

## Supporting Information

### Multifunctional ionic liquid additive providing solvation structure and electrostatic shielding layer for high-stable aqueous zinc ion batteries

#### 1. Experimental section

**Electrolyte preparation:** Zinc sulfate ( $\text{ZnSO}_4$ , Macklin, 99%) was dissolved in deionized (DI) water to prepare a 2 M  $\text{ZnSO}_4$  electrolyte, which was used as a blank electrolyte (BE). The control group used different concentrations (0.5%, 1%, 1.5%) of 1-butyl-3-methylimidazolium hexafluorophosphate ( $\text{C}_8\text{H}_{15}\text{F}_6\text{N}_2\text{P}$ , Aladdin, 99%,  $[\text{BMIM}]\text{PF}_6$ ) was added to the prepared 2 M  $\text{ZnSO}_4$  electrolyte to obtain the  $[\text{BMIM}]\text{PF}_6$  additive-containing. The optimum concentration of  $[\text{BMIM}]\text{PF}_6$  systems is 1%  $[\text{BMIM}]\text{PF}_6 + 2 \text{ M } \text{ZnSO}_4$ , and the corresponding electrolyte is abbreviated as  $[\text{BMIM}]\text{PF}_6/\text{BE}$ .

**Preparation of electrodes** Purchased zinc foils (thickness: 100  $\mu\text{m}$ , 99.99%) were polished with sandpaper to remove the passivation layer. The Zn foil was then cut into a disc with a diameter of 16 mm to serve as the Zn electrode.  $\text{NH}_4\text{V}_4\text{O}_{10}$  was synthesized using a hydrothermal method. i.e. 1.17 g of ammonium vanadate ( $\text{NH}_4\text{VO}_3$ , Aladdin, AR) was dissolved in 70 mL of deionized water. Then 1.891 g of oxalic acid (Aladdin, AR) powder was added to the  $\text{NH}_4\text{VO}_3$  solution under magnetic stirring. The solution was transferred to a 100 mL tetrafluoroethylene lined autoclave and heated at 140  $^\circ\text{C}$  for 12 h. After cooling, the product was collected, washed repeatedly with deionized water, and then dried at 70  $^\circ\text{C}$  overnight to give the final  $\text{NH}_4\text{V}_4\text{O}_{10}$  powder. A  $\text{NH}_4\text{V}_4\text{O}_{10}$  electrode slurry was formed by fusion stirring with  $\text{NH}_4\text{V}_4\text{O}_{10}$  powder, Ketjen black (KB), and PTFE (mass ratio 75:15:10), and then the slurry was cast on a stainless steel mesh. After drying in air at 70  $^\circ\text{C}$  overnight,  $\text{NH}_4\text{V}_4\text{O}_{10}$  electrodes containing 1.3-2.6  $\text{mg cm}^{-2}$  were finally obtained.

The monomer (2 g acrylamide) was dissolved in 10 mL of an aqueous electrolyte (2 M  $\text{ZnSO}_4$ ), and then the initiator [15 mg  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Aladdin, AR)] and cross-linking agent [2.5 mg N, N'-methylene bis(acrylamide) (Aladdin, 99%)] were added and stirred for 30 min. Alternatively, it was injected into a mold of the designed

24 thickness. After polymerization at 60 °C for 1.5 h, a Polyacrylamide (PAM) hydrogel film was formed, named  
25 PAM. the composite gel electrolyte obtained by adding 1% [BMIM]PF<sub>6</sub> before polymerization was noted as  
26 PAM-1% [BMIM]PF<sub>6</sub>.

## 27 **2. Test section**

28 **Materials Characterization:** The prepared NH<sub>4</sub>VO<sub>3</sub> powder and zinc anode were physically analyzed using  
29 a MiniFlex600 X-ray diffractometer. The XRD scanning range used in the experiments was 5~80°, and the  
30 XRD scanning speed was set at 10°/min. Fourier transform infrared (FTIR) spectroscopy was tested by a  
31 Nicolet IS10 Fourier transform infrared spectrometer, with a scanning range of 4000 cm<sup>-1</sup>~400 cm<sup>-1</sup>. X-ray  
32 photoelectron spectroscopy was collected by an EscaLab Xi<sup>+</sup> XPS system. X-ray photoelectron spectra were  
33 collected by the EscaLab Xi<sup>+</sup> XPS system, which uses a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$   
34 eV). The morphology of the samples was observed by a field emission scanning electron microscope (SEM,  
35 Gemini SEM 300) field emission scanning electron microscope on the morphological structure of the  
36 experimental samples.

37 **Electrochemical Characterization:** Purchased zinc foils (thickness: 100  $\mu\text{m}$  and 20  $\mu\text{m}$ , 99.99%) were  
38 polished with sandpaper to remove the passivation layer. The zinc foil was then cut into a 16 mm diameter  
39 disc to serve as the zinc electrode. All tested CR2032 type coin batteries were assembled in an open-air  
40 environment using glass fiber filters (GF/D, Whatman) as diaphragms. The amount of electrolyte used for the  
41 coin battery was 120  $\mu\text{L}$ . two identical zinc plates with a thickness of 100  $\mu\text{m}$  were used to make a symmetrical  
42 battery. Zn//Cu half batteries were assembled using a copper foil of 20  $\mu\text{m}$  thickness as the working electrode  
43 and a zinc foil of 100  $\mu\text{m}$  thickness as the reference and counter electrodes. The NH<sub>4</sub>V<sub>4</sub>O<sub>10</sub>//Zn full battery  
44 was assembled using a Zn plate with a thickness of 100  $\mu\text{m}$  as the anode and NH<sub>4</sub>V<sub>4</sub>O<sub>10</sub> as the cathode. The  
45 blank electrolyte and [BMIM]PF<sub>6</sub> electrolyte were used for the electrolyte. The NH<sub>4</sub>V<sub>4</sub>O<sub>10</sub> cathode (16 mm

diameter, circular piece) was combined with the Zn anode (100  $\mu\text{m}$  thickness), and glass fiber was used as the diaphragm to assemble the  $\text{NH}_4\text{V}_4\text{O}_{10}/\text{Zn}$  full battery. The  $\text{NH}_4\text{V}_4\text{O}_{10}$  cathode (2  $\text{cm}^2$ ) was combined with a Zn anode (100  $\mu\text{m}$  thickness) and assembled into  $\text{NH}_4\text{V}_4\text{O}_{10}/\text{Zn}$  flexible batteries using PAM-[BMIM]PF<sub>6</sub> hydrogel electrolyte as a flexible diaphragm. The  $\text{NH}_4\text{V}_4\text{O}_{10}/\text{Zn}$  battery was discharged/charged under a potential control of 0.3 ~ 1.4 V using a NEWARE battery tester.

Electrochemical characterization: Tafel plots were measured with Zn plate as the working electrode, Pt foil as the counter electrode, and saturated dimercury dichloride as the reference electrode, scanning at -0.7 ~ -1.2 V in 2  $\text{mV s}^{-1}$  band. Chronoamperometry (CA), when measured at a fixed overpotential of -0.15 V. Cyclic voltammetry (CV) curves of plated/stripped zinc, were measured with a Zn//Ti battery in the voltage range of -1.5 V ~ 2.0 V at 1  $\text{mV s}^{-1}$ . Hydrogen precipitation potentials were determined using linear scanning voltammetry (LSV) with a scan rate of 1  $\text{mV s}^{-1}$  in the BE and [BMIM]PF<sub>6</sub>/BE systems. The electrochemical impedance spectroscopy (EIS) of the Zn//Zn symmetric battery was analyzed in the frequency range of 0.01 Hz ~ 100 k Hz. By fitting the obtained  $R_{\text{ct}}$ , the activation energy  $E_a$  was calculated according to Arrhenius' law.

#### **DFT calculation method:**

The density functional theory (DFT) simulations are performed using the CASTEP program package in Materials Studio. The exchange-correlation interaction is described by generalized, gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional.

For the construction of surface models, a 15  $\text{\AA}$  vacuum is used to eliminate interactions between periodic structures. And the Zn (002) slab is constructed with lattice constants of  $a = b = 15.6862 \text{ \AA}$ ,  $c = 22.3097 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$ . And one molecular of [BMIM]<sup>+</sup> or H<sub>2</sub>O is put on the Zn (002) surface. And the adsorption energy ( $E_{\text{abs}}$ ) of [BMIM]<sup>+</sup> or H<sub>2</sub>O on Zn (002) surface was calculated, by the formula:  $E_{\text{abs}} = E_{\text{total}} - E_{\text{M}} - E_{\text{S}}$ , where  $E_{\text{total}}$ ,  $E_{\text{M}}$  and  $E_{\text{S}}$  are the energy of, respectively, the total system, the [BMIM]<sup>+</sup> or H<sub>2</sub>O

69 molecular, and Zn (002) surface.

70 The binding energy ( $E_{\text{binding}}$ ) between  $\text{Zn}^{2+}$ ,  $[\text{BMIM}]^+$ ,  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{O}$  molecular was calculated by the,  
71 formula:  $E_{\text{binding}} = E_{\text{total}} - E_a - E_b$ , where  $E_{\text{total}}$  is the energy of the total system,  $E_a$  and  $E_b$  are the, energies of  
72 components in the system.

### 73 **Molecular dynamic (MD) simulations**

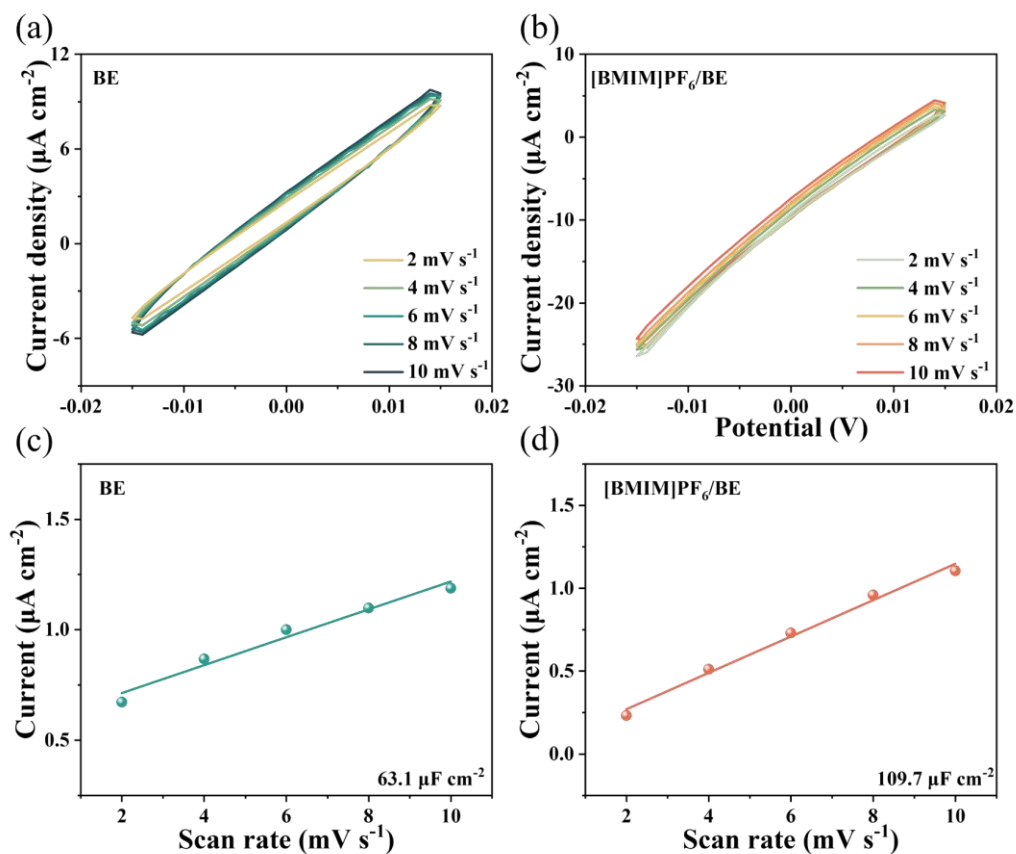
74 Molecular dynamic (MD) simulations were applied to investigate the solvation structures for two  
75 considered electrolytes denoted as S1 and S2. For S1 system, the solution was comprised of 50  $\text{ZnSO}_4$  and  
76 1375  $\text{H}_2\text{O}$  molecules. For S2, the solution contained 50  $\text{ZnSO}_4$ , 10  $[\text{BMIM}]\text{PF}_6$  and 1375  $\text{H}_2\text{O}$  molecules. All  
77 solution components were randomly packed into cubic simulation boxes. All MD simulations were carried  
78 out by Forcite module with COMPASS III force field <sup>1,2</sup> in MS 2020. Van der Waals and Coulomb interactions  
79 were respectively considered by atom based and Ewald methods with a cut-off value of 12.5 Å. Equations of  
80 motion were integrated with a time step of 1 fs. After energy minimization, the electrolyte system was fully  
81 relaxed under periodic boundary conditions for 400 ps in the NPT ( $P = 1$  atmosphere,  $T = 298.0$  K) ensemble  
82 using the Nose thermostat and Berendsen barostat, which was long enough for system temperature, potential  
83 and total energy to get stable. After reaching equilibrium state, another 400 ps simulation under NVT ensemble  
84 was performed to extract trajectory and data for radial distribution function (RDF) and coordination number  
85 (CN) calculation. The dynamic trajectory for each system was outputted at an interval of 4 ps. The  
86 coordination number  $N_i$  of atom  $i$  in the first solvation shell surrounding  $\text{Zn}^{2+}$  was calculated as:

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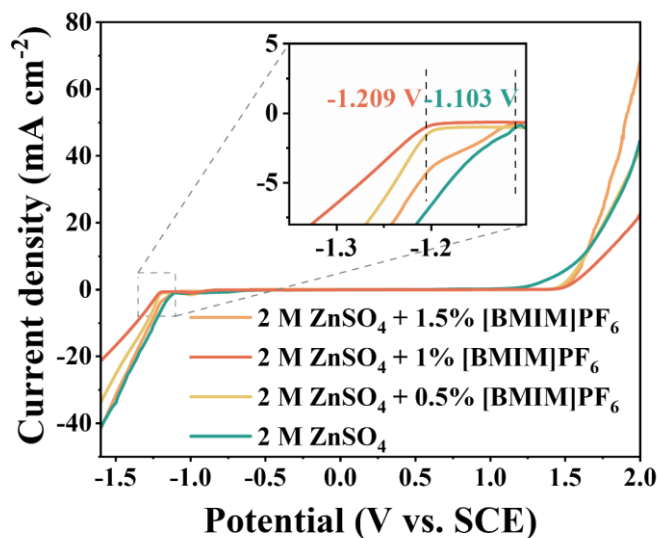
$$N_i = 4\pi\rho\int_0^{R_M} g(r)r^2 dr \quad (1)$$

88 in which  $R_M$  is the distance of the first minimum following the first peak in the RDF  $g(r)$  and  $\rho$  is the number  
89 density of atom  $i$ .

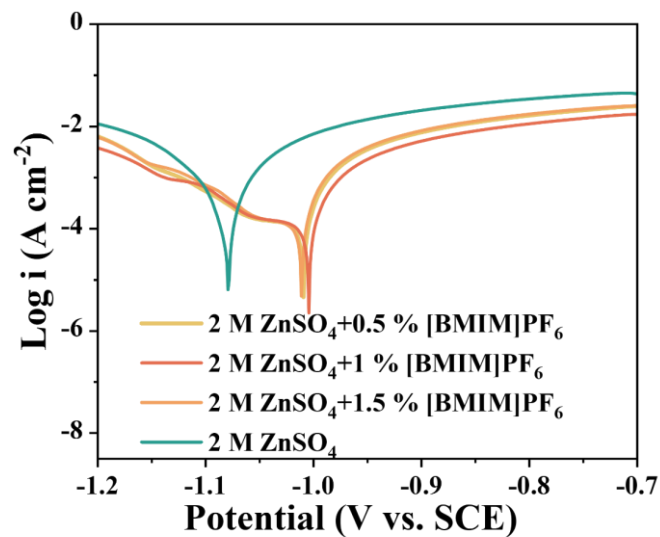
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92 **Fig. S1** The cyclic voltammetry (CV) curves for Zn//Zn cells in (a) BE system, (b) [BMIM]PF<sub>6</sub>/BE system.  
93 The calculated electric double layer capacitance for cells in (c) BE system, (d) [BMIM]PF<sub>6</sub>/BE system.

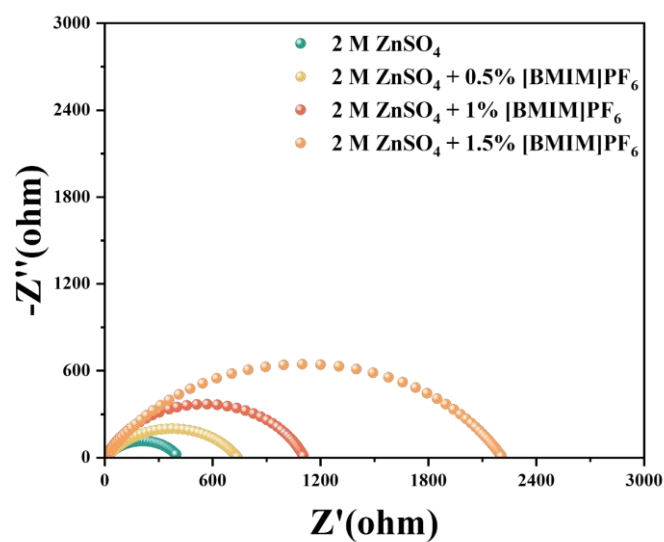


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95 **Fig. S2.** The electrochemical stability window of the electrolytes with various doping concentrations of  
96 [BMIM]PF<sub>6</sub> additives was tested on Ti electrodes by scanning at a rate of 1 mV s<sup>-1</sup>.



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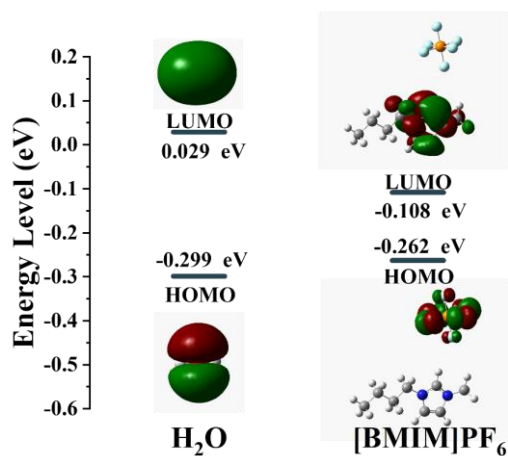
98 **Fig. S3.** Tafel curves for BE system and different concentrations of [BMIM]PF<sub>6</sub>/BE systems.



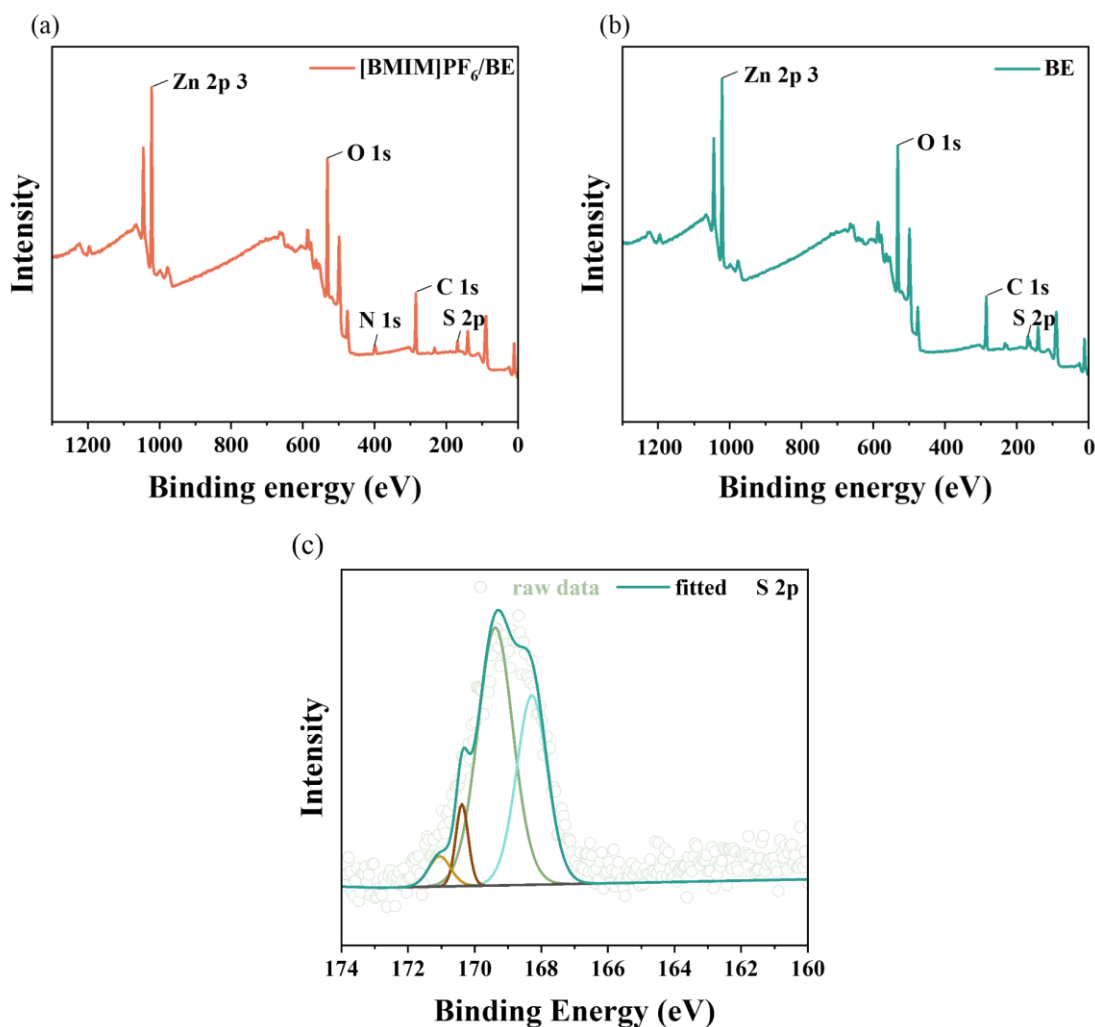
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100 **Fig. S4.** Electrochemical impedance spectroscopy of batteries assembled with [BMIM]PF<sub>6</sub> at different  
 101 concentrations.

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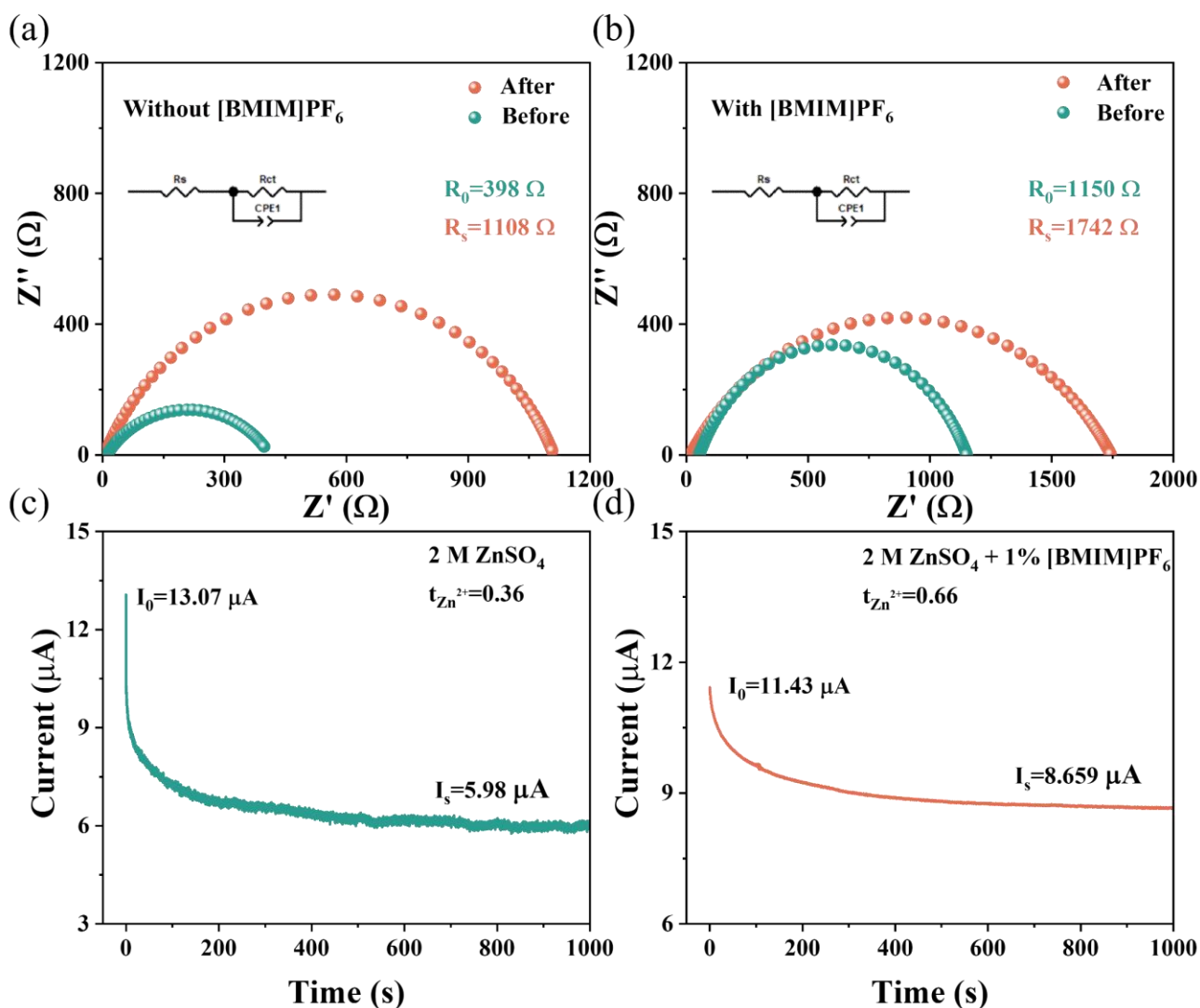
**Fig. S5.** LUMO, HOMO energy of H<sub>2</sub>O molecules (**left**) and [BMIM]PF<sub>6</sub> (**right**).



**Fig. S6.** High resolution XPS spectra of zinc metal electrodes after 50 cycles with (a) [BMIM]PF<sub>6</sub>/BE

system and (b) BE system at 1 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>. High-resolution XPS spectra of the Zn metal

electrodes after 50 cycles with BE system at 1 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>: (c) S 2p.



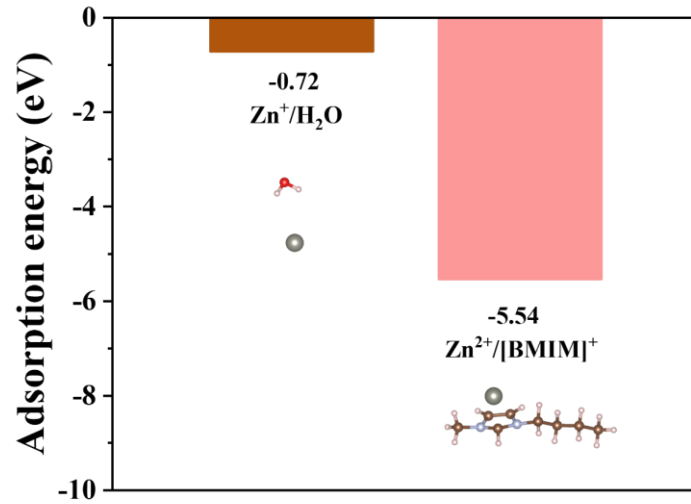
**Fig. S7.** Comparison of EIS curves of Zn//Zn symmetric cells in different electrolytes (a) initial and (b) after i-t test; current-time plots of electrolytes (c) without [BMIM]PF<sub>6</sub> and (d) with [BMIM]PF<sub>6</sub>, respectively, at a constant voltage of 15 mV for 1000 seconds.

