

Supplementary information for

**Rational design of aqueous zinc-ion battery electrolytes
based on intermolecular interactions between co-solvents
and anions**

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This includes Supplementary Table 1 and Supplementary Fig. S1 to S12.

Table S1 Compositions and miscibility of the electrolytes investigated in this study.

S/N	Electrolyte composition	Abbreviation	Miscibility
1	2.0 M ZnSO ₄ in H ₂ O	ES	O *
2	2.0 M ZnSO ₄ in H ₂ O/THF (10:0.5mol/mol)	ES-THF-0.5	X *
3	1.0 M Zn(OTF) ₂ in H ₂ O	ET	O *
4	1.0 M Zn(OTF) ₂ in H ₂ O/THF (10:0.5 mol/mol)	ET-THF-0.5	O *
5	1.0 M Zn(OTF) ₂ in H ₂ O/THF (10:1.5 mol/mol)	ET-THF-1.5	O *
6	1.0 M Zn(OTF) ₂ in H ₂ O/THF (10:2.5 mol/mol)	ET-THF-2.5	O *
7	1.0 M Zn(OTF) ₂ in H ₂ O/THF (10:3.5 mol/mol)	ET-THF-3.5	O *

* “X” and “O” represent immiscible (two-phase) and miscible system, respectively.

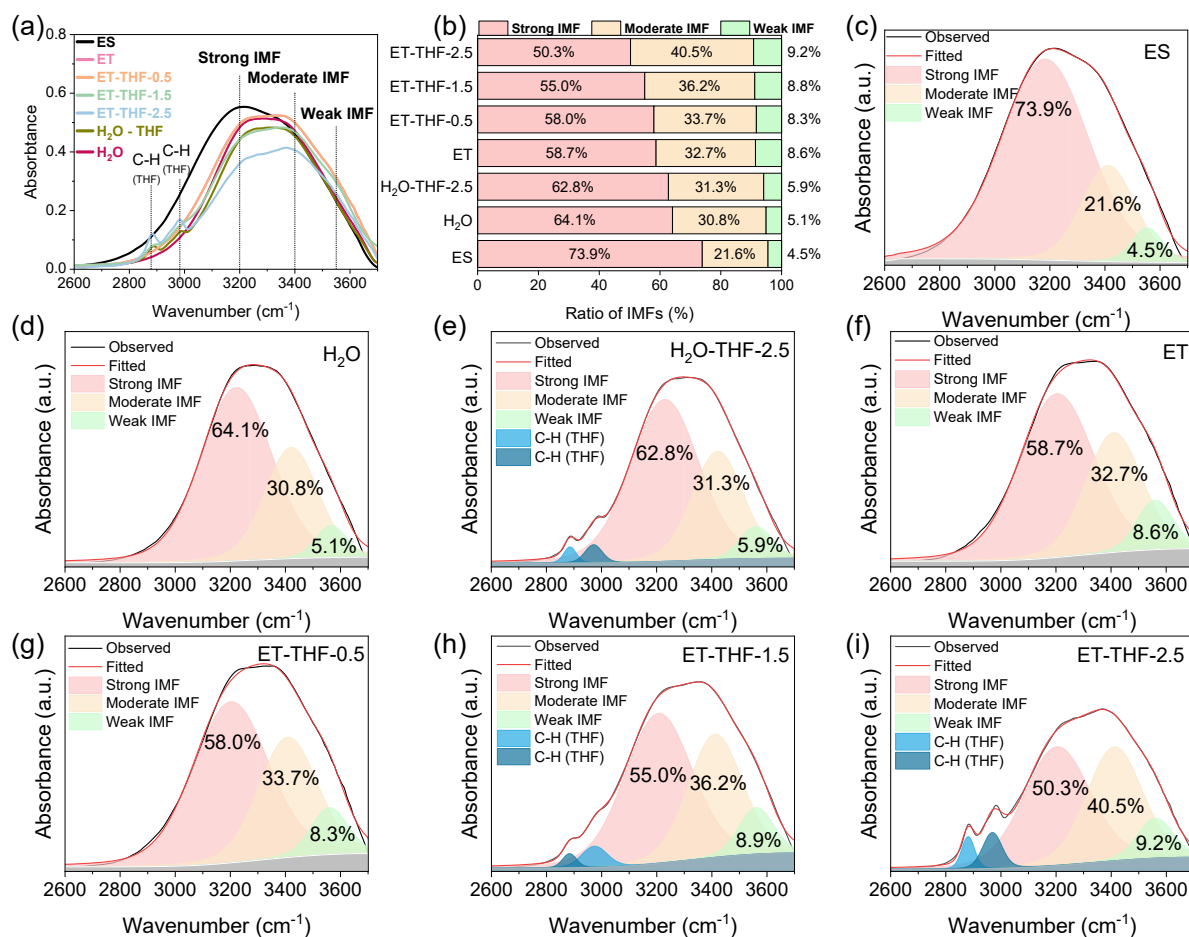


Fig. S1 FT-IR spectra of the various electrolytes considered in this study focusing on the O–H stretching band region (2600–3750 cm^{-1}). Gaussian deconvolution was applied to resolve overlapping sub-bands, enabling detailed examination of hydrogen-bonding structures and strong, moderate, and weak intermolecular forces (IMFs).

