# **Supporting Information**

# Nano-scaled Hydrophobic Confinement of Aqueous Electrolyte by Nonionic Amphiphilic Polymer for Long-lasting and Widetemperature Zn-based Energy Storage

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#### **Experimental section**

**Materials.** All materials were used as received unless otherwise specified. Acrylamide (AM) and methyl acrylate (MA) were passed through an Al<sub>2</sub>O<sub>3</sub> column just before polymerization to eliminate the inhibitor. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized once from ethanol before use. Zn (thickness 200  $\mu$ m), Cu foils (thickness 100  $\mu$ m), Ti mesh, polytetrafluoroethylene (PTFE, 60 wt.% aqueous dispersion), acetylene black and Ketjen black (KB) were purchased from Shenzhen Kejing. Zinc triflate (98%), or (Zn(OTf)<sub>2</sub>), was obtained from Shanghai Aladdin. Activated carbon YEC-8A (AC) was provided by Fuzhou Yihuan Carbon. Vanadium oxide (V<sub>2</sub>O<sub>5</sub>, 99%) was purchased from Macklin. Glass fiber separator was obtained from Whatman.

**Synthesis of amphiphilic polymer additive (APA)**. In a 50 mL Schlenk flask, AM (4.12 g, 58.0 mmol), MA (0.88 g, 10.2 mmol), AIBN (0.125 g, 0.76 mmol) and DMF (45 mL) were mixed under stirring for 30 min. The flask was then sealed and purged with high-purity nitrogen for 30 min, and placed in an oil bath at 70 °C for 6 h. After concentrating the solution, the product was precipitated in ethyl alcohol for three times. The sample was dried in a vacuum oven at 60 °C for 24 h. Compositional ratios of AM and MA in the copolymers are determined by <sup>1</sup>H NMR.

**Preparation of electrolyte solution.** The 3M aqueous pristine electrolyte solution was prepared by dissolving stoichiometric amount of  $Zn(OTf)_2$  in deionized water. The electrolyte solutions containing APA were prepared by adding 0.1 wt.%, 0.5 wt.%, 1.0 wt.%, 1.5 wt.% and 2.0 wt.% of APA into 3M  $Zn(OTf)_2$  aqueous solutions. The wt.% denotes the weight percent of APA in the electrolyte.

**Preparation of Na<sub>2</sub>V<sub>6</sub>O<sub>16</sub>·1.5H<sub>2</sub>O (NVO) Cathode.** V<sub>2</sub>O<sub>5</sub> cathode material was synthesized according to published literature. <sup>[1,2]</sup> Specifically, 3g of V<sub>2</sub>O<sub>5</sub> was dissolved in 45 mL of 2 M sodium chloride (NaCl) aqueous solution, following by stirring for 72 h. An orange red gel was then obtained, which was washed with deionized water and ethanol for three times to remove the excess V<sub>2</sub>O<sub>5</sub>. The obtained product was dried in a vacuum oven at 60 °C for 12 h before use.

**Material characterization.** Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were obtained on a Bruker AVANCE III 400 MHz spectrometer. Infrared spectroscopy (IR) was recorded on a Thermo Scientific Nicolet 6700 instrument. The hydrodynamic diameters (Dh) of polymers were measured on a Brookhaven Instruments BI-200SM laser scatterometer with a digital correlator (BI-9001). The specific viscosity ( $\eta_{sp}$ ) of APA with different concentrations in aqueous solution and pristine electrolyte was measured by Ubbelohde viscometer, where the average capillary diameter of Ubbelohde viscometer was 0.57 mm, according to Poiseuille equation:

$$\eta_{sp} = \frac{t}{t_0} - 1$$

where *t* is the outflow time of APA solution,  $t_0$  is the outflow time of solvent (water or pristine electrolyte). The contact angles between metal Zn and different electrolyte were measured on an Dataphysics OCA25 optical contact angle goniometer. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer (Cu Ka radiation,  $\lambda$ =1.504 Å). The morphologies and element mapping were observed on a ZEISS EVO/MA 15 scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDS). The surface compositions of Zn anodes were investigated on a Thermo Scientific K-Alpha+ X-ray photoelectron spectroscope (XPS). The ion conductivity of different electrolytes was collected through a conductivity meter (YOKE, DDS-307A). The in-situ optical images were observed by an optical microscope with an in-situ optical electrochemical cell.

