Ice-Template-Induced Highly Ionic Conductive PVA/PEG-SiO$_2$ Gel Polymer Electrolyte for Zinc-Ion Batteries

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Synthesis of polymer electrolytes

First, 0.15 g SiO$_2$(99.5 %, 15nm, Macklin) was dispersed in 40 mL deionized water and stirred for 30 minutes to obtain a uniform silica dispersion. Then, the silica dispersion was heated to 90 °C by oil bath heating and 3 g PVA (molecular weight 195000, Adamas) was gradually added under continuous stirring. After a period of stirring, the PVA was completely dissolved and then 0.8 g PEG (average molecular weight 6000, Adamas) was added and the stirring was continued for 5 h. Next, the homogeneously viscous solution was poured into the mold and frozen at -18 °C for 12 h for crosslinking, and finally freeze-drying for 8 h to remove ice crystals to obtain a polymer film. The dried polymer film was fully immersed in 2M ZnSO$_4$ solution to obtain a polymer gel electrolyte. Pure PVA, PVA-SiO$_2$ and PVA/PEG were synthesized by the above steps and used as comparison samples.

Synthesis of cathodes

V$_2$O$_5$/CNT was synthesized by hydrothermal method[6]. Firstly, 0.72 g V$_2$O$_5$ (99.99%, Macklin) powder was dissolved in 120 mL deionized water and stirred to form a yellow suspension. Then 10 mL 30% H$_2$O$_2$ was added to the suspension and stirred for 10min. Then 0.31 g multi-walled carbon nanotubes (95%, Macklin) were added to

the suspension and sonicated for 4 h, then stirred overnight. Next, the uniformly stirred suspension was transferred into the reactor and the hydrothermal reaction was carried out at 180 °C for 48 h. After the reaction, the sediment was collected, washed several times with deionized water and anhydrous ethanol, and then dried in a vacuum drying oven at 70 °C for 12 h. Finally, the obtained V_2O_5/CNT was annealed at 300 °C for 2 h. The V_2O_5/CNT, acetylene black and PVDF were mixed at a ratio of 8:1:1 and fully ground and added with N-methylpyrrolidone (NMP) to make a slurry, which was then coated on carbon paper (loading 1-2mg cm^{-2}) and dried at 70 °C for 12 h to obtain the cathode of ZIBs.

Characterization of materials

Field Emission Scanning Electron Microscopy (FESEM, Zeiss Gemini Sigma 300) was used to characterize the surface morphology and elemental distribution of the samples. X-ray diffraction (XRD) spectra of the samples were tested by a Bruker advance D8 X-ray diffractometer (40 kV, 40 mA, Cu-Ka radiation, λ= 0.15418 nm) in the range of 10° to 90° at a sweep speed of 10° min^{-1}. Fourier Transform Infrared Spectroscopy (FTIR) was determined by Agilent Technologies Cary 630 FTRI at room temperature in the wave number range of 500 cm^{-1} to 4000 cm^{-1}. Raman spectra[1-2] (Raman) were determined with a HORIBA HR Evolution (532nm laser). Tensile strain was determined at room temperature using an electronic universal testing machine (UTM5305H).

Electrochemical testing

All electrochemical testing was accomplished on a CHI760E electrochemical

workstation and a LAND battery test system. Electrochemical performance was evaluated using a CR2032 coin cell, which was assembled using a synthetic cathode and gel electrolyte with zinc foil in air. Cycling, multiplicative performance and cyclic voltammetry curves (CV) of the cells were tested over a potential range of 0.2 to 1.6 V. The EIS of the gel electrolyte was measured at 0.1 Hz to 100000 Hz. The gel electrolyte was sandwiched between two stainless steel sheets, and the EIS of the gel electrolyte was tested to obtain the resistance over the range of 0.1 Hz to 100000 Hz. The ionic conductivity was calculated by the following equation:

$$\sigma = \frac{L}{RA}$$

where L, R, and A represent the thickness (cm), resistance (Ω), and test area (cm^2) of the gel electrolyte, respectively. The zinc ion transference number (t_{zn2+}) of the gel electrolyte was tested by constant potential polarization method with sandwiching the gel electrolyte between two zinc foils and calculated using the following Evans equation:

$$t_{Zn^{2+}} = \frac{I_S(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)}$$