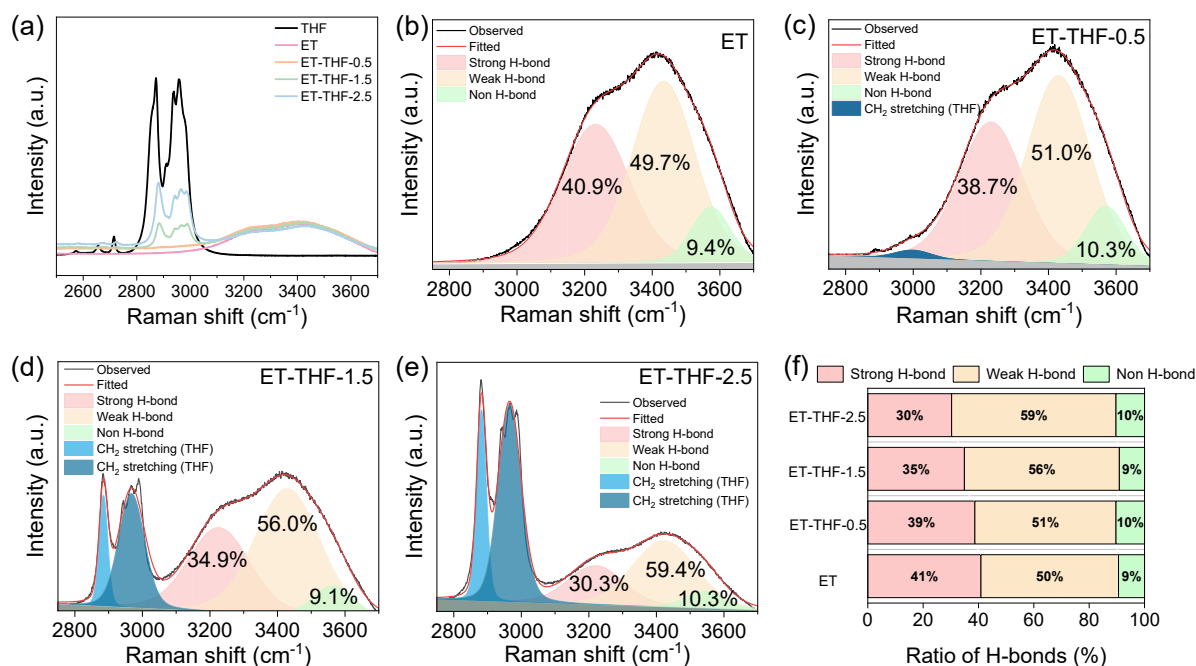


Fig. S2 Raman spectroscopic analysis of ET-based electrolytes with different THF contents. (a) Raman spectra in the O-H stretching region for ET, and ET-THF-series. (b-e) Deconvolution of the O-H stretching bands for (b) ET, (c) ET-THF-0.5, (d) ET-THF-1.5, and (e) ET-THF-2.5, showing contributions from strong hydrogen-bonded, weak hydrogen-bonded, and non-hydrogen-bonded water species, including CH_2 stretching modes of THF. (f) Relative ratios of different hydrogen-bonding states derived from Raman peak fitting for each electrolyte.

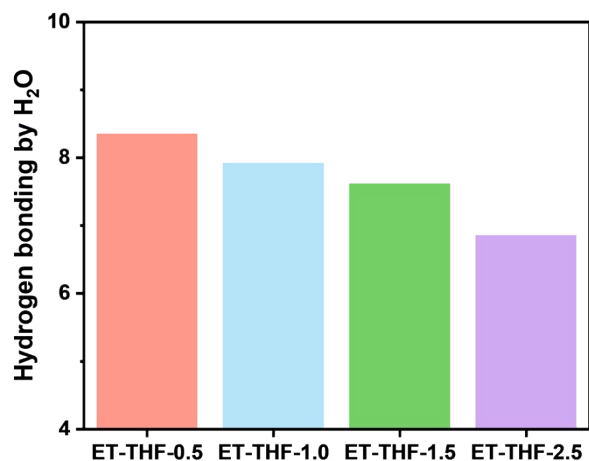


Fig. S3 The number of hydrogen bonds formed by water molecules in the first solvation shell of Zn^{2+} in ET-THF series, which was calculated in relation to the hydrogen-bonding network. Due to the strong electrostatic attraction of Zn^{2+} , hydrogen bonding between water molecules within the first shell is hindered. The connectivity between water molecules was analyzed, revealing that the average number of hydrogen bonds decreased from 8.35 to 6.78 with increasing THF content. This quantitatively demonstrates that THF entry into the first shell physically blocks and disrupts the previously robust hydrogen bonding network, which is structure-breaking.

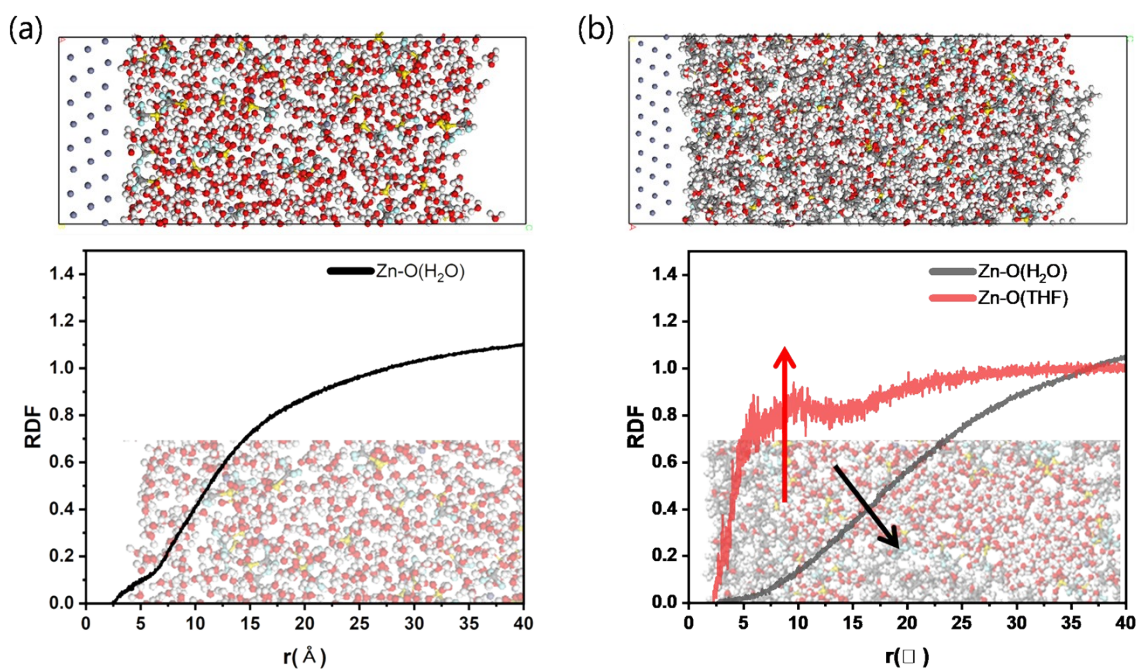


Fig. S4 Molecular dynamics (MD) simulation results for ET and ET-THF-2.5 on Zn (101) surface, where the distribution of H₂O or THF molecules along the distance from a zinc atom on (101) surface is simulated. (a) RDF of Zn-H₂O in ET, (b) and RDF of Zn-H₂O and Zn-THF in ET-THF-2.5. For (101) plane, much stronger adsorption energy is expected in Zn-THF over Zn-H₂O from DFT study.

