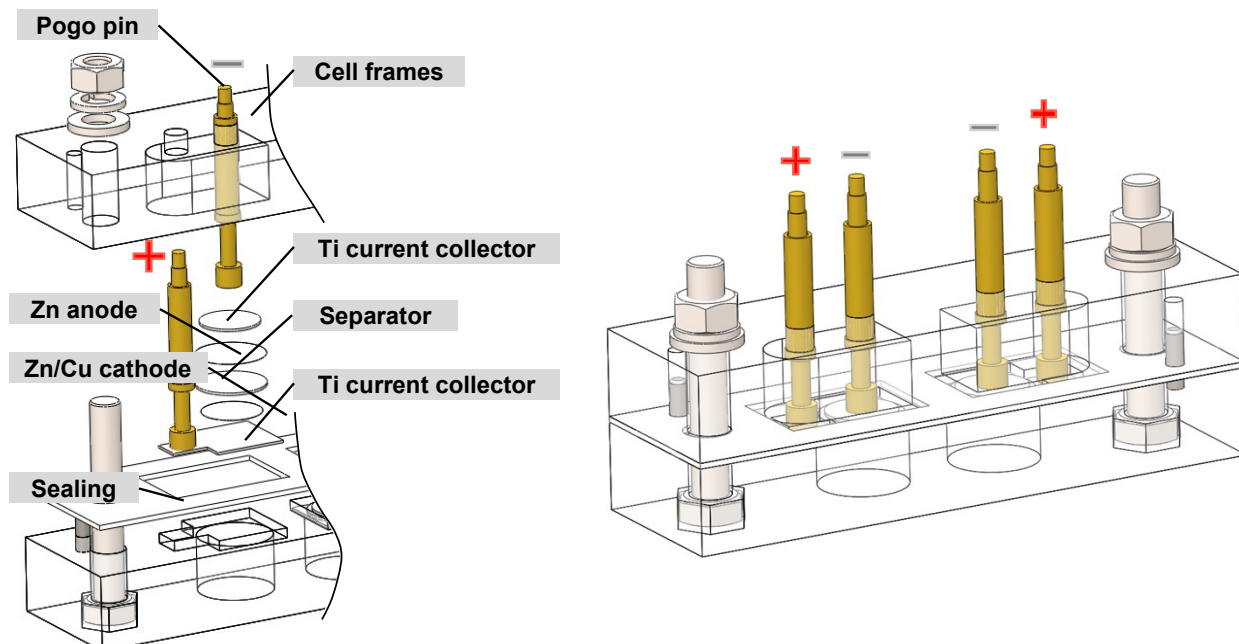| Item	C / mol·m^{-3}	E^0 / mV	j^0 / Am^{-2}	Ionic conductivity / S·m^{-1}	Diffusion coefficient m^2·s^{-1}
0.2 M	200	15.997	2.075	0.5245	2.76E-11
1.0M	1000	11.9567	4.830	0.3565	8.39E-12
2.0M	2000	13.931	8.810	0.2475	4.12E-12
4.0M	4000	10.925	16.331	0.0825	9.71E-13

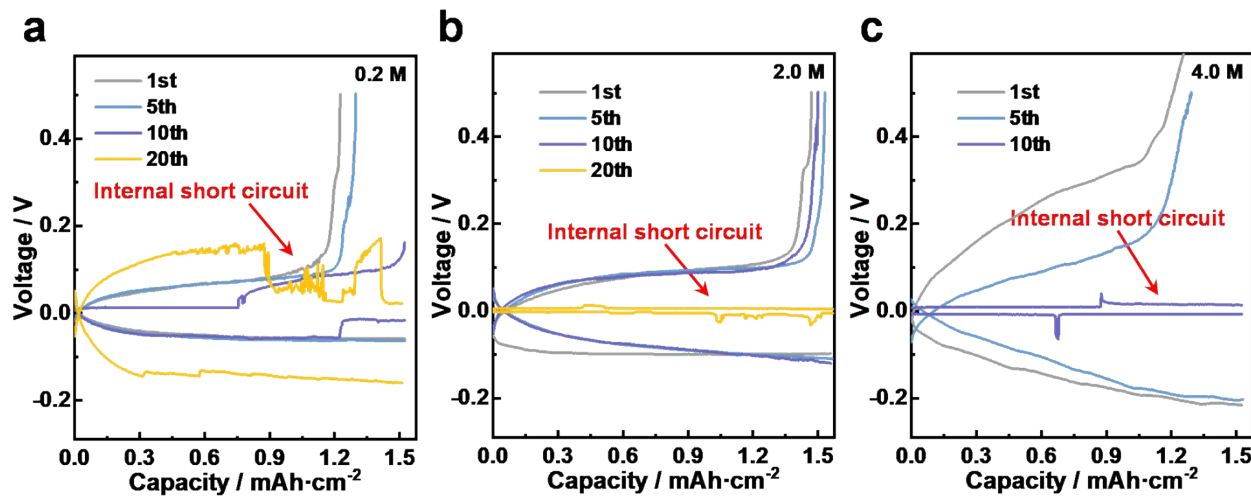**Fig. S8** The schematic drawing of Zn/Cu||Zn cell