Auxiliary note: The Zn<sup>2+</sup> transfer number ( $t_{zn^{2+}}$ ) was calculated according to the Bruce Vincent method:

$$t_{zn^{2+}} = \frac{I_s(V - I_0R_0)}{I_0(V - I_sR_s)}$$

where V is the applied potential (15 mV); I<sub>0</sub> and R<sub>0</sub> are the initial current and the interface resistance; I<sub>s</sub> and R<sub>s</sub> represent the steady-state current and interface resistance, respectively. Therefore, the value of  $t_{zn^{2+}}$  can be calculated to be 0.66 for the [BMIM]PF<sub>6</sub>/BE system, while the value is only 0.36 for the BE system.

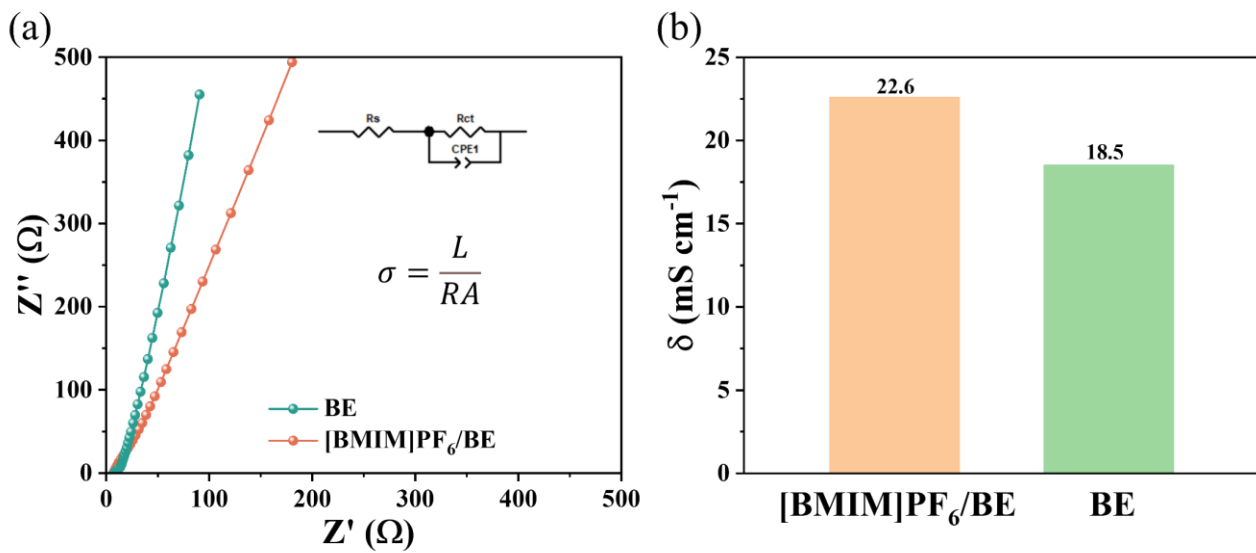




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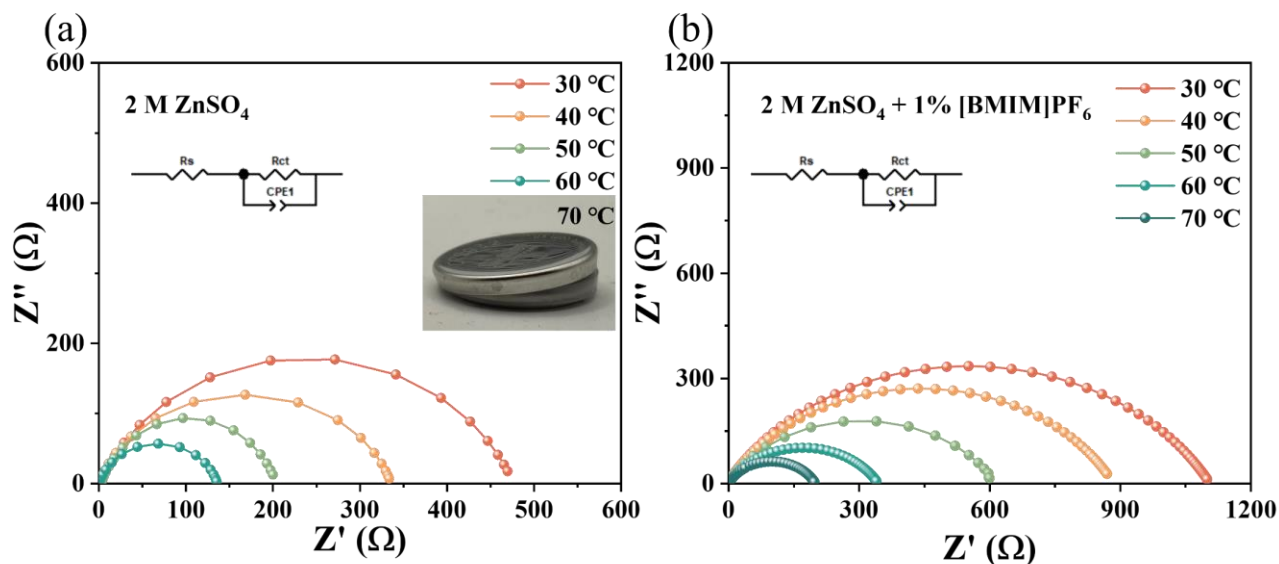
**Fig. S8.** The comparison of binding energies between Zn<sup>2+</sup>&H<sub>2</sub>O, Zn<sup>2+</sup>&[BMIM]<sup>+</sup> and [BMIM]<sup>+</sup>&H<sub>2</sub>O.



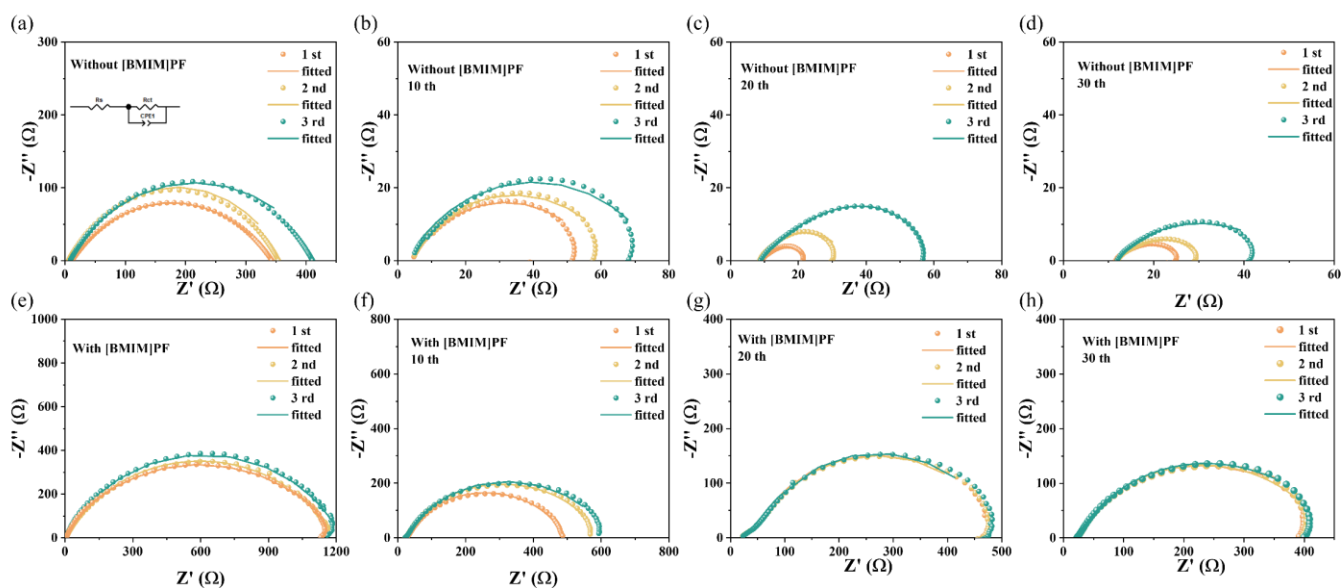
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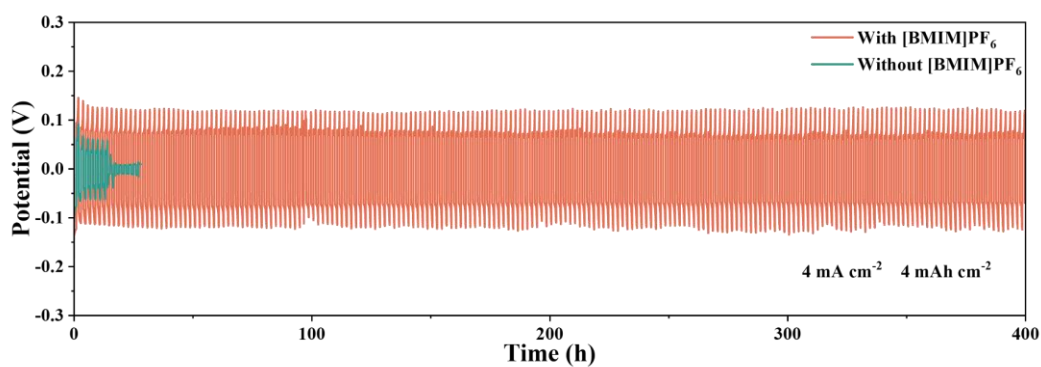
**Fig. S9.** (a) Impedance spectra and (b) ionic conductivities in the BE and [BMIM]PF<sub>6</sub>/BE systems.