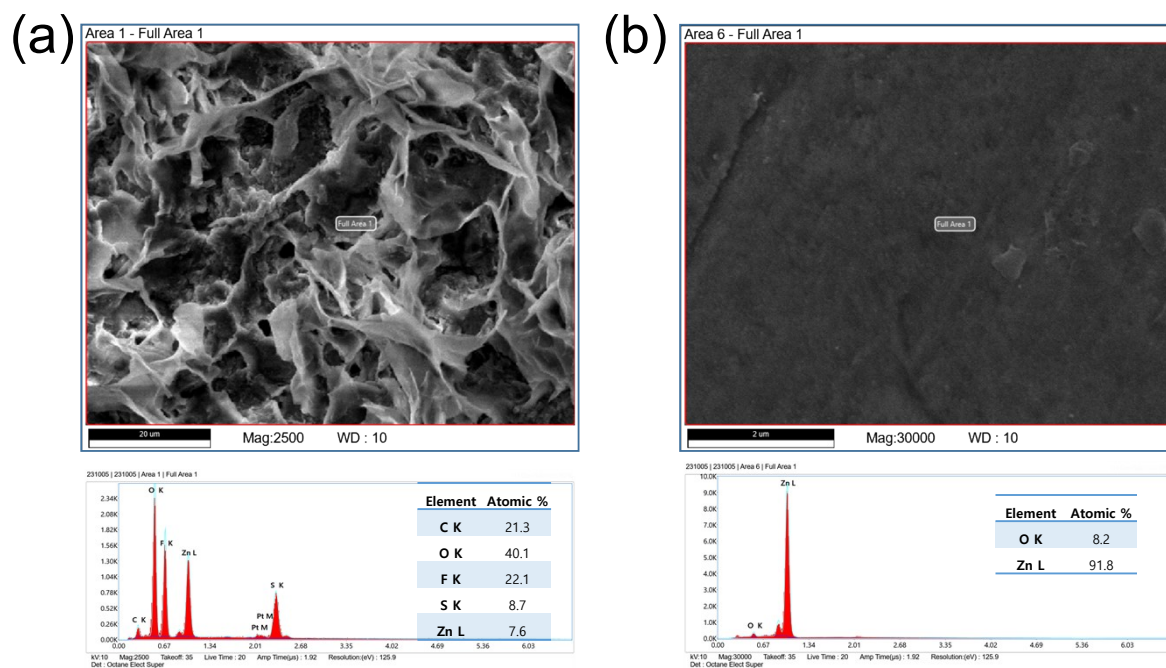


Fig. S5 SEM images and EDS analyses of (a) Zn foil after 48 h immersion in ET electrolyte and (b) pristine Zn foil.

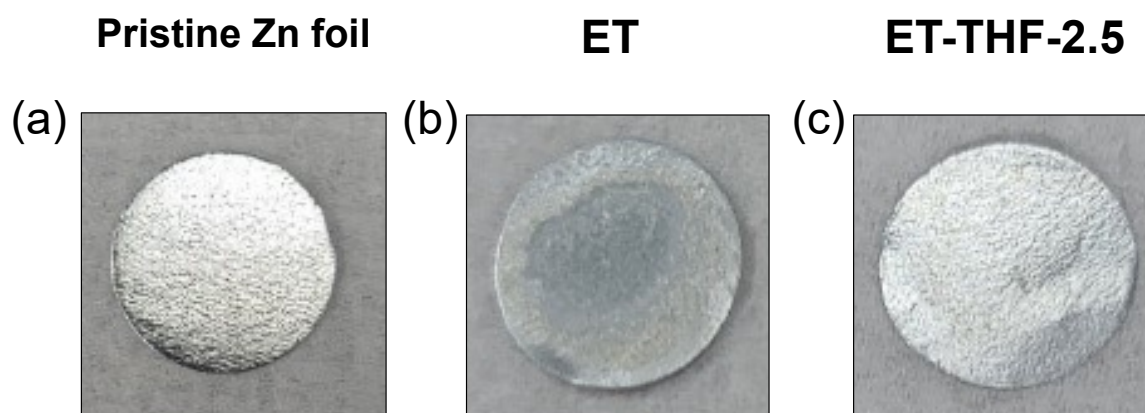


Fig. S6 Photographs of (a) pristine Zn foil, Zn foils after immersion for 48 h in (b) ET and (c) ET-THF-2.5 electrolytes.

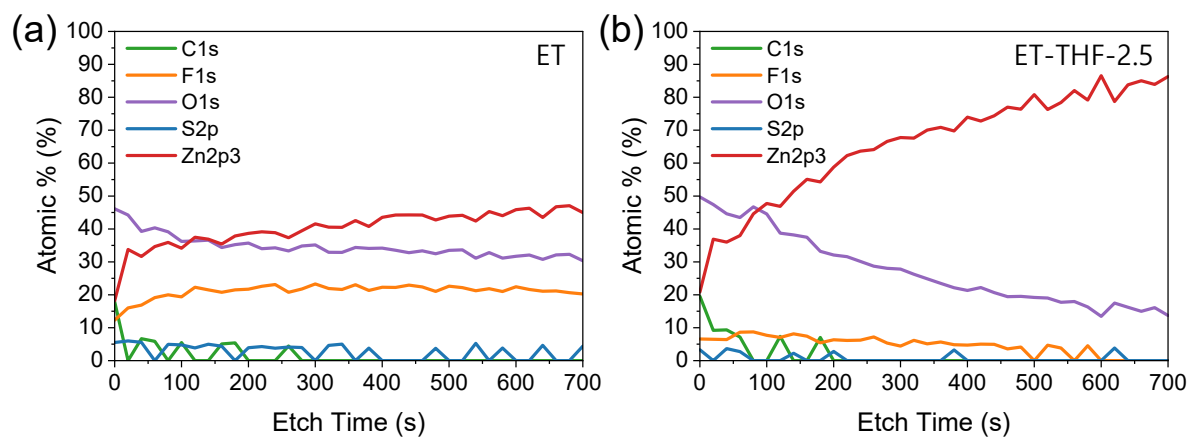


Fig. S7 XPS depth profiles of Zn foils immersed for 24 h in (a) ET and (b) ET-THF-2.5 electrolyte, showing compositional variation along the depth.