The rate of uptake (Wt) and the rate of desorption (Wt') of the gel electrolyte to the liquid electrolyte were tested at room temperature and calculated using the following equations:

$$W_t = \frac{W_1 - W_0}{W_0} \times 100\%$$

$$W_t' = \frac{W_3}{W_2} \times 100\%$$

Where W_1, W_0 are the weight of dry gel soaked in 2M $ZnSO_4$ over time and the weight of dry gel before soaking. W_2 and W_3 are the weight of wet gel after 48h of soaking in 2M $ZnSO_4$ and the weight of wet gel exposed to air over time, respectively.
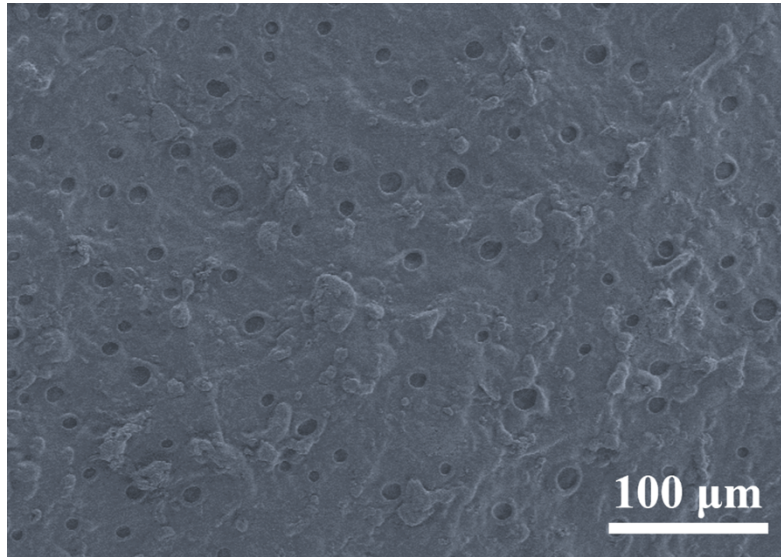
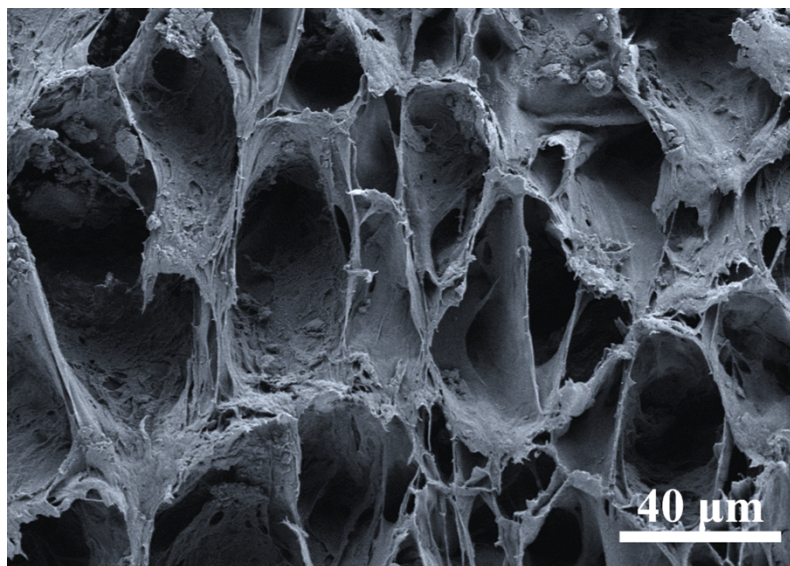**Fig. S1**. FESEM images of pure PVA surface.