**Electrochemical Tests.** The Zn-Zn symmetric cells, Zn-Cu asymmetric cells, Zn-AC hybrid ion supercapacitors and Zn-NVO batteries were assembled with CR2032 coin using glass fiber as the separator and 3M Zn(OTf)<sub>2</sub> as the electrolyte. The cycling performances of cells were then evaluated by a Neware battery cycler (CT-4008T-5V10mA-164, Shenzhen, China). For Zn-Zn symmetric cells, the current densities were varied from 1.0 to 20.0 mA cm<sup>-2</sup> (each plating or stripping process for 1 h) during galvanostatic plating/stripping process. For Zn-Cu asymmetric cells, the coulombic efficiency (CE) of Zn stripping/plating were investigated at various current densities from 1 to 5 mA cm<sup>-2</sup> (each plating or stripping process for 1 h). In-situ electrochemical impedance spectra (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried on a Gamry Reference 3000 electrochemical workstation. In-situ Infrared spectroscopy (IR) was collected on a Bruker Vertex 70V IR spectrometer. Tafel plots were obtained on a three-electrode system using Zn plate as the work and electrode and Ag/AgCl as the reference electrode. Chronoamperograms (CAs) of the Zn-Zn symmetric

cells were recorded at a scan rate of 10 mV s<sup>-1</sup> and under a -200 mV overpotential, respectively. The Zn-AC hybrid ion supercapacitors were assembled using activated carbon (AC) as cathode and Znmetal as anode, with a 3 M pristine Zn(OTf)<sub>2</sub> electrolytes or APA-containing electrolyte. In a typical fabrication of AC cathode, a slurry was prepared by mixing AC, Ketjen black (KB), and polytetrafluoroethylene (PTFE) at a mass ratio of 8:1:1. The obtained slurry was rolled to a freestanding film of about 120 µm thick. The film was then cut into discs ( $\Phi = 10$  mm) and pressed on a Ti mesh ( $\Phi = 15$  mm), followed by drying in vacuum at 110 °C overnight. The mass loading of active material was adjusted to about 1.0-1.5 mg cm<sup>-2</sup>. In a typical fabrication of NVO cathode, a slurry was prepared by mixing NVO, acetylene black, and polyvinylidene difluoride (PVDF) at a mass ratio of 7:2:1. The obtained slurry was then cast onto a carbon cloth (thickness: 0.35mm) by a doctorblade method and cut into discs ( $\Phi = 8$  mm), followed by drying in vacuum at 60 °C overnight. The mass loading of active material was adjusted to about 2 mg cm<sup>-2</sup>.

**Molecular dynamics (MD) Simulations**. The simulations were performed using a BIOVIA package (version 2020) with the Amber force field. The whole simulation consists of five steps. First, different molecular components, including H<sub>2</sub>O, Zn<sup>2+</sup>, OTf<sup>-</sup>, and APA, were chosen and their molecular structures were drawn. Specially, a modeling chain unit of AM-AM-AM-AM-AM-AM-AM-MA with random arrangement was used to represent the entire APA. Then the energy of all selected molecules of each structure is minimized to obtain a stable structure in force. The third step consists of substeps, (I) construction of the simulated solution box and (II) energy minimization of the simulated solution box. The size of the box is  $10 \times 10 \times 10$  nm<sup>3</sup>, where periodic boundary conditions were set in all three axes. The simulation cells contain 5560 H<sub>2</sub>O, 300 Zn(OTf)<sub>2</sub>, and 30 modeling chain units. The fourth step is the equilibrium dynamics under 50 picosecond system (constant pressure, constant temperature) with random initial velocity. The integration time step was 1 femtosecond.<sup>[3-5]</sup> The last step is the radial distribution function (RDF) analysis of the final trajectory to examine the intermolecular interactions between different atoms. The calculations used in MD simulation and RDF analysis are all done on the Visual Molecular Dynamics software (VMD).<sup>[6]</sup>

**Density functional theory (DFT) calculation**. All combination structures were optimized by Density functional theory (DFT) at  $PBE0^{[7]}$  hybrid functional with 6-31+g(d,p) basis set using Gaussian

