

## Supporting Information

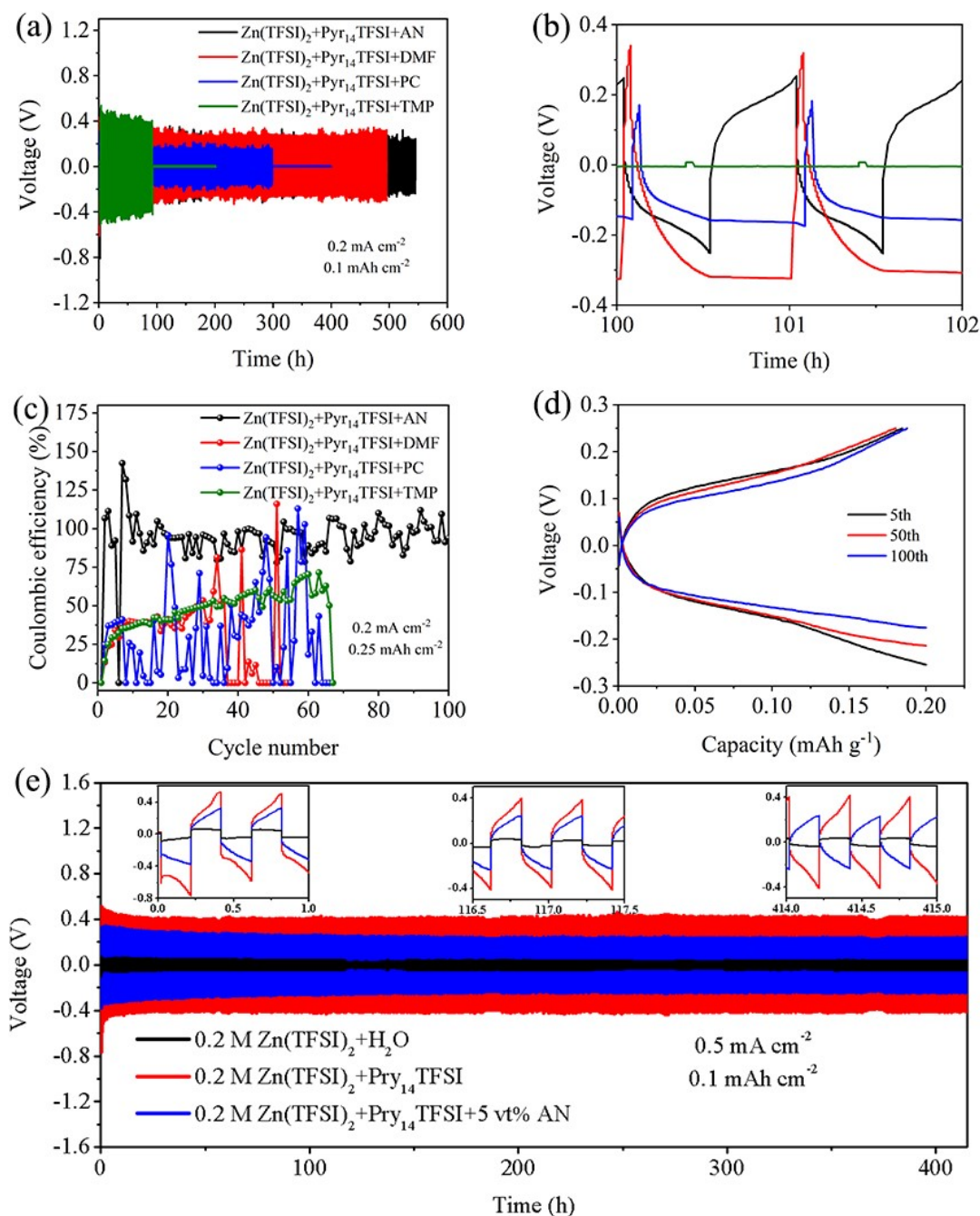
### **Developing high voltage Zn(TFSI)<sub>2</sub> / Pyr<sub>14</sub>TFSI / AN hybrid electrolyte for carbon-based Zn ion hybrid capacitor**