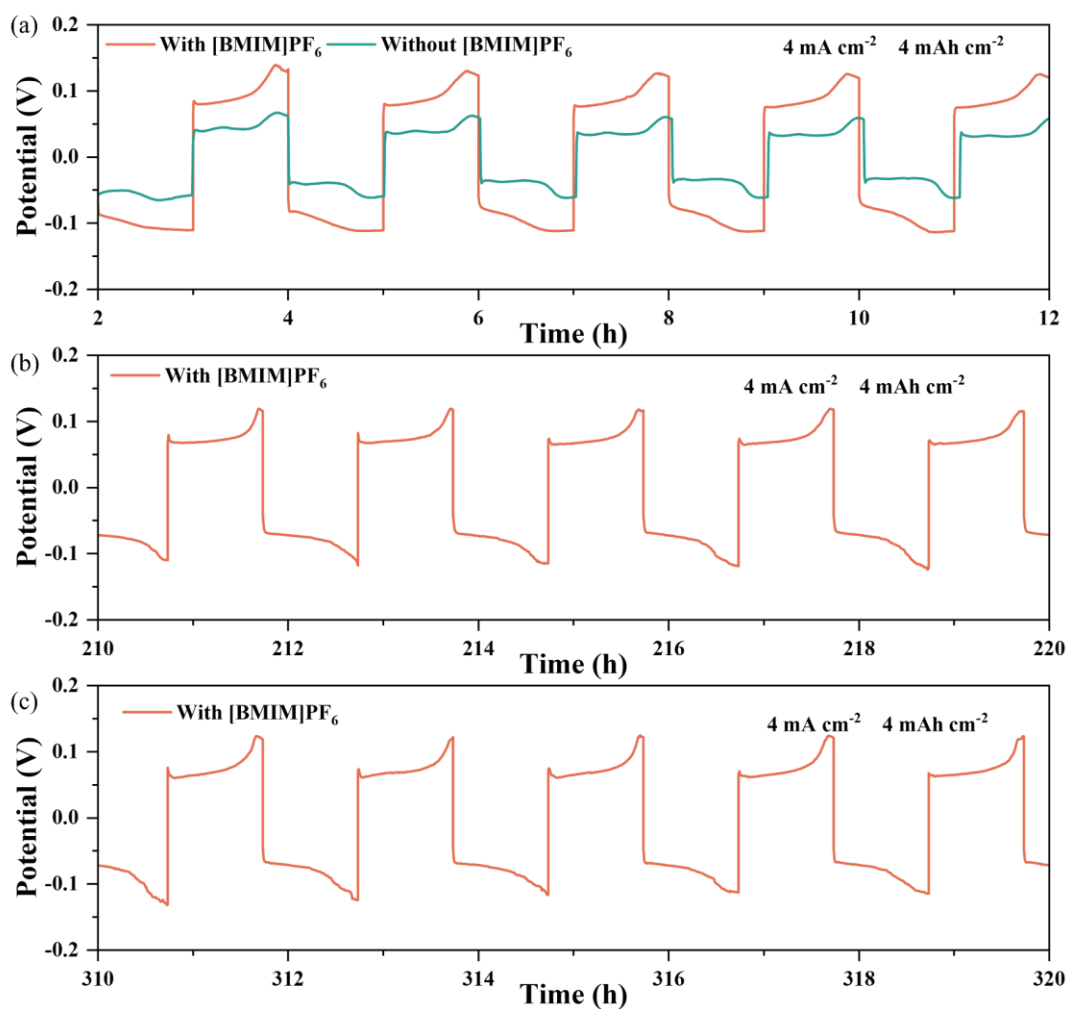
**Fig. S10.** Nyquist plots of Zn//Zn symmetric cells at different temperatures in (a) BE and (b) [BMIM]PF<sub>6</sub>/BE systems.



**Fig. S11.** Nyquist plots and fitted curves in the BE system without [BMIM]PF<sub>6</sub> (upper panel) and with [BMIM]PF<sub>6</sub> (lower panel) at (a), (e) 0 cycling cycle, (b), (f) 10 cycling cycles, (c), (g) 20 cycling cycles, (d), (h) 30 cycling cycles (three tests at the same cycle are shown in the same figure).

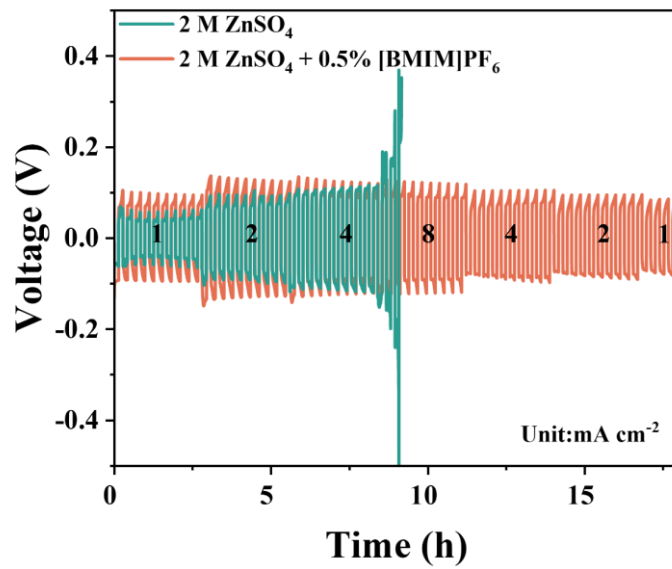


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 132 **Fig. S12.** Stability of Zn//Zn cells using electrolytes with [BMIM]PF<sub>6</sub> and without [BMIM]PF<sub>6</sub> additive at 4  
 133 mA cm<sup>-2</sup> conditions.  
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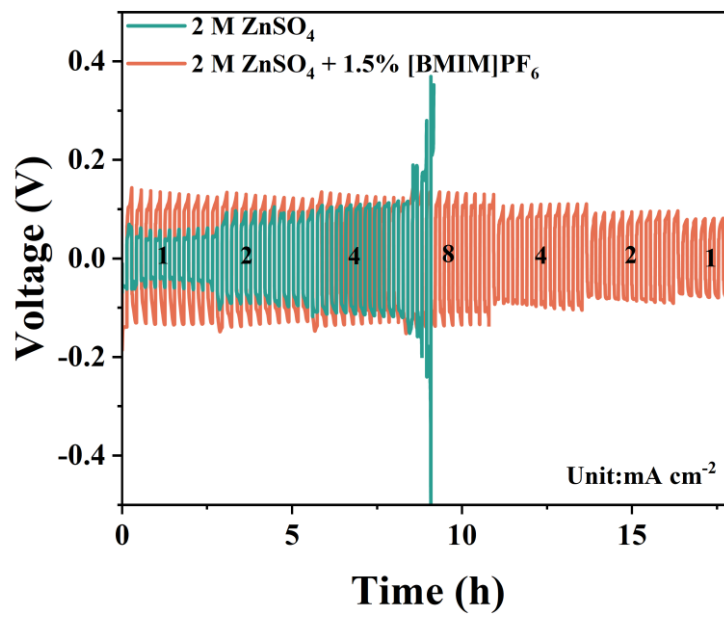
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 136 **Fig. S13.** Cycling stability of Zn//Zn batteries with and without [BMIM]PF<sub>6</sub> electrolytes under 4 mA cm<sup>-2</sup>:  
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(a) 10-20h; (b) 210-220h; (c) 310-320h.



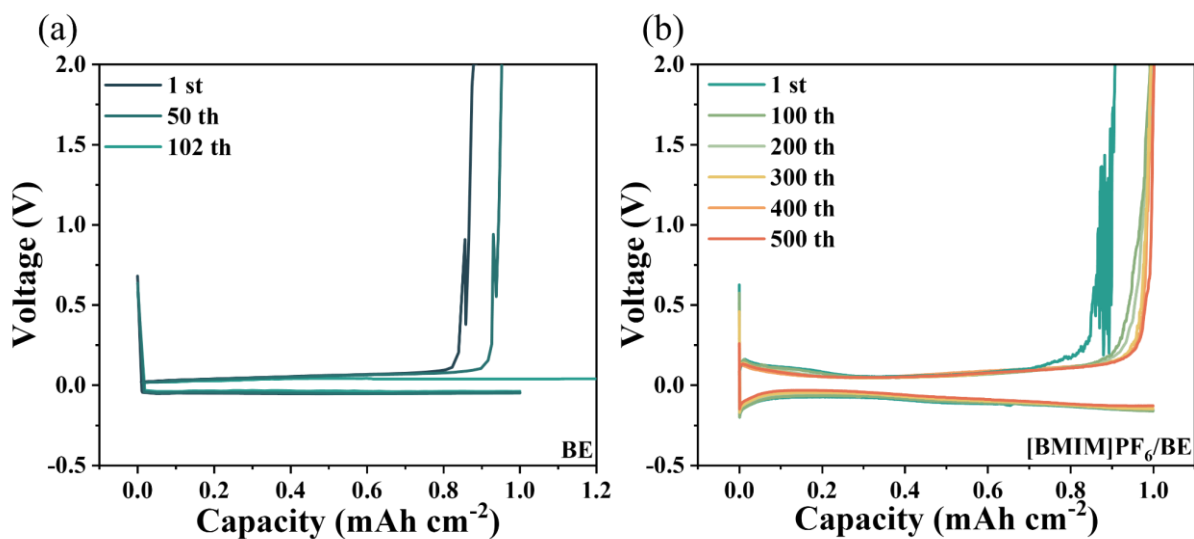
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139 **Fig. S14.** Rate performance of Zn//Zn batteries in 2 M ZnSO<sub>4</sub>+0.5% [BMIM]PF<sub>6</sub>.