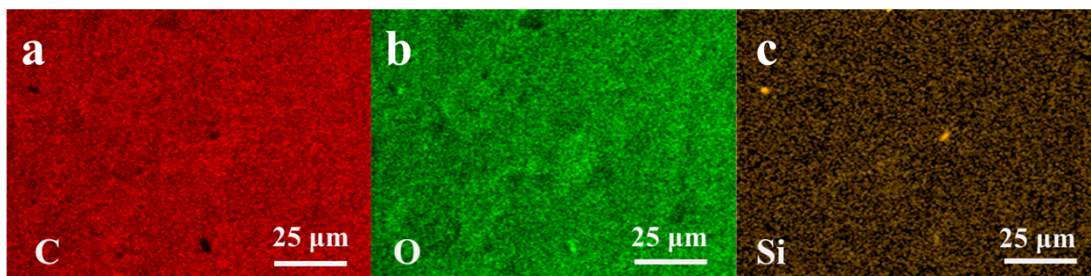**Fig. S2**. FESEM image of the cross section of PVA/PEG-SiO$_2$

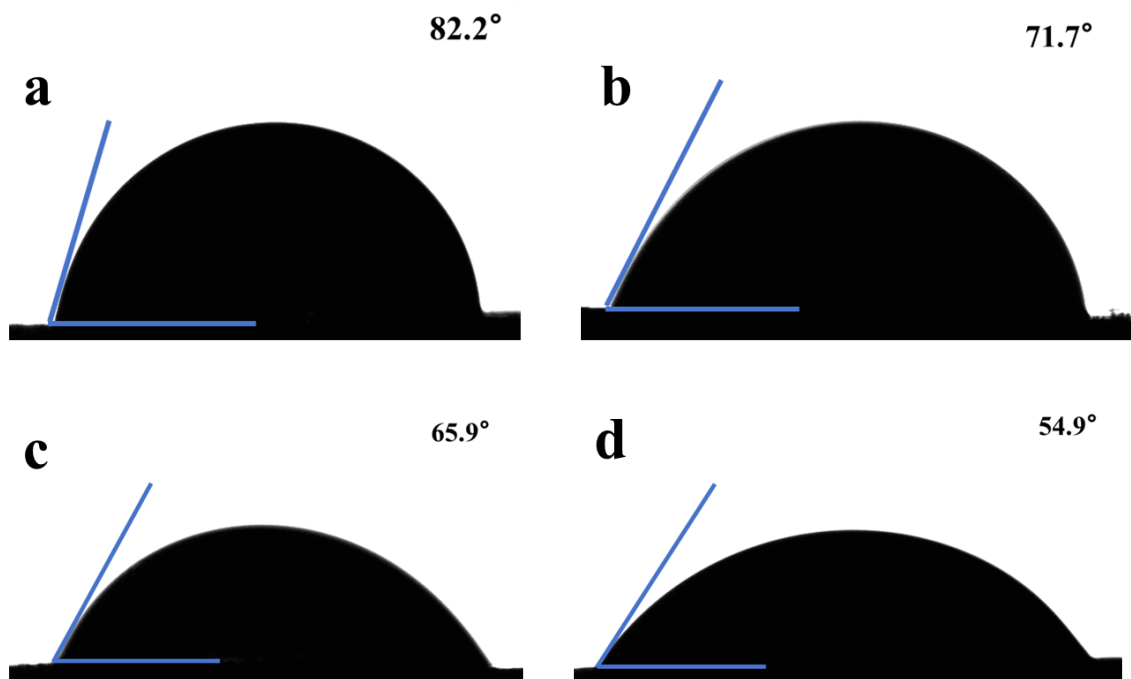**Fig. S3** The elemental mapping of (a) C, (b) O, (c) Si of PVA/PEG-SiO$_2$