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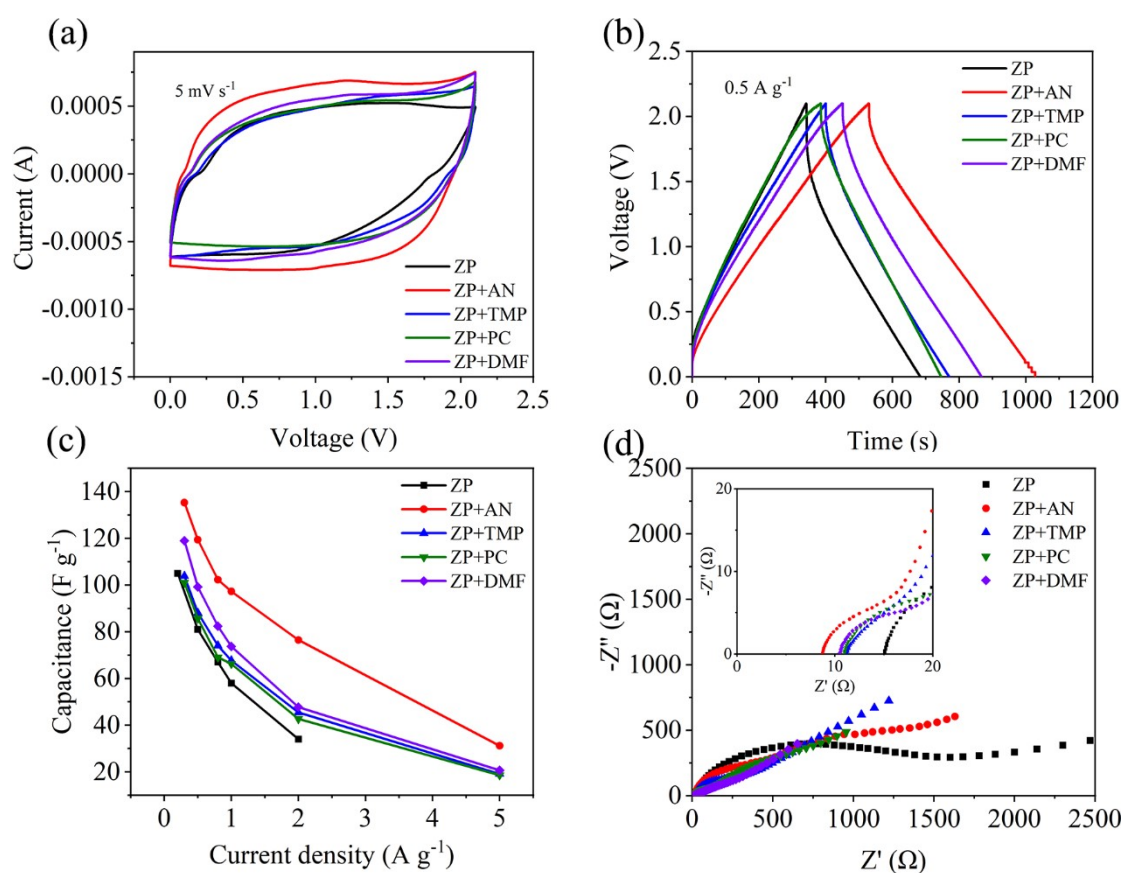
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**Fig. S1.** Compatibility of electrolytes with organic additives (AN, TMP, PC, DMF) and metal Zn. (a) Zn/Zn symmetrical cells is circulating in constant current of 0.2 mA cm<sup>-2</sup>. (b) Display the selected Zn deposition/exfoliation curve. (c) Coulomb efficiency (CE) of deposition/exfoliation in a Zn/Ti cells at a current density of 0.2 mA cm<sup>-2</sup>. (d) Typical Zn deposition/exfoliation curve at the selected number of cycles (5<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup>). (e) Voltage profiles of Zn/Zn symmetric cells with different electrolytes at 0.5 mA cm<sup>-2</sup> (insets of Fig. S1e is magnification charge/discharge profiles during 0.0-1.0h, 116.5-117.5h and 414.0-415.0h).

