

Supporting Information

Engineering a Zinc Anode Interphasial Chemistry for Acidic, Alkaline and Non-aqueous

Electrolytes

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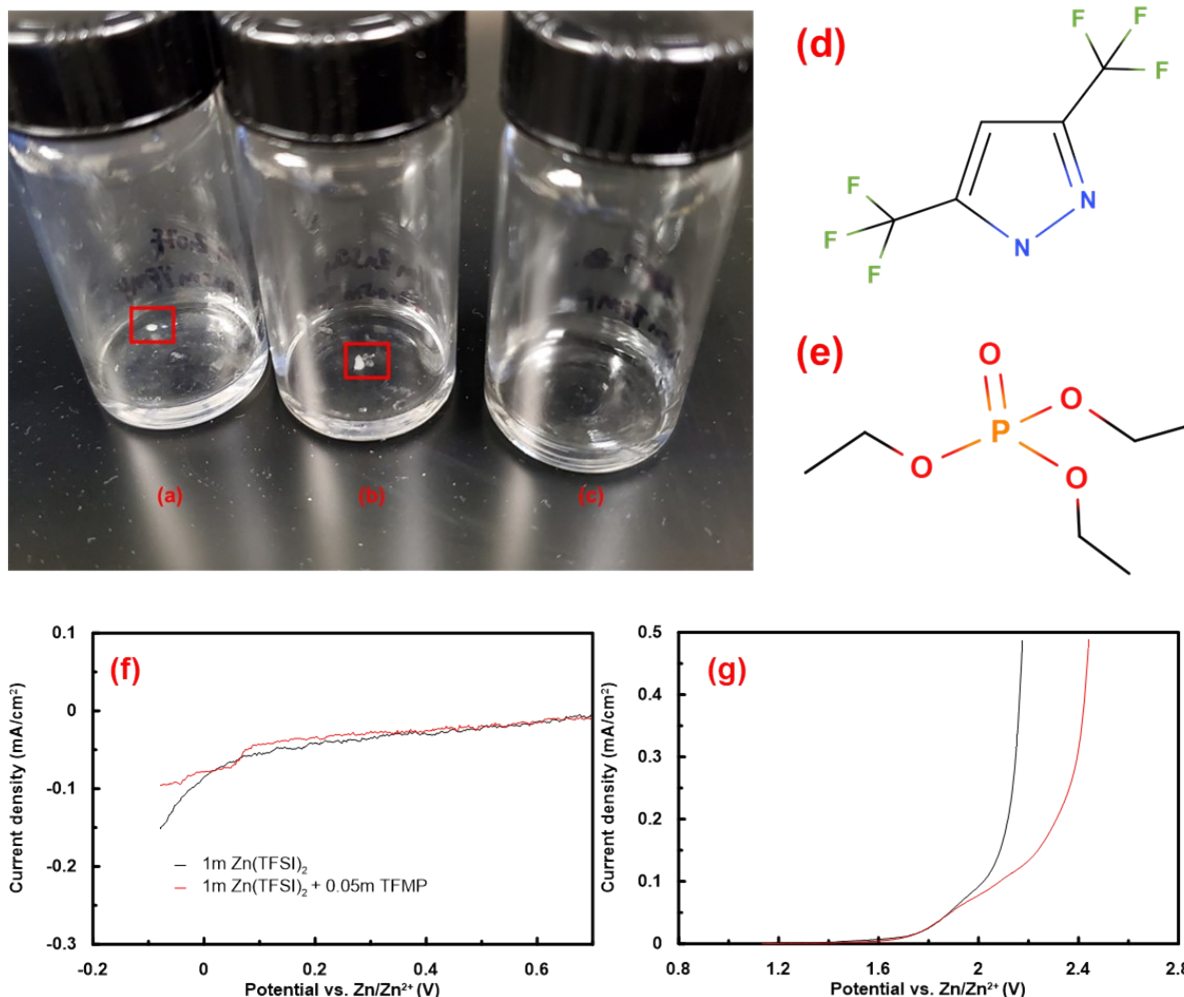


Figure S1. Solubility testing of TFMP (to accelerate the dissolution process, heating at 50°C is necessary) in different aqueous electrolytes: (a) 1m Zn(OTf)₂ + 0.05m TFMP in H₂O; (b) 1m ZnSO₄ + 0.05m TFMP in H₂O; (c) 1m Zn(TFSI)₂ + 0.05m TFMP in H₂O. Red squares indicate the undissolved TFMP in the electrolytes. Chemical structures of TFMP (d) and TEP (e). Electrochemical stability analysis of the aqueous Zn electrolytes including (f) cathodic region and (g) anodic region during 4th cycle. A three electrode Swagelok cell containing stainless steel (SS) as the working electrode, carbon black as the counter electrode and Ag/AgCl as the reference electrode was used for testing at a scan rate of 5mV/s at room temperature.

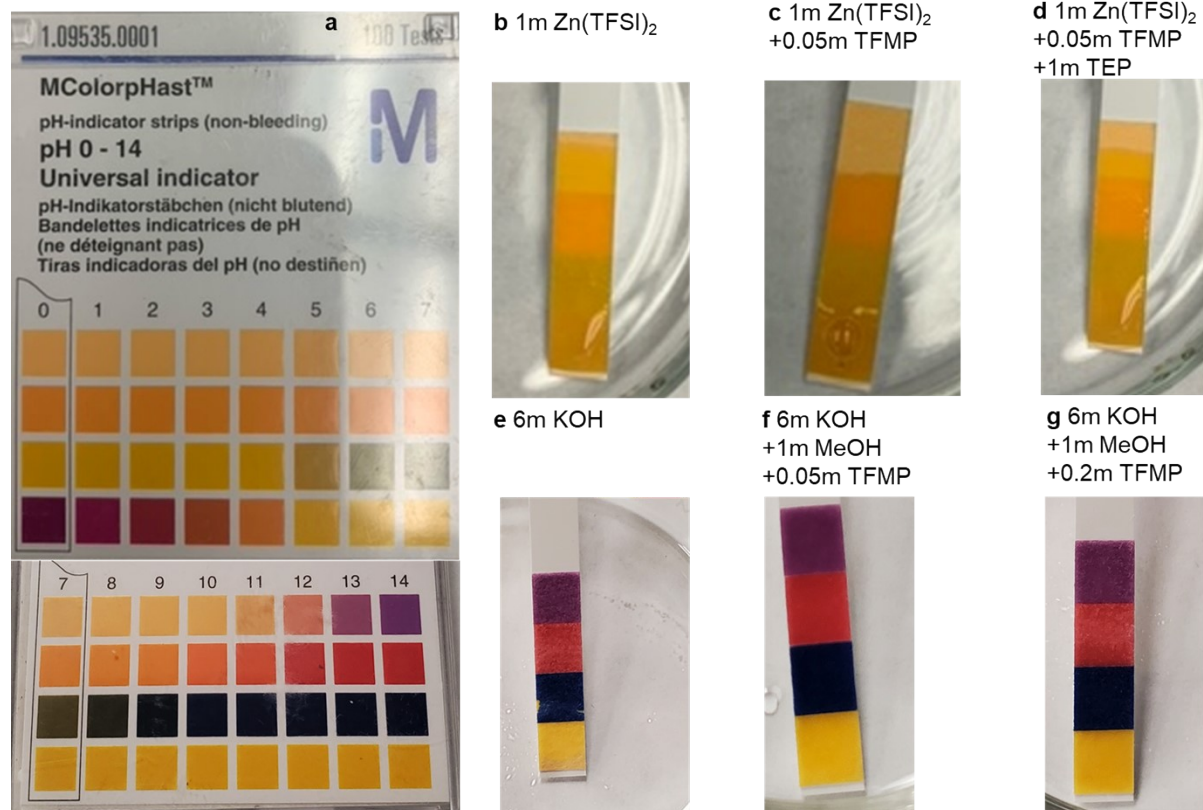


Figure S2. pH paper (a) testing results for different electrolytes: (b) 1m Zn(TFSI)_2 in H_2O ; (c) 1m Zn(TFSI)_2 + 0.05m TFMP in H_2O , (d) 1m Zn(TFSI)_2 + 0.05m TFMP + 1m TEP in H_2O , (e) 6m KOH in H_2O , (f) 6m KOH + 1m MeOH + 0.05m TFMP in H_2O and (g) 6m KOH + 1m MeOH + 0.2m TFMP in H_2O .