Fig. S4 Contact angles of 2M $ZnSO_4$ electrolyte on (a) PVA, (b) PVA-SiO_2, (c) PVA/PEG, and (d) PVA/PEG-SiO_2
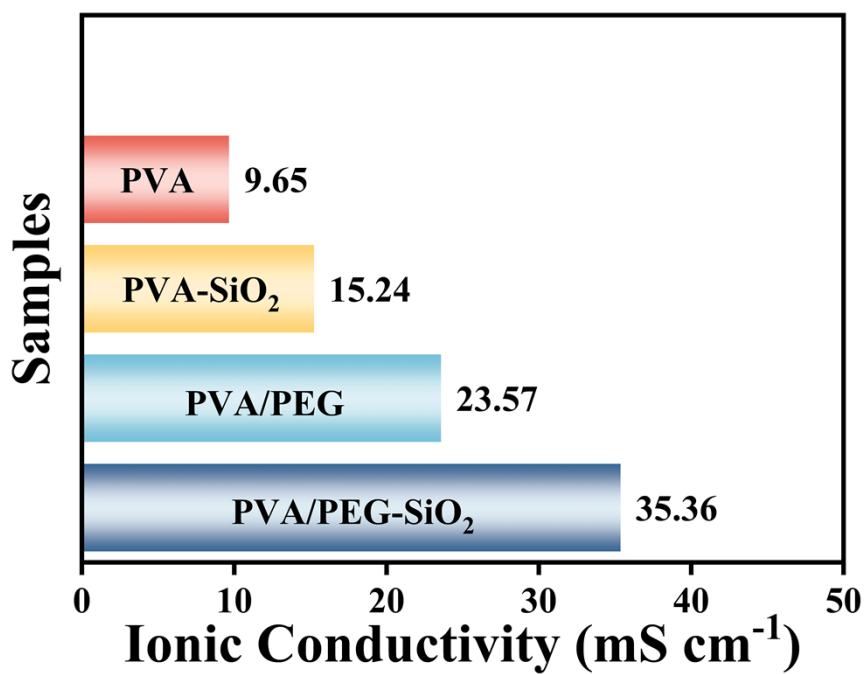

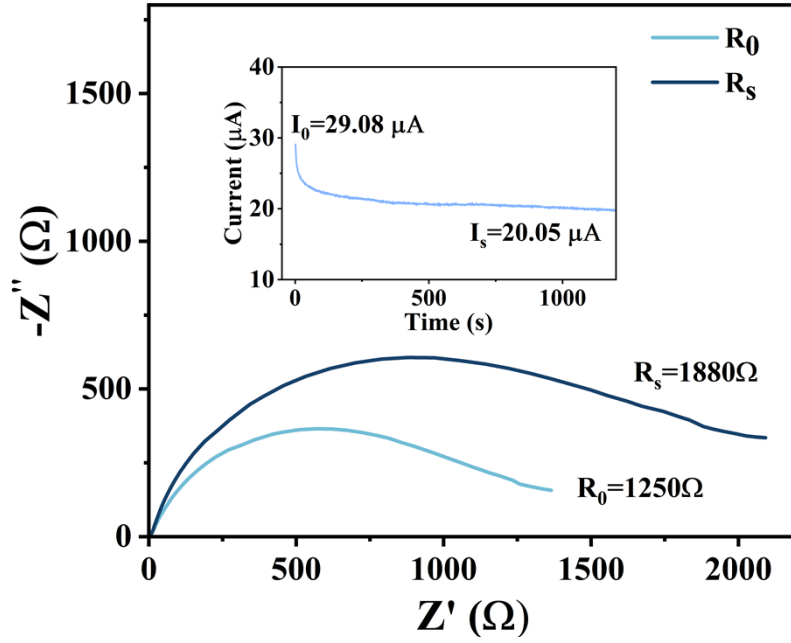**Fig. S5**. Ionic conductivity of pure PVA, PVA-SiO_2, PVA/PEG, and PVA/PEG-SiO_2