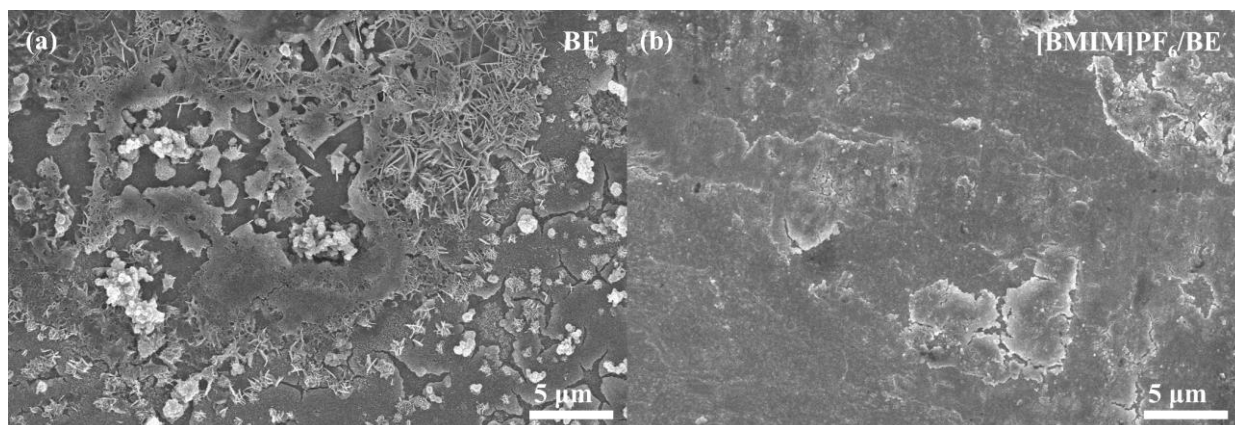


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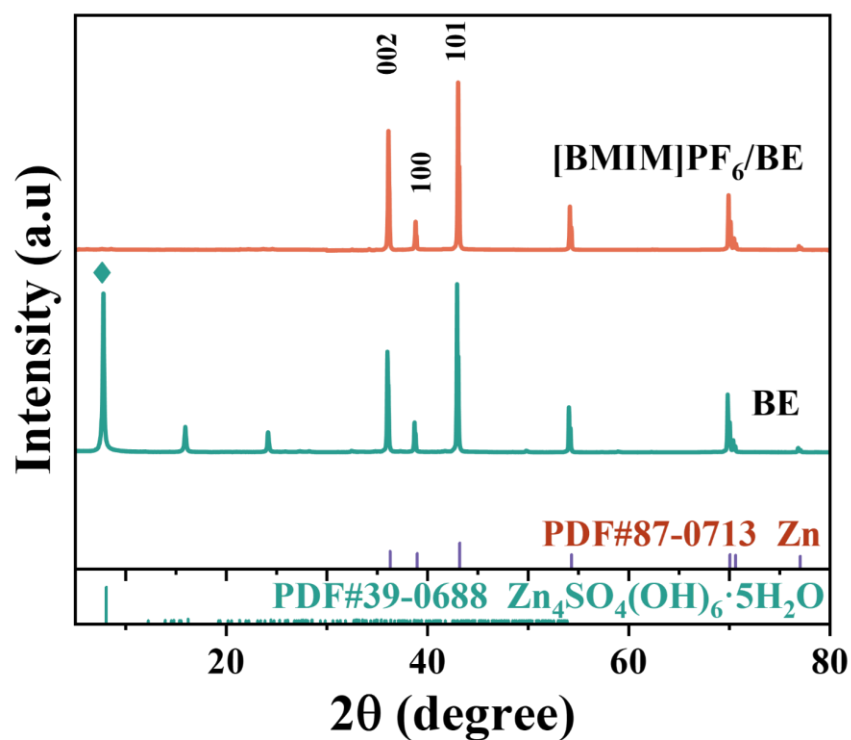
141 **Fig. S15.** Rate performance of Zn//Zn batteries in 2 M ZnSO<sub>4</sub>+1.5% [BMIM]PF<sub>6</sub>.



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 143 **Fig. S16.** corresponding voltage profiles at various cycles in ZnSO<sub>4</sub> electrolyte (a) without and (b) with  
 144 [BMIM]PF<sub>6</sub> additive.  
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 147 **Fig. S17.** SEM images of Zn anode surface morphology after cycling: (a) in BE system, (b) in [BMIM]PF<sub>6</sub>/BE  
 148 system.

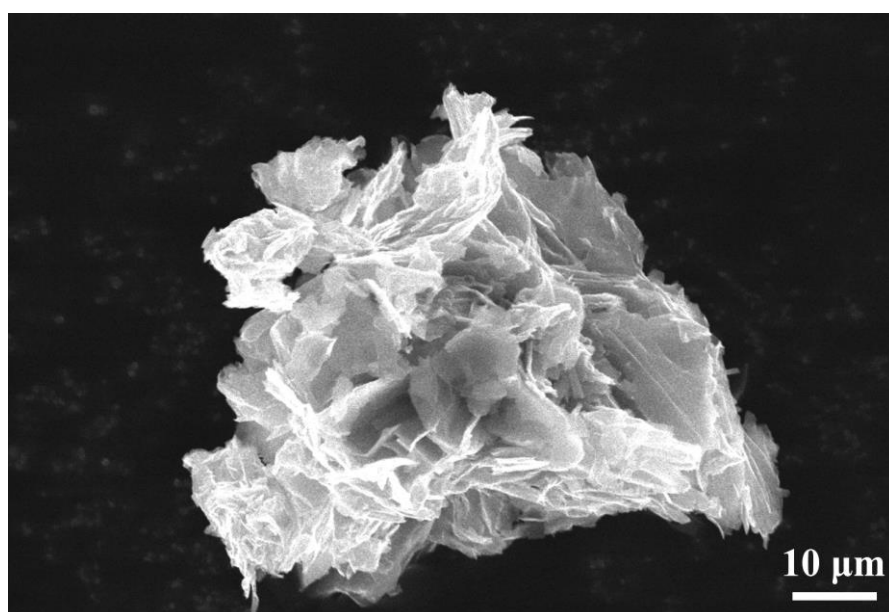


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150 **Fig. S18.** XRD patterns of the Zn anodes with Zn//Cu half-cells in different electrolytes after 20 cycles at 1  
 151 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>.

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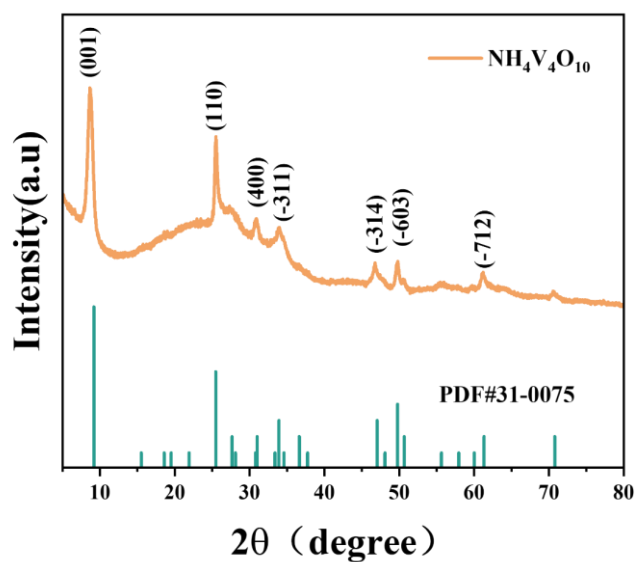
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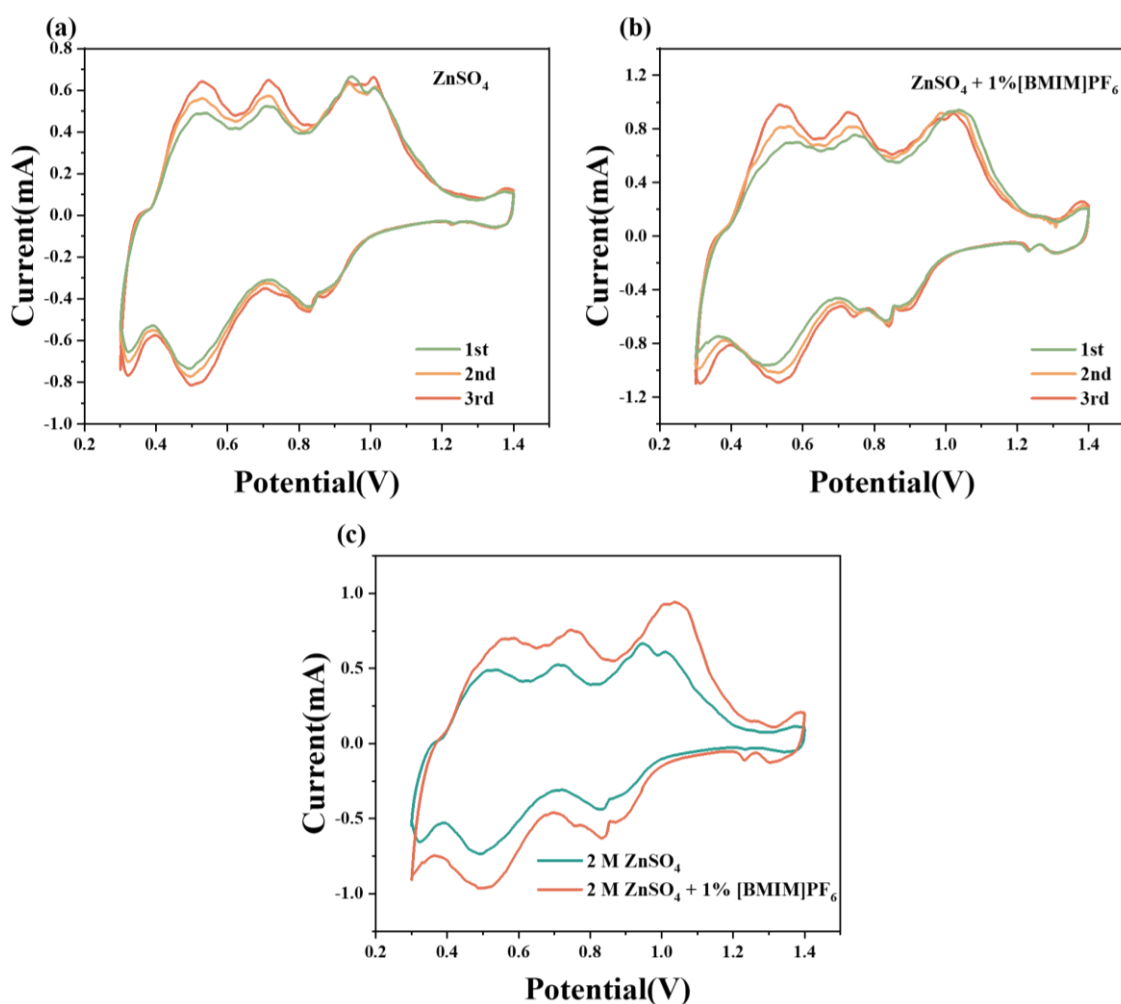
155 **Fig. S19.** SEM image of the NH<sub>4</sub>V<sub>4</sub>O<sub>10</sub> cathode material particle.

