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# **Electronic Supplementary Information**

## Supporting Information

## Hydrated Deep Eutectic Electrolyte with Finely-Tuned Solvation Chemistry for High-

### **Performance Zinc-Ion Batteries**

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#### **Experimental section**

Electrolyte preparation: 2 mol L<sup>-1</sup> of Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> aqueous electrolyte was prepared by dissolving zinc trifluorosulfonate into deionized water. To prepare deep eutectic solvent electrolytes (DES), Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and ethylene glycol with different molar ratios of 1:3, 1:5, 1:6, and 1:10 were mixed under constant stirring at 70 °C until forming a transparent liquid. To prepare hydrated deep eutectic solvent electrolytes, deionized water with different volume ratios of 10%, 30%, 40%, and 50% were added into DES (1:6) under constant stirring, named HDES<sub>10</sub>, HDES<sub>30</sub>, HDES<sub>40</sub>, and HDES<sub>50</sub>, respectively.

**Electrode preparation:** NVO cathode material was prepared by a single-step hydrothermal reaction according to our previous work.<sup>1</sup> In a typical synthesis process, 5 mmol of ammonium metavanadate was dissolved into 30 ml of deionized water with 10 min stirring under ambient environment. After that, a mixture of 6 mmol of oxalic acid and 1 mmol of ammonium fluoride were added. Then, the mixed solution was transferred into 50 ml Teflon-lined autoclaves and heat up to 180 °C for 6 hours. The as-obtained bronze-color precipitates were washed by deionized water for several times. Finally, the washed sample was freeze-dried for 2 days. The cathode electrodes were fabricated by mixing polyvinylidene fluoride (Sigma-Aldrich), Super-P (Sigma-Aldrich) and as-prepared materials with a ratio of 1:2:7 using N-methyl-2-pyrrolidone as the solvent. The mixture slurry was printed on a hydrophilic carbon paper and then transferred to a vacuum oven to dry under 80 °C for 10 hours.

**Materials characterizations:** SEM was conducted on JEOL-JSM-6700F. The *in-situ* optical microscope was conducted on VisiScope® BL254 T1 (VWR) instrument. The XRD patterns were performed on a PANalytical Empyrean device with Cu  $K_{\alpha}$  radiation. A LabRAM HR Evolution instrument (laser wavelength: 532 nm) was carried out to collect the Raman spectra. FTIR-spectra were conducted on an ATRFTIR (BRUKER, platinum-ATR). X-ray photoelectron spectroscopy were collected by a Thermo scientific K-alpha

photoelectron spectrometer. The 3D morphologies were conducted on a 3D optical profilometer (RTEC UP Dual Model).

**Electrochemical tests:** The electrochemical performances of Zn//Zn symmetric cells, Zn//Cu asymmetric cells, Zn//NVO full cells were tested using CR 2025 coin cells. The evaluation of cyclic voltammetry, linear sweep voltammetry, chronoamperometry measurement, and electrochemical impedance spectroscopy tests were achieved by a VMP3 Biologic potentiostat. The evaluation of galvanostatic charge-discharge was tested by a Neware battery testing system. All Zn foil (99.9%) anodes were utilized after polished by 1000 grit sandpaper. Glass-fiber (GF/A, Whatman) was chosen as the separator. Additionally, linear sweep voltammetry was tested using Swagelok cells with a Ti foil working electrode and a Zn foil reference electrode at a scan rate of 5 mV s<sup>-1</sup>. To test the activation energy, electrochemical impedance spectroscopy was conducted at different temperatures ranging from 303.15 to 353.15 K. Then, the activation energy was calculated by Arrhenius equation:

$$- \ln R_{ct} = \ln A - \frac{E_a}{RT}$$

where,  $R_{ct}$  is the charge-transfer resistance, A is the frequency factor, and  $E_a$  is the activation energy related to the zinc-ion transport and the desolvation process.

#### **Computational Details**

MD simulations were performed by the forcite module implemented in the Materials Studio. The general COMPASS III force field, an ab initio forcefield, was used to describe all the interactions between the ions. The atomic partial charges were derived using *ab initio* electrostatic potentials. To ensure transferability, a constrained ESP approach was used. The valence parameters were derived using CFF *ab initio* parameterization techniques. The DFT calculations were performed by the CASTEP module in the Materials Studio. The cutoff energy was set as 550 eV, the  $\Gamma$ -centered *k*-mesh was adopted as  $3 \times 3 \times 3$  for the geometry optimization for all structures. The criteria of convergence for max force, stress, and displacement were 0.02 eV/A, 0.02 GPa, and 0.001 Å, individually. The PBE functional was employed,<sup>2</sup> and the ultrasoft pseudopotential for each atom was adopted.<sup>3</sup>

The binding energy ( $\Delta E_{bind}$ ) was calculated by the following equations:

$$\Delta E_{bind} = \frac{E_{total} - E_{Zn^2} + -\sum E_{molecule}}{6} \#(1)$$

 $E_{total}$ ,  $E_{Zn^{2}+}$ ,  $E_{ligand}$  are the final energies of the complex,  $Zn^{2+}$ , and the molecule in the corresponding solvation sheath.

The charge density difference is calculated based on:

$$\Delta \rho = \rho(molecule + Zn^{2+}) - \rho(Zn^{2+}) - \sum \rho(molecule)$$

The  $\rho$  denotes the charge density.