Fig. S9 Voltage profiles of the Cu∥Zn cell at different cycles of C_{ZnCl_2} at: a) 0.2 M; b) 2.0 M, and c) 4.0 M;

Table S2 Comparison of over-potential, viscosity, and ionic conductivity of 1.0 M $ZnCl_2$ with

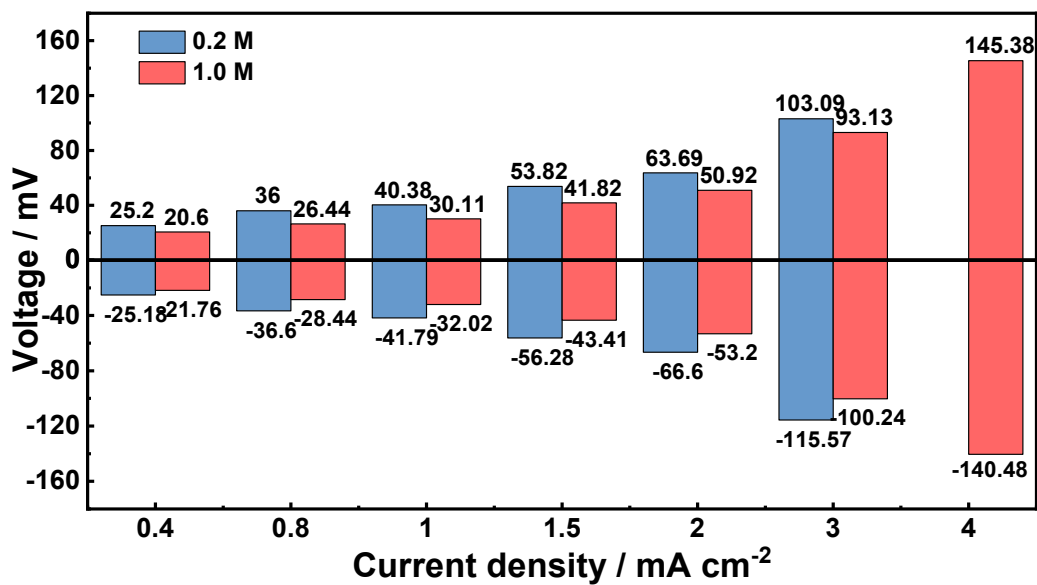| Electrolyte composition	Current density mA·cm^{-2}	Over-potential mV	Viscosity mPa·s	Ionic conductivity mS·cm^{-1}	Reference
1.0M $ZnCl_2$ ChCl-2Urea-2EG	**1**	**33**	**69.2**	**3.56**	*This Work*
$ZnCl_2$-4EG	1	125.9	126.73	1.15	*Angew Chem Int Edit* **2022**, *61.*[6]
$Zn(TFSI)_2$-7Acetamide	0.1	55	798	0.31	*Nat. Commun.* **2019**, *10.*[7]
LiTFSI-20$Zn(TFSI)_2$-3.8Urea/**2H$_2$O**	0.1	69.1	139	1.85	*Nano Energy* **2019**, *57, 625-634.*[8]
30 m $ZnCl_2$ + 15 m ChCl **H$_2$O**	0.2	35	220.8	1.255	*Chem. Eng. J.* **2023**, *456.*[9]
$ZnCl_2$:acetamide:**H$_2$O** **is 1:3:1**	0.1	65	250	1.1	*Adv. Funct. Mater.* **2021**, *31.*[10]

