Supporting Information

Advanced electrolyte with high stability and low temperature resistance for zinc-ion batteries

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Supplementary Text

Density Functional Theory (DFT) Study

To study the molecular conformations and interaction strengths among water molecules (W), trehalose molecules (TreH), and SA molecules (SA) in the trehalose-modified hydrogels, we computed the interaction energies of the following cases based on DFT, respectively: (1) water molecule and water molecule (W-W); (2) SA molecule and water molecule (SA-W); (3) trehalose molecule and water molecule (TreH-W); (4) SA molecule and trehalose molecule (SA-TreH); (5) SA molecule coexisting with trehalose molecule and water molecule (SA-TreH-W); (6) trehalose molecule and trehalose molecule (TreH-TreH); (7) SA molecule and SA molecule (SA-SA). The corresponding molecular models are shown in Fig. 2d.

All the DFT calculations were performed with Gaussian 16, using the B3LYP hybrid density functional. Geometry optimizations were carried out with the 6-31G(d,p) basis set in vacuum. Single-point calculations were performed with the 6-311+G(2d,2p) basis set. DFT-D3(BJ) corrections were also added to the single-point energies. When computing the interaction energies among water molecules, trehalose molecules and SA molecules, four repeating structural units (MGGM) of the SA chain were chose to represent a SA molecule.

The interaction energy (E_i) represents the interaction strength among the system components, which can be calculated by the following equation:

$$E_i = E_{total} - \sum E_{component}$$

where E_{total} and $E_{component}$ are the total energy of the system and the energy of each component in the model, respectively. Since the interaction energy is negative, a smaller value indicates a stronger interaction existing in the model. The calculated interaction energies among water molecules, trehalose molecules, and SA molecules are given in Table. S1.

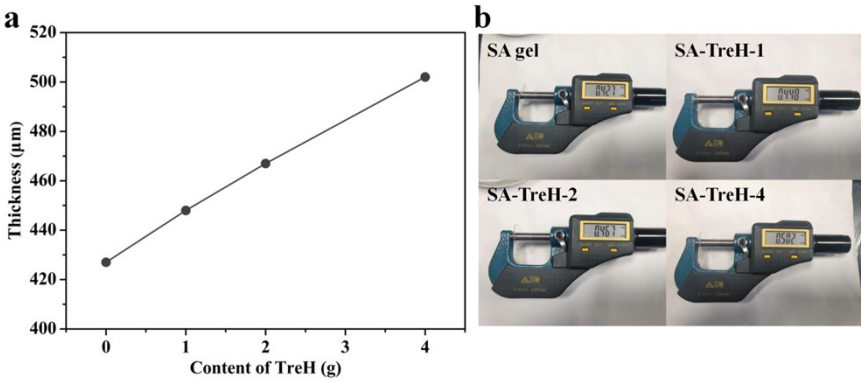

Fig. S1 (a) Variation curve of hydrogel thickness with TreH content; (b) Optical image of the thickness measurement.

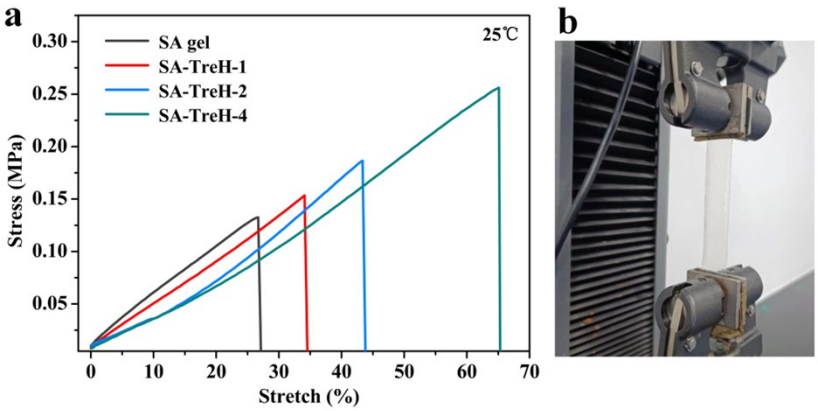

Fig. S2 (a) Stress-strain curves of four hydrogels; (b) Optical image of the tensile test.