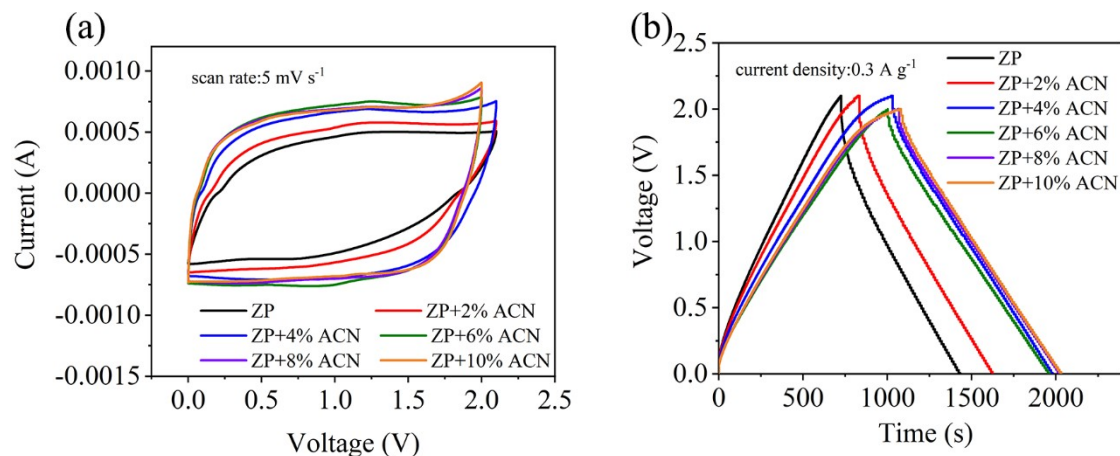
To study the effect of organic solvents as additives on the  $\text{Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}$  electrolyte, the Zn/Zn symmetric cells of (Propylene carbonate) PC, (Trimethyl phosphate) TMP, AN and (N, N-Dimethylformamide) DMF based hybrid electrolyte were assembled (Fig. S1a). For the  $\text{Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}$  electrolyte with adding PC and TMP, the constructed Zn/Zn symmetric cells have a significant short-circuit phenomenon. Interestingly, when AN and DMF are introduced into the  $\text{Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}$  electrolyte, this symmetric system can be cycled stably for 500 h. In order to observe the specific deposition/exfoliation behavior, the voltage-time curve of about 100 h was enlarged. As shown in Fig. S1b, the  $\text{Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}$  electrolyte with AN can maintain the stable operation of the Zn/Zn symmetric cells, whereas  $\text{Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}$  electrolyte with DMF failed to perform the normal  $\text{Zn}^{2+}$  deposition/exfoliation behavior. With current density growing to  $0.5 \text{ mA cm}^{-2}$ , the metallic Zn in  $0.2 \text{ M Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}$  and  $0.2 \text{ M Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}/5 \text{ vt\% AN}$  electrolyte are able to steadily work for not fewer than 160 h. Besides, the polarization voltage decreases by 136 mV in comparison to original 363 mV in  $0.2 \text{ M Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}/5 \text{ vt\% AN}$  electrolyte (Fig. S1e).



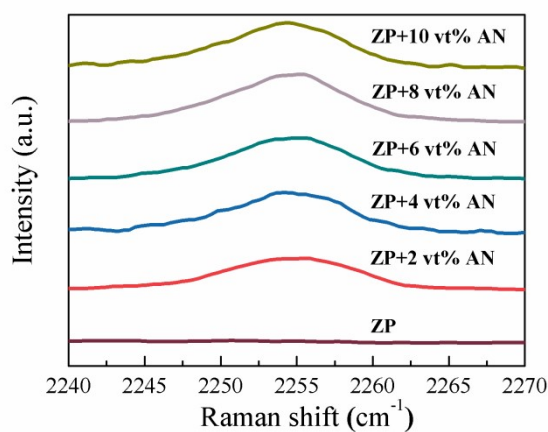
**Fig. S2.** Electrochemical performance of ZIHCs assembled with electrolytes containing different organic solvents (AN, TMP, PC, DMF): (a) CV curve, the scan rate is  $5 \text{ mV s}^{-1}$ ; (b) GCD curve when the current density is  $0.5 \text{ A g}^{-1}$ ; (c) Rate performance; (d) Compare the EIS of ZIHCs with different electrolytes. The inset is an enlarged view.

In addition, the electrochemical performance of ZIHCs composed of  $\text{Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}/\text{organic solvent}$  (AN, PC, DEC, and DMF) electrolyte was also studied (Fig. S2). As shown in Fig. S2a,b, the working voltage of ZIHCs constructed by  $\text{Zn}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}/\text{organic solvent}$  electrolyte (AN, PC, DEC, and DMF) is 0–2.1 V, indicating that these additives have no effect on the stability of the electrolyte. Meanwhile, the cyclic voltammetry (CV) and GCD curves of the device maintain a quasi-rectangular shape and a quasi-isosceles triangle shape within the operating voltage range, suggesting that the device has rapid capacitance behavior. Notably, the addition of AN, can significantly boost the capacitance and improve the rate performance of ZIHCs compared with other organic solvents (Fig. S2c). Furthermore,