16 program. All calculations were carried out with the atom-pairwise dispersion correction (DFT-D3) and the implicit universal solvation model based on Solute Electron Density (SMD).<sup>[8-10]</sup> The calculation formula of combined energy is as follows:

$$E = E_{ab} - E_a - E_b$$

Where *E* is the binding energy,  $E_a$  and  $E_b$  are the respective energies of Zn ion and the bonded molecule, respectively, and  $E_{ab}$  is the total energy after binding. All the energy was Electronic Energy + Zeropoint Energy Correction. The Electrostatic potential (ESP) were under the PBE0/6-31g(d)<sup>[7,8]</sup> hybrid functional/basis set and analyzed by the Multiwfn<sup>[11]</sup> package. The ESP were drawn by VMD package.<sup>[12]</sup>

The 101 crystal plane of Zn was extracted from the database and expanded to an appropriate size. The calculations of crystal and adsorbed molecule under GGA/PBE functional were performed with fine precision. The conversion formula is as follows:

$$E = E_{ab} - E_a - E_b$$

Where *E* is the adsorption energy,  $E_a$  and  $E_b$  are the energies of Zn unit cell and adsorbed molecule respectively, and  $E_{ab}$  is the total energy after adsorption.

**Finite element analysis method**. The simulation of the electric and concentration field was implemented in finite element solver. The secondary current distribution of electrochemistry was calculated in a two-dimensional model using finite element simulation to perform the simulations of the electric and concentration field. The width of the simulation area is 90 µm and the height is 70 µm. The ion concentration in the near-surface area of the Zn electrode and the spatial distribution of the electrochemical current density were simulated during the Zn deposition process. The pristine and APA-containing electrolyte were set with different macro ion diffusion coefficients to describe the diffusion ability of complex ions in different electrolyte additive strokes. Specifically, the electric field in the electrolyte domain followed the constitutive relation, the electrochemical process on the electrode surface followed the boundary condition of the Buter-Volmer kinetic equation and the migration of Zn-ions followed the Fick's law and the Nernst-Einstein relationship.

## Figure



Fig. S1 <sup>1</sup>H NMR spectrum of APA-LMW with peak assignments and integrals.

The molar content of AM, calculated using  $(\int_{c/2}) / (\int_{c/2} + \int_{d/3})$  from the integration in <sup>1</sup>H NMR (Fig. S1), is 0.84, which is in good agreement with the molar feeding ratio of AM in preparation (0.85).



Fig. S2 IR spectrum of APA-LMW with peak assignments.



**Fig. S3** Visual appearance of APA with different molecular weights dissolved in water and in pristine electrolyte, respectively.



**Fig. S4** Specific viscosity ( $\eta_{sp}$ ) of APA-LMW with the concentration of 1wt.% in pure water and pristine electrolyte.



Fig. S5 Ionic conductivity of APA-containing electrolytes at different APA contents.



Fig. S6 3D snapshots of MD simulations for  $Zn^{2+}$  ion in pristine electrolyte. One  $Zn^{2+}$  ion combines with four H<sub>2</sub>O molecules and two OTf<sup>-</sup> counterions in the solvation structure.





**Fig. S8** RDFs and coordination numbers for (a)  $Zn^{2+}$ -O (H<sub>2</sub>O) and (b)  $Zn^{2+}$ -O (OTf<sup>-</sup>) in pristine electrolyte environment.



**Fig. S9** RDFs and coordination numbers for (a)  $Zn^{2+}-N$  (APA) and (b)  $Zn^{2+}-O$  (OTf<sup>-</sup>) in the APA-containing electrolyte environment.



**Fig. S10** Nyquist plots of Zn-Zn symmetric cells with pristine electrolyte and APA-containing electrolyte.



**Fig. S11** XRD diffractograms of bare Zn and the Zn soaked in pristine electrolyte and APAcontaining electrolyte for 10 days under 25 °C.

Several new characteristic peaks of zinc triflate hydroxide hydrate  $(Zn_xOTf_y(OH)_{2x-y} \cdot nH_2O$  at 8.2, 12.4 and 17.5°) and zinc oxide (ZnO at 37.2°) is observed in the XRD pattern of bare Zn soaked in pristine electrolyte, whereas only one new diffraction peak of zinc triflate hydroxide hydrate (at 8.1°) with very low intensity is found for the Zn-metal soaked in APA-containing electrolyte, indicating the corrosion inhibiting effect of APA.



**Fig. S12** SEM images of Zn-metal anode soaked in (a) pristine electrolyte and (b) APAcontaining electrolyte for 10 days under 25 °C.