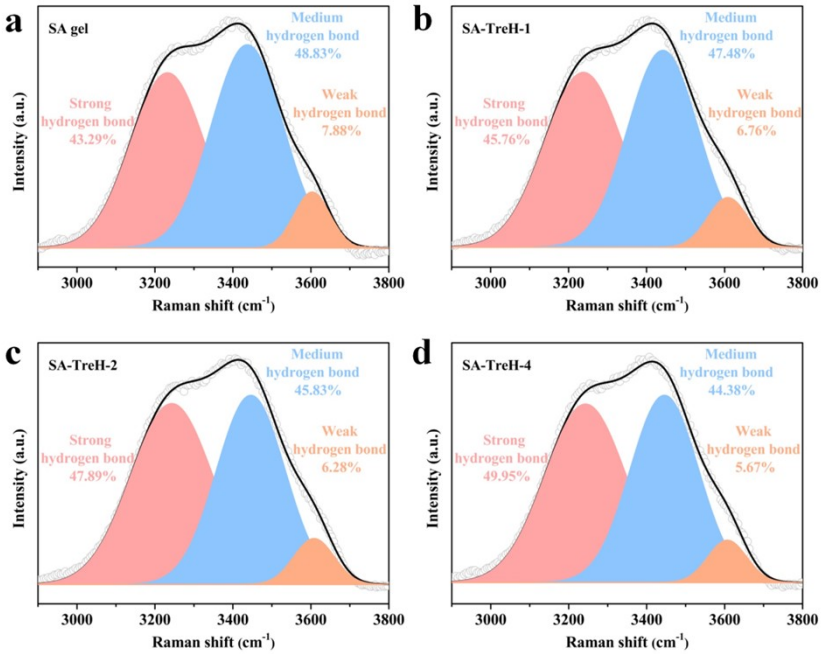

Fig. S3 Fitted Raman spectra of four SA hydrogels: (a) SA gel; (b) SA-TreH-1; (c) SA-TreH-2; (d) SA-TreH-4.

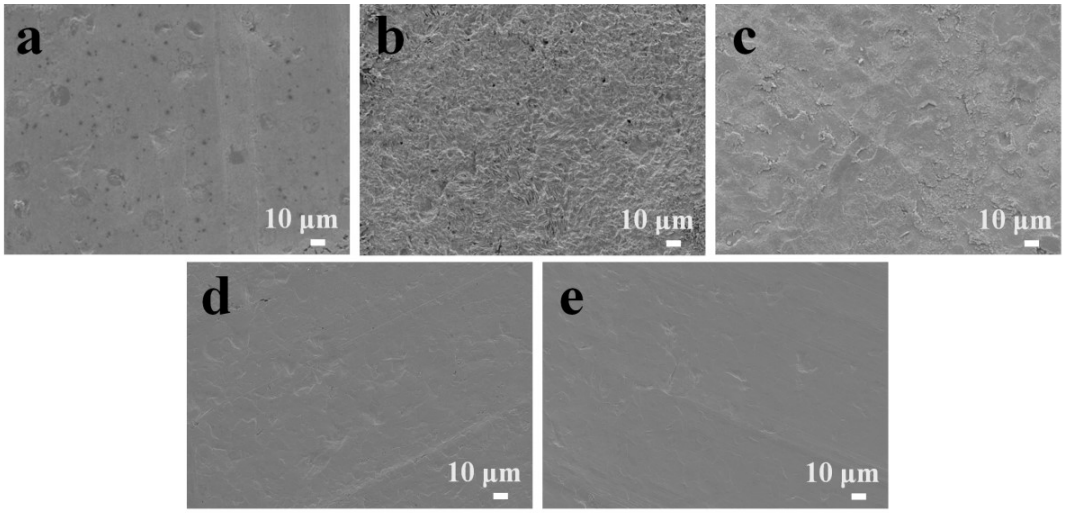

Fig. S4 (a) SEM image of the fresh zinc anode; SEM images of zinc anodes after 50 cycles in the Zn-Zn symmetric batteries assembled with four HEs: (b) SA gel; (c) SA-TreH-1; (d) SA-TreH-2; (e) SA-TreH-4.