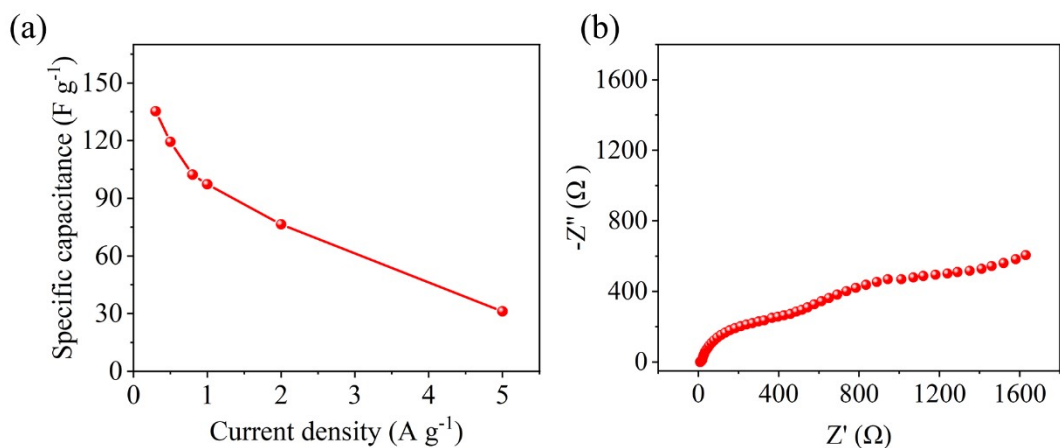
EIS measurement was performed to explore the influence of additives on the dynamic behavior of the interface (Figure S2d). The addition of AN reduces the internal resistance of the device from 15  $\Omega$  to 8  $\Omega$ , indicating that the addition of AN reduce the viscosity and increase the conductivity of the hybrid electrolyte.



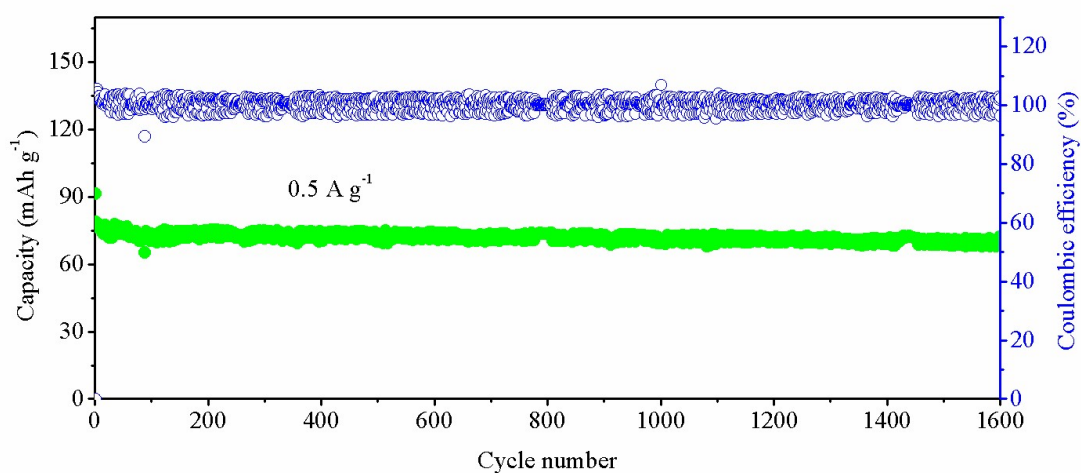
**Fig. S3.** (a) and (b) respectively represent the CV and PT of ZIHCs with different AN additions to determine the device window change.



**Fig. S4.** Raman spectra between 2240 and 2270 cm<sup>-1</sup> of hybrid electrolytes with different AN content (C≡N stretching vibration of AN).



**Fig. S5.** (a) Rate performance of ZIHC based on  $[\text{Zn}(\text{TFSI})_2]_3/[\text{Pyr}_{14}\text{TFSI}]_{16}/[\text{AN}]_4$  electrolyte. (b) EIS.



**Fig. S6.** Cycling performance of the 2.1 V C-ZIHC coin cell using commercial activated carbon cathode and metallic Zn anode with  $[\text{Zn}(\text{TFSI})_2]_3/[\text{Pyr}_{14}\text{TFSI}]_{16}/[\text{AN}]_4$  electrolyte, at a current density of  $0.5 \text{ A g}^{-1}$ .