Supporting Information

Hydrogen-bonded zwitterionic hydrogel electrolyte constructs freeze-resistant and flame-retardant flexible zinc-ion capacitors

Min Li[1], Xiaoyan Li[1], Xin Wang, Zheng Wang, Quanyu Wen, Hui Peng, Yin Yuan*, Guofu Ma*

Key Laboratory of Eco-functional Polymer Materials of the Ministry of Education, Key Laboratory of Eco-environmental Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, School of Physical Education, Northwest Normal University, Lanzhou 730070, China.

*Corresponding authors: xbshdyy@163.com (Y. Yuan), magf@nwnu.edu.cn (G. Ma).

S1. Material characterization

Fourier transform infrared spectroscopy (FT-IR, Digilab Merlin FTS 3000) was used to evaluate the chemical structure of hydrogels in the range of 500-4000 cm^{-1}. The morphology of the hydrogels was observed by scanning electron microscopy (SEM, FE-SEM, Ultra Plus,) The crystal structure of the material was determined by X-ray diffraction (XRD, D/Max-2400, physics) equipped with Cu Ka radiation (k=1.5418 A).

S2. Assembly of Zn//Zn symmetrical cell

The Zn//Zn battery consists of a metallic zinc plate (20×15×2 mm) and PAM/CS/Pro hydrogel (20×15×2 mm). Among them, zinc plate is used node/cathode electrode and PAM/CS/Pro hydrogel is used as electrolyte.

S3. Preparation of electrodes and assembly of zinc ion capacitors

The electrochemical properties of GPEs were analyzed by assembling zinc ion capacitors with activated carbon as electrode materials. First, 80 wt% activated carbon (AC) (8 mg), 10 wt% acetylene black (1 mg) and 10 wt% binder polyvinylidene fluoride (PVDF) (8 mg) were mixed in 1-methyl-2-pyrrolidone (NMP) solvent and ground in an agate mortar for 10 minutes to prepare a uniform positive slurry. Then the slurry is evenly coated on the titanium foil, and the pole sheet is placed in the oven at 100℃ for 10 h to dry, the positive load is about 1 mg cm^{-2}. Finally, ZICs with direct AC as positive electrode, zinc foil as negative electrode and PAM/CS/Pro hydrogel as electrolyte were assembled into sandwich structure.

S4. Mechanical properties measurement

The hydrogel tensile test was carried out using AGS-X universal testing machine (AGS-X100 N Shimadzu, Japan), and the gel sample (20×15×2mm) was tested with a tensile rate of 20 mm min^{-1}. Compression tests of the hydrogel were performed on the AGS-X universal test machine. The lap shear test was measured the interfacial adhesion strength between hydrogel electrolytes/zinc plate. The effective lap area of the hydrogel electrolyte and the substrate is 50×30 mm. Furthermore, weight was

applied to make them fit better before the tests.

S5. Water retention test

The water retention capacity of the gel electrolyte is calculated by placing the hydrogel at room temperature and weighing the mass of the hydrogel at corresponding intervals. The calculation formula is as follows:

$W_{RC} = Wt / W0 \times 100\%$

W_t: the mass of the hydrogel after it is placed in the air for a period of time, W_0: the initial mass of the hydrogel.

S6. Flame retardant and thermal performance

The thermal insulation performance is tested by placing the hydrogel sample on a heating table at 100℃, and recording the temperature of the sample with infrared thermal imaging as the heating time changes. Thermal gravimetric analysis (TGA) was carried out under nitrogen atmosphere from 25 to 1000 ℃ at 10 ℃ min^{-1} by using Mettler TGA thermal analyzer. The value of limiting oxygen index (LOI) was determined by Fire Testing Technology 007. A cone calorimeter was used to characterize the combustion status of the sample. Under fully ventilated conditions, the sample size was 10 cm×10 cm×0.3 cm, and the sample mass was about 3 g. The test parameters include total heat release (THR) and heat release rate (HRR). The combustion experiment is to place the sample directly above the alcohol lamp and light it with the alcohol lamp to observe its combustion.

S7. Electrochemical properties measurement

The electrochemical performance of the assembled zinc-ion capacitor is tested by electrochemical workstation (CHI660D, Shanghai Chenhua, China). Cyclic voltammetry (CV) was performed at different scanning rates (1~10 mV s^{-1}) and constant current charge-discharge (GCD) tests were performed at different current densities (0.1~2 A g^{-1}).