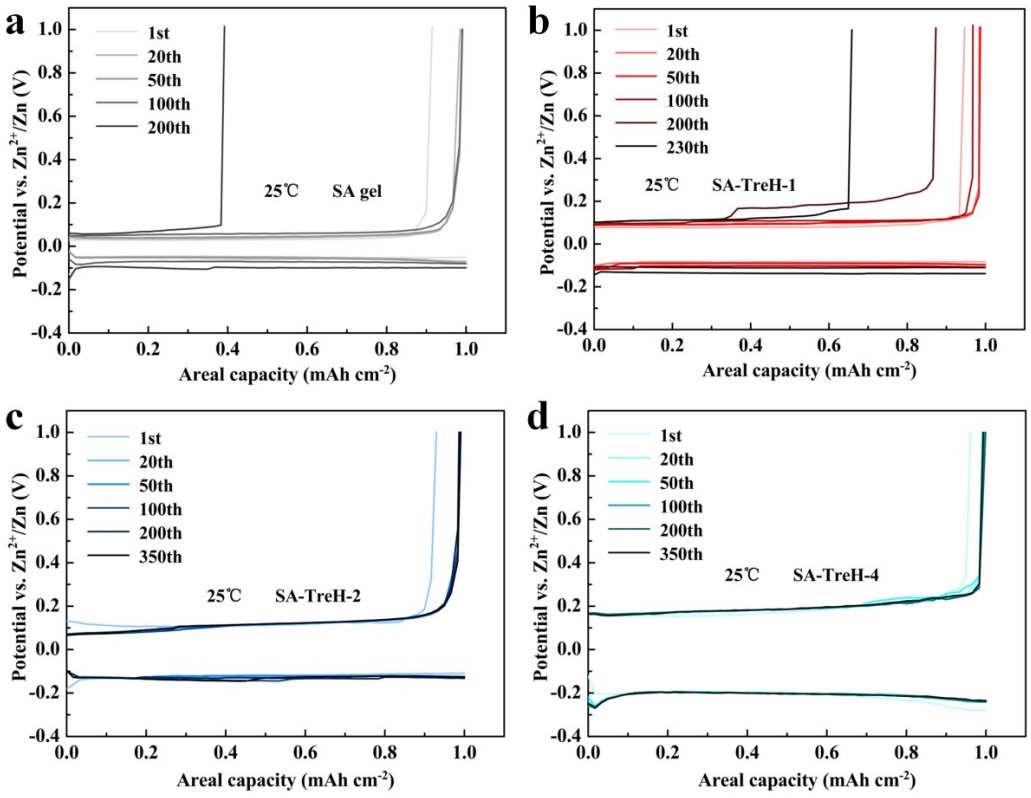

Fig. S5 Voltage profiles of the Zn-Cu asymmetric batteries assembled with four HEs at 25 ℃ (2 mA·cm^{-2} - 1 mAh·cm^{-2}): (a) SA gel; (b) SA-TreH-1; (c) SA-TreH-2; (d) SA-TreH-4.