The corrosion of Zn-metal anode soaked in pristine electrolyte is more clearly seen, where the surface is filled with bulky irregular micro-flakes and Zn dendrite (Fig. S12a). By contrast, the Zn anode in APA-containing electrolyte shows a much smoother surface (Fig. S12b). No obvious dendrite is found even under SEM, although a few scattered particulate substances seem to appear on the surface.



**Fig. S13** XRD diffractograms of Zn-metal soaked in pristine electrolyte and APA-containing electrolyte at 60 °C for 12 h.

Fig. S13 shows that several new characteristic peaks of  $Zn_xOTf_y(OH)_{2x-y} \cdot nH_2O$  (at 8.2, 12.4 and 17.5°) and ZnO (at 37.2°) are observed in the XRD diffractograms of bare Zn soaked in pristine electrolyte. In contrast, only the new diffraction peaks of  $Zn_xOTf_y(OH)_{2x-y} \cdot nH_2O$  (at 8.1, 12.4 and 17.5°) with relatively low intensity are observed for the Zn soaked in APA-containing electrolyte, further indicating the anti-corrosion effect of APA.



Fig. S14 Tafel plots of Zn-metal tested in pristine and APA-containing electrolyte.



**Fig. S15** (a) Hydrogen evolution reaction (HER) and (b) oxygen evolution reaction (OER) of electrolytes determined using LSV at a scan rate of  $1 \text{ mV s}^{-1}$ .

As shown in Fig. S15, the HER overpotential of APA-containing electrolyte decreases to - 0.165 V from -0.131 V for pristine electrolyte, while the OER overpotential of the APA-containing electrolyte increases to 2.72 V from 2.66 V for pristine electrolyte. These results well demonstrate that APA can expand the electrochemical stability window.



Fig. S16 Energy dispersive spectroscopy (EDS) mapping of Zn soaked in APA-containing electrolyte.



Fig. S17 IR spectra of APA, bare Zn soaked for 10 d in APA-containing electrolyte, and bare Zn.

Fig. S17 shows that the Zn foil soaked in APA-containing electrolyte displays similar IR bands with pristine APA, suggesting the adsorption of polymer additive on the Zn surface. Moreover, the C=O peak of bare Zn soaked in APA-containing electrolyte has a blue shift from 1665 cm<sup>-1</sup> to 1678 cm<sup>-1</sup>, which is attributed to the strong interaction between Zn and the polar amide groups in APA, confirming the chemical adsorption of the polymer additive on the Zn surface.



**Fig. S18** Electric double layer capacitance (EDLC) measurements for Zn-Zn symmetric cells using pristine electrolyte and APA-containing electrolyte. (a, b) CV curves. (c, d) Plots of calculated capacitive currents versus scan rates. Note: The EDLC was calculated through the equation C = i/v (C: capacitance, i: current. The value of i was determined by taking the half of the current difference between positive and negative scan under each scanning rate).



**Fig. S19** (a) Measurement setup of the in-situ electrochemical impedance spectroscopy during continuous Zn deposition in Zn-Zn symmetrical cell. Each discharge process is separated by a 3 min interval, with a total measurement time of 120 min (20 cycles). (b) In-situ EIS of Zn-Zn symmetric cell using pristine electrolyte at 25 °C during electro-plating of  $Zn^{2+}$ .



Fig. S20 Simulation of (a, b) electric field distribution and (c, d)  $Zn^{2+}$  ion concentration at the electrode/electrolyte interface.

As shown in Fig. S20a, at the electrode/electrolyte interface without APA, the electric field becomes non-uniformly distributed as Zn continuously deposits, and the maximum value of current density occurs near the tip of the electrode surface that eventually leads to uncontrollable growth. In turn, the uneven distribution of electrical field would consume  $Zn^{2+}$  flux quickly and form a low concentration area, resulting in uneven concentration on the electrode surface and further exacerbating the dendrite growth (Fig. S20c). In comparison, the electric field and Zn-ion distribution on the electrode/electrolyte interface with APA are uniformly distributed (Fig. S20b and S20d). The distinct deposition behaviour could be attributed to the fact that APA is preferentially adsorbed on the Zn-metal interface after desolvation of hydrated  $Zn^{2+}$  in the Zn plating process. Such adsorption of polymer layer on Zn-metal anode forms an ion-regulating interface layer that largely promotes the uniform Zn plating.