Fig. S6 EIS spectrum of Zn//PVA/PEG-SiO2//Zn symmetric batteries before and after polarization. The inset shows variation of current with time during polarization at 10 mV voltage applied.
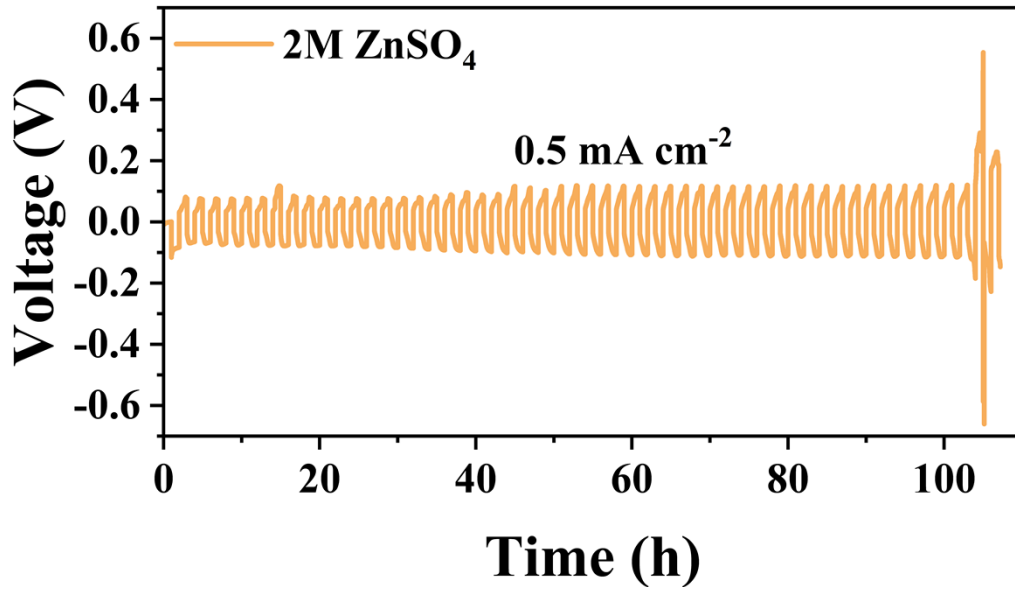

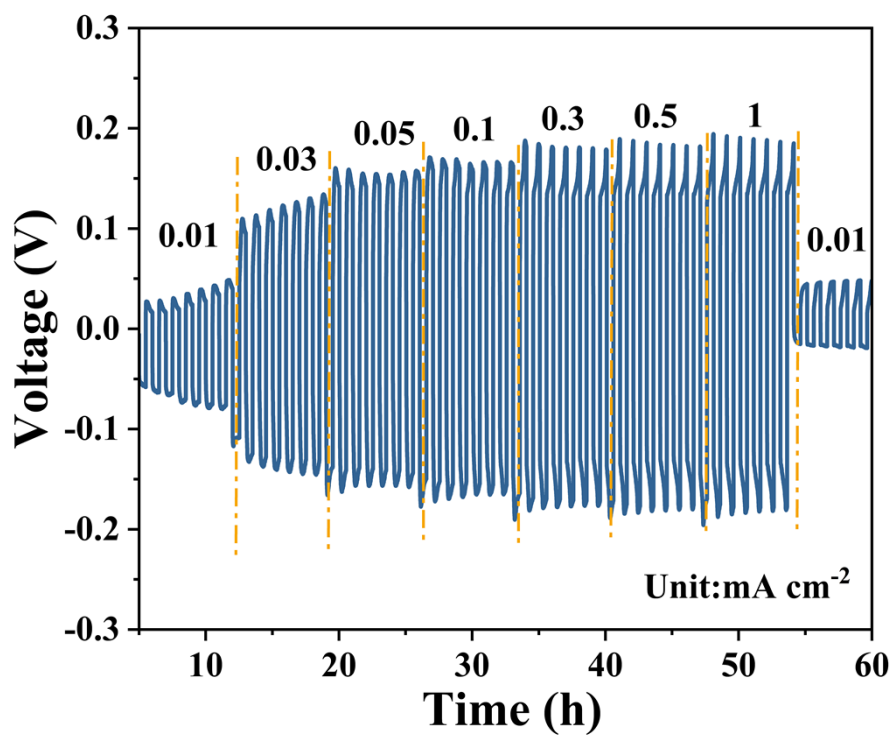**Fig. S7** Zn plating/stripping performance of Zn//ZnSO$_4$//Zn symmetrical battery.