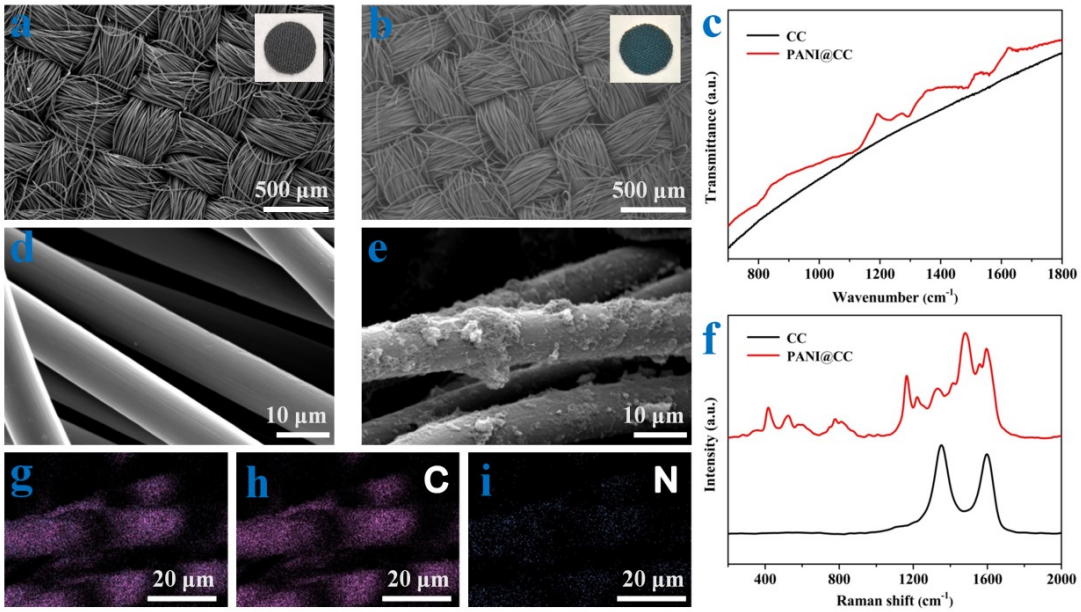

Fig. S6 SEM images (×50) of (a) CC and (b) PANI@CC (Optical images of both are in the top right corner, respectively.); (c) FTIR spectra of CC and PANI@CC; SEM images (×2000) of (d) CC and (e) PANI@CC; (f) Raman spectra of CC and PANI@CC; (g-i) EDS mapping images of PANI@CC.

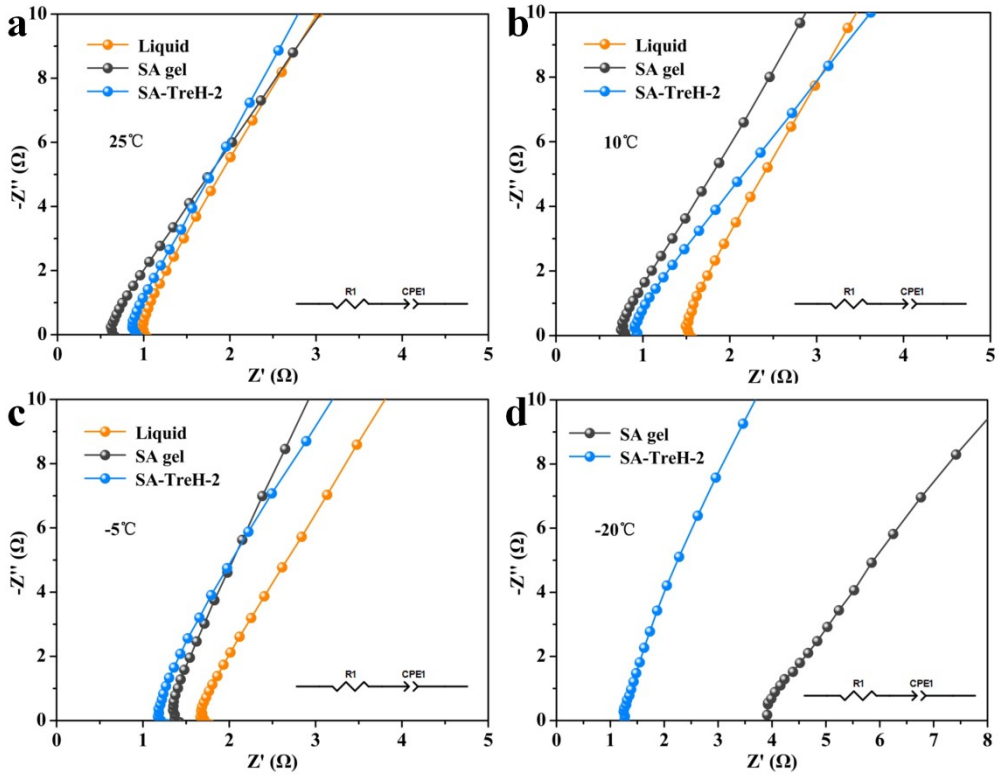

Fig. S7 Nyquist plots of liquid electrolyte, SA gel and SA-TreH-2 at four temperatures: (a) 25 ℃; (b) 10 ℃; (c) -5 ℃; (d) -20 ℃.