**Fig. S21** XPS depth profile for F 1s of Zn anode surface after 30 cycles in pristine electrolyte and APA-containing electrolyte at a current density of  $1 \text{mA cm}^{-2}$  and capacity of  $1 \text{mAh cm}^{-2}$ .

As shown in Fig. S21, the content of  $-CF_3$  on the cycled Zn anode surface with APA-containing electrolyte is higher than that with pristine electrolyte. Furthermore, as the Ar<sup>+</sup> sputtering depth increases, the peak intensity of Zn-F derived from the decomposition of  $-CF_3$  also increases. These results indicate more OTf<sup>-</sup> anions decomposition at the Zn/electrolyte interface.



**Fig. S22** XPS depth profile for S 2p of Zn anode surface after 30 cycles in pristine electrolyte and APA-containing electrolyte at a current density of 1mA cm<sup>-2</sup> and capacity of 1mAh cm<sup>-2</sup>.

As shown in Fig. S22, the appearance of  $ZnS_x$  and  $ZnSO_3/ZnSO_4$  in the S 2p spectrum suggests the decomposition of OTf<sup>-</sup> anions at the Zn/electrolyte interface during the plating/stripping process. Moreover, the content of  $ZnS_x$  and  $ZnSO_3/ZnSO_4$  on the cycled Zn anode surface with APA-containing electrolyte is higher than that with pristine electrolyte, further indicating more OTf<sup>-</sup> anions decomposition at the Zn/electrolyte interface.



**Fig. S23** XPS depth profile for O 1s of Zn anode surface after 30 cycles in pristine electrolyte and APA-containing electrolyte at a current density of 1mA cm<sup>-2</sup> and capacity of 1mAh cm<sup>-2</sup>.

As shown in Fig. S23, the O content on the cycled Zn anode surface with pristine electrolyte is higher than that of APA-containing electrolyte at the Zn/electrolyte interface. Notably, the O content is mainly derived from the decomposition of  $H_2O$  and  $OTf^-$  anions in the electrolyte, while the content of  $OTf^-$  anions on the cycled Zn anode surface with APA-containing electrolyte is higher than that with pristine electrolyte. These results well demonstrate that APA can suppress  $H_2O$  decomposition at the Zn/electrolyte interface.



**Fig. S24** Zn-Zn symmetric cells cycled at a current density of 10 mA cm<sup>-2</sup> using pristine electrolyte and additive-electrolytes containing a PAM homopolymer and four APA copolymers with MA content of 10 mol.%, 15 mol.%, 20 mol.% and 25 mol.%, respectively. The content of different polymers in the solution is 1 wt.% for all electrolytes.

As shown in Fig. S24, a Zn-Zn symmetric cell using pristine electrolyte cycles for only 10 h at a current density of 10 mA cm<sup>-2</sup> before short circuit. In contrast, the introductio of a polyacrylamide (PAM) homopolymer additive to pristine electrolyte extends the symmetric cell cycle life to 80 h. After copolymerized with 10 mol.% of MA, the lifespan of the symmetric cell is significantly increased to 620 h, while the polarization voltage does not change significantly. When the MA content further increases to 15 mol.%, the Zn-Zn symmetric cell achieves a longest cycle lifer of 780 h. These results demonstrate that the enhancement of cycle stability can be well achieved by using APA-containing electrolyte with a properly-tuned MA content. The increased MA content enhances the hydrophobicity of APA compared to the PAM homopolymer, which can foster a localized hydrophobic environment on the Zn/electrolyte interface thus reduce the side reactions induced by solvated H<sub>2</sub>O. However, too much MA units will also shorten the cycle life, as shown by the cycle life of 405 h for the APA with 20 mol.% of MA and 160 h for the APA with 25 mol.% of MA, respectively, which may be because of the reduced hydrophilicity and zincophilicity at the Zn/electrolyte interface introduced by the excess hydrophobic MA.



Fig. S25 Voltage profiles Zn-Zn symmetrical cells using pristine and APA-containing electrolyte at a current density of 20 mA cm<sup>-2</sup> with a capacity of 20 mA h cm<sup>-2</sup>. (b) The magnified view of voltage profiles.