Fig. S8. Rate performance of Zn//PVA/PEG-SiO$_2$//Zn symmetrical battery
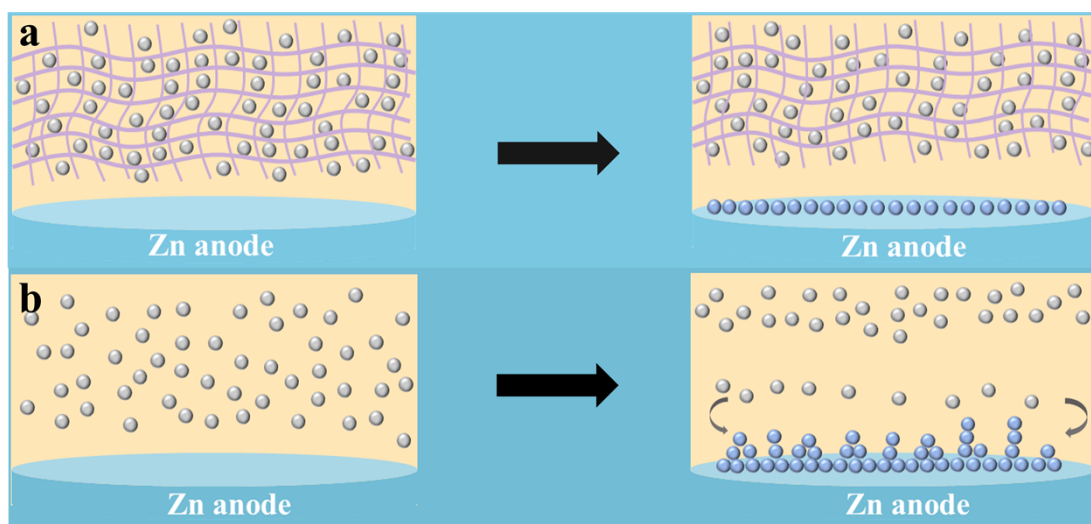