The specific capacitance of zinc ion capacitor is calculated according to the following formul

$C_A = I \times \Delta t / \Delta V$

Δt is the discharge time (h), I is the current density (A g^{-1}) and ΔV voltage range (V)

The energy density (E_A, Wh kg^{-1}) and power density (P_A, W kg^{-1}) are calculated by the following formula:

$$E_A = C_A V2/2 \times 1000/3600$$

$$P_A = EA/\Delta t \times 3600$$

The electrochemical impedance spectroscopy (EIS) was conducted using an electrochemical workstation (CHI660D, Shanghai Chenhua, China) within the frequency range of 10^{-2} to 10000 Hz. The calculation formula is as follows:

$$\sigma = 1000\ L / (R \times S)$$

where L is the thickness of the gel electrolyte(cm), S is the area of the hydrogel electrolyte (3 cm^2), R denotes the measured resistance.

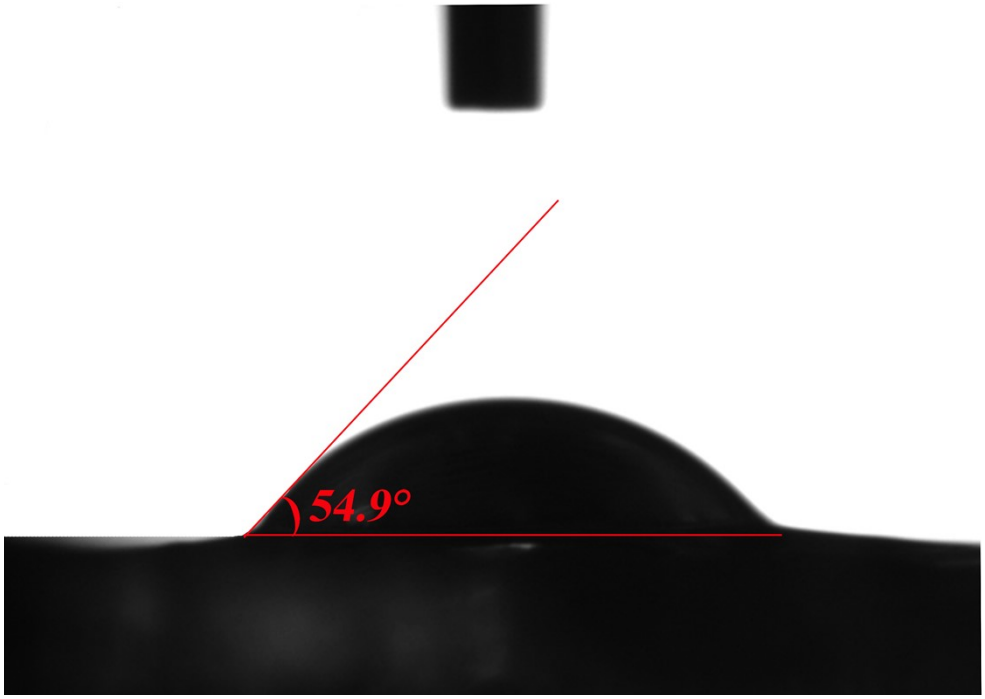

Fig. S1 Contact angle of PAM hydrogels.

Table S1. Comparison of flame retardant and antifreeze properties of polymer electrolytes with previous reports.

Electrolyte System	LOI Value (%)	Temperature Range (°C)	Ref.
PAM/CS/Pro	29.0	-20 to 80	This Work
SPHZL-4	—	−30 to 20	[S1]
D-CGE	—	-20 to 60	[S2]
SL-Zn	—	- 40 to 25	[S3]
DESG	38.0	20 to 90	[S4]
PFGPE	43.0	—	[S5]

[S1] T. Gao, N. Li, Y. Yang, J. Li, P. Ji, Y. Zhou and J. Xu, Journal of Energy Chemistry, 2024, 92, 63-73.

[S2] L. Shen, C. Hu, Z. Huang, J. Yang, Y. Jia, Y. Zhao, R. Berger, Q. Liu and Y. Zhou, Nano-Micro Letters, 2026, 18.

[S3] J. Bi, F. Zhang, X. Zhao, Z. Cai and H. Pan, Journal of Materials Chemistry A, 2025, 13, 17569-17577.

[S4] Q. Zeng, X. Lai, H. Li, Z. Chen, X. Zeng and L. Zhang, Advanced Functional Materials, 2024, 34, 2411029.

[S5] B. Yang, Y. Pan, T. Li, A. Hu, K. Li, B. Li, L. Yang and J. Long, Energy Storage Materials, 2024, 65, 103124.