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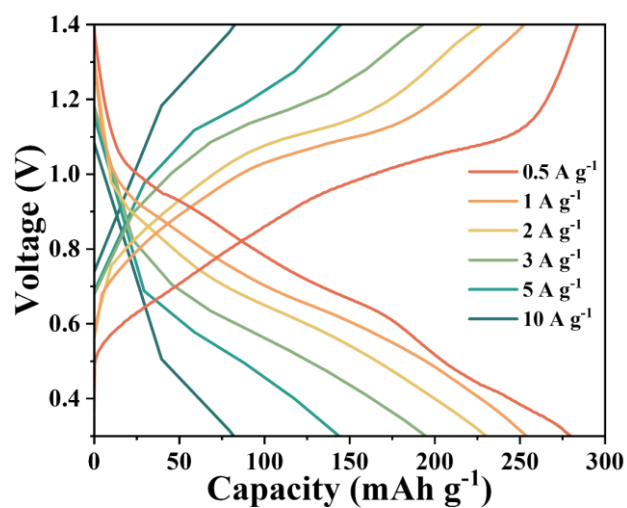
158 **Fig. S20.** XRD patterns of  $\text{NH}_4\text{V}_4\text{O}_{10}$  powder.



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160 **Fig. S21.** CV profiles of the  $\text{Zn}/\text{NH}_4\text{V}_4\text{O}_{10}$  batteries with different electrolytes. (a) Pure  $\text{ZnSO}_4$  and (b)

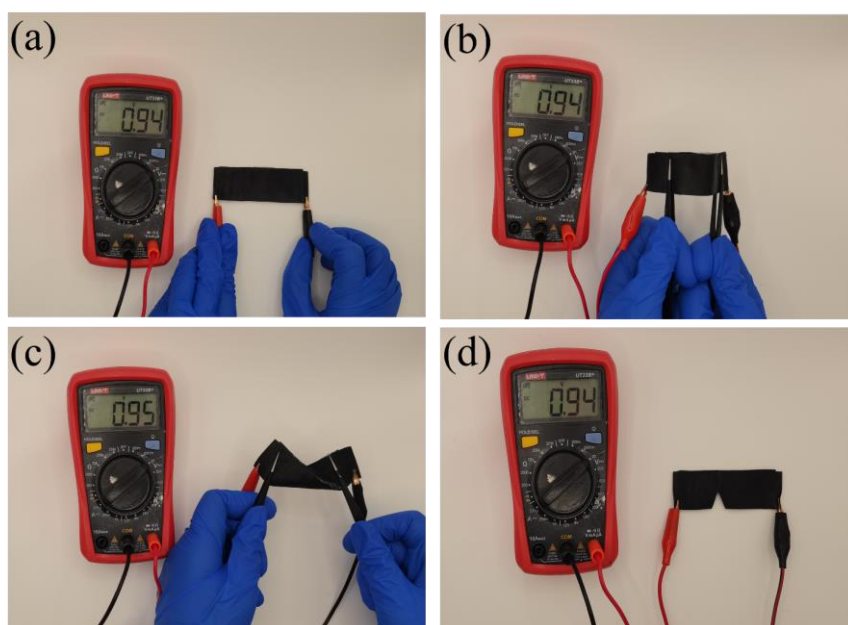
161  $\text{ZnSO}_4 + 1\% [\text{BMIM}]\text{PF}_6$  electrolytes. (c) Comparison of the 3rd cycle of CV curves.



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**Fig. S22.** Electrostatic charge/discharge curves of the Zn//NH<sub>4</sub>V<sub>4</sub>O<sub>10</sub> full cells at different current densities.



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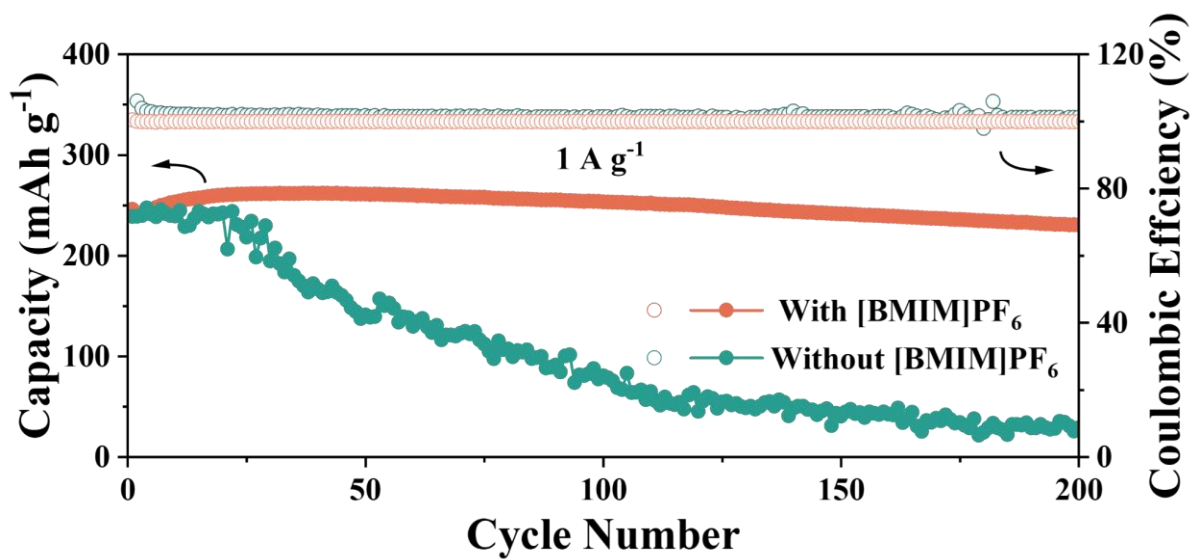
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**Fig. S23.** Demonstrate the voltage variation of a PAM-[BMIM]PF<sub>6</sub> battery under (a) flat, (b) bent, (c) twisted,

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and (d) shear conditions.





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**Fig. S24.** Corresponding cycle performance of PAM-[BMIM]PF<sub>6</sub> flexible full cell at 1 A g<sup>-1</sup>.

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170 **Table S1.** Fitting parameters of Nyquist plots.

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With [BMIM]PF <sub>6</sub>			
T(K)	R <sub>ct</sub> (Ω)	Error (%)	ln(R <sub>ct</sub> <sup>-1</sup> /Ω <sup>-1</sup> )
303	1030.1	0.90	-6.94
313	885.4	0.83	-6.79
323	621.1	1.02	-6.43
333	344.3	1.07	-5.84
343	199.9	1.32	-5.29

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Without [BMIM]PF <sub>6</sub>			
T(K)	R <sub>ct</sub> (Ω)	Error (%)	ln(R <sub>ct</sub> <sup>-1</sup> /Ω <sup>-1</sup> )
303	469.6	1.56	-6.16
313	333.6	2.09	-5.81
323	199.9	2.15	-5.29
333	135.4	2.23	-4.91

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193 The formula of the Arrhenius equation is expressed as follows :

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$$\frac{1}{R_{ct}} = A \exp\left(-\frac{E_a}{RT}\right)$$

195 where  $R_{ct}$  is the charge-transfer resistance, and A, T, R, and  $E_a$  represent the pre-exponential factor,  
196 absolute temperature, ideal gas constant, and activation energy, respectively.