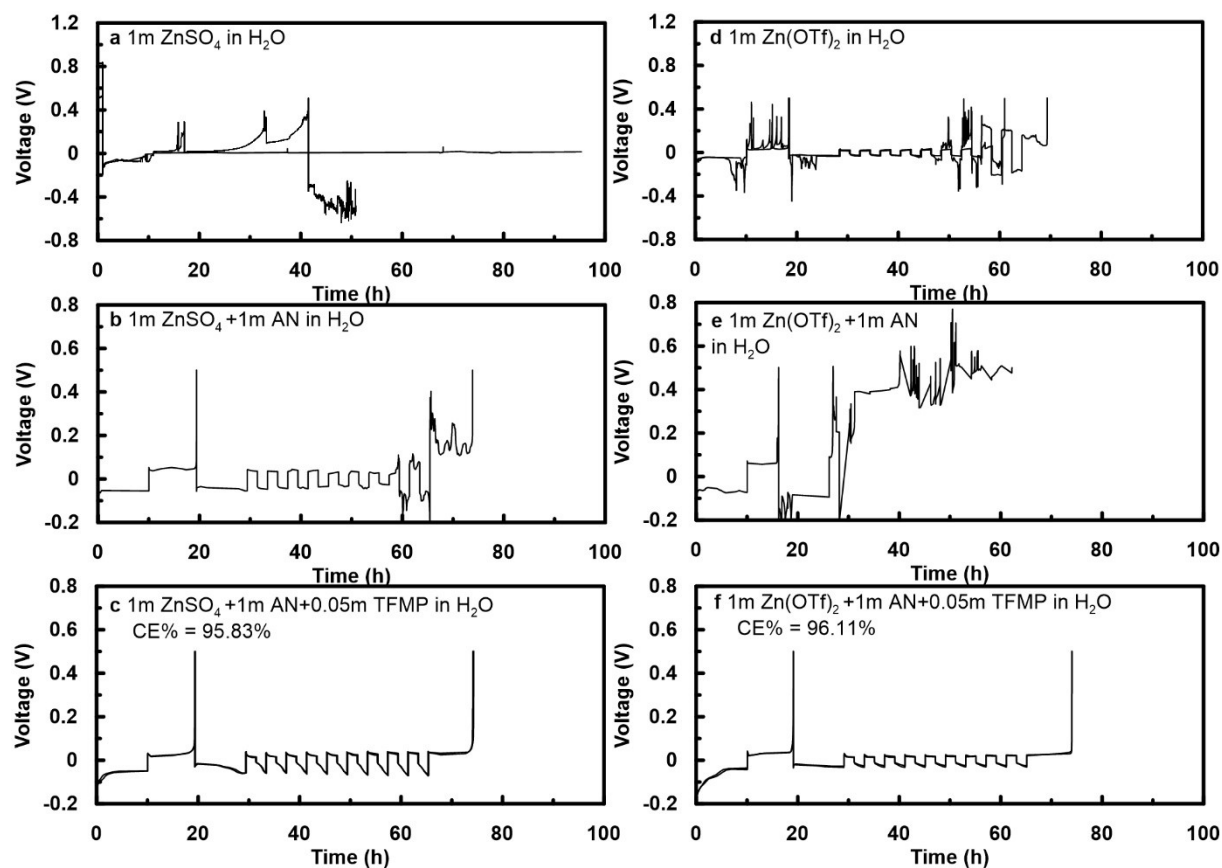


Figure S3. Voltage vs time for Cu|Zn cells at 25°C with different electrolytes: (a) 1m ZnSO₄ in H₂O; (b) 1m ZnSO₄ + 1m AN in H₂O; (c) 1m ZnSO₄ + 1m AN + 0.05m TFMP in H₂O (d) 1m Zn(OTf)₂ in H₂O (e) 1m Zn(OTf)₂ + 1m AN in H₂O, and (f) 1m Zn(OTf)₂ + 1m AN + 0.05m TFMP in H₂O. Cu was conditioned by plating (0.5 mA/cm², 5 mAh/cm²) and stripping Zn (0.5 V) during the first cycle. Then a Zn reservoir with a capacity of 5 mAh/cm² was built on the Cu substrate using 0.5 mA/cm². 0.5 mA/cm² was used for stripping and plating Zn during the following 9 cycles. A capacity of 1mAh/cm² Zn was plated or stripped in each cycle. The cell was charged to 0.5 V to strip Zn during the last step.

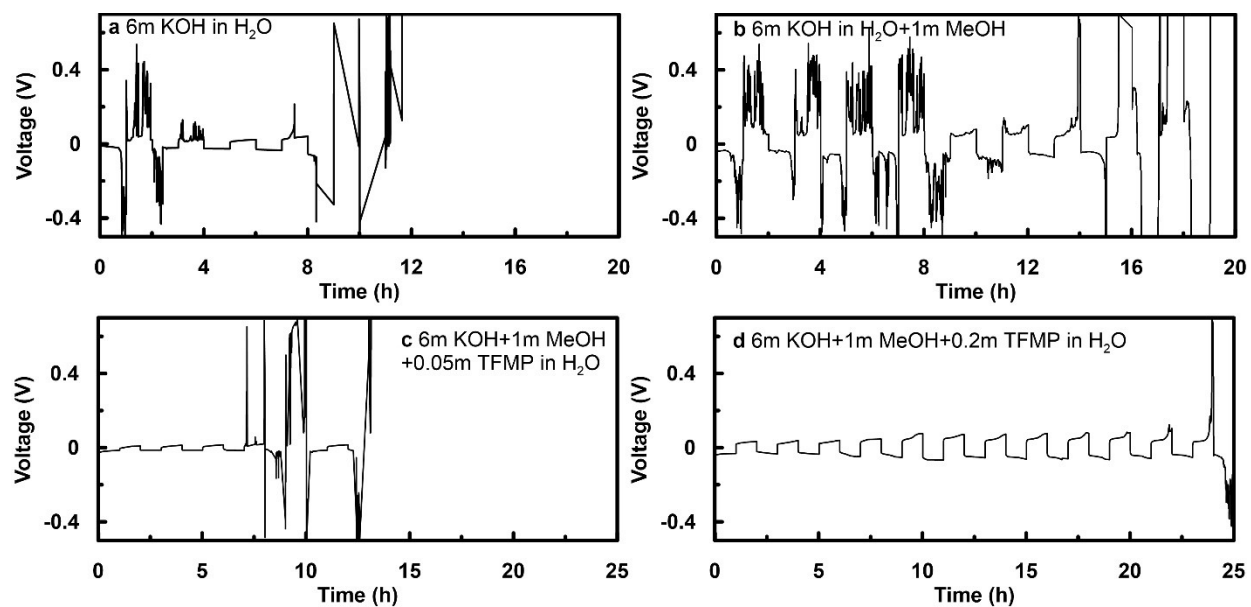


Figure S4. Voltage vs time for Zn|Zn cells (0.5 mA cm^{-2} , 0.5 mAh cm^{-2} per cycle) at 25°C with different electrolytes: (a) 6m KOH in H₂O, (b) 6m KOH+1m MeOH in H₂O, (c) 6m KOH+1m MeOH+0.05m TFMP in H₂O and (d) 6m KOH+1m MeOH+0.2m TFMP in H₂O.

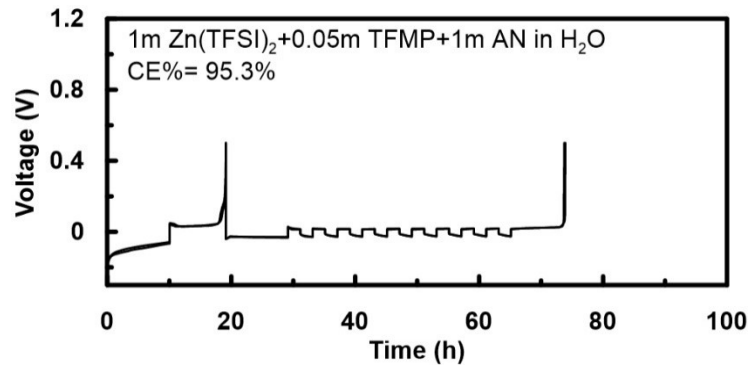


Figure S5. Voltage vs time for Cu|Zn cells at 25°C with 1m Zn(TFSI)₂ + 1m AN + 0.05m TFMP in H₂O. Cu was conditioned by plating (0.5 mA/cm², 5 mAh/cm²) and stripping Zn (0.5 V) during the first cycle. Then a Zn reservoir with a capacity of 5 mAh/cm² was built on the Cu substrate using 0.5 mA/cm². 0.5 mA/cm² was used for stripping and plating Zn during the following 9 cycles. A capacity of 1mAh/cm² Zn was plated or stripped in each cycle. The cell was charged to 0.5 V to strip Zn during the last step.

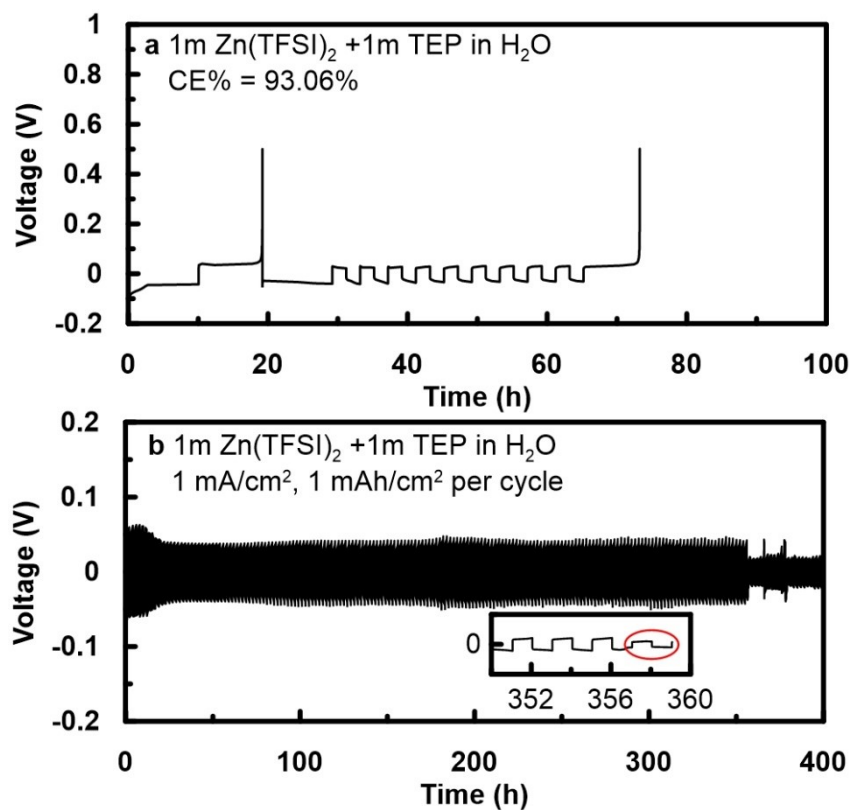


Figure S6. Voltage vs time for (a) Cu|Zn cells and (b) Zn|Zn cells at 25°C with electrolyte of 1m Zn(TFSI)₂ + 1m TEP in H₂O. Cu was conditioned by plating (0.5 mA/cm², 5 mAh/cm²) and stripping Zn (0.5 V) during the first cycle. Then a Zn reservoir with a capacity of 5 mAh/cm² was built on the Cu substrate by using the same current density used for the following cycling. Different current density (i.e. 0.25 mA/cm², 0.5 mA/cm², 1mA/cm² and 2.5 mA/cm²) was used for stripping and plating Zn during the following 9 cycles. A capacity of 1mAh/cm² (Q_c) Zn was plated or stripped in each cycle. In the final step, a capacity was observed when plated Zn was stripped by charging to 0.5 V. The red circle in (b) suggests cell short circuit.

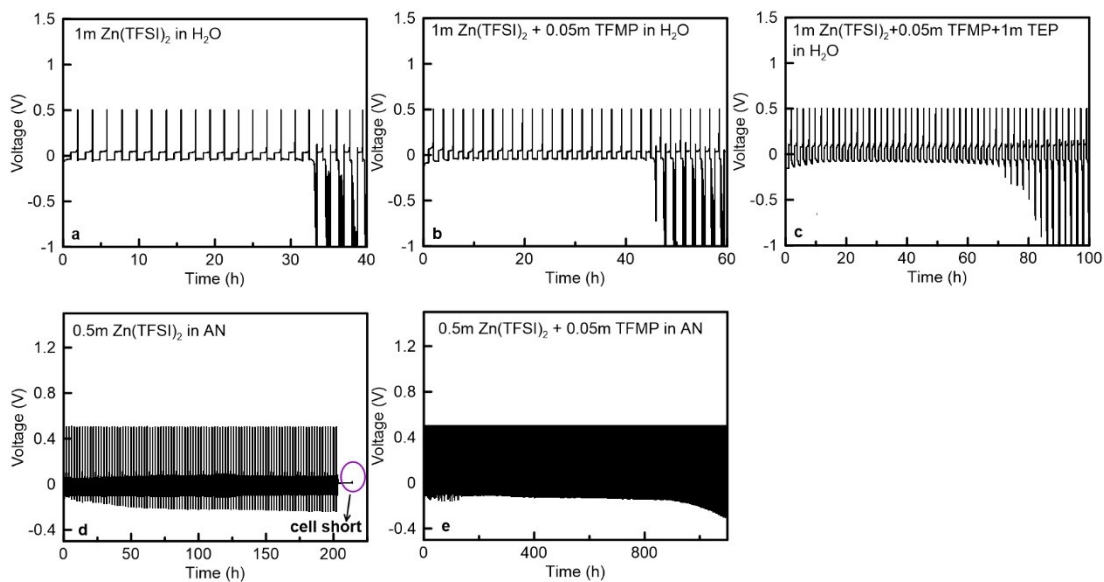


Figure S7. Voltage vs time for Cu|Zn (10 μm) cells (during each cycle 1.17 mA/cm^2 , 1.17 mAh/cm^2 (20% Zn utilization) were used to plate Zn on Cu substrate, then charged to 0.5 V to strip Zn) at room temperature with different electrolytes: (a) 1m $\text{Zn}(\text{TFSI})_2$ in H_2O ; (b) 1m $\text{Zn}(\text{TFSI})_2$ + 0.05m TFMP in H_2O ; (c) 1m $\text{Zn}(\text{TFSI})_2$ + 0.05m TFMP + 1m TEP in H_2O ; (d) 0.5m $\text{Zn}(\text{TFSI})_2$ in AN; (e) 0.5m $\text{Zn}(\text{TFSI})_2$ + 0.05m TFMP in AN. Corresponding CE for (a) has been shown in Figure 1.

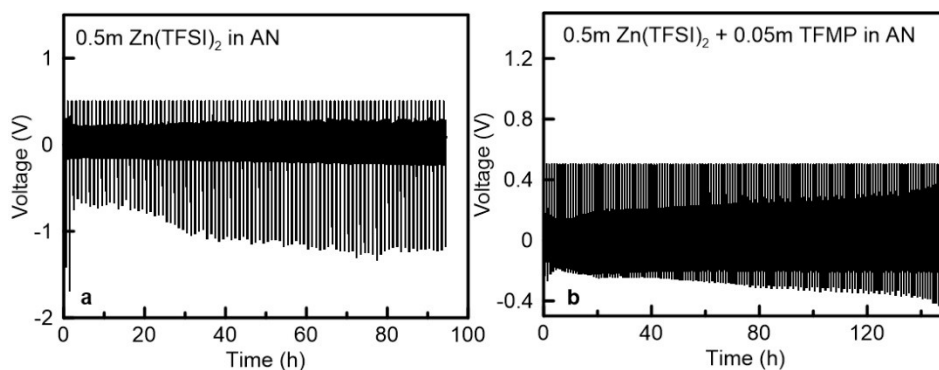


Figure S8. Voltage vs time for Cu|Zn (10 mm) cells (during each cycle 9.36 mA/cm², 4.68 mAh/cm² (80% Zn utilization) were used to plate Zn on Cu substrate, then charged to 0.5 V to strip Zn) at room temperature with different electrolytes: (a) 0.5m Zn(TFSI)₂ in AN; (b) 0.5m Zn(TFSI)₂ + 0.05m TFMP in AN. Corresponding CE for (a) has been shown in Figure 1.

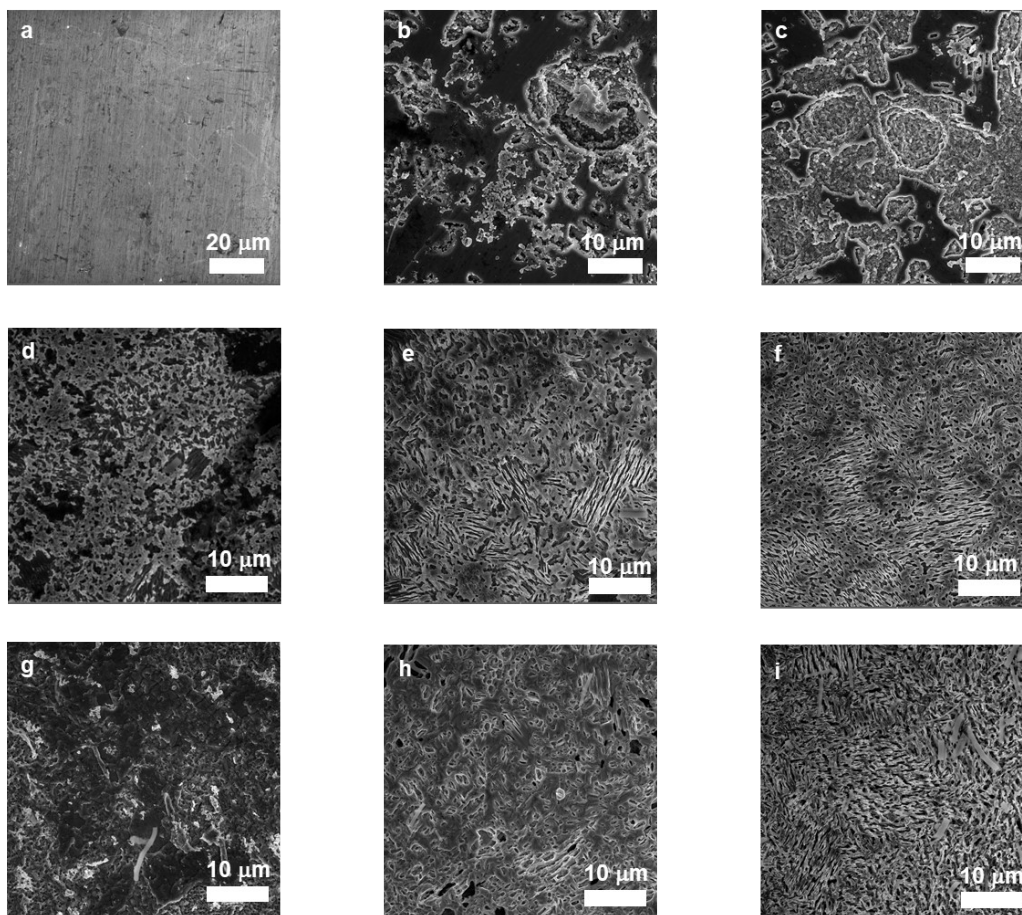


Figure S9. (a) SEM images of Zn metal anode (100 μm) before cycling and after 10 h room temperature cycling (b-i) obtained from Zn|Zn symmetric cells at zero state of charge with different electrolytes: (b) 0.5m $\text{Zn}(\text{TFSI})_2$ in AN, (c) 0.5m $\text{Zn}(\text{TFSI})_2$ + 0.05m TFMP in AN, (d, g) 1m $\text{Zn}(\text{TFSI})_2$ in H_2O , (e, h) 1m $\text{Zn}(\text{TFSI})_2$ + 0.05m TFMP in H_2O , (f, i) 1m $\text{Zn}(\text{TFSI})_2$ + 0.05m TFMP + 1m TEP in H_2O . Different cycling conditions were used: (d-f) 0.5 mA cm^{-2} , 0.5 mAh cm^{-2} per cycle, (b-c, g-i) 2.5 mA cm^{-2} , 2.5 mAh cm^{-2} per cycle.

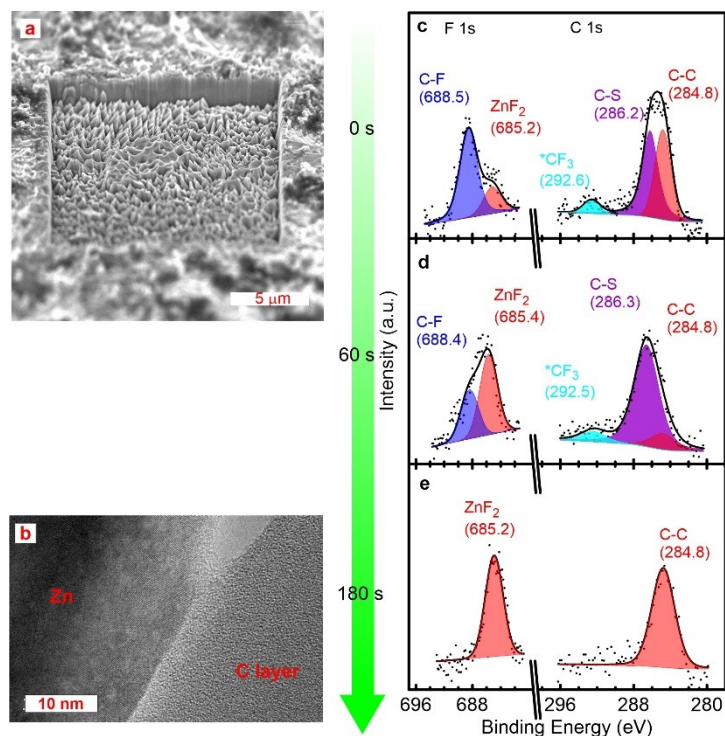


Figure S10. Zn metal anode morphology and SEI information after 10 h cycling (Zn|Zn cell setup, 0.5 mA cm⁻², 0.5 mAh cm⁻² per cycle) at room temperature with 1m Zn(TFSI)₂ in H₂O. Zn morphology was obtained using FIB-SEM (a). SEI information was obtained using TEM (b) and depth profile XPS (c-e).

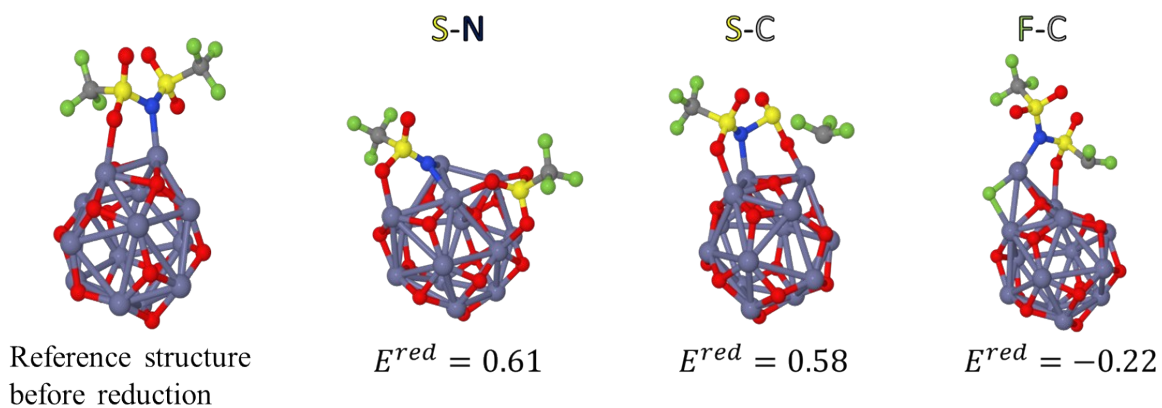


Figure S11. Computed reduction potentials from DFT for the decomposition of a $[\text{ZnTFSI}]^+$ species on a nano-scale ZnO cluster $(\text{ZnO})_{12}$ which might be present on the Zn metal surface. The calculated reduction potential is in V vs. Zn^{2+}/Zn and labeled in the Figure. Decomposition of the TFSI⁻ anion on a neutral $(\text{ZnO})_{12}$ cluster results in potentials of 0.13 V, -0.17 V, and -1.00 V for S-N, S-C, and F-C cleavage products, respectively.

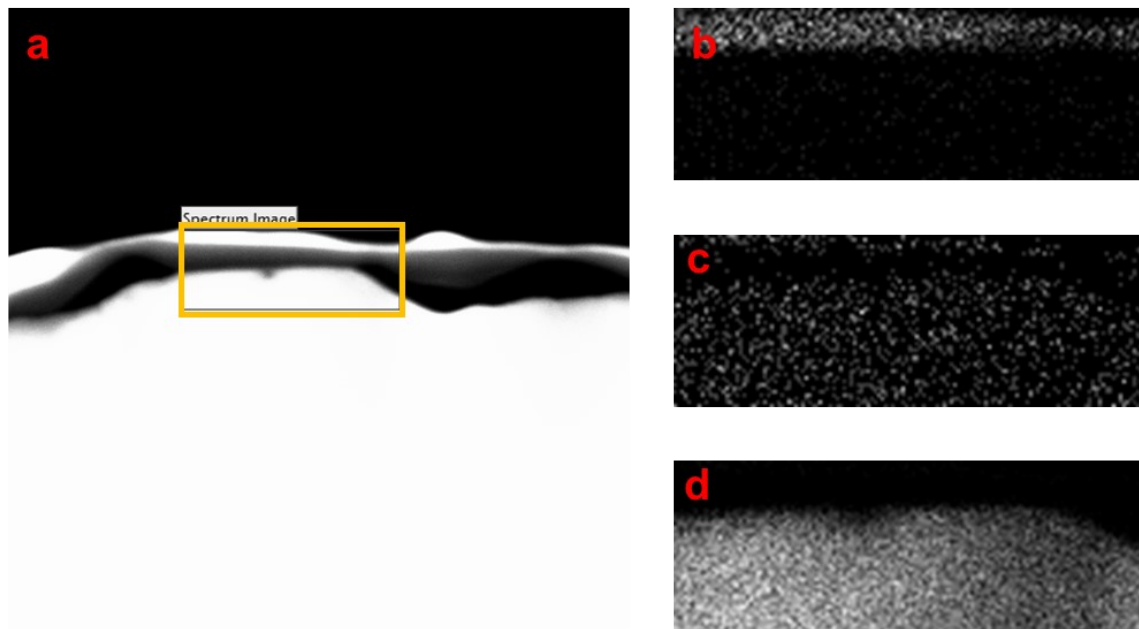


Figure S12. (a) STEM HAADF mode observation of Zn metal with the evolved interphase layer. STEM EDS mapping area is indicated by the yellow rectangular box. (b-d) EDS mapping of C (b), F (c) and Zn (d). Zn sample was obtained from Zn|Zn cells with 1m Zn(TFSI)₂+0.05m TFMP in H₂O after 10h cycling (0.5 mA/cm², 0.5 mAh/cm²) at zero state of charge.

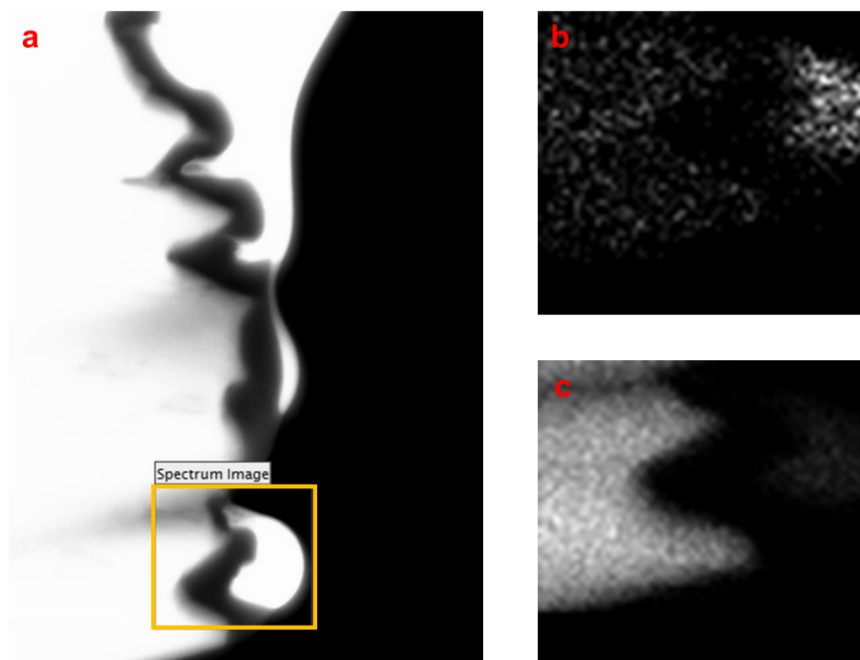


Figure S13. (a) STEM HAADF mode observation of Zn metal with the evolved interphase layer. STEM EDS mapping area is indicated by the yellow rectangular box. (b-c) EDS mapping of F (b), and Zn (c). Zn sample was obtained from Zn|Zn cells with 1m Zn(TFSI)₂+0.05m TFMP+1m TEP in H₂O after 10h cycling (0.5 mA/cm², 0.5 mAh/cm²) at zero state of charge.

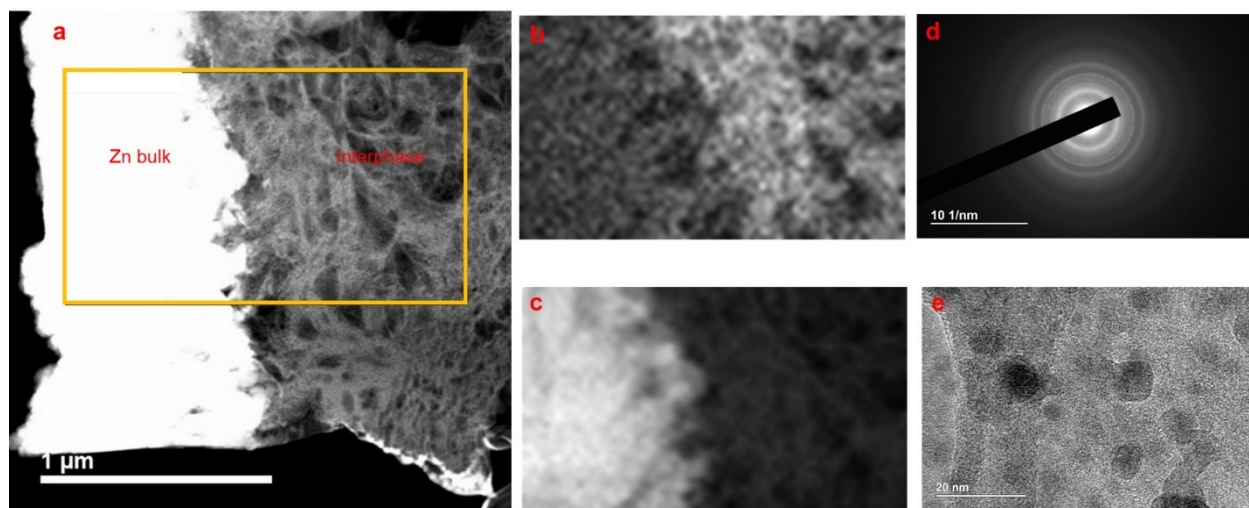


Figure S14. (a) STEM HAADF mode observation of Zn metal with the evolved interphase layer. STEM EDS mapping area is indicated by the yellow rectangular box. (b-c) EDS mapping of F (b), and Zn (c). (d) Selected-area electron diffraction of the interphase region in (a). (e) High resolution TEM image of the interphase region in (a). Zn sample was obtained from Zn|Zn cells with 1m Zn(TFSI)₂+0.05m TFMP in H₂O after 200h cycling (0.5 mA/cm², 0.5 mAh/cm²) at zero state of charge.

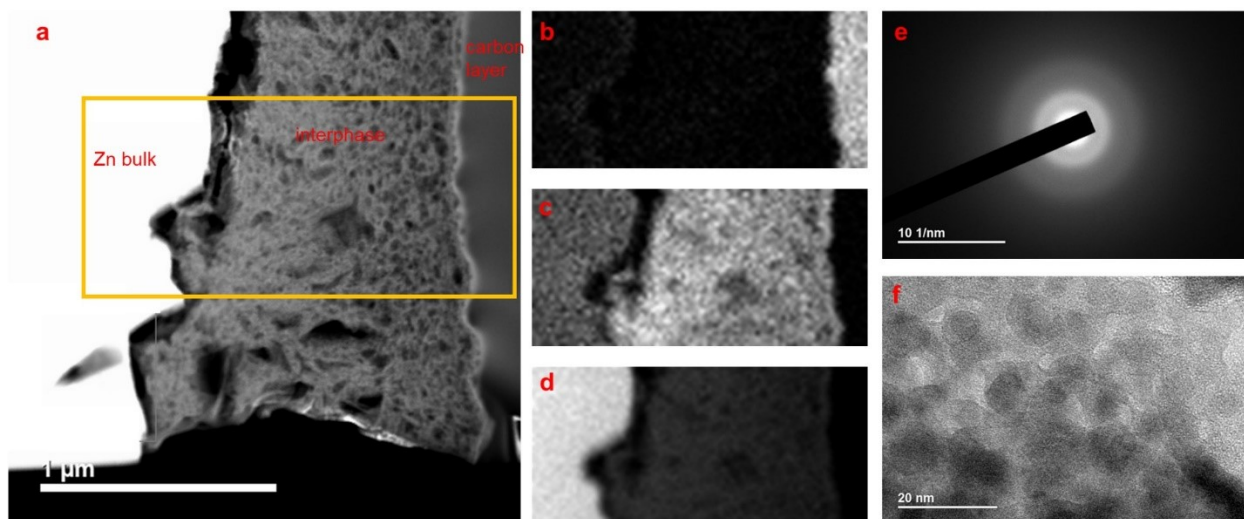


Figure S15. (a) STEM HAADF mode observation of Zn metal with the evolved interphase layer. STEM EDS mapping area is indicated by the yellow rectangular box. (b-d) EDS mapping of C (b), F (c), and Zn (d). (e) Selected-area electron diffraction of the interphase region in (a). (f) High resolution TEM image of the interphase region in (a). Zn sample was obtained from Zn|Zn cells with 1m Zn(TFSI)₂+0.05m TFMP+1m TEP in H₂O after 200h cycling (0.5 mA/cm², 0.5 mAh/cm²) at zero state of charge.

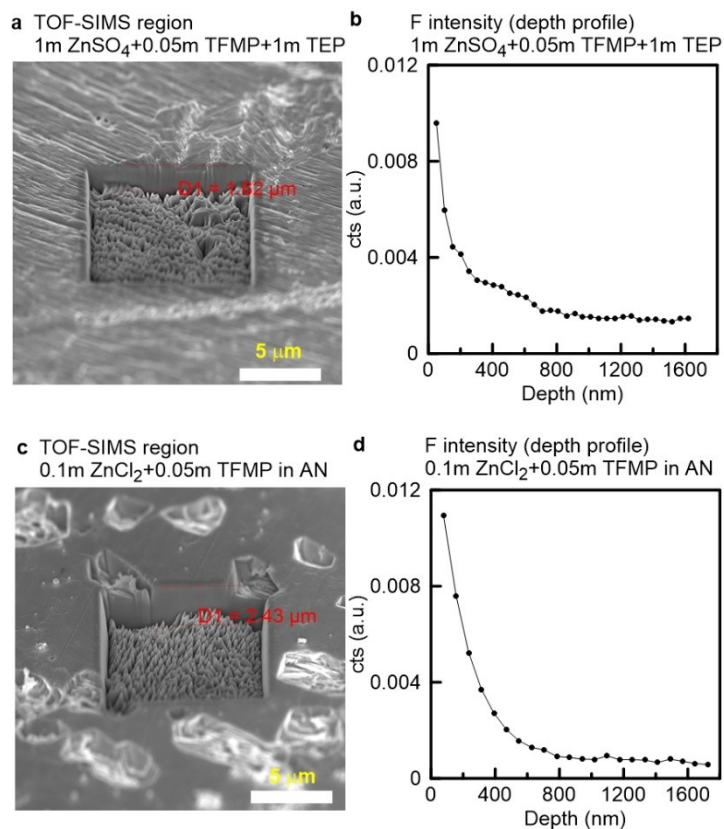


Figure S16. FIB-SEM images (a, c) and corresponding fluorine signal intensity depth profile (b, d) during time of flight secondary ion mass spectrometry (ToF-SIMS) analysis on the Zn metal anodes obtained from Zn|Zn symmetric cells at zero state of charge after 10h cycling (0.5 mA/cm^2 , 0.5 mAh/cm^2) at room temperature using different electrolytes: (a-b) $1 \text{ m ZnSO}_4 + 0.05 \text{ m TFMP} + 1 \text{ m TEP}$ in H_2O ; (c-d) $0.1 \text{ m ZnCl}_2 + 0.05 \text{ m TFMP}$ in AN.

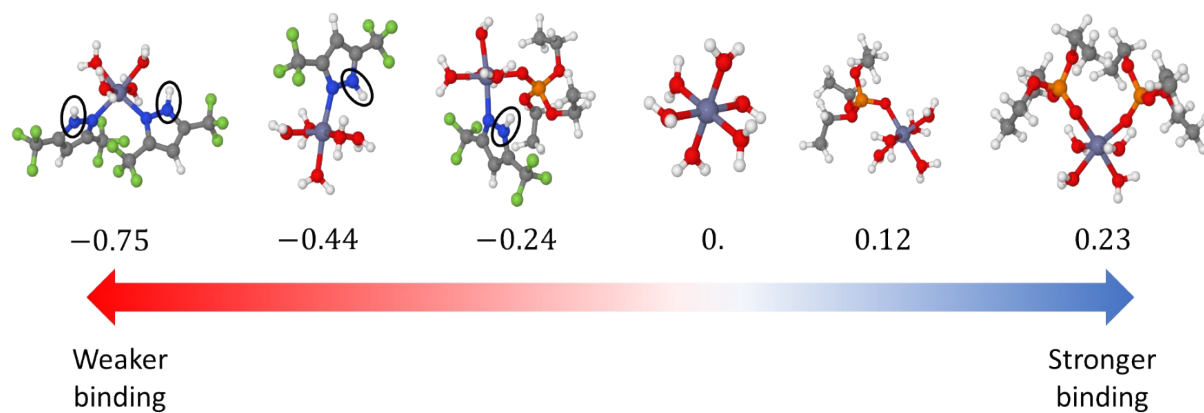


Figure S17. Binding free energies from density functional theory relative to $\text{Zn}(\text{H}_2\text{O})_6$ in eV for various solvates comprising Zn, H_2O , TEP, and TFMP. Values >0 eV indicate stronger binding than $\text{Zn}(\text{H}_2\text{O})_6$. The N-H protons are highlighted by ovals on the left-hand side of this figure.

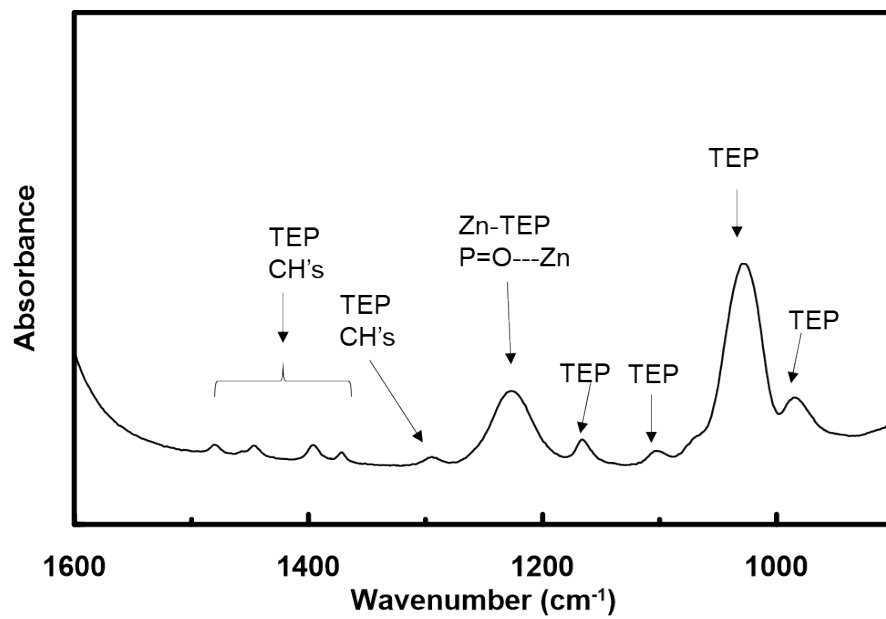


Figure S18. IR spectrum of 1m ZnCl₂ + 1m TEP in H₂O.

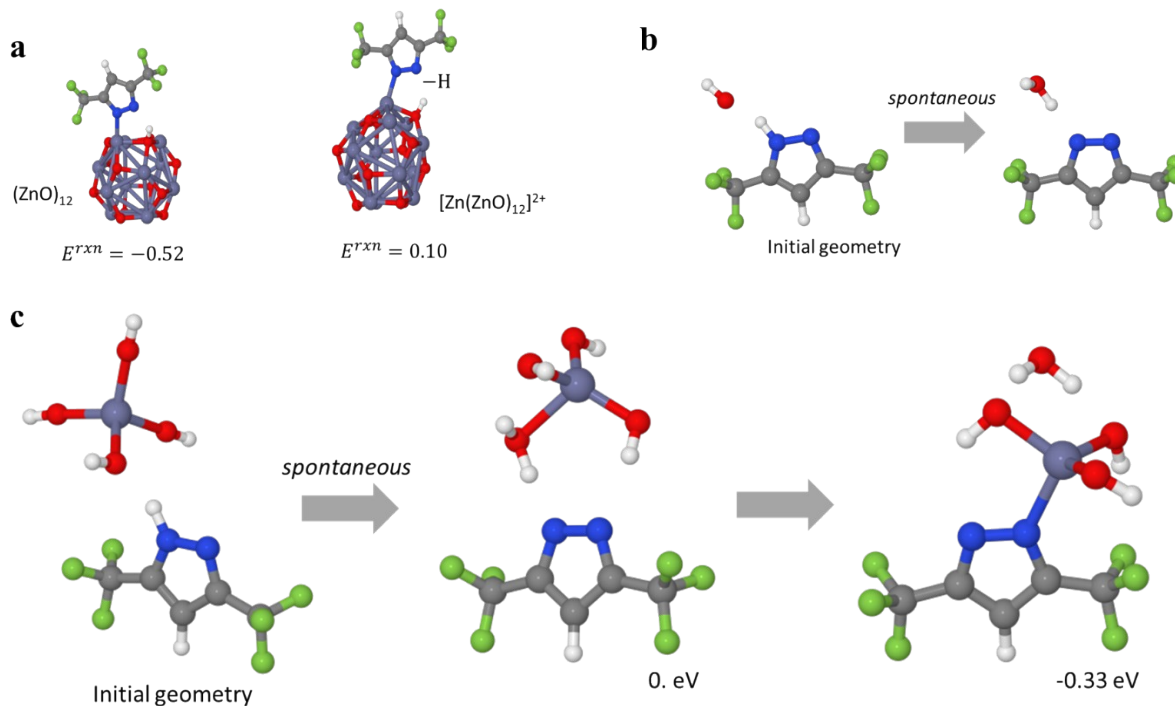


Figure S19. Computed reaction free energies in eV to deprotonate TFMP (a) on a neutral and charged ZnO nanoparticle, (b) with OH^- anions, (c) with $[\text{Zn}(\text{OH})_4]^{2-}$. In (c), TFMP-H displaces the reformed water molecule and has a free energy 0.33 eV lower than that of the middle structure with water still in the first solvation shell (meaning, it is favorable for the anion to displace the water). Structures labeled ‘initial geometry’ are optimized with the non-reactive Merck94 force field so the proton does not initially transfer. Where labeled ‘spontaneous’, the initial geometry during optimization with DFT converges on a geometry with the proton transferred. It’s an entirely energetically ‘downhill’ process.

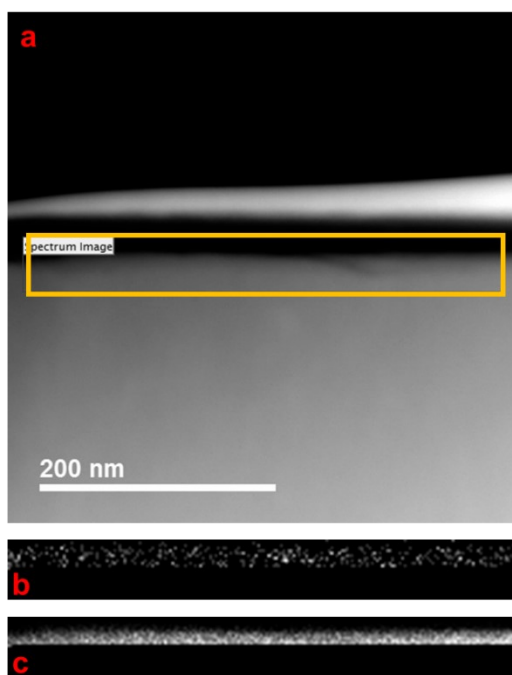


Figure S20. (a) STEM HAADF mode observation of Zn metal with the evolved interphase layer. STEM EDS mapping area is indicated by the yellow rectangular box. (b-c) EDS mapping of F (b), and Zn (c). Zn sample was obtained from Zn|Zn cells with 0.5m Zn(TFSI)₂+0.05m TFMP in AN after 10h cycling (0.5 mA/cm², 0.5 mAh/cm²) at zero state of charge.

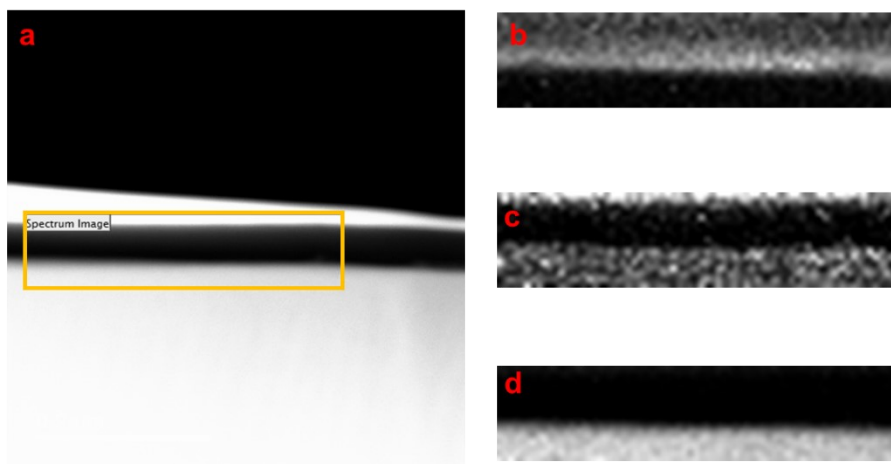


Figure S21. (a) STEM HAADF mode observation of Zn metal with the evolved interphase layer. STEM EDS mapping area is indicated by the yellow rectangular box. (b-d) EDS mapping of C (b), F (c), and Zn (d). Zn sample was obtained from Zn|Zn cells with 0.5m Zn(TFSI)₂+0.05m TFMP in AN after 200h cycling (0.5 mA/cm², 0.5 mAh/cm²) at zero state of charge.

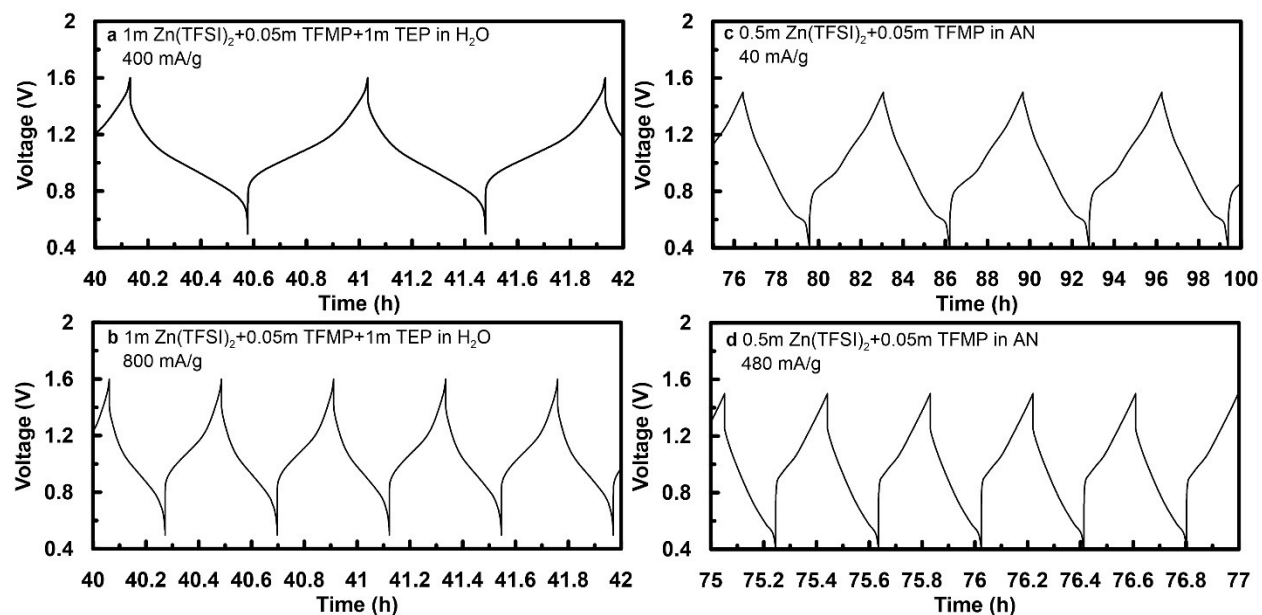


Figure S22. Voltage vs time for PBQS|Zn ($10\ \mu\text{m}$) and PANI|Zn ($10\ \mu\text{m}$) during long term cycling at 30°C with different electrolytes as labeled. Corresponding cycling results have been shown in Figure 5b, e. In Figure S21a, each discharge step takes $\sim 0.5\text{h}$ and corresponding areal capacity will

be $400\ \frac{\text{mA}}{\text{g}} \times 6\ \frac{\text{mg}}{\text{cm}^2} \times 0.5\text{h} = 1.2\ \frac{\text{mAh}}{\text{cm}^2}$. As a result, Zn utilization percentage per cycle will be

$$1.2\ \frac{\text{mAh}}{\text{cm}^2} \div 5.85\ \frac{\text{mAh}}{\text{cm}^2} = 20.5\%$$

. Zn utilization percentage per cycle for Figure S21b, S21c, and S21d are 16.4%, 18.5%, and 14.8%, respectively, calculated using the same way for Figure S21a.

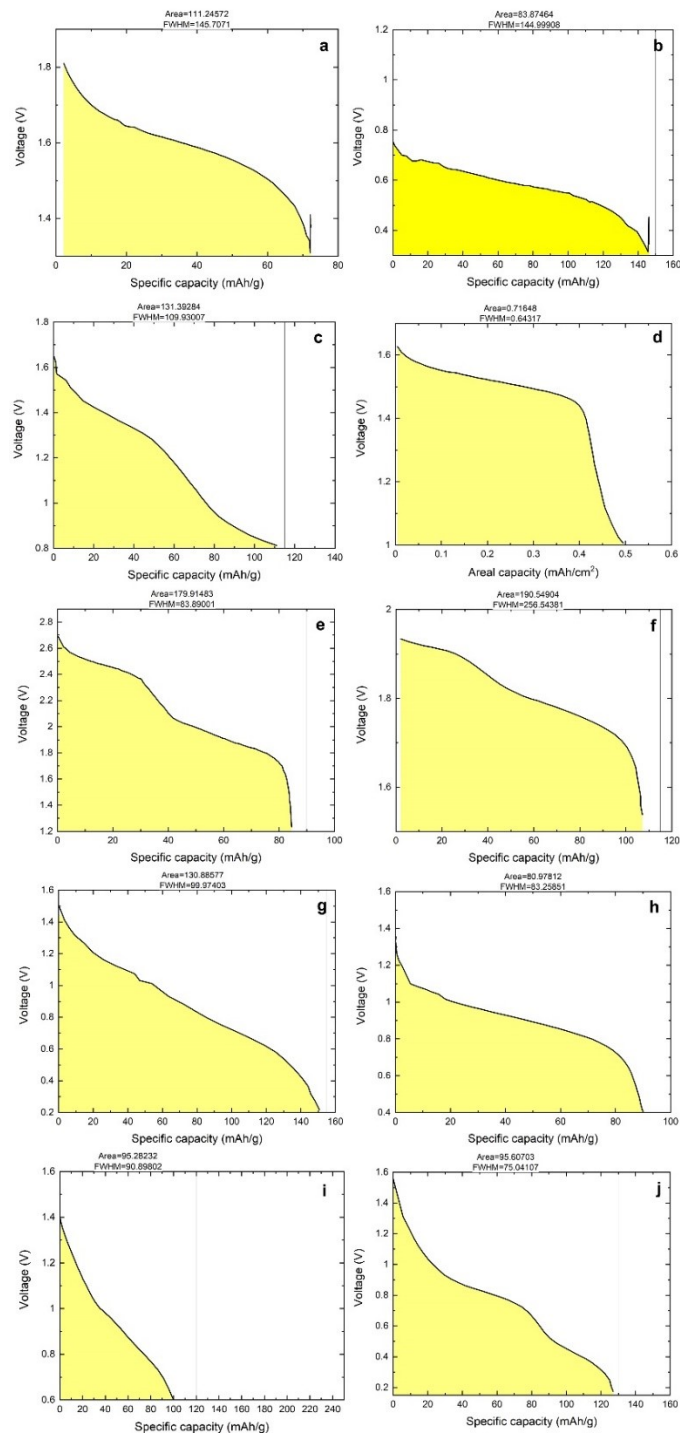


Figure S23. Digitized voltage vs. capacity from reported Zn electrolyte work (2018-2021): (a) 0.5M Zn(OTf)₂ in TEP/H₂O (7/3 by vol.)¹; (b) 0.5M Zn(OTf)₂ in TMP/DMC (1/1 by vol.)²; (c) 3M Zn(OTf)₂+2 vol.% Et₂O in H₂O³; (d) 1M Zn(Ac)₂+0.4M Mn(Ac)₂ in H₂O⁴; (e) Zn(TFSI)₂/EMC/TMP 3/5/11 by mol⁵; (f) 30m ZnCl₂+5m LiCl in H₂O⁶; (g) 30m ZnCl₂+5m LiCl in H₂O⁶; (h) Zn(ClO₄)₂•6H₂O/SN 1/8 by mol⁷; (i) 2M ZnSO₄ in H₂O/MeOH (1/1 by vol.)⁸; (j) 1M

$\text{Zn}(\text{OTf})_2 + 0.025\text{M Zn}(\text{H}_2\text{PO}_4)_2$ in H_2O^9 . Integrated area is shown in yellow in each panel to calculate average voltage.

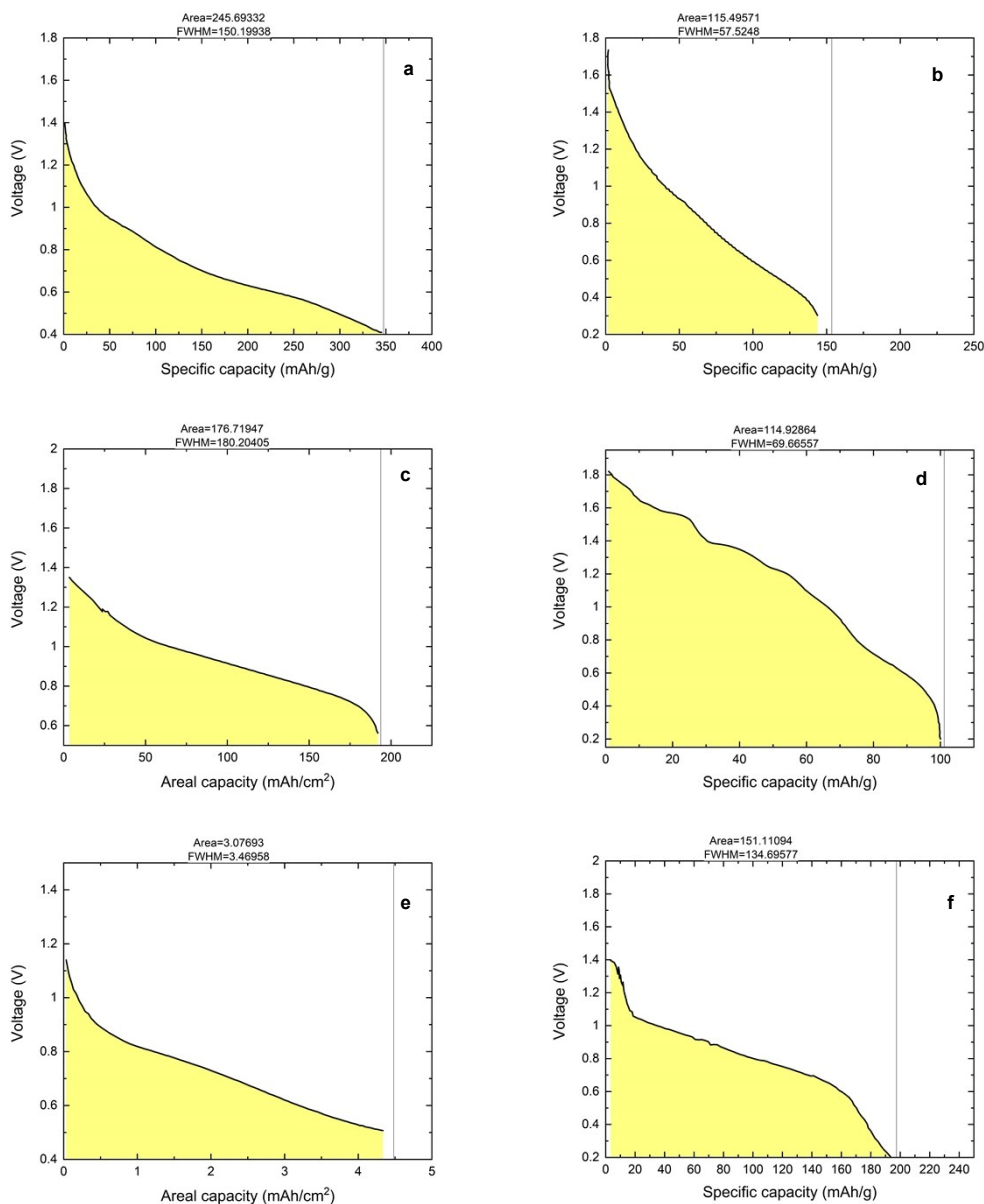


Figure S24. Digitized voltage vs. capacity from reported Zn electrolyte work (2022-2023): (a) $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}/\text{MSM}/\text{H}_2\text{O}$ 1.2/3.6/3 by mol¹⁰; (b) hydrous 4m $\text{Zn}(\text{BF}_4)_2$ in EG¹¹; (c) chitosan¹²; (d) 30m ZnCl_2 +5m LiCl +10m TMACl in $\text{H}_2\text{O}:\text{DMC}$ (5:1 by mol)¹³; (e) 2mmol $\text{Zn}(\text{OTf})_2$ in $\text{H}_2\text{O}/\text{SL}$ (10/7 by wt)¹⁴; (f) 10m $\text{Zn}(\text{Ac})_2$ +15m KAc ; 10m $\text{Zn}(\text{Ac})_2$ +24m urea; 8m $\text{Zn}(\text{Ac})_2$ +30m acetamide¹⁵. Integrated area is shown in yellow in each panel to calculate average voltage.

Supplementary Table 1. Metrics of interest for previously published rechargeable Zn metal battery electrolyte efforts (2018-2023) corresponding to Figure 5g. Average voltage was obtained by using integration area divided by the capacity in voltage-capacity curve (Figures S23-24), if not directly reported in the literature. The calculation is only based on the volume of cathode and anode. 30% porosity has been considered during the cathode thickness calculation, if the thickness is not reported in the reference.

Ref.	cathode active material and loading	cathode mixture ratio (active material/carbon black/binder)	cathode and Zn thickness (μm)	electrolyte	volumetric energy density based on total volume of	voltage range and average voltage	Specific capacity used for energy density estimation	N/P	temperature	note
this work	PBQS, 6 mg cm ⁻²	7/2/1	30 and 10	1m Zn(TFSI) ₂ +1m TEP+0.05m TFMP in H ₂ O	267.3 Wh L ⁻¹	0.5-1.6V, 0.99V	180 mAh g ⁻¹ (based on cathode)	5.42	30°C	
this work	PANI, 9 mg cm ⁻²	7/2/1	45 and 10	0.5m Zn(TFSI) ₂ +0.05m TFMP in AN	182 Wh L ⁻¹	0.4-1.5V, 0.89V	125 mAh g ⁻¹ (based on cathode)	5.2	30°C	
Wang et al. ¹⁶	LiMn ₂ O ₄ , unknown	8/1/1	unknown	1m Zn(TFSI) ₂ +20m LiTFSI in H ₂ O	208 Wh L ⁻¹	0.8-2.1V, 1.8V	66 mAh g ⁻¹ (based on both cathode and anode)	4.43	N/A	N/P mass ratio is 0.8/1. Zn powder mixed with carbon black, PVDF (8/1/1) is used as anode here so 30% porosity is also estimated for anode
Naveed et al. ¹	KCuHCF, 1 mg cm ⁻²	7.5/1/1.5	10.8 and 250	0.5M Zn(OTf) ₂ in TEP/H ₂ O (7/3 by vol.)	4.22 Wh L ⁻¹	1.3-2V, 1.5V	73.3 mAh g ⁻¹ (based on cathode)	1995	25°C	
Naveed et al. ²	VS ₂ , 4 mg cm ⁻²	7/2/1	34.6 and unknown	0.5M Zn(OTf) ₂ in TMP/DMC (1/1 by vol.)	51.6 Wh L ⁻¹ and 17.1 Wh L ⁻¹	0.3-1V, 0.57V	102.57 mAh g ⁻¹ (based on cathode)	14.3 and 143	N/A	Zn thickness is unknown in this work. An estimation of 10 and 100 μm was used for Zn to estimate energy density and N/P.
Xu et al. ³	α -MnO ₂ , 3.5 mg cm ⁻²	7/2/1	21.1 and unknown	3M Zn(OTf) ₂ +2 vol.% Et ₂ O in H ₂ O	135 Wh L ⁻¹ and 34.7 Wh L ⁻¹	0.8-1.8V, 1.2V	100 mAh g ⁻¹ (based on cathode)	16.7 and 167	N/A	Zn thickness is unknown in this work. An estimation of 10 and 100 μm was used for Zn to estimate energy density and N/P.
Zeng et al. ⁴	MnO ₂ , 1.8 mg cm ⁻²	unknown	11 and 100	1M Zn(Ac) ₂ +0.4M Mn(Ac) ₂ in H ₂ O	126.1Wh L ⁻¹	1-1.8V, 1.4V	1 mAh cm ⁻¹ (based on cathode)	58.5	N/A	A 7/2/1 slurry ratio in cathode was used to estimate its thickness.
Qiu et al. ¹⁷	V ₂ O ₅ , 14.3 mg cm ⁻²	7/2/1	106 and 20	Zn(TFSI) ₂ /acetamide 1/7 by mol	58.7Wh L ⁻¹	0.6-1.8V, 1.01V	25.5 mAh g ⁻¹ (based on both cathode and anode)	7.45	N/A	N/P mass ratio is 1/1.
Zhao et al. ¹⁸	LiMn ₂ O ₄ , 5 mg cm ⁻²	8/1/1	36.1 and 19.1	LZ-DES/2H ₂ O	225Wh L ⁻¹	1.5-2.1V, 1.92V	110 mAh g ⁻¹ (based on cathode)	20.3	N/A	
Chen et al. ⁵	graphite, 2.3 mg cm ⁻²	8.5/0.5/1	17.6 and 250	Zn(TFSI) ₂ /EMC/TMP 3/5/11 by mol	13.5Wh L ⁻¹	1.2-2.8V, 2.1V	75 mAh g ⁻¹ (based on cathode)	8478	N/A	
Zhang et al. ⁶	LiMn ₂ O ₄ , 6.5 mg cm ⁻²	8/1/1	46.8 and 5.5	30m ZnCl ₂ +5m LiCl in H ₂ O	233Wh L ⁻¹	1.55-1.95V, 1.8V	100 mAh g ⁻¹ (based on cathode)	4.95	N/A	

Ref.	cathode active material and loading	cathode mixture ratio (active material/carbon black/binder)	cathode and Zn thickness (μm)	electrolyte	volumetric energy density based on total volume of	voltage range and average voltage	Specific capacity used for energy density estimation	N/P	temperature	note
Zhang et al. ⁶	$\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$, 1.5 mg cm^{-2}	7/2/1	11.3 and 2.5	30m ZnCl_2 +5m LiCl in H_2O	188.2 Wh L^{-1}	0.2-1.6V, 0.87V	150 mAh g^{-1} (based on cathode)	6.5	N/A	
Yang et al. ⁷	PDB, 0.21 mg cm^{-2}	6/2/2	2.6 and 0.74	$\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}/\text{SN}$ 1/8 by mol	50.9 Wh L^{-1}	0.4-1.5V, 0.9V	90 mAh g^{-1} (based on cathode)	22.9	N/A	
Hao et al. ⁸	PANI, 10 mg cm^{-2}	N/A (polymerized on current collector)	50 and 10	2M ZnSO_4 in $\text{H}_2\text{O}/\text{MeOH}$ (1/1 by vol)	158 Wh L^{-1}	0.6-1.6V, 0.95V	100 mAh g^{-1} (based on cathode)	5.9	room temperature	Cathode thickness is estimated based on the loading proportion of PANI used in this work
Zeng et al. ⁹	V_2O_5 , 8.7 mg cm^{-2}	7/2/1	64.7 and 10	1M $\text{Zn}(\text{OTf})_2$ +0.025M $\text{Zn}(\text{H}_2\text{PO}_4)_2$ in H_2O	96.1 Wh L^{-1}	0.2-1.6V, 0.75V	110 mAh g^{-1} (based on cathode)	6.1	N/A	
Han et al. ¹⁰	CaV_4O_9 , 1.33 mg cm^{-2}	7/2/1	10 and 80	$\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}/\text{MSM}/\text{H}_2\text{O}$ 1.2/3.6/3 by mol	36.7 Wh L^{-1}	0.4-1.6V, 0.71V	350 mAh g^{-1} (based on cathode)	101	N/A	Cathode thickness is estimated based on the loading proportion of CaV_4O_9 used in this work
Han et al. ¹¹	V_2O_5 , 2-3 mg cm^{-2}	7/2/1	22 and 17	Hydrous 4m $\text{Zn}(\text{BF}_4)_2$ in EG	105.8 Wh L^{-1}	0.2-1.8V, 0.8V	140 mAh g^{-1} (based on cathode)	19.1	N/A	Cathode thickness is estimated based on the loading of 3 mg cm^{-2}
Wu et al. ¹²	PBQS, 10 mg cm^{-2}	7/2/1	77 and 100	Chitosan-Zn	99.8 Wh L^{-1}	0.5-1.7V, 0.92V	190 mAh g^{-1} (based on cathode)	30.8	room temperature	Cathode thickness is estimated based on the loading proportion of PBQS used in this work
Jiang et al. ¹⁹	$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, 22.5 mg cm^{-2}	8.75/0.25/1	121 and 1.2	30m ZnCl_2 +5m LiCl+10m TMACl in $\text{H}_2\text{O}/\text{DMC}$ (5:1 by mol)	202.5 Wh L^{-1}	0.2-1.8V, 1.1V	100 mAh g^{-1} (based on cathode)	2.3	room temperature	Cathode thickness is estimated based on its loading proportion of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ used in this work
Li et al. ¹⁴	$\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ 42.46 mg cm^{-2}	8/1/1	580 and 11	2mmol $\text{Zn}(\text{OTf})_2$ in $\text{H}_2\text{O}/\text{SL}$ (10/7 by wt)	52.8 Wh L^{-1}	0.5-1.4V, 0.71V	4.4 mAh cm^{-1} (based on cathode)	1.08	N/A	Cathode thickness is reported by the authors
Dong et al. ¹⁵	PTO, 2 mg cm^{-2}	6/3/1	19 and 3.5	10m $\text{Zn}(\text{Ac})_2$ +15m KAc; 10m $\text{Zn}(\text{Ac})_2$ +24m urea; 8m $\text{Zn}(\text{Ac})_2$ +30m acetamide	133.9 Wh L^{-1}	0.2-1.4V, 0.78V	200 mAh g^{-1} (based on cathode)	5.12	N/A	Cathode thickness is estimated based on the loading proportion of PTO used in this work
Yang et al. ²⁰	Air	N/A	215 and unknown	$\text{Li}_2\text{ZnCl}_4 \cdot \text{RH}_2\text{O}$	186 Wh L^{-1} and 127 Wh L^{-1}	1-1.75V, 1V	4 mAh cm^{-1}	N/A	20°C	Cathode thickness is the air electrode. Zn thickness is unknown in this work. An estimation of 10 and 100 μm was used for Zn to estimate energy density

PANI: polyaniline; DES: deep eutectic solvents; PDB: poly(2,3-dithiino-1,4-benzoquinone); TMP: triethyl phosphate; TEP: triethyl phosphate; MSM: methylsulfonylmethane; EG: ethylene glycol; PBQS: poly(benzoquinonyl sulfide); DMC: dimethyl carbonate; TMACl: trimethylammonium chloride; SL: sulfolane; PTO: pyrene-4,5,9,10-tetraone

Supplementary Table 2. The ionic conductivity of different electrolytes at room temperature.

Electrolyte	Conductivity (mS/cm)
1m Zn(TFSI) ₂ in H ₂ O	36.55
1m Zn(TFSI) ₂ + 0.05m TFMP in H ₂ O	36.28
1m Zn(TFSI) ₂ + 0.05m TFMP + 1m TEP in H ₂ O	27.95
0.5m Zn(TFSI) ₂ in AN	33.00
0.5m Zn(TFSI) ₂ + 0.05m TFMP in AN	32.45

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