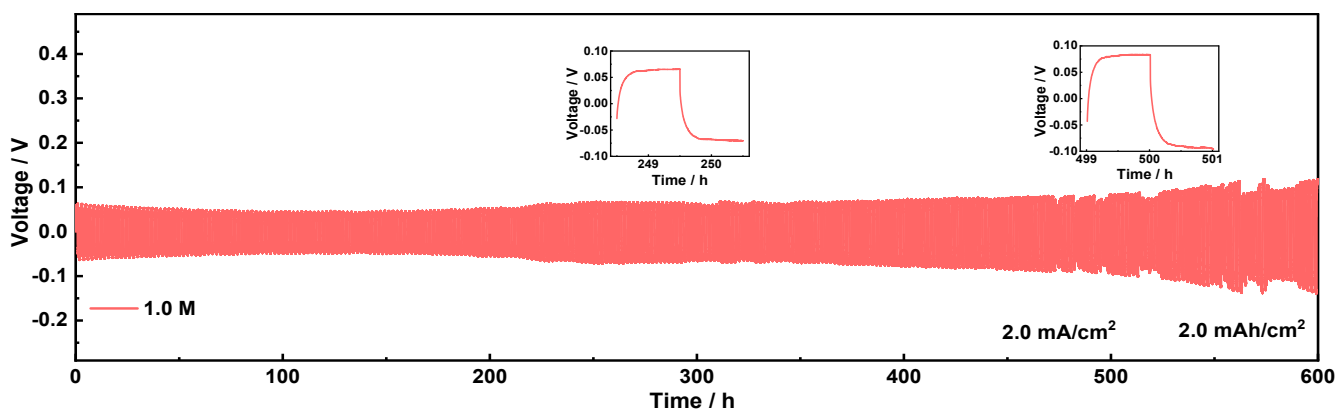**Fig. S10** Over-potential of Zn‖Zn symmetric cells at current densities from 0.4 to 4.0 mA·cm⁻²