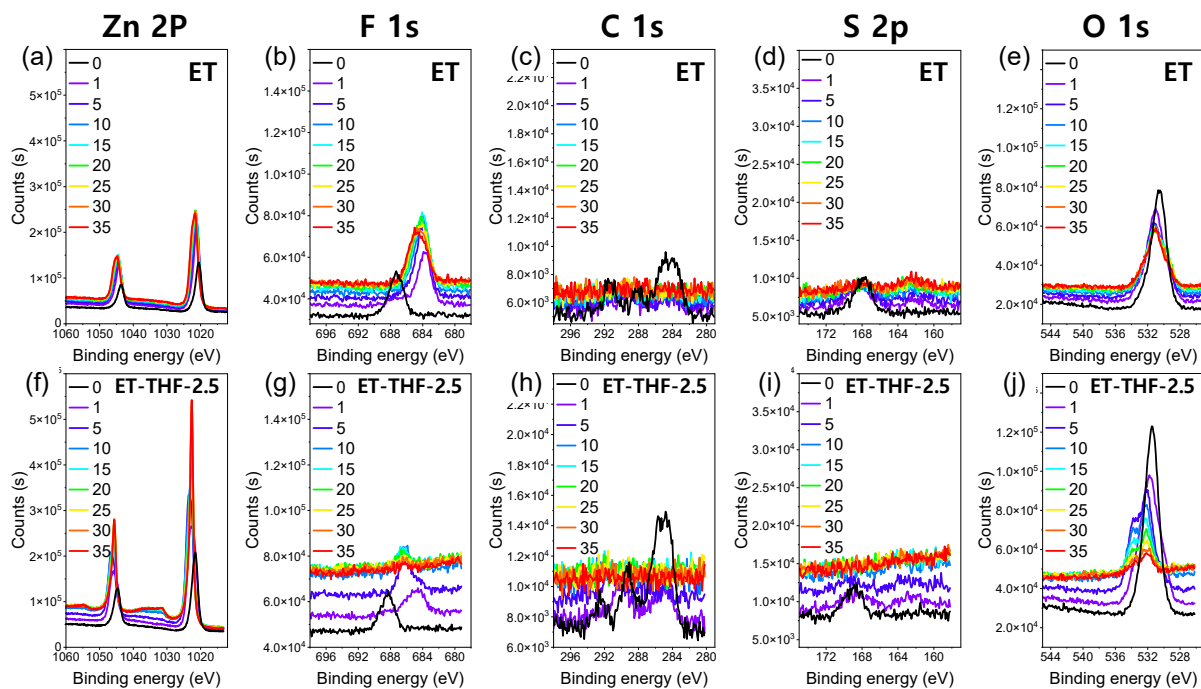


Fig. S8 XPS depth profiling spectra of Zn foils immersed for 24 h in ET or ET-THF-2.5 electrolytes for two days. The spectra were collected at successive etching levels for (a,f) Zn 2p, (b,g) F 1s, (c,h) C 1s, (d,i) S 2p, and (e,j) O 1s regions, where the upper (a,b,c,d,e) and lower (f,g,h,i,j) panels correspond to the ET and ET-THF-2.5, respectively.

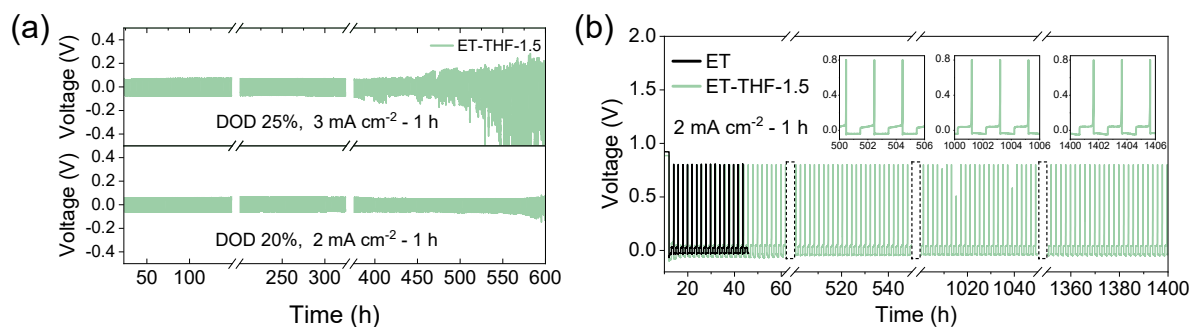


Fig. S9 Zn plating-stripping characteristics in ET-THF-1.5. (c) Zn plating-stripping profiles in Zn||Zn symmetrical cells with DOD 25% (3 mA cm^{-2} / 3 mAh cm^{-2}) and 20% (2 mA cm^{-2} / 2 mAh cm^{-2}). (b) Zn plating-stripping profiles in asymmetrical cells (Zn||Cu) with 2 mA cm^{-2} / 2 mAh cm^{-2} condition over 1,400 h