Fig. S9 (a) Zn deposition schematic diagram in PVA/PEG-SiO$_2$.
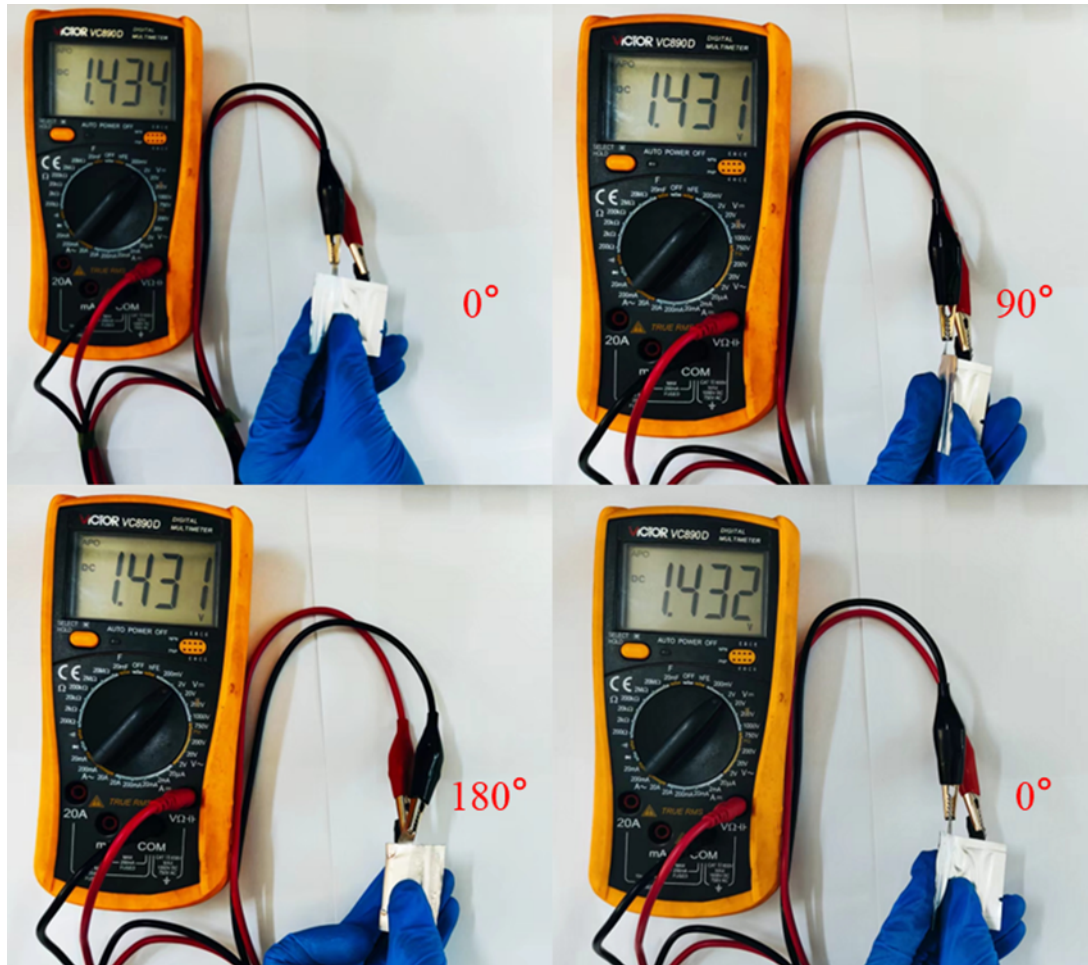(b) Zn deposition schematic diagram in ZnSO$_4$.

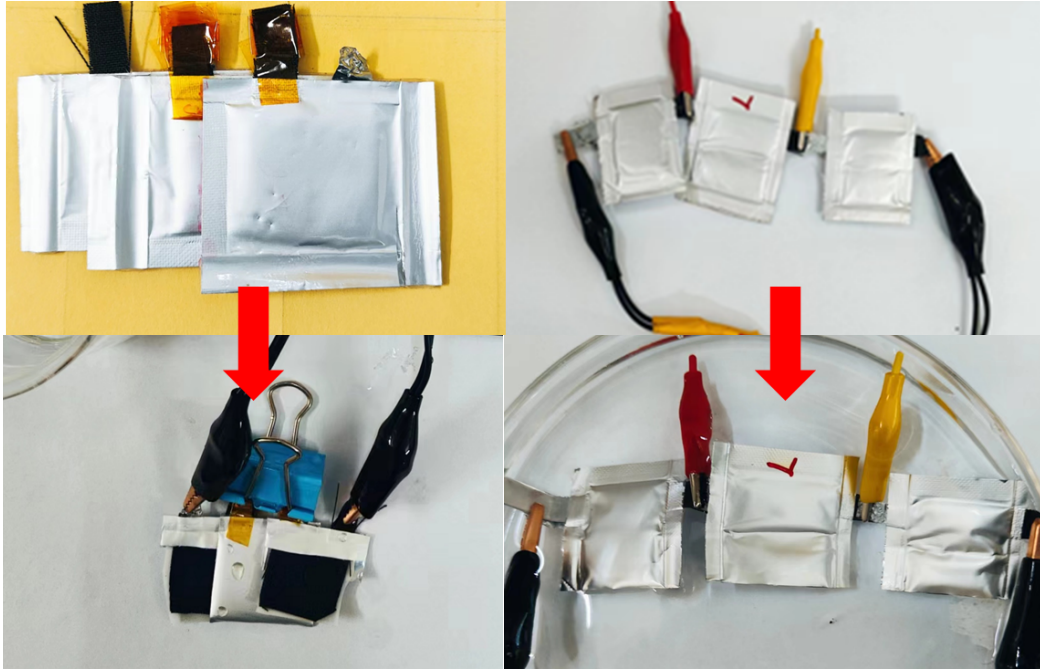**Fig. S10** Open-circuit voltage of ZIBs at different degrees of bending