Fig. S11 Cycling performance of the Zn‖Zn symmetric cells at a current density of 2.0 mA·cm^{-2} for 2 mAh·cm^{-2} with 1.0 M ZnCl$_2$ electrolyte
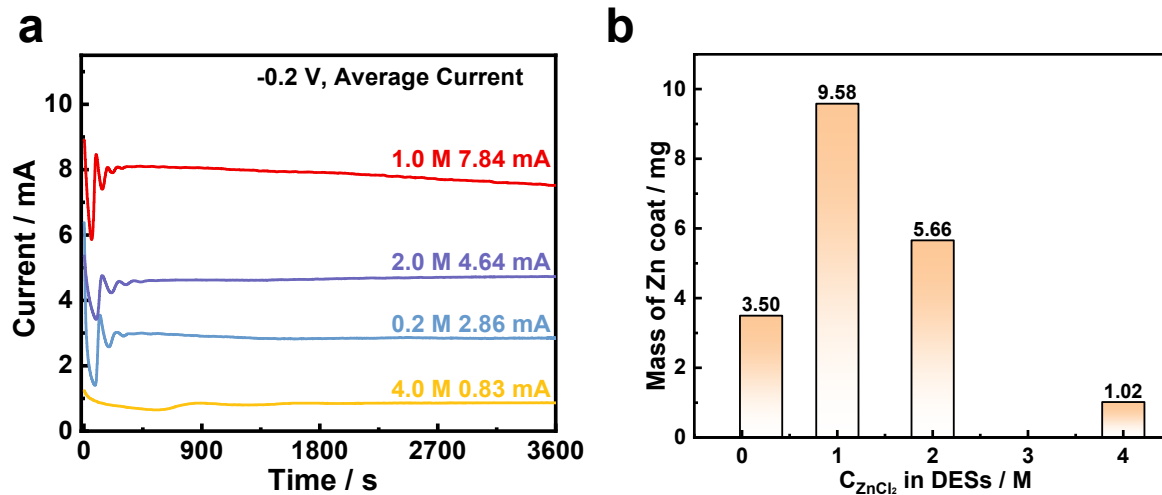
Fig. S12 a) The current-time curves for -0.2 V (vs. Zn/Zn^{2+}) over a duration of 3600 s at the various C_{ZnCl_2}; b) The mass of Zn coating at the various C_{ZnCl_2};
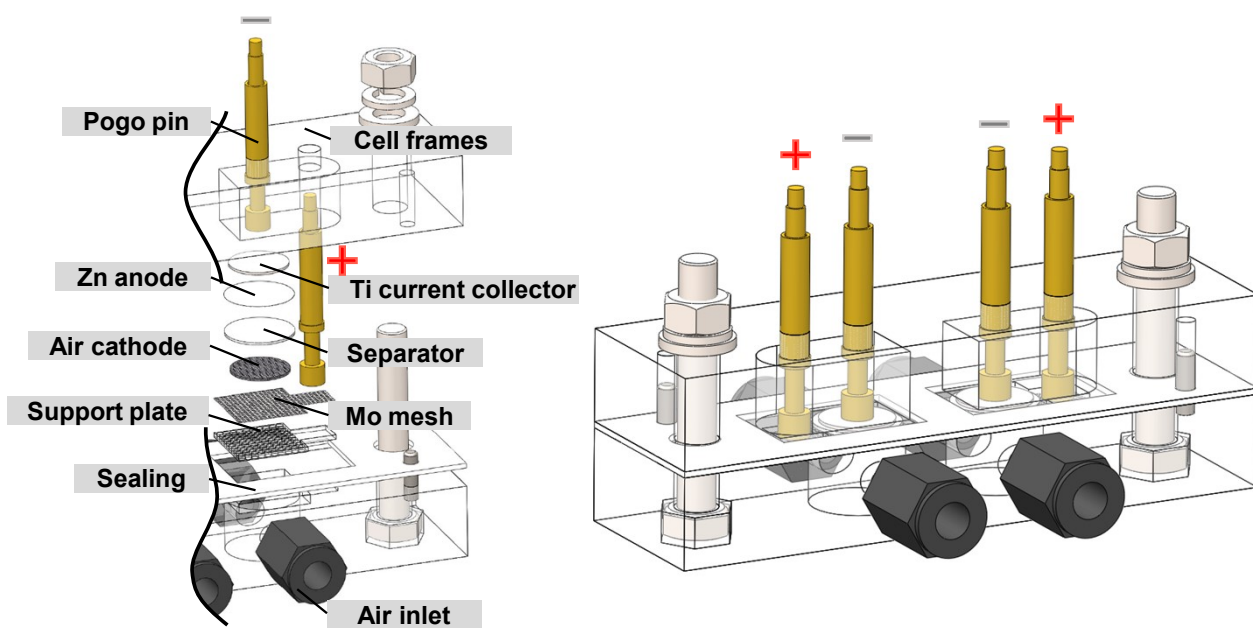
Fig. S13 The schematic drawing of Zn-air cell set up in which the cathode is C loaded on a gas diffusion layer and the anode is Zn foil;
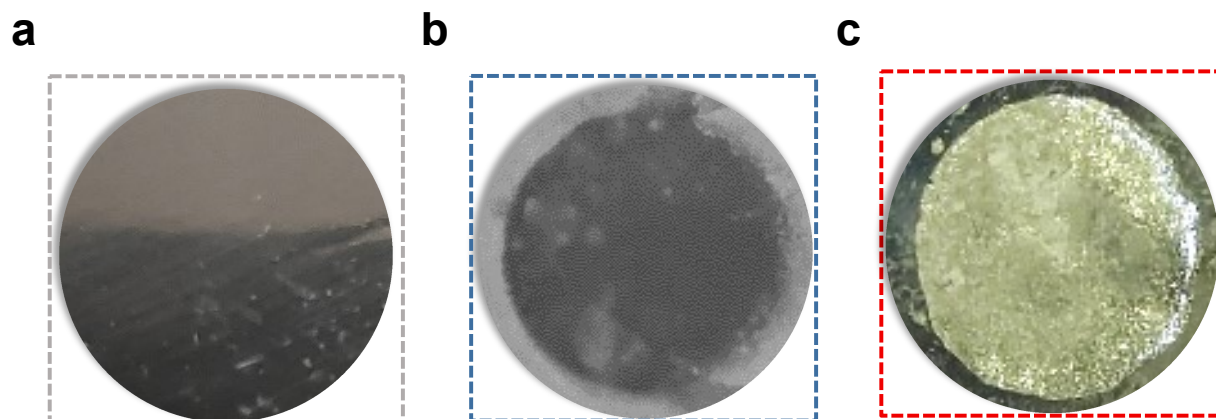
Fig. S14 a) The photographs of the fresh Zn anode; b) The Zn anode after discharge in 6 M KOH + 0.2 M $ZnCl_2$; c) The Zn anode after discharge1.0 M $ZnCl_2$ DES electrolytes

References

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