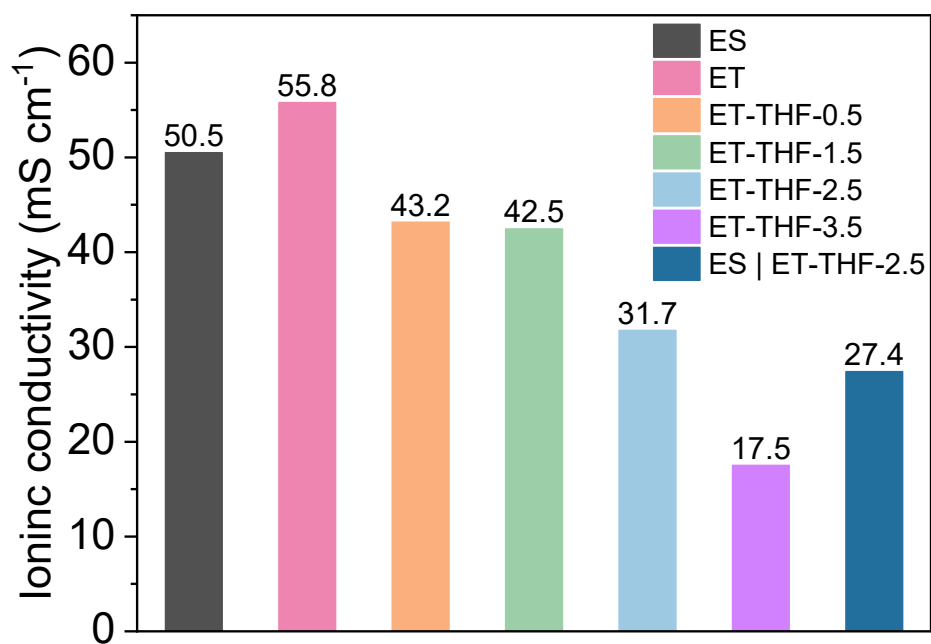


Fig. S10 Ionic conductivity of the electrolytes considered in this study measured by electrochemical impedance spectroscopy (EIS).

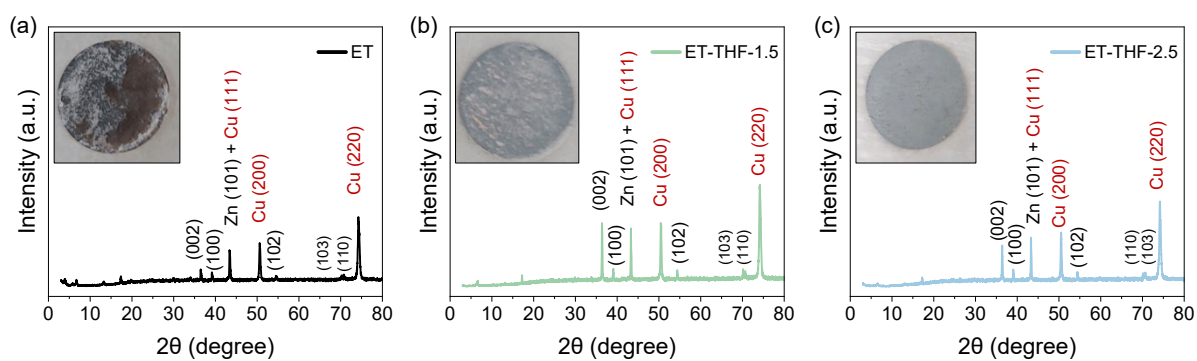


Fig. S11 XRD patterns of Zn deposited on Cu substrates in different electrolytes considered in this study, obtained after 20 cycles (1 mA cm^{-2} , 1 mAh cm^{-2}) followed by Zn plating during the 21st discharge.