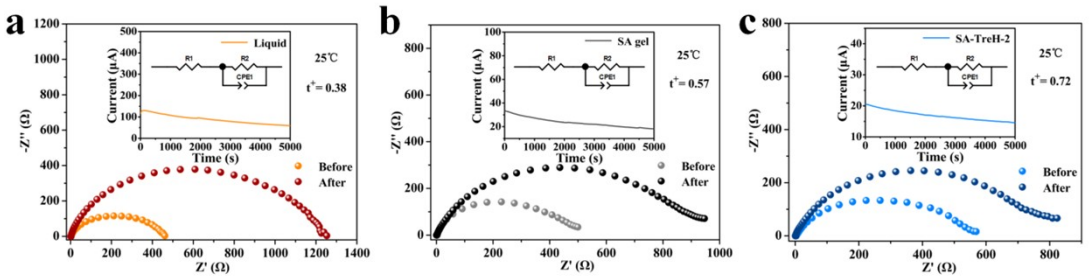

Fig. S8 Initial impedances and impedances after polarization and the I-t curves (Applied voltage: 25 mV) of the Zn-Zn symmetric batteries assembled with three electrolytes at 25 ℃: (a) Liquid; (b) SA gel; (c) SA-TreH-2.

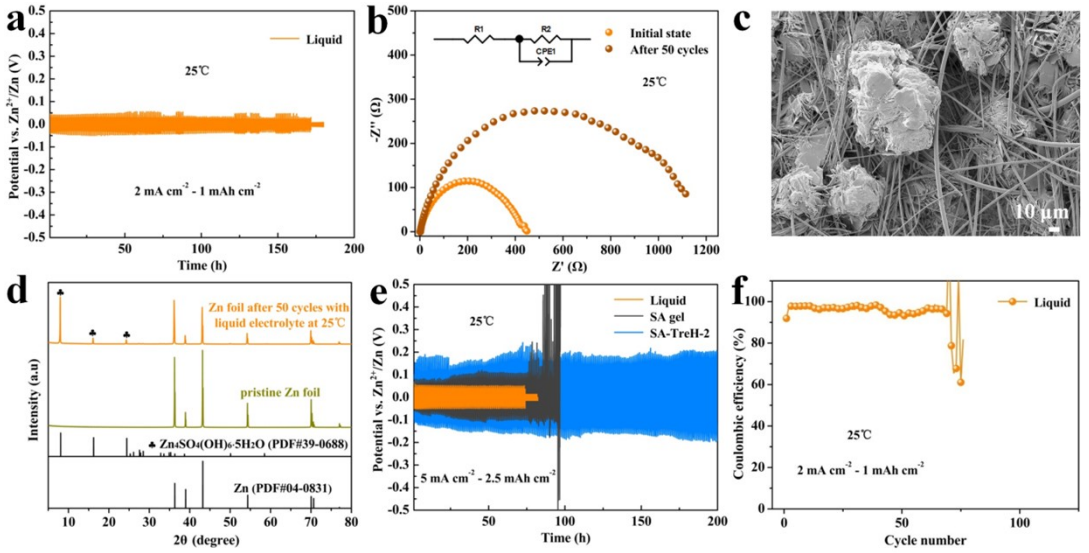

Fig. S9 Zn-Zn symmetric battery performance with liquid electrolyte at 25 ℃: (a) Zinc plating/stripping performance (2 mA·cm^{-2} - 1 mAh·cm^{-2}); (b) Initial impedance and impedance after 50 cycles; (c) SEM image of the zinc anode after 50 cycles; (d) XRD pattern of the zinc anode after 50 cycles. (e) Zinc plating/stripping performance of the Zn-Zn symmetric batteries assembled with liquid electrolyte, SA gel and SA-TreH-2 at 25 ℃ (5 mA·cm^{-2} - 2.5 mAh·cm^{-2}); (f) CE of the Zn-Cu asymmetric battery assembled with liquid electrolyte at 25 ℃.

