

Supporting Information

A robust dual-network hydrogel electrolyte coupled with porous carbon material for flexible quasi-solid-state zinc ion hybrid supercapacitor

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1. Materials.

Agarose (AR), Zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$, 98%), acrylamide (AAm, AR), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (initiator, 98%) and Gelatin (AR), were purchased from Aladdin Industrial Corporation. Coal tar pitch (CTP) were purchased from Guangdong Zhuguang New Energy Technology Co., Ltd (Tianjin, China). Ltd. N, N'-methylenebisacrylamide (MBAA, AR) was supplied by Damao Chemical Reagent Factory (Tianjin, China). KCl were purchased from Tianjin Baishi Chemical Co., Ltd. KOH were purchased from Tianjin Beilian Fine Chemicals Development Co., Ltd.

2. Material characterization

The samples were analyzed using scanning electron microscopy (SEM, ZEISS Sