### Supplementary Information

### Unveiling solvation structure and desolvation dynamics of hybrid electrolytes for ultralong cyclability and facile kinetics of Zn–Al alloy anodes

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#### **Experimental Section**

#### **Electrolyte preparations**

Three hybrid electrolytes, ACN-HE, PC-HE, and DMF-HE, were obtained by dissolving aluminum trifluoromethanesulfonate (Al(OTf)<sub>3</sub>, Sigma-Aldrich) into the mixture of deionized water and organic solvents, including acetonitrile (ACN, DAEJUNG), propylene carbonate (PC, DAEJUNG), and dimethylformamide (DMF, DAEJUNG), where the H<sub>2</sub>O to Al(OTf)<sub>3</sub> molar ratio was kept at 2:1 and required amount of organic solvents were added to make the hybrid electrolytes have the same concentration of 0.8 mol L<sup>-1</sup>. Hybrid electrolytes with increased H<sub>2</sub>O to Al(OTf)<sub>3</sub> molar ratios (4, 6, 8, 10) were obtained by adding the required amounts of H<sub>2</sub>O to the above electrolytes. 1.4 mol L<sup>-1</sup> aqueous electrolyte (H<sub>2</sub>O-E) was obtained by dissolving Al(OTf)<sub>3</sub> into deionized water. 0.8 mol L<sup>-1</sup> anhydrous Al(OTf)<sub>3</sub>/DMF electrolyte was obtained by dissolving Al(OTf)<sub>3</sub> into DMF solvent.

#### Electrode preparation and cell fabrication

Symmetric cells and full cells were assembled in the CR2032 coin-type cells under the ambient atmosphere without requiring a glovebox. If not noted, symmetric cells consisted of two Zn foils (Alfa Aesar, thickness 250  $\mu$ m, diameter 15 mm) as the electrodes, glass fiber (Whatman, GF/A, diameter 16 mm) as the separator, and 90 uL Al(OTf)<sub>3</sub>-based electrolytes. Full cells consisted of Zn foil (~25  $\mu$ m, ~17.5 mg cm<sup>-2</sup>) as the anode, polyaniline (PANI), activated carbon (AC), vanadium dioxide/carbon nanotubes (VO<sub>2</sub>/CNTs) as the cathodes (diameter 15 mm), glass fiber as the separator, and ~125 uL Al(OTf)<sub>3</sub>-based electrolyte. The ~25  $\mu$ m Zn foils were obtained by mechanically rolling commercial Zn foils (thickness 250  $\mu$ m) with a roll squeezer.

The PANI cathodes were prepared by blending 80 wt% of PANI power (Sigma-Aldrich, average Mw ~100,000), 12.5 wt% carbon black (conductive additive, Alfa Aesar), and 7.5 wt% sodium alginate (SA, binder, Alfa Aesar) in H<sub>2</sub>O. The obtained slurry was cast on Al foil as the current collector and dried at 80 °C for 2 h. The PANI loading in each electrode was ~4.0 mg cm<sup>-2</sup>. For high-loading PANI cathodes (~10 mg cm<sup>-2</sup>), the PANI-based slurry was cast onto stainless steel foil. After drying in the ambient atmosphere for 24 h, the PANI discs can be separated from the stainless steel foil as free-standing electrodes (Fig. **S22a**) and further dried

at 80 °C for 2 h.

The free-standing AC cathodes (~10 mg cm<sup>-2</sup>) were prepared as follows: 80 wt% AC powder (YP-50F, Kuraray Chemical), 10 wt% carbon black, 10 wt% poly(tetrafluoroethylene) (PTFE, binder, Sigma-Aldrich) in H<sub>2</sub>O, and drops of ethanol were blended to create a paste, which was mechanically rolled to a film with a roll squeezer, and then cut into 15 mm-diameter discs and dried at 80 °C for 2 h (Fig. **S23a**).

The VO<sub>2</sub>/CNTs composites were prepared as follows: 50 mg multi-walled carbon nanotubes (MWCNTs, OD: <7nm, US Research Nanomaterials, Inc.) in nitric acid were first heated in Teflon-lined stainless steel autoclave at 120 °C for 12 h to enhance the hydrophilicity. The acid-treated MWCNTs were washed with deionized water and then re-dispersed in 40 mL deionized water. To the above suspension  $V_2O_5$  (Sigma-Aldrich, 568 mg) and glucose (Sigma-Aldrich, 451mg) were added and stirred magnetically for 1 h. Subsequently, the above mixture was transferred to a 50 mL Teflon-lined autoclave and heated at 180 °C for 24 h. The resultant precipitate was washed with ethanol and H<sub>2</sub>O, and freeze-dried to afford the product. The VO<sub>2</sub>/CNTs cathodes were prepared as follows: 70 wt% of VO<sub>2</sub>/CNTs power, 20 wt% carbon black, and 10 wt% polyvinylidene difluoride (PVDF, binder) in N-methyl-2-pyrrolidone (NMP) solvent were blended to obtain a slurry, which was cast on carbon paper as the current collector and dried at 80 °C for 2 h in a vacuum oven. The VO<sub>2</sub>/CNTs loading in each electrode was ~8.0 mg cm<sup>-2</sup>.

#### **Material characterizations**

The morphologies of Zn–Al electrodes were investigated by scanning electron microscopy (SEM, JEOL, JSM7000F). The cross-sectional views of Zn–Al electrodes were characterized by transmission electron microscopy (TEM, JEM ARM 200F), combined with energy-dispersive X-ray spectroscopy (EDX) for the element determination. The TEM specimen was prepared by a focused ion beam (FIB, NX2000) tool. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements were conducted with a TOF-SIMS (ION-TOF GmbH, Münster). Sputtering was performed using a 1 keV O<sub>2</sub> beam over a 150×150  $\mu$ m<sup>2</sup> area, and analysis area was 40×40  $\mu$ m<sup>2</sup> using a pulsed 25 keV Bi<sup>+</sup> primary beam. The surface components of electrodes were characterized on X-ray photoelectron spectroscopy (XPS)

(Thermo-Scientific ESCALAB 250Xi). Depth-dependent XPS spectra were achieved after etching the electrode surface by argon-ion (Ar<sup>+</sup>) sputtering for 300 s, 600 s, and 900 s. The binding energies of XPS spectra were determined by reference to the adventitious C 1s peak at 284.6 eV. Near-edge X-ray absorption fine structure (NEXAFS) studies of Zn-supported Zn– Al alloy, Zn foil, and Al foil were performed at the soft X-ray beamline, Australian Synchrotron.<sup>1</sup> The NEXAFS data were processed using Igor Pro 8, with the aid of QANT program developed at Australian Synchrotron.<sup>2</sup> X-ray diffraction (XRD) pattern was recorded using an X-ray diffractometer (PANalytical, Almelo, the Netherlands) with Cu K $\alpha$  radiation ( $\lambda$ = 0.154 nm).

The ionic conductivities of electrolytes were measured by a conductivity meter (Mettler-Toledo). The viscosities were measured on a rheometer (ARES-G2). The nuclear magnetic resonance (NMR) measurements of electrolytes with non-deuterated solvents were performed without field locking. The <sup>1</sup>H NMR and <sup>27</sup>Al NMR spectra were recorded on a 500 MHz NMR spectrometer (Unity Inova). The <sup>17</sup>O NMR spectra were recorded on a 700 MHz spectrometer (AVANCE III 700). The Fourier-transform infrared (FT-IR) spectra were recorded using an FT-IR instrument (JASCO 4600) and adopted an attenuated total reflection (ATR) method. The in situ FT-IR spectra were measured by using a designed two-electrode cell (with a porous carbon paper as the working electrode allowing the IR light to push through the electrode and obtain the spectra, and Zn foil as the counter and reference electrodes in hybrid electrolytes, Fig. **S18**) combined with an electrochemical workstation applying different negative potentials (25, 50, 75, 100 mV) on the working electrode.

#### Two-dimensional correlation spectroscopy (2D-COS) analysis

Before the analysis of 2D-COS, FT-IR spectra were pretreated with baseline correction and smooth factor analysis (SFA).<sup>3</sup> SFA is an effective denoising method using the modified nonlinear iterative partial least squares (NIPALS) procedure.

Baseline corrections were performed using Solo9.0 (Eigenvector Research, Inc., WA, USA). SFA and 2D-COS were carried out using homemade code in MATLAB R2019b software (The Mathworks Inc., MA, USA).

SFA-treated FT-IR spectra were prepared using five factors of the smoothed loading vectors.

In the 3700–2400 cm<sup>-1</sup> and 1950–800 cm<sup>-1</sup> spectral regions, 15-points and 5-points S-G filter were applied to loading vectors.

#### **Electrochemical measurements**

The cyclic voltammetry (CV), chronopotentiometry (CP), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) measurements were conducted using an electrochemical workstation (Bio-Logic Science Instrument-VSP). The galvanostatic charge/discharge (GCD) measurements were conducted using an automatic battery test system (WonATech, WBCS3000L).

The open-circuit potentials ( $E_0$ ) were measured in three-electrode cells, with Zn foil as the working electrode, platinum (Pt) foil as the counter electrode, and Ag/AgCl as the reference electrode, in the four electrolytes. The Al<sup>3+</sup> deposition profiles on the Zn substrate were measured using CP under a current density of 0.1 mA cm<sup>-2</sup> in three-electrode cells.

The electrochemical stability windows (ESWs) of electrolytes were measured by CV at a scan rate of 5 mV s<sup>-1</sup>, in three-electrode cells consisting of two stainless steel foils as the working electrode and counter electrode, and Ag/AgCl as the reference electrode.

The Nyquist plots were obtained using EIS with a frequency range from 100 kHz to 0.1 Hz and a potential amplitude of 10 mV.

The transference number<sup>4,5</sup> of Al<sup>3+</sup> ( $t_{Al}$ ) was measured in symmetric cells with two Zn electrodes and Al(OTf)<sub>3</sub>-based electrolytes, using a procedure that involves EIS and CA with an applied voltage of 10 mV (Fig. **S11**) for 10 minutes. The cells were left standing for 24 h before recording data. The  $t_{Al}$  was calculated by the following *Equation* (1):

$$t_{\rm Al} = \frac{I_{\rm s}(\Delta V - I_{\rm o}R_{\rm o})}{I_{\rm o}(\Delta V - I_{\rm s}R_{\rm s})} \tag{1}$$

where  $\Delta V$  is the applied potential (10 mV),  $I_0$  and  $I_s$  are the initial and steady-state currents, and  $R_0$  and  $R_s$  are the initial and steady-state electrode resistances, respectively.

#### **Computational details**

Density functional theory (DFT) calculations were conducted in Gaussian (G09) program with Becke's three-parameter hybrid method using the Lee–Yang–Parr correlation functional (B3LYP) at 6-311++G(d,p) level.<sup>6,7</sup> The solvation effect was considered with the universal solvation model of SMD.<sup>8</sup> Frequency analysis was performed to ensure the ground state of optimized ion–solvent complexes. The binding energy  $(E_b)$  between an Al<sup>3+</sup> ion and solvent(s)/anion is defined by the following *Equation* (2):

$$Eb = Ecomplex - EAl - Esolvent(s)/anion$$
 (2)

where  $E_{\text{complex}}$  is total energy of Al<sup>3+</sup>–solvent/anion complex,  $E_{\text{Al}}$  is the energy of Al<sup>3+</sup>, and  $E_{\text{solvent}(s)/\text{anion}}$  is the energy of solvent(s)/anion.

Molecular dynamics (MD) simulations were performed using the Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code and based on Optimized Potential for Liquid Simulations-all atom (OPLS-AA) force field.<sup>9-11</sup> The organic solvent force field parameters were generated by the LigParGen web server except for adopting restrained electrostatic potential (RESP) atomic partial charges, which were obtained based on electrostatic potential (ESP) charges using the Multiwfn program.<sup>12-15</sup> Parameters for Al<sup>3+</sup>, OTf<sup>-</sup>, and H<sub>2</sub>O were from Faro et al.,<sup>16</sup> Doherty et al.,<sup>17</sup> and OPLS-AA force field, respectively. The ACN-HE, PC-HE, and DMF-HE each contains 55 Al(OTf)<sub>3</sub> and 110 H<sub>2</sub>O with 1045, 649, and 715 organic solvent molecules, respectively, while the H<sub>2</sub>O-E is composed of 55 Al(OTf)<sub>3</sub> and 1540 H<sub>2</sub>O molecules. The initial atomic coordinates were generated with Packing Optimization for Molecular Dynamics Simulations (Packmol) program, and the final model boxes, and solvation structures were visualized by Materials Studio of Accelrys Inc.<sup>18</sup>

The periodic boundary conditions were applied in all three directions for all simulations. A cutoff of 12 Å was used for both van der Waals interactions and long-range correction (particleparticle particle-mesh) of Coulombic interactions. The time step was fixed to be 1 fs. All electrolyte models were first equilibrated in an NPT ensemble using the Parrinello–Rahman barostat for 3 ns to maintain a temperature of 298 K and a pressure of 1 atm with time constants of 0.1 and 1 ps, respectively.<sup>19</sup> After that, the electrolytes were heated from 298 to 400 K for 2 ns and maintained at 400 K for 2 ns. Subsequently, the models were annealed from 400 to 298 K in 2 ns and equilibrated at 298 K in the NPT ensemble for another 6 ns. A 14-ns production run was finally conducted for all systems in the NVT ensemble under Nose–Hoover thermostat.<sup>20,21</sup> Only the final 5-ns run was sampled for the analysis of solvation structures. The radial distribution function (*g*(*r*)) was calculated based on the following *Equation* (3):

$$g(r) = \frac{\frac{\mathrm{d}N_i}{4\pi r^2 \mathrm{d}r}}{\frac{N_{tot,i}}{V}}$$
(3)

where *r* is the distance from the reference atom Al<sup>3+</sup>,  $N_i$  the average number of oxygen or nitrogen atoms belonging to species *i* in shell between *r* and *r* + d*r*,  $N_{tot,i}$  the total number of oxygen or nitrogen atoms belonging to species *i*, and *V* the volume of the system. The g(r) of different species were further normalized into relative g(r) by multiplying  $N_{tot,i}/N_{tot}$ , where  $N_{tot}$ =  $\sum N_{tot,i}$  represents the total number of all oxygen or nitrogen atoms in the system.

Redox	Ionic radius	Charge density	Standard potential Theoretical cap		l capacity
couple	<i>R</i> (Å)	Z/R (Å <sup>-1</sup> )	$M^{n+}/M$ (V vs. SHE)	$(Ah g^{-1})$	(Ah cm <sup><math>-3</math></sup> )
Li <sup>+</sup> /Li	0.76	1.32	-3.04	3.86	2.08
Na <sup>+</sup> /Na	1.02	0.98	-2.71	1.17	1.13
K+/K	1.38	0.72	-2.92	0.68	0.58
Mg <sup>2+</sup> /Mg	0.72	1.39	-2.37	2.21	3.84
Ca <sup>2+</sup> /Ca	1.00	2.00	-2.87	1.34	2.08
Zn <sup>2+</sup> /Zn	0.74	2.70	-0.76	0.82	5.85
Al <sup>3+</sup> /Al	0.535	5.61	-1.66	2.98	8.04

Table S1. Properties of reactive metals used as battery anodes.

Solvent	Chemical structure	Molar mass (mol kg <sup>-1</sup> )	Density (g cm <sup>-3</sup> )	Viscosity (mPa s)	Dielectric constant	Donor number $(\text{kcal mol}^{-1})^a$
Water (H <sub>2</sub> O)	н <sup>-0</sup> , Н	18	1.00	0.89	80.1	18.0
Dimethylformamide (DMF)	N H H	73	0.95	0.80	36.7	26.6
Dimethylacetamide (DMA)	N N	87	0.93	0.95	37.8	
Propylene carbonate (PC)		102	1.20	2.50	64.9	15.1
Ethylene carbonate (EC)		$88^b$	1.32 <sup>b</sup>	1.9 <sup>b</sup>	89.8	
Dimethylene carbonate (DMC)		90	1.06	0.59	3.1	
Diethylene carbonate (DEC)	° nono	118	0.97	0.75	2.8	
Acetonitrile (ACN)	N	41	0.78	0.33	37.5	14.1
3-methoxypropionitrile (MPN)	N	85	0.94	1.1	36	
glutaronitrile (GLN)	N	94	0.99	5.3	37	

Table S2. Chemical structures and physical properties of  $H_2O$  and organic solvents for hybrid electrolytes.

 $^a$  Values are cited from references.  $^{22,23}$   $^b$  At 40 °C.

Electrolyte	Compositions (molar ratio)	Conductivity (mS cm <sup>-1</sup> )	Viscosity (mPa s)	Transference number $(t_{Al})$	Density (g mL <sup>-1</sup> )
H <sub>2</sub> O-E	Al(OTf) <sub>3</sub> :H <sub>2</sub> O (1:28)	47.5	5.7	-	1.45
DMF-HE	Al(OTf) <sub>3</sub> :DMF:H <sub>2</sub> O (1:13:2)	9.8	12.3	0.11	1.16
PC-HE	Al(OTf) <sub>3</sub> :PC:H <sub>2</sub> O (1:12:2)	0.57	25.3	0.24	1.37
ACN-HE	Al(OTf) <sub>3</sub> :ACN:H <sub>2</sub> O (1:19:2)	6.6	1.9	0.31	1.02

**Table S3.** Compositions and physical properties of hybrid electrolytes.

Electrode	Electrolyte	Current density @ Capacity	Cycle time	Ref.
Zn–Al 25 μm	Al(OTf) <sub>3</sub> /ACN/H <sub>2</sub> O (ACN-HE)	$0.2 \text{ mA cm}^{-2} @ 0.2 \text{ mAh g}^{-1}$	8000 h	this work
Zn–Al	Al(OTf) <sub>3</sub> /H <sub>2</sub> O	$0.2 \text{ mA cm}^{-2} @ 0.1 \text{ mAh g}^{-1}$	1700 h	24
Cu–Al 400 µm	Al(OTf) <sub>3</sub> /H <sub>2</sub> O	$0.5 \text{ mA cm}^{-2} @ 0.5 \text{ mAh g}^{-1}$	2000 h	25
TAl 250 μm	Al(OTf) <sub>3</sub> /H <sub>2</sub> O	$0.2 \text{ mA cm}^{-2} @ 0.2 \text{ mAh g}^{-1}$	50 h	26
A1 	Al(OTf) <sub>3</sub> /H <sub>2</sub> O+H <sub>3</sub> PO <sub>4</sub>	$1 \text{ mA cm}^{-2} @ 1 \text{ mAh g}^{-1}$	160 h	27
Al 100 μm	Al(ClO <sub>4</sub> ) <sub>3</sub> /H <sub>2</sub> O/ succinonitrile	$0.5 \text{ mA cm}^{-2} @ 0.5 \text{ mAh g}^{-1}$	100 h	28
Zn–Al 200 µm	ZnSO <sub>4</sub> /H <sub>2</sub> O	$1 \text{ mA cm}^{-2} @ 1 \text{ mAh g}^{-1}$	3000 h	29
Zn–Al 400 μm	ZnSO <sub>4</sub> /H <sub>2</sub> O	$0.5 \text{ mA cm}^{-2} @ 0.5 \text{ mAh g}^{-1}$	2000 h	30
Zn–Mn 250 μm	ZnSO <sub>4</sub> /H <sub>2</sub> O	$80 \text{ mA cm}^{-2} @ 16 \text{ mAh g}^{-1}$	760 h	31
Zn 50 μm	Zn(OTf) <sub>2</sub> /DMC-H <sub>2</sub> O	1 mA cm <sup>-2</sup> @ 0.5 mAh g <sup>-1</sup> 5 mA cm <sup>-2</sup> @ 2.5 mAh g <sup>-1</sup>	1000 h 800 h	32
Zn 50 μm	ZnSO <sub>4</sub> /EG-H <sub>2</sub> O	$\begin{array}{c} 0.5 \text{ mA cm}^{-2} @ 0.5 \text{ mAh g}^{-1} \\ 5 \text{ mA cm}^{-2} @ 0.5 \text{ mAh g}^{-1} \end{array}$	2668 h 160 h	33
(002) Zn 50 μm	Zn(OTf) <sub>2</sub> /H <sub>2</sub> O	$\frac{1}{1} \text{ mA cm}^{-2} @ 0.167 \text{ mAh g}^{-1}$ $\frac{10}{10} \text{ mA cm}^{-2} @ 1.67 \text{ mAh g}^{-1}$	800 h 200 h	34
Zn 50 μm	ZnSO <sub>4</sub> /EG-H <sub>2</sub> O	$2 \text{ mA cm}^{-2} @ 1 \text{ mAh g}^{-1}$	145 h	35
MOF-coated Zn 20 µm	ZnSO <sub>4</sub> /H <sub>2</sub> O	$0.5 \text{ mA cm}^{-2} @ 0.5 \text{ mAh g}^{-1}$	3000 h	36
ZF@F-TiO <sub>2</sub> Zn 30 μm	ZnSO <sub>4</sub> /H <sub>2</sub> O	$1 \text{ mA cm}^{-2} @ 1 \text{ mAh g}^{-1}$ 2 mA cm <sup>-2</sup> @ 2 mAh g <sup>-1</sup>	460 h 280 h	37
Mxene-coated Zn 50 μm	ZnSO <sub>4</sub> /H <sub>2</sub> O	$0.2 \text{ mA cm}^{-2} @ 0.2 \text{ mAh g}^{-1}$	800 h	38
PA-coated Zn 20µm	ZnSO <sub>4</sub> /H <sub>2</sub> O	$10 \text{ mA cm}^{-2} @ 10 \text{ mAh g}^{-1}$	150 h	39
ZGL@Zn 20µm	ZnSO <sub>4</sub> /H <sub>2</sub> O	$\begin{array}{c} 0.5 \text{ mA cm}^{-2} @ 0.5 \text{ mAh } \text{g}^{-1} \\ 1 \text{ mA cm}^{-2} @ 10 \text{ mAh } \text{g}^{-1} \end{array}$	2180 h 250 h	40

**Table S4.** Comparison of cycling performance of symmetric cells using alloy anodes, Al anodes, and Zn anodes.

Electrolyte	CN of organic solvent (coordinated/total)	<i>CN</i> of H <sub>2</sub> O (coordinated/total)	<i>CN</i> of OTf⁻
H <sub>2</sub> O-E		3.18 (11.3%)	2.82
DMF-HE	4.49 (34.5%)	0.51 (25.5%)	1.00
ACN-HE	2.34 (12.3%)	1.98 (99.0%)	1.72
PC-HE	2.91 (24.7%)	1.91 (95.5%)	1.18

**Table S5.** Radial distribution function g(r) analyses showing the coordination number (*CN*) of Al<sup>3+</sup> ions with solvents/anions.

**Table S6.** Determination of the sequence of band intensities upon the increased negative potentials on working electrode.

Electrolyte	Cross peak (cm <sup>-1</sup> )	Sign in synchronous 2D correlation spectrum	Sign in asynchronous 2D correlation spectrum	Sequence		
	(1640,1660)	+	_	1660→1640		
	(1620,1640)	+	+	1620→1640		
DMF-HE	(1620,1660)	+	_	1660→1620		
	Total sequence 1	660→1620→1640 cm <sup>-1</sup>				
	(1680,1814)	_	+	1814→1680		
	(1745,1783)	+	+	1745→1783		
	(1730,1783)	+	+	1730→1783		
	(1680,1783)	+	+	1680→1783		
PC-HE	(1730,1745)	+	_	1745→1730		
	(1680,1745)	+	+	1680→1745		
	(1680,3050)	+	_	3050→1680		
	(1745,3050)	+	_	3050→1745		
	<b>Total sequence 3050→1680→1745→1730→1783</b> cm <sup>-1</sup>					
	(2270,2276)	+	_	2276→2270		
	(2254,2276)	+	_	2276→2254		
	(2254,2270)	+	-	2270→2254		
ACN-HE	(2270,3050)	+	+	2270→3050		
	(2254,3050)	+	_	3050→2254		
	<b>Total sequence 2276→2270→3050→2254</b> cm <sup>-1</sup>					

Anode	Cathode	Electrolyte	Voltage	Capacity based on active material on cathode /current	Cycling stability retention/time/ cycles/current	Ref
Zn–Al 25 μm	PANI $\begin{array}{r} 4.1 \\ mg \ cm^{-2} \\ 10 \\ mg \ cm^{-2} \end{array}$	Al(OTf) <sub>3</sub> /ACN/ H <sub>2</sub> O (ACN-HE)	0.3–1.6 V	$\frac{141 \text{ mAh } \text{g}^{-1}}{0.5 \text{ mA } \text{cm}^{-2}}$ $\frac{110 \text{ mAh } \text{g}^{-1}}{0.5 \text{ mA } \text{cm}^{-2}}$	91%/1000cycles /2 mA cm <sup>-2</sup> 67%/300cyles /2 mA cm <sup>-2</sup>	this work
Al 	PANI 1.1 mg cm <sup>-2</sup>	Al(OTf) <sub>3</sub> /H <sub>2</sub> O+ H <sub>3</sub> PO <sub>4</sub>	0.6–1.7 V	$167 \text{ mAh } \mathrm{g}^{-1/}$ $0.5 \mathrm{A} \mathrm{g}^{-1}$	58%/3850 cycles/2 A g <sup>-1</sup>	27
Al 100 μm	SPANI 1.4 mg cm <sup>-2</sup>	Al(ClO <sub>4</sub> ) <sub>3</sub> /H <sub>2</sub> O/ succinonitrile	0.1–1.6 V	185 mAh g <sup>-1</sup> / 0.1 A g <sup>-1</sup>	89%/300 cycles/0.1 A g <sup>-1</sup>	28
Al 25 µm	PANI(H <sup>+</sup> ) 1.1 mg cm <sup>-2</sup>	AlCl3- [EMIM]Cl	0.3–2.0 V	$\frac{200 \text{ mAh } g^{-1}}{1 \text{ A } g^{-1}}$	84.5%/1000 cycles/6 A g <sup>-1</sup> 87.6%/8000 cycles/10 A g <sup>-1</sup>	41
Zn 10 μm	PANI $\frac{1.1}{10 \text{ mg cm}^{-2}}$ $\frac{10 \text{ mg}}{\text{ cm}^{-2}}$	Zn(OTf) <sub>2</sub> /H <sub>2</sub> O+ MeOH	0.6–1.6 V	219 mAh g <sup>-1</sup> / 0.1 A g <sup>-1</sup> 101 mAh g <sup>-1</sup> / 100 mA	85.5%/1000 cycles/5 A g <sup>-1</sup> 95.6%/300 cycles/100 mA	42
Zn 130 μm	PANI 17 mg cm <sup>-2</sup>	CNF-SO <sub>3</sub> Zn (separator)	0.5–1.6 V	$\frac{100 \text{ mAh } \text{g}^{-1}}{0.1 \text{ A } \text{g}^{-1}}$	95%/150 cycles/100 mA	43
Zn 20 μm	PANI 1.5 mg cm <sup>-2</sup>	Zn(OTf) <sub>2</sub> /H <sub>2</sub> O	0.5–1.5 V	95 mAh $g^{-1}/$ 5 A $g^{-1}$	94%/200 cycles/0.5 A g <sup>-1</sup> 92%/3000 cycles/5 A g <sup>-1</sup>	44
Zn	PANI-S 0.6 mg cm <sup>-2</sup>	ZnSO <sub>4</sub> /H <sub>2</sub> O	0.5–1.6 V	$\frac{184 \text{ mAh } \text{g}^{-1}}{0.2 \text{ A } \text{g}^{-1}}$	~100%/2000 cycles/0.5 A g <sup>-1</sup>	45
Zn	PANI-CNT 2 mg cm <sup>-2</sup>	ZnSO <sub>4</sub> /H <sub>2</sub> O	0–2.0 V	240 mAh g <sup>-1</sup> / 0.5 A g <sup>-1</sup>	50%/2000 cycles/14 A g <sup>-1</sup>	46
Zn	Q-PANI 	ZnSO <sub>4</sub> /H <sub>2</sub> O	0.5–1.6 V	$\frac{186 \text{ mAh } \text{g}^{-1}}{0.2 \text{ A } \text{g}^{-1}}$	88%/1500 cycles/2 A g <sup>-1</sup>	47
Zn	PANI 	ZnCl <sub>2</sub> /H <sub>2</sub> O	0.5–1.6 V	221 mAh g <sup>-1</sup> / 0.2 A g <sup>-1</sup>	96.6%/1000 cycles/3 A g <sup>-1</sup>	48
Zn on carbon cloth	PANI	$Zn(ClO_4)_2/H_2O$ /CSAM (gel)	0.5–1.5 V	156 mAh g <sup>-1</sup> / 0.1 A g <sup>-1</sup>	~100%/2000 cycles/5 A g <sup>-1</sup>	49
Zn on Au/nylon	SPANI $0.5 \text{ mg cm}^{-2}$	Zn(OTf) <sub>2</sub> /H <sub>2</sub> O /PVA (gel)	0.5–1.6 V	$\frac{180.5 \text{ mAh } \text{g}^{-1}}{0.5 \text{ A } \text{g}^{-1}}$	80%/1000 cycles/5 A g <sup>-1</sup>	50

## Table S7. Comparison of electrochemical performance of full cells using Al/Zn anodes and PANI cathodes.

Anode	Cathode	Electrolyte	Voltage	Capacity based on active material on cathode /based on two electrodes/current	Cycling stability retention/time/ cycles/current	Ref
Zn–Al 25 μm	AC 10.4 mg cm <sup>-2</sup>	Al(OTf) <sub>3</sub> /ACN/ H <sub>2</sub> O (ACN-HE)	0.5–1.8 V	50 mAh g <sup>-1</sup> / 18.1 mAh g <sup>-1</sup> / 2 mA cm <sup>-2</sup>	96%/ >2700 h/ >5000 cycles/ /2 mA cm <sup>-2</sup>	this work
Zn 30 μm	MOF-PC 10 mg cm <sup>-2</sup>	Zn(OTf) <sub>2</sub> /DMF	0.2–1.8 V	$\begin{array}{c} 36 \text{ mAh } g^{-1/} \\ 11.5 \text{ mAh } g^{-1/} \\ 10 \text{ mA } \text{ cm}^{-2} \end{array}$	~100%/ ~650 h/ 9000 cycles/ 10 mA cm <sup>-2</sup>	51
ZGL@Zn 20 µm	AC 30 mg cm <sup>-2</sup>	ZnSO <sub>4</sub> /H <sub>2</sub> O	0.2–1.8 V	~24 mAh g <sup>-1</sup> / ~16.2 mAh g <sup>-1</sup> / 15 mA cm <sup>-2</sup>	~100%/ ~620 h/ 6500 cycles/ 15 mA cm <sup>-2</sup>	40
Zn@HsGDY 	N-PC 22.95 mg cm <sup>-2</sup>	ZnSO <sub>4</sub> /H <sub>2</sub> O	0.2–1.8 V	32.6 mAh g <sup>-1</sup> / / 22.95 mA cm <sup>-2</sup>	~67%/ / 10000 cycles/ 22.95 mA cm <sup>-2</sup>	52
MCHSs- coated Zn	MCHSs 20 mg cm <sup>-2</sup>	ZnSO <sub>4</sub> /H <sub>2</sub> O	0.2–1.8 V	110 mAh g <sup>-1</sup> / / 20 mA cm <sup>-2</sup>		53
Zn 50 μm	N-AC $2-3 \text{ mg cm}^{-2}$	ZnSO <sub>4</sub> /H <sub>2</sub> O+ ethylene glycol	0.2–1.8 V	60 mAh g <sup>-1</sup> / / 5 A g <sup>-1</sup>	>100%/ /200 h/ 50000 cycles/ 5 A g <sup>-1</sup>	35
Zn 200 μm	$\begin{array}{c} \text{OCCs} \\ 0.3 \text{ mg cm}^{-2} \end{array}$	Zn(OTf) <sub>2</sub> /H <sub>2</sub> O	0–2.0 V	225 mAh g <sup>-1</sup> / / 0.1 A g <sup>-1</sup>	>100%/ 1200 h/ 300000 cycles/ 50 A g <sup>-1</sup>	54
Zn 	AC	ZnSO <sub>4</sub> /H <sub>2</sub> O+ MgSO <sub>4</sub>	0.2–1.8 V	154 mAh g <sup>-1</sup> / / 1 A g <sup>-1</sup>	98.7%/ / 10000 cycles/ 5 A g <sup>-1</sup>	55
Zn 	PC 1.4–2 mg cm <sup>-2</sup>	Zn(ClO <sub>4</sub> ) <sub>2</sub> /H <sub>2</sub> O	0–1.9 V	78.4 mAh g <sup>-1</sup> / / 20 A g <sup>-1</sup>	99.2%/ / 30000 cycles/ 20 A g <sup>-1</sup>	56
Zn 	NTC 1–1.5 mg cm <sup>-2</sup>	ZnSO <sub>4</sub> /H <sub>2</sub> O	0–2.0 V	100.7 mAh g <sup>-1</sup> / / 10 A g <sup>-1</sup>	~80.5%/ / 10000 cycles/ 5 g <sup>-1</sup>	57
Zn@Nafion- Zn-X 300 μm	AC	ZnSO <sub>4</sub> /H <sub>2</sub> O		~82 mAh g <sup>-1</sup> / / 0.5 A g <sup>-1</sup>	~94%/ / 1000 cycles/ 0.5 g <sup>-1</sup>	58
Al 15 μm	ZTC 10 mg cm <sup>-2</sup>	AlCl <sub>3</sub> - [EMIM]Cl	0.01– 2.2 V	157 mAh g <sup>-1</sup> / / 1 A g <sup>-1</sup>	86%/ / 1000 cycles/ 1 g <sup>-1</sup>	59
Al 100 μm	AC 1.4–2 mg cm <sup>-2</sup>	AlCl <sub>3</sub> - [EMIM]Cl	0.01– 2.2 V	150 mAh g <sup>-1</sup> / / 0.1 A g <sup>-1</sup>	90%/ / 1500 cycles/ 1 g <sup>-1</sup>	60
Al 	PCP-1600 1.2 mg cm <sup>-2</sup>	AlCl <sub>3</sub> - [EMIM]Cl	0.5– 2.25 V	136 mAh g <sup>-1</sup> / / 0.1 A g <sup>-1</sup>	96.3%/ / 2000 cycles/ 1 g <sup>-1</sup>	61

# Table S8. Comparison of electrochemical performance of hybrid capacitors using Zn/Al anodes and capacitive cathodes.



**Fig. S1.** (**a**–**d**) Nyquist plots for the symmetric cells consisting of Zn electrodes in H<sub>2</sub>O-E (**a**), DMF-HE (**b**), PC-HE (**c**), and ACN-HE (**d**) before cycling and after the 1<sup>st</sup>, 10<sup>th</sup>, and 20<sup>th</sup> cycles under 0.2 mA cm<sup>-2</sup> @ 0.2 mAh g<sup>-1</sup>.



**Fig. S2.** Potential profiles for the symmetric cell consisting of Zn (25  $\mu$ m) foils and ACN-HE cycled under 0.2, 0.4, 1.0, 2.0, 4.0 mA cm<sup>-2</sup> with a plating/stripping time of 1 h. Inset showing the photograph of the electrode after 1000 h of cycles.



**Fig. S3.** (**a**, **b**) TOF-SIMS 3D images of Al<sup>+</sup> (**a**), and Zn<sup>+</sup> (**b**) spatial distribution for the Zn–Al alloy anode after 20 cycles under 0.2 mA cm<sup>-2</sup> @ 0.2 mAh g<sup>-1</sup> in ACN-HE.



**Fig. S4.** (**a**, **b**) XPS spectra of O 1s (**a**) and C 1s (**b**) for the Zn–Al alloy anodes after 20 cycles under 0.2 mA cm<sup>-2</sup> @ 0.2 mAh g<sup>-1</sup> in H<sub>2</sub>O-E (gray), DMF-HE (blue), PC-HE (green), and ACN-HE (red). The O and C elements arise from adventitious impurities.<sup>62</sup>



**Fig. S5.** (**a**, **b**) XPS spectra for the Zn–Al alloy anode after 20 cycles under 0.2 mA cm<sup>-2</sup> @ 0.2 mAh g<sup>-1</sup> in ACN-HE. Evolution of Al 2p (**a**) and Zn 2p (**b**) after Ar<sup>+</sup> sputtering on the Zn–Al alloy surface for 300 s, 600 s, and 900 s, along with Al and Zn foil as the references, respectively.



**Fig. S6.** XRD pattern for the Zn–Al alloy anode in the symmetric cell after 20 cycles under 0.2 mA cm<sup>-2</sup> @ 0.2 mAh g<sup>-1</sup> in ACN-HE, with Zn foil as the reference.



**Fig. S7.** (**a**, **b**) Magnifications near cathodic stability (**a**) and anodic stability (**b**) of the ESWs for the four electrolytes determined by CV tests at a scan rate of 5 mV s<sup>-1</sup> in three-electrode cells. A current density of 0.1 mA cm<sup>-2</sup> was defined as the cutoff for determining the onset potentials of electrolyte decomposition.



Fig. S8. (a, b) Photographs showing the bubble formation in  $H_2O-E$  (a) and the absence of bubbles in DMF-HE (b) upon  $Al^{3+}$  deposition on the Zn substrate at negative potentials in three-electrode cells.



**Fig. S9.** Potential profiles for the symmetric cells using Zn foils and anhydrous  $Al(OTf)_3/DMF$  electrolyte cycled under 0.2 mA cm<sup>-2</sup> and 0.2 mAh g<sup>-1</sup>.



**Fig. S10.** Dynamic viscosity for the H<sub>2</sub>O-E (gray), DMF-HE (blue), PC-HE (green), and ACN-HE (red).



**Fig. S11.** (**a**–**d**) CA polarization curves with an applied voltage of 10 mV for the symmetric cells consisting of Zn electrodes in H<sub>2</sub>O-E (**a**), DMF-HE (**b**), PC-HE (**c**), and ACN-HE (**d**). Insets showing the corresponding Nyquist plots before and after CA polarization. The transference number of Al<sup>3+</sup> ( $t_{Al}$ ) was calculated based on *Equation* (1). The  $t_{Al}$  of H<sub>2</sub>O-E cannot be measured using this method because of the accompanied hydrogen evolution leading to the overestimation of  $I_s$  value.



**Fig. S12.** (**a**–**e**) Optimized geometrical structures from DFT calculations for the Al<sup>3+</sup>–DMF (**a**), Al<sup>3+</sup>–PC (**b**), Al<sup>3+</sup>–ACN (**c**), Al<sup>3+</sup>–H<sub>2</sub>O (**d**), and Al<sup>3+</sup>–OTf<sup>-</sup> (**e**). Al purple, H white, C gray, O red, N blue, S yellow, F green.



**Fig. S13.** (**a**–**d**) MD simulated geometrical structures for the  $H_2O$ -E (**a**), DMF-HE (**b**), PC-HE (**c**), and ACN-HE (**d**). Al purple, H white, C gray, O red, N blue, S orange, F cyan. Only solvation sheaths of  $Al^{3+}$  are shown for clarity.



**Fig. S14.** (**a**–**d**) Coordination distribution analyses of Al<sup>3+</sup> in the H<sub>2</sub>O-E (**a**), DMF-HE (**b**), PC-HE (**c**), and ACN-HE (**d**).



Fig. S15. <sup>1</sup>H NMR spectrum for the DMF-HE showing the integral of peak areas.

Deconvolution of the peaks in Fig. S15 shows that the molar ratio of bound and free H<sub>2</sub>O is 0.32:1.00, and that of bound and free DMF is 0.82:1.88 in DMF-HE. Moreover, the Al<sup>3+</sup>:H<sub>2</sub>O:DMF molar ratio is 1:2:13 according to the composition of DMF-HE (Table S3). Therefore, the coordination number of Al<sup>3+</sup> to H<sub>2</sub>O is  $0.32/(0.32+1.00)\times 2 = 0.48$ , and the coordination number of Al<sup>3+</sup> to DMF is  $0.82/(0.82+1.88)\times 13 = 3.9$ .



**Fig. S16.** FT-IR spectrum showing the SO<sub>3</sub> stretching of OTf<sup>-</sup> anions for the three hybrid electrolytes.



**Fig. S17.** (**a**–**f**) FT-IR spectra in different regions for the DMF-HEs (**a**,**b**), PC-HEs (**c**,**d**), and ACN-HEs (**e**,**f**) with increased H<sub>2</sub>O to Al<sup>3+</sup> molar ratios of 2, 4, 6, 8, and 10 as the perturbation.



**Fig. S18.** Schematic of in situ FT-IR analysis conducted in a two-electrode cell setup with a porous Zn-deposited carbon paper as the working electrode, and Zn foil as the counter and reference electrodes in hybrid electrolytes. FT-IR spectra were measured at the backside of the working electrode closely attached to the crystal.



**Fig. S19.** (**a**–**f**) FT-IR spectra in different regions for the DMF-HEs (**a**,**b**), PC-HEs (**c**,**d**), and ACN-HEs (**e**,**f**) with increased potentials of 25, 50, 75, 100 mV on working electrode as the perturbation.



**Fig. S20.** (**a**–**d**) Synchronous (**a**, **c**) and asynchronous (**b**, **d**) 2D correlation spectra for PC-HE in 1900–1600 and 3660–2840) cm<sup>-1</sup> hetero-region (**a**, **b**), and ACN-HE in 2280–2245 and 3660–2840 cm<sup>-1</sup> hetero-region (**c**, **d**). The positive and negative cross peaks are described as red and blue colors, respectively.



**Fig. S21.** Electrochemical performance of the Zn–Al//PANI full cells under a cathode loading of ~4.0 mg cm<sup>-2</sup>. (**a**, **b**) CV curves at various scan rates (**a**) and rate capability at various current densities (**b**) for the Zn–Al//PANI full cell in ACN-HE. (**c**) Comparison of typical GCD curves at 10<sup>th</sup> cycle during cycling tests for the Zn–Al//PANI full cells in H<sub>2</sub>O-E (gray), DMF-HE (blue), PC-HE (green), and ACN-HE (red).



Fig. S22. (a) Photographs showing the free-standing PANI cathode with a loading of ~10 mg cm<sup>-2</sup>. (b) Rate capability at various current densities for the Zn–Al//PANI full cells under a cathode loading of ~10 mg cm<sup>-2</sup> in ACN-HE.



Fig. S23. (a) Photographs showing the free-standing AC cathode with a loading of  $\sim 10$  mg cm<sup>-2</sup>. (b) CV curves at various scan rates for the Zn–Al//AC full cells in ACN-HE.



Fig. S24. XRD pattern for the VO<sub>2</sub>/CNTs composites.



Fig. S25. (a–d) SEM image (a), TEM image (b), associated EDX elemental mapping of V, O, and C (c), and HRTEM image (d) for the VO<sub>2</sub>/CNTs composites. As shown in (d), the lattice fringes with an interplanar spacing of 3.56 Å correspond to the (110) plane of the monoclinic  $VO_2$  phase.



Fig. S26. (a, b) Rate capability at various current densities (a) and CV curves at various scan rates (b) for the  $Zn-Al//VO_2/CNTs$  full cells in ACN-HE with a  $H_2O$  to  $Al^{3+}$  molar ratio of 10.



Fig. S27. Comparison of cycling stabilities at 2 mA cm<sup>-2</sup> for the Zn–Al//VO<sub>2</sub>/CNTs full cells in ACN-HEs with  $H_2O$  to  $Al^{3+}$  molar ratios of 2 (cyan) and 10 (purple).

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