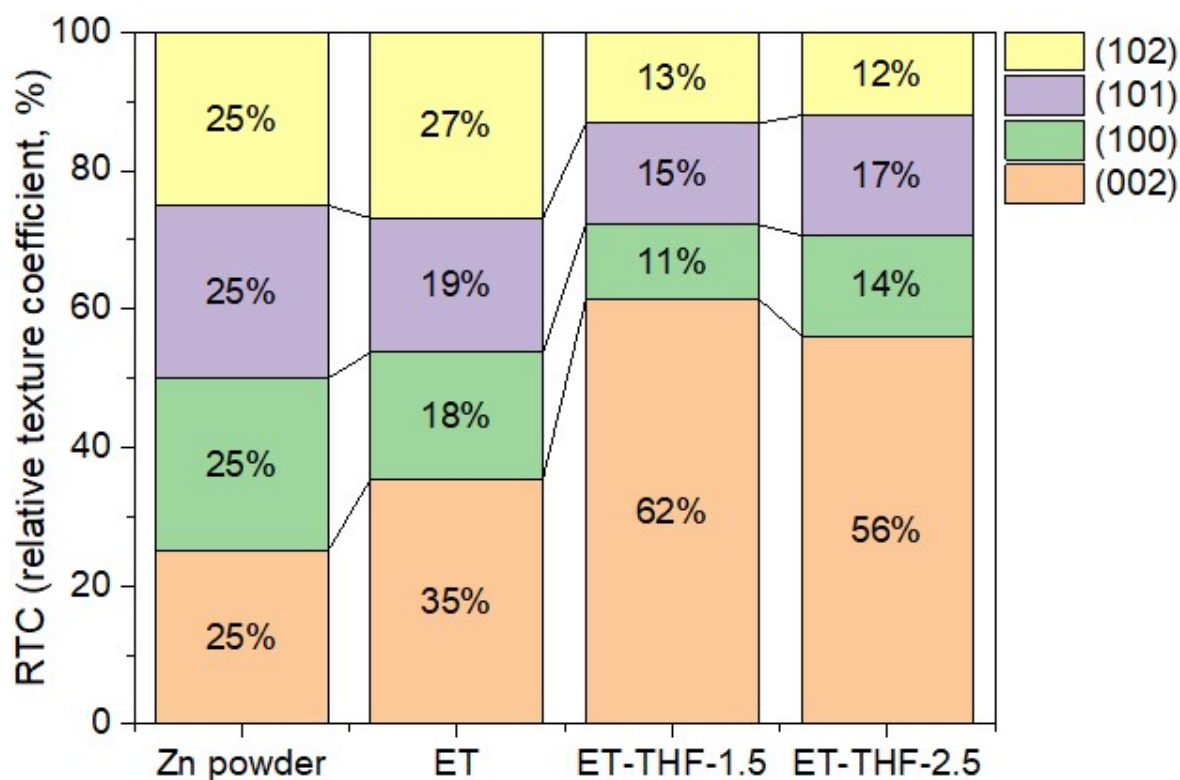


Fig. S12 Relative texture coefficient (RTC) analysis ^[1] derived from Zn (002), (100), (101), and (102) diffraction peaks in XRD patterns of Zn deposited on Cu substrates after the 21st discharge in different electrolytes. If RTC value for specific plane has value more than 25%, it indicates that the deposit (thin film) has a texture on that plane. The RTC values were calculated to quantify the preferred crystallographic orientation of the deposited Zn. For each (hkl) plane, the measured XRD peak intensity was normalized to the corresponding reference intensity taken from the Zn powder diffraction pattern. The relative texture coefficient was then obtained using the following expression:

$$RTC(hkl) = \frac{I(hkl)/I_0(hkl)}{\sum I(hkl)/I_0(hkl)} \times 100$$

where $I(hkl)$ is the measured peak intensity of the deposited Zn and $I_0(hkl)$ is the peak intensity of the same reflection in the Zn powder, which represents a randomly oriented sample. THF-containing electrolyte significantly increased the RTC value of the (002) plane beyond its reference fraction in Zn powder, demonstrating that Zn deposit tends to form (002)-texture when THF is present.

[1] Y. Ma, J. Pepas, G. Zhang, Z. Liu, Y. Su, J. Bai, H. Zhong, T. Li, W. Xu, M. Kang, J. Carsley, J. Kacher and H. Chen, Nat Commun, 2025, 16, 7448.

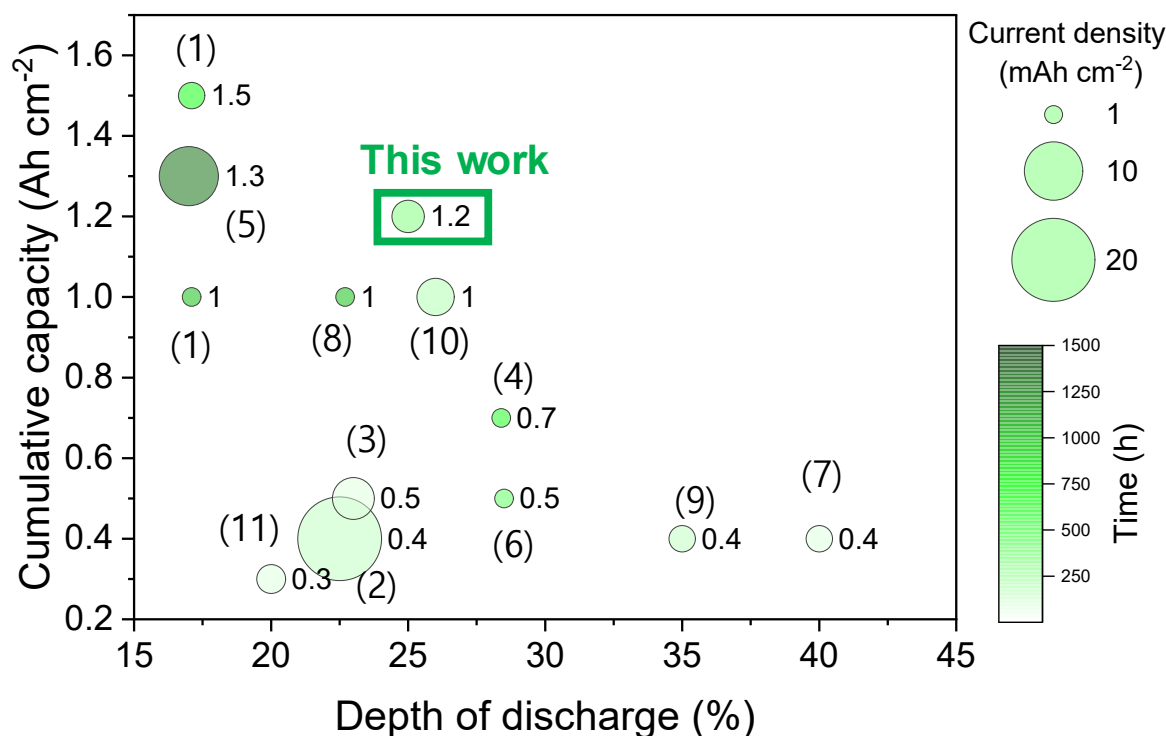


Fig. S13 Comparison of Zn symmetric cell performance between previously reported studies and this work, presented as cumulative capacity versus depth of discharge (DOD). Bubble size represents the applied areal current density, and the colour scale indicates cycling lifetime. Reference numbers are shown in brackets. Notably this work exhibits a higher cumulative capacity at moderate DOD compared with previously reported studies.

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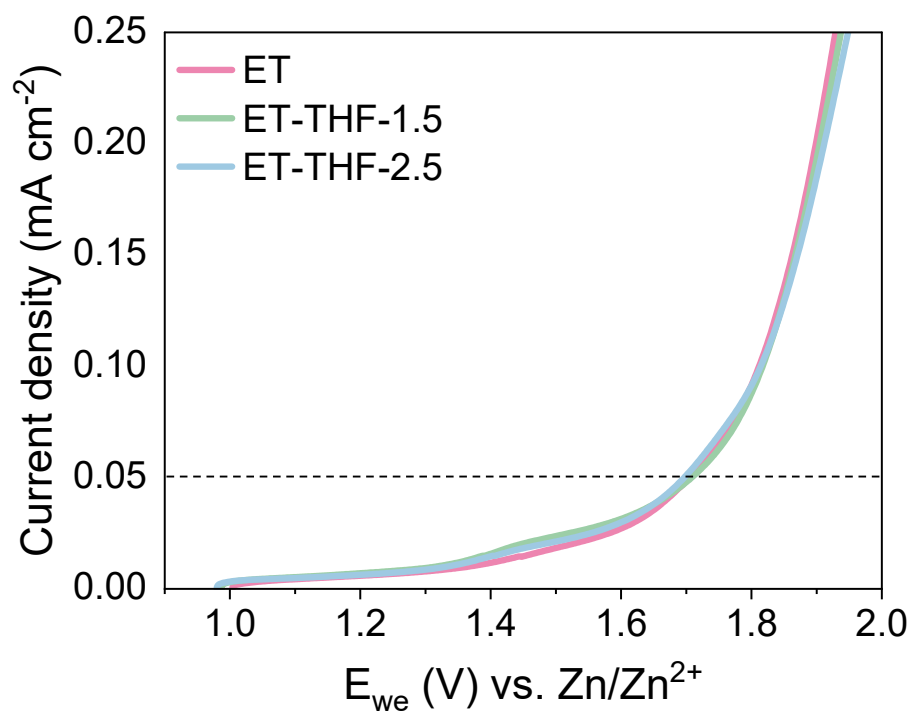