As shown in Fig. S25, at a very high current density current density of 20 mA cm<sup>-2</sup> with a capacity of 20 mAh cm<sup>-2</sup>, the Zn-Zn symmetrical cell using APA-containing electrolyte achieves stable cycles of more than 295 h, whereas theone using pristine electrolyte displays unstable polarization voltage during initial cycling (only 2 h). The improved stability further verifies the effective inhibition of Zn dendrite growth and by-products enabled by APA.



**Fig. S26** Ion transport behaviours at the electrode/electrolyte interface under -30 °C. (a) Ionic conductivity of electrolyte at different temperatures. (b) CV curves demonstrating the Zn nucleation behaviour on the Cu electrodes. In-situ EIS of Zn-Zn symmetric cells using (c) pristine electrolyte and (d) APA-containing electrolyte during electro-plating of  $Zn^{2+}$ . Atomic composition of XPS of Zn-metal anodes surface after 10 cycles in (e) pristine electrolyte and (f) APA-containing electrolyte.

The Zn-ion transport behaviours at the interface under low temperature are further characterized and discussed in the revised manuscript. Fig. S26a shows that the introduction of APA has little effect on the ionic conductivity of pristine electrolyte in a wide temperature range. In Fig. S26b, the nucleation overpotential (NOP) of Zn-Cu asymmetric cell using APAcontaining electrolyte at -30 °C is increased by 49 mV, suggesting uniform Zn deposition behavior. The result of operando electrochemical impedance spectra (EIS) of Zn-Zn cell using APA-containing electrolyte at -30 °C also confirms the high stability of the Zn/electrolyte interface and the uniform Zn deposition behavior, although the interface impedance slightly increases (Fig. S26c and Fig. S26d). Moreover, the results of X-ray photoelectron spectroscopy (XPS) and Ar+ sputtering depth profiling clearly show that a F-rich and O-deficient stable SEI is built in the batteries using APA-containing electrolyte (Fig. S26e and Fig. S26f). Despite the reduced ionic conductivity at low temperature, the above results have supported that the smooth ion transportation at low temperature is attributed to the nano-scaled hydrophobic confinement of APA-containing aqueous electrolyte, which not only reduces the H<sub>2</sub>O number in the solvated Zn<sup>2+</sup>, but also fosters a localized nano-scaled H<sub>2</sub>O-poor environment at the Zn/electrolyte interface thus prolongs the cycle stability of Zn-ion devices at low temperature even at -30 °C.



**Fig. S27** Top-view SEM images of different magnification of the Zn anodes using (a, b) pristine electrolyte and (c-d) APA-containing electrolyte after cycling for 100 h at a current density of 5 mA cm<sup>-2</sup> with a capacity of 5 mAh cm<sup>-2</sup>.

As shown in Fig. S27a and S27b, in pristine electrolyte, the Zn suface is filled with deposited zinc protuberances that are loosely packed on the surface, whereas in APA-containing electrolyte, the Zn anode shows a much smoother and dendrite-free surface (Fig. S27c and S27d), suggesting modulated deposition behaviour of Zn that effectively suppress the formation of Zn dendrite.



**Fig. S28** XRD diffractograms of Zn anodes before and after cycling at different current densities and capacities. B-1-50th denotes the Zn anodes cycling in pristine electrolyte after 50 cycles at a current density of 1mA cm<sup>-2</sup> with a capacity of 1mAh cm<sup>-2</sup>. P-1-50th denotes the Zn anodes cycling in the APA-containing electrolyte after 50 cycles at a current density of 1mA cm<sup>-2</sup> with a capacity of 1mAh cm<sup>-2</sup>.

Fig. S28a shows the X-ray diffraction (XRD) patterns of Zn anodes after cycled with pristine electrolyte and APA-containing electrolyte. Specially, with longer cycling time and higher current density and capacity, several new diffraction peaks emerge and the intensity also increases gradually for Zn anode with pristine electrolyte, which should be attributed to the formation of byproducts such as  $Zn_xOTf_y(OH)_{2x-y}$ ·nH<sub>2</sub>O. Interestingly, we found that the value of  $I_{(002)}/I_{(101)}$  for Zn anode after cycled in the APA-containing electrolyte decreases gradually as cycling time prolongs and the current density and capacity increase, demonstrating the preferential Zn deposition along the (101) plane (Fig. S28b).