**Fig. S1** (a) Schematic diagram of the preparation of DES and HDES electrolytes. (b) Corresponding optical photographs of DES electrolytes with different molar ratios of ethylene glycol and zinc trifluorosulfonate. (c) Optical photographs of HDES and AE electrolytes.



**Fig. S2** Charge density difference of the zinc ion with different ligands. (a)  $Zn^{2+}$ -otf<sup>-</sup>. (b)  $Zn^{2+}$ -eg. (c)  $Zn^{2+}$ -H<sub>2</sub>O. The white, gray, red, yellow, light blue and purple balls represent hydrogen, carbon, oxygen, sulfur, fluorine atoms and zinc ions, respectively.



Fig. S3 The change of the average binding energy of  $Zn^{2+}$  towards the molecule in the first solvation structure.



**Fig. S4** Long-term cycling performances of Zn//Zn symmetric cells at 1 mA cm<sup>-2</sup>-1 mAh cm<sup>-2</sup> in different electrolytes.



Fig. S5 Comparison of Coulombic efficiency of different electrolytes.



Fig. S6 Comparison of ionic conductivity of different electrolytes.



**Fig. S7** Comparison of overpotential of different electrolytes. (a) Voltage-time curve of Zn//Zn symmetric cell in DES electrolyte. (b) Voltage-time curves of Zn//Zn symmetric cells in AE and HDES electrolytes.



**Fig. S8** (a-f) Nyquist plots at various temperatures of Zn//Zn symmetric cells in AE, HDES<sub>50</sub>, HDES<sub>40</sub>, HDES<sub>30</sub>, HDES<sub>10</sub>, and DES, respectively. (g) Arrhenius curves of Zn//Zn symmetric cells in different electrolytes: activation energy.

Electrolyte	Viscosity	Density	Thermal stability	Cost
AE	13.5 mPa.s	1.371 g cm <sup>-3</sup>	nonflammable	6.2 \$ cm <sup>-3</sup>
HDES	22.8 mPa.s	1.378 g cm <sup>-3</sup>	nonflammable	6.3 \$ cm <sup>-3</sup>
DES	167.2 mPa.s	1.515 g cm <sup>-3</sup>	inflammable	8.3 \$ cm <sup>-3</sup>

Table S1. Physicochemical properties of different electrolytes.



**Fig. S9** Thermal stability of different electrolytes. (a) Thermogravimetric (TG) analysis of different electrolytes. (b) DTG curves of different electrolytes. (c) Differential scanning calorimetry (DSC) analysis of different electrolytes.



Fig. S10 Flammability test. (a) eg. (b) DES. (c) HDES. (d) AE.



**Fig. S11** Formation of deep eutectic solvent. (a,c) Original Raman spectra. (b) Fitted Raman spectra. (d-e) FTIR-spectra of DES with different ratios of zinc trifluorosulfonate and ethylene glycol.



Fig. S12 DSC curves of different liquids.



**Fig. S13** (a-b) FTIR-spectra of HDES electrolytes with different water contents. (c) Raman spectra of HDES electrolytes with different water contents.



Fig. S14 Chronoamperometry curves of Zn//Zn symmetric cells of AE and HDES electrolytes.



**Fig. S15** Characterization of Zn anodes after cycling in AE and HDES. (a) Raman spectra. XPS spectra: (b) S 2p, (c) F 1s.



**Fig. S16** (a-b) SEM images of zinc anode after cycled in the AE electrolyte. (c) SEM image of zinc anode after cycling in the DES electrolyte (d) SEM image if zinc anode after cycling in the HDES electrolyte.



**Fig. S17** Morphologies of cycled Zn anodes. (a) 3D optical profile of Zn anode after cycling in AE. (b) 3D optical profile of Zn anode after cycling in HDES.



Fig. S18 (a) Long-term cycling performance of Zn//Zn symmetric cell in HDES electrolyte at 3 mA cm<sup>-2</sup>-3 mAh cm<sup>-2</sup>. (b) Long-term cycling performance of Zn//Zn symmetric cell in HDES electrolyte at 5 mA cm<sup>-2</sup>-5 mAh cm<sup>-2</sup>.



Fig. S19 Rate performance of Zn//Zn symmetric cell in DES electrolyte.



**Fig. S20** (a) CV curves of Zn-NVO battery in AE electrolyte for 10 cycles at 0.2 mV s<sup>-1</sup>. (b) Voltage profiles of Zn-NVO in AE electrolyte at different current densities.



Fig. S21 (a) SEM image of pristine NVO cathode. (b) SEM image of the zinc anode after cycling in the AE electrolyte. (c) SEM image of zinc anodes after cycling in the HDES electrolyte.



**Fig. S22** (a) Ex-situ XRD patterns of NVO cathodes in AE electrolytes at different charge/discharge states. (b) Corresponding GCD curves of (a) at 0.3 A g<sup>-1</sup>.



**Fig. S23** (a) *In-situ* Raman spectra of NVO cathodes in the AE electrolyte. (b) *In-situ* Raman spectra of the NVO cathode in an HDES electrolyte.



**Fig. S24** De-solvation process of HDES. (a) Desolvation energy of HDES during the individual de-solvation process. (b) Schematic diagram of the individual de-solvation process.

### References

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