Fig. S14 Linear sweep voltammetry (LSV) curves of ES, ET, and ET-THF-2.5 electrolytes, measured in the potential range of 0–2 V at a scan rate of 25 mV s⁻¹, demonstrating their oxidative stability.

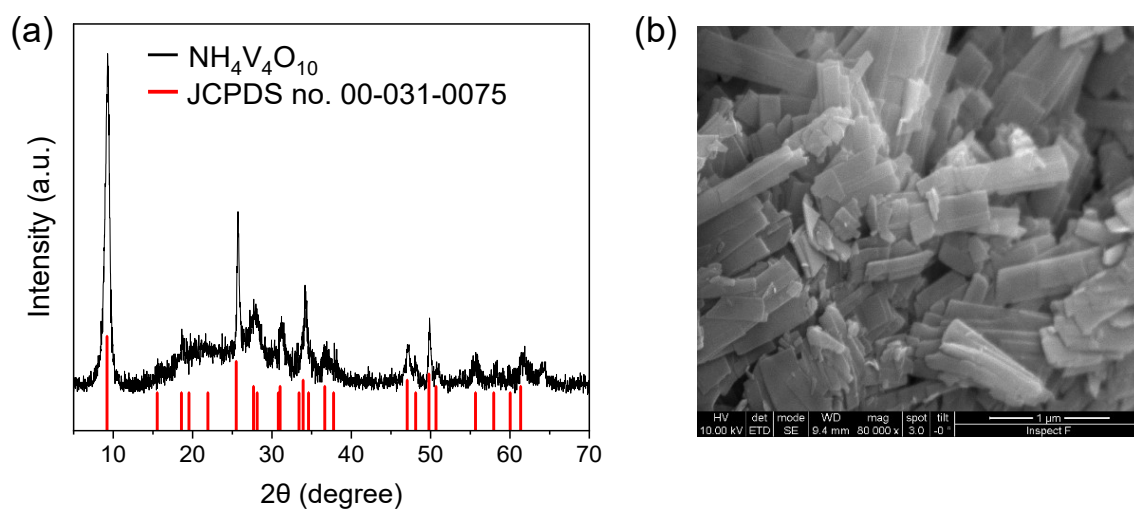


Fig. S15 (a) XRD pattern of $\text{NH}_4\text{V}_4\text{O}_{10}$ prepared by hydrothermal route, along with the stick pattern for reference JCPDS no. 00-031-0075 for phase identification. (b) SEM images showing the rod-like morphology.

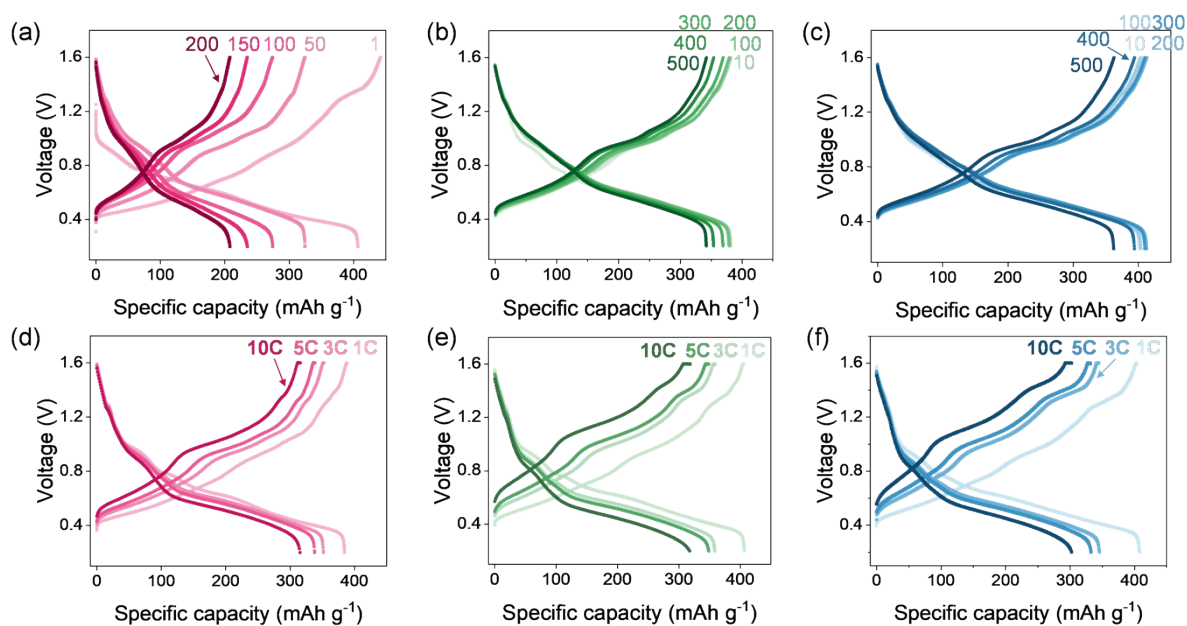


Fig. S16 Galvanostatic discharge/charge voltage profiles of Zn||NH₄V₄O₁₀ full cells with different electrolytes, (a) ET, (b) ET-THF-1.5, and (c) ET-THF-2.5 at 1C. Rate capability of Zn||NH₄V₄O₁₀ full cells with (d) ET, (e) ET-THF-1.5, and (f) ET-THF-2.5 at various C-rates.