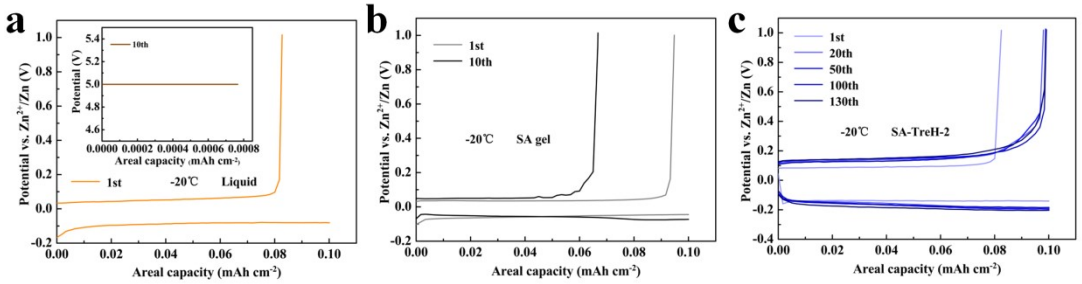

Fig. S10 Voltage profiles of the Zn-Cu asymmetric batteries assembled with three electrolytes at -20 ℃ (0.2 mA·cm^{-2} – 0.1 mAh·cm^{-2}): (a) Liquid; (b) SA gel; (c) SA-TreH-2.

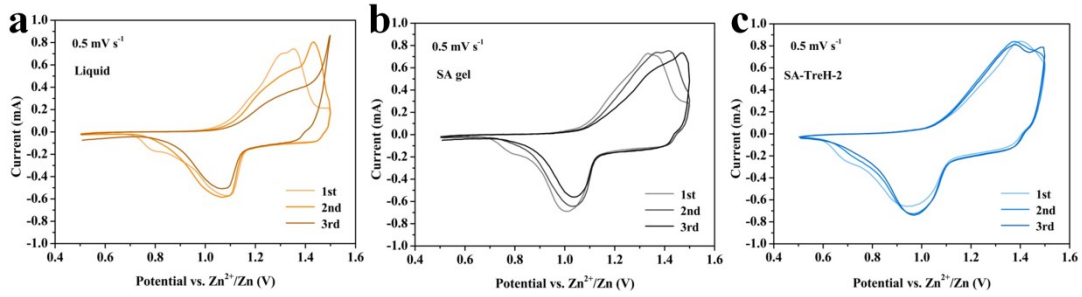

Fig. S11 CV curves at 0.5 mV·s^{-1} of the Zn-PANI full batteries assembled with three electrolytes: (a) Liquid; (b) SA gel; (c) SA-TreH-2.