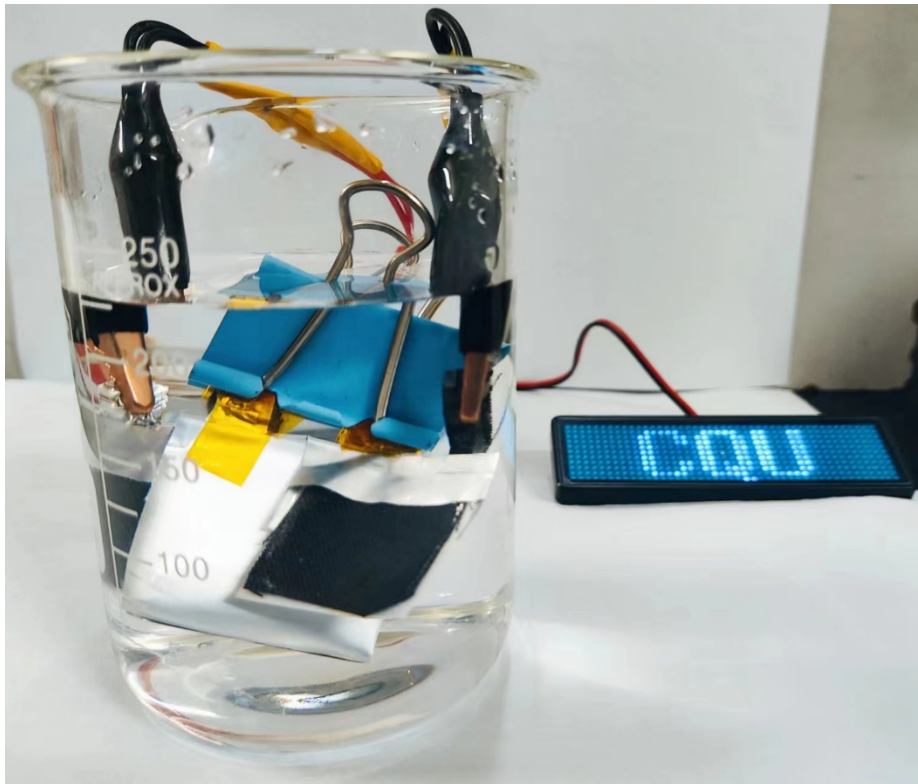**Fig. S11** ZIBs before and after breaking the sealing state

Fig. S12 ZIBs that have lost their sealing status power LED signs in the water

Table S1 The performance of recently reported gel polymer electrolytes in ZIBs.

Hydrogel polymer matrix	Ionic conductivity (mS/cm)	cycle life (h)	references
PVA/PEG-SiO$_2$	35.36	940	This work
PVA/PAM	14.63	\	3
PAM/Xanthan	16.8	400	4
CMC	34.5	500	5
PAM	24.6	500	6
IC-AAM	2.15	400	7
SA-GA	37	400	8
PVA	12.6	800	9
SiO$_2$-SA	11.44	500	10
PAM/HEMA	17.2	600	11
AM-SAS	29.2	1000	12

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