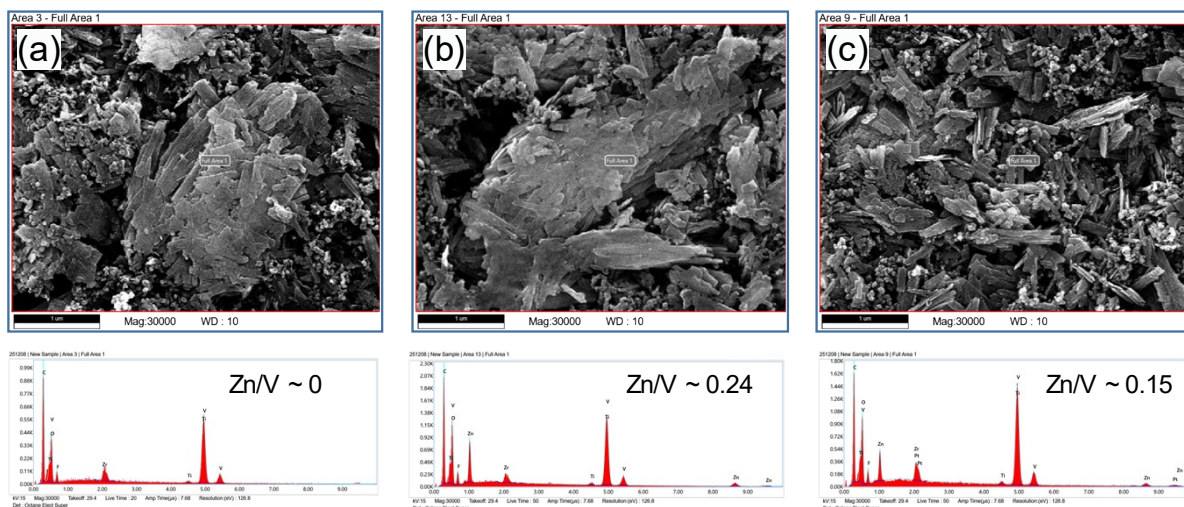


Fig. S17 SEM images and corresponding EDS spectra of $\text{NH}_4\text{V}_4\text{O}_{10}$ cathodes: (a) pristine cathode without electrochemical cycling, and (b,c) cathodes collected after 20 discharge-charge cycles at 1C ($=400 \text{ mAh g}^{-1}$), terminated in the charged state, using (b) ET and (c) ET-THF-2.5 electrolytes. The cycled cathodes exhibit a significant Zn content regardless of electrolyte type, suggesting partial trapping of Zn^{2+} within the interlayer galleries.

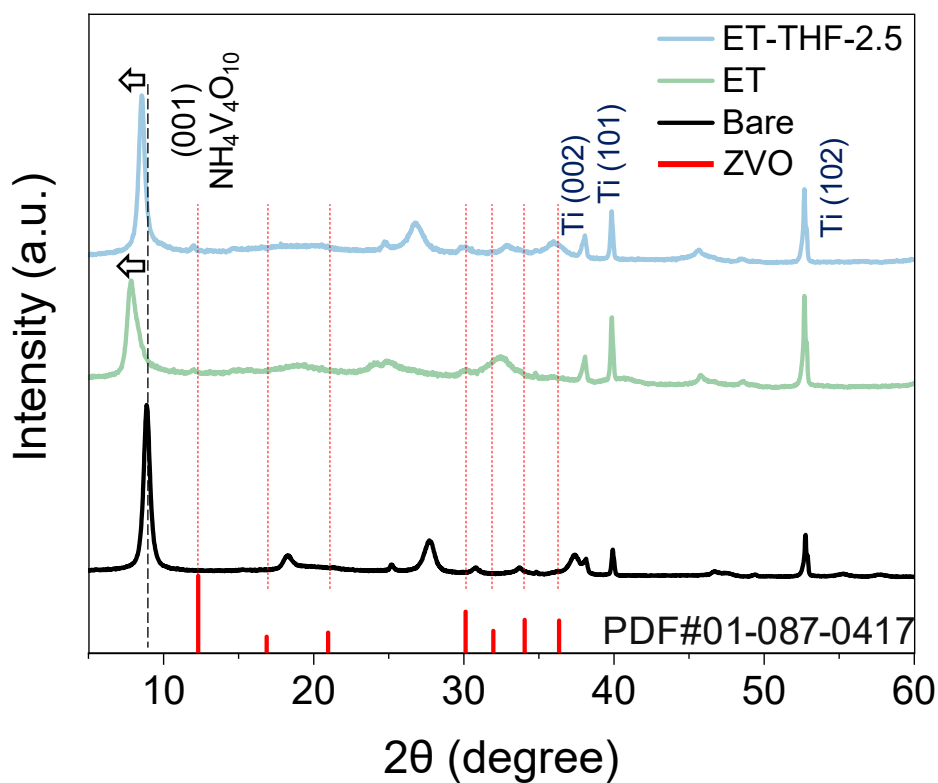


Fig. S18 XRD patterns of (i) pristine $\text{NH}_4\text{V}_4\text{O}_{10}$ cathode and (ii, iii) $\text{NH}_4\text{V}_4\text{O}_{10}$ cathodes after 20 discharge-charge cycles at 1C ($=400 \text{ mAh g}^{-1}$), collected in the charged state using (ii) ET and (iii) ET-THF-2.5 electrolytes. Stick pattern corresponds to the reference diffraction peaks of a possible corrosion product, zinc pyrovanadate (ZVO, $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot n\text{H}_2\text{O}$) (PDF# 01-087-0417). The cycled cathodes exhibited a significant expansion of (001) spacing after cycling in both cases, suggesting interlayer restructuring associated with Zn^{2+} trapping. Moreover, no discernible accumulation of corrosion products was observed on the cycled electrodes.