**Fig. S29** (a) Coulombic efficiency (CE) of Zn plating/stripping in Zn-Cu asymmetric cells at a current density of 5 mA cm<sup>-2</sup> and capacity of 5 mAh cm<sup>-2</sup>. (b, c) Corresponding voltage profiles at various cycles.

Fig. S29 shows the CE of Zn plating/stripping in Zn-Cu asymmetric cells using pristine electrolyte and APA-containing electrolyte at a current density of 5 mA cm<sup>-2</sup>. As seen from the plots, the asymmetric cell using pristine electrolyte failed after only 10 cycles (Fig. S29a and S29b). In contrast, the asymmetric cell using APA-containing electrolyte exhibits a regular and smooth voltage under Zn plating/stripping process with an average CE of 99.7 % in 100 cycles (Fig. S29a and S29c).



Fig. S30 Rate capacities at different current densities.



**Fig. S31** Galvanostatic charge-discharge curves of Zn-AC hybrid ion supercapacitors in the voltage range of 0-1.9 V using pristine electrolyte at 5 A  $g^{-1}$  under 25 °C.



**Fig. S32** Galvanostatic charge-discharge curves of Zn-AC hybrid ion supercapacitors in the voltage range of 0-1.9 V using (a) APA-containing electrolyte and (b) pristine electrolyte at 5 A  $g^{-1}$  under 50 °C.



**Fig. S33** Cycling stability of Zn-AC hybrid ion supercapacitors at -20 °C with a current density of 1 A  $g^{-1}$ . Galvanostatic charge-discharge curves of Zn-AC hybrid ion supercapacitors using APA-containing electrolyte at 1 A  $g^{-1}$  under -20 °C.



**Fig. S34** Comparison of comprehensive performance of Zn-AC hybrid ion supercapacitors using pristine and APA-containing electrolyte.



Fig. S35 XRD diffractogram of the synthesized NVO.



**Fig. S36** Galvanostatic charge-discharge curves of Zn-NVO batteries using (a) APAcontaining electrolyte and (b) pristine electrolyte at 5 A  $g^{-1}$  under 25 °C.

# Table

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Polymer	$M_n$ (g/mol)	$M_w$ (g/mol)	$M_w/M_n$
APA-HMW	46637	210797	4.52
APA-MMW	18790	81524	4.34
APA-LMW	6977	29807	4.27

 Table S1 Molecular weight of APA.

Electrolyte additive		Current density	Cycle life	Ref
		(mA·cm <sup>-2</sup> , mAh·cm <sup>-2</sup> )	(h)	iter.
	Polyethylene glycol	1, 1	650	13
	Polyethylene glycol	2, 1	8000	14
	Polyacrylamide (PAM)	1, 1	180	15
	Polyethylene oxide	1, 1	—	16
Macromolecule	Polyethylene oxide	1, 1	—	17
	Polyaspartic acid (PASP)	5, 2.5	600	18
	1,4-Dioxane	5, 2.5	600	19
	Saccharin (Sac)	10, 10	550	20
	Silk fibroin (SF)	10, 5	500	21
	CH <sub>3</sub> COONH <sub>4</sub>	2, 1	2400	22
	TMBA	10, 5	500	23
	NHP	5, 5	315	24
	Acetic acid (HAC)	5, 5	300	25
	Glucose	5, 5	270	26
	Silk peptide	1, 1	3000	27
	Betaine (Bet)	2, 2	830	28
	Boric acid (BA)	5, 1	2100	29
	$Al_2(SO_4)_3$	2, 1	1000	30
Small molecule	Amino acid	5, 4	2200	31
	DMSO	2, 1	2100	32
	NMP	1, 1	550	33
	Ethylene glycol	2, 1	150	34
	Sulfolane	2, 1	1200	35
<b>Organic Solvent</b>	DMF	1, 2	2800	36
	1m Zn(TFSI) <sub>2</sub> + 20 m LiTFSI	0.2, 0.1	170	37
	1 m Zn(OAc) <sub>2</sub> +31 m KOAc	5, 1	34	38
	$30 \text{ m ZnCl}_2$	0.2, 0.1	600	39
Water in Salt	$7.6\ m\ ZnCl_2 + 0.05\ m\ SnCl_2$	1, 1	500	40
	АРА	1, 1	8800	
This work		5, 5	2500	
		10, 10	780	
		20, 20	295	

Table S2 Cycling performance of zinc anodes obtained with different types of additives.

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