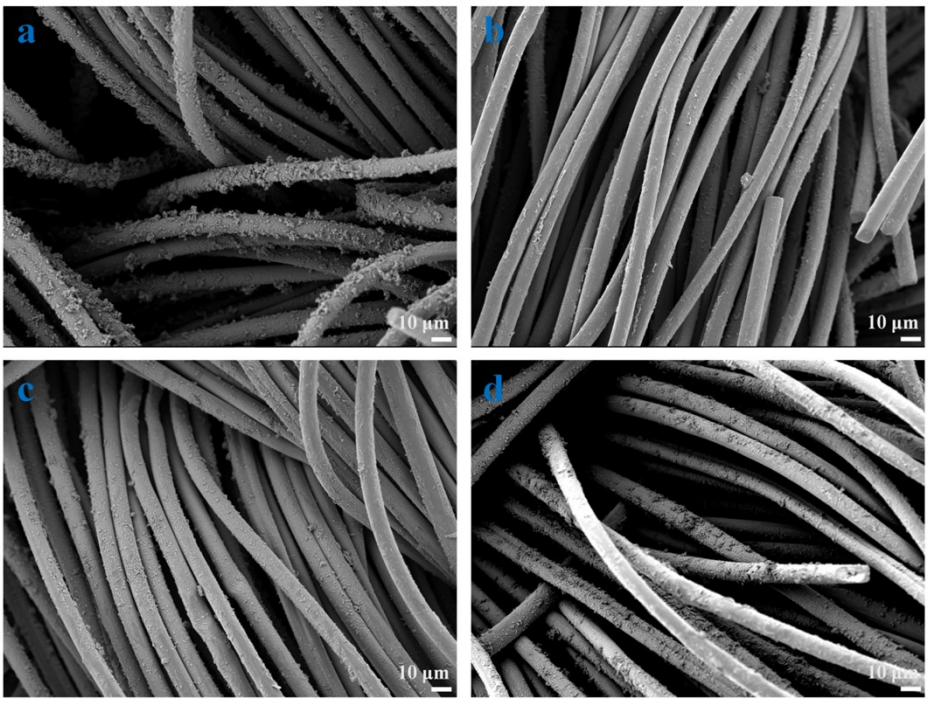

Fig. S12 (a) SEM image of the fresh PANI@CC cathode; SEM images of PANI@CC cathodes after 100 cycles in the Zn-PANI full batteries assembled with three electrolytes: (b) Liquid; (c) SA gel; (d) SA-TreH-2.

Table. S1 The interaction energies among water molecules, trehalose molecules, and SA molecules calculated by DFT.

Model	Interaction energy (Kcal·mol^{-1})
W-W	-8.58
TreH-W	-17.29
SA-W	-19.34
SA-TreH	-46.38
SA-TreH-W	-61.22
TreH-TreH	-44.83
SA-SA	-69.80

Table. S2 Comparison of the performance of zinc-ion polymer electrolytes

Polymer Matrices	Salts	Zn-Zn symmetric batteries performance	Full batteries performance	Reference
SA	2 M $ZnSO_4$	25℃: 200 h (180 mV polarization) 5 mA·cm^{-2} - 2.5 mAh·cm^{-2} -20℃: 200 h (280 mV polarization) 0.5 mA·cm^{-2} - 0.25 mAh·cm^{-2}	25℃: PANI@CC 213 mAh·g^{-1} 0.2 A·g^{-1} -20℃: PANI@CC 120 mAh·g^{-1} 0.2 A·g^{-1}	**This work**
PVA	0.5 M $ZnCl_2$ + 1 M NH_4Cl	/	25℃: PANI@KCY 167 mAh·g^{-1} 0.2 A·g^{-1}	*Energy Storage Materials* **2021**, 35, 739-749
Cellulose	16 M $ZnCl_2$ + 0.6 M $CaCl_2$	20℃: 800 h (25 mV polarization) 2 mA·cm^{-2} - 2 mAh·cm^{-2} -40℃: 800 h (30 mV polarization) 2 mA·cm^{-2} - 2 mAh·cm^{-2}	20℃: PANI@CNT 125 mAh·g^{-1} 0.2 A·g^{-1} -40℃: PANI@CNT 80 mAh·g^{-1} 0.2 A·g^{-1}	*Chemical Engineering Journal* **2022**, 446, 137056

PVA	0.2 M $Zn(CF_3SO_3)_2$	25℃: 200 h (80 mV polarization) 2 $mA \cdot cm^{-2}$ - 2 $mAh \cdot cm^{-2}$	25℃: PANI@CC 145 $mAh \cdot g^{-1}$ 0.2 $A \cdot g^{-1}$	*Journal of Materials Chemistry A* **2021**, 9, 24325-24335
PAM	≈0.7 M $Zn(CF_3SO_3)_2$	/	20℃: PANI@CC 120 $mAh \cdot g^{-1}$ 0.2 $A \cdot g^{-1}$	*SCIENCE CHINA Materials* **2022**, 65(8), 2189-2196