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**Table S2.** Fitting parameters of Nyquist plots.

With [BMIM]PF <sub>6</sub>		
	R <sub>s</sub> (Ω)	R <sub>ct</sub> (Ω)
Pristine	1.42 / 1.44 / 1.46	409.19 / 471.17 / 495.32
10 th	1.58 / 1.59 / 1.54	55.49 / 62.95 / 74.47
20 th	1.75 / 1.77 / 1.82	24.65 / 32.39 / 57.14
30 th	1.63 / 1.67 / 1.65	25.36 / 30.35 / 43.26
Without [BMIM]PF <sub>6</sub>		
	R <sub>s</sub> (Ω)	R <sub>ct</sub> (Ω)
Pristine	1.49 / 1.52 / 1.50	1163.69 / 1181.13 / 1208.49
10 th	1.74 / 1.77 / 1.79	488.49 / 567.05 / 592.21
20 th	1.92 / 1.93 / 1.91	468.21 / 472.59 / 475.05
30 th	1.85 / 1.88 / 1.84	389.56 / 393.26 / 396.34

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203 **Table S3.** Performance comparison of symmetric Zn//Zn cells from the previously reported works  
 204 involving electrolyte additives and our work.

No.	Electrolyte component	Current density/capacity (Zn//Zn)	Life (h)	Current density/capacity (Zn//Cu)	Coulombic efficiency (%)	Max cumulative capacity plated (Ah cm <sup>-2</sup> )	Ref
1	2 M ZnSO <sub>4</sub> + 0.08 M ZnF <sub>2</sub>	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	600	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	99.6 (1000cycles)	3.2	4
2	1 M ZnSO <sub>4</sub> + 4 M EMImCl	1mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	500	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	99.9 (90cycles)	0.25	5
3	2 M ZnSO <sub>4</sub> in glycerol/water (50/50)	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup> , 2 mA cm <sup>-2</sup> /6 mAh cm <sup>-2</sup>	1500, 900	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	98.3 (500cycles)	0.9	6
4	1 M ZnSO <sub>4</sub> + 75 mM Na <sub>4</sub> EDTA	2 mA cm <sup>-2</sup> /2 mAh cm <sup>-2</sup> , 5 mA cm <sup>-2</sup> /2 mAh cm <sup>-2</sup>	450, 2000	0.5 mA cm <sup>-2</sup> /0.5 mAh cm <sup>-2</sup>	98.3 (300cycles)	5	7
5	1 M ZnSO <sub>4</sub> + 0.1 M MgSO <sub>4</sub>	1mA cm <sup>-2</sup> /0.25 mAh cm <sup>-2</sup>	600	2 mA cm <sup>-2</sup> /0.5 mAh cm <sup>-2</sup>	expands to 400 h with about 100 C.E.	0.3	8
6	1 M ZnSO <sub>4</sub> + 0.01 M Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup> , 5 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	400, 700	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	97.0 (2000cycles)	1.75	9
7	2 M ZnSO <sub>4</sub> + 1 vol% DME	2 mA cm <sup>-2</sup> /2 mAh cm <sup>-2</sup>	380	1 mA cm <sup>-2</sup> /0.4 mAh cm <sup>-2</sup>	99.1 (200cycles)	0.38	10
8	2 M ZnSO <sub>4</sub> + 0.05mg mL <sup>-1</sup> Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	2 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup> , 4 mA cm <sup>-2</sup> /5 mAh cm <sup>-2</sup>	1180, 250	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	98.6 (100cycles)	1.18	11
9	2 M ZnSO <sub>4</sub> + 0.5 g L <sup>-1</sup> TMBAC	2 mA cm <sup>-2</sup> /2 mAh cm <sup>-2</sup> , 10 mA cm <sup>-2</sup> /5 mAh cm <sup>-2</sup>	900, 470	0.5 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	99.0 (200cycles)	2.35	12
10	7.6 mM ZnCl <sub>2</sub> + 0.05 mM SnCl <sub>2</sub>	3 mA cm <sup>-2</sup> /3 mAh cm <sup>-2</sup>	500	0.5 mA cm <sup>-2</sup> /0.5 mAh cm <sup>-2</sup>	99.7 (200cycles)	0.75	13
11	4 M Zn(TFSI) <sub>2</sub> + 4 M P <sub>444</sub> (201)-TFSI	0.5 mA cm <sup>-2</sup> /0.5 mAh cm <sup>-2</sup> , 1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup> , 2.5 mA cm <sup>-2</sup> /2.5 mAh cm <sup>-2</sup>	6000, 800, 280	0.5 mA cm <sup>-2</sup> /5 mAh cm <sup>-2</sup>	>99 (16cycles)	1.5	14
12	1 M Zn(TFSI) <sub>2</sub> + 0.25 M Ace	1 mA cm <sup>-2</sup> /0.5 mAh cm <sup>-2</sup>	100	0.5 mA cm <sup>-2</sup> /0.5 mAh cm <sup>-2</sup>	98 (10cycles)	1	15
13	1 M ZnSO <sub>4</sub> +0.25PA	5 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	400	/	/	/	16
14	1 M ZnSO <sub>4</sub> +10% TG	2 mA cm <sup>-2</sup> /0.67 mAh cm <sup>-2</sup>	670	2 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	99.49 (300cycles)	/	17
This work	2 M ZnSO <sub>4</sub> + 1 % [BMIM]PF <sub>6</sub>	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup> , 4 mA cm <sup>-2</sup> /0.5 mAh cm <sup>-2</sup> , 4 mA cm <sup>-2</sup> /4 mAh cm <sup>-2</sup>	800, 1000, 400	1 mA cm <sup>-2</sup> /1 mAh cm <sup>-2</sup>	99.7 (500cycles)	2.31	This work

205

206

### 3. References

1. H. Sun, *J. Phys. Chem. B*, 1998, **102**, 7338-7364.
2. H. Sun, P. Ren, J.R. Fried, *Comput. Theor. Polym. Sci.*, 1998, **8**, 229-246.
3. O. Borodin, M. Olguin, P. Ganesh, P.R.C. Kent, J.L. Allen, W.A. Henderson, *Phys. Chem. Chem. Phys.*, 2016, **18**, 164-175.
4. Y. An, Y. Tian, K. Zhang, Y. Liu, C. Liu, S. Xiong, J. Feng, Y. Qian, *Adv. Funct. Mater.*, 2021, **31**, 2101886.
5. Q. Zhang, Y. Ma, Y. Lu, L. Li, F. Wan, K. Zhang, J. Chen, *Nat. Commun.*, 2020, **11**, 4463.
6. Y. Zhang, M. Zhu, K. Wu, F. Yu, G. Wang, G. Xu, M. Wu, H.-K. Liu, S.-X. Dou, C. Wu, *J. Mater. Chem. A*, 2021, **9**, 4253-4261.
7. S.-J. Zhang, J. Hao, D. Luo, P.-F. Zhang, B. Zhang, K. Davey, Z. Lin, S.-Z. Qiao, *Adv. Energy Mater.*, 2021, **11**, 2102010.
8. P. Wang, X. Xie, Z. Xing, X. Chen, G. Fang, B. Lu, J. Zhou, S. Liang, H.J. Fan, *Adv. Energy Mater.*, 2021, **11**, 2101158.
9. K.A. Owusu, X. Pan, R. Yu, L. Qu, Z. Liu, Z. Wang, M. Tahir, W.A. Haider, L. Zhou, L. Mai, *Mater. Today Energy*, 2020, **18**, 100529.
10. H. Huang, D. Xie, J. Zhao, P. Rao, W.M. Choi, K. Davey, J. Mao, *Adv. Energy Mater.*, 2022, **12**, 2202419.
11. J. Cao, D. Zhang, C. Gu, X. Wang, S. Wang, X. Zhang, J. Qin, Z.-S. Wu, *Adv. Energy Mater.*, 2021, **11**, 2101299.
12. K. Guan, L. Tao, R. Yang, H. Zhang, N. Wang, H. Wan, J. Cui, J. Zhang, H. Wang, H. Wang, *Adv. Energy Mater.*, 2022, **12**, 2103557.
13. L. Cao, D. Li, F.A. Soto, V. Ponce, B. Zhang, L. Ma, T. Deng, J.M. Seminario, E. Hu, X.-Q. Yang, P.B. Balbuena, C. Wang, *Angew. Chem. Int. Ed.*, 2021, **60**, 18845-18851.
14. L. Ma, T.P. Pollard, Y. Zhang, M.A. Schroeder, M.S. Ding, A.V. Cresce, R. Sun, D.R. Baker, B.A. Helms, E.J. Maginn, C. Wang, O. Borodin, K. Xu, *Angew. Chem. Int. Ed.*, 2021, **60**, 12438-12445.
15. H. Qiu, X. Du, J. Zhao, Y. Wang, J. Ju, Z. Chen, Z. Hu, D. Yan, X. Zhou, G. Cui, *Nat. Commun.*, 2019, **10**.

- 230 16. Y. Chen, F. Gong, W. Deng, H. Zhang, X. Wang, *Energy Storage Mater.*, 2023, **58**, 20-29.
- 231 17. Z. Liu, R. Wang, Q. Ma, J. Wan, S. Zhang, L. Zhang, H. Li, Q. Luo, J. Wu, T. Zhou, J. Mao, L. Zhang, C. Zhang, Z.
- 232 Guo, *Adv. Funct. Mater.*, 2024, **34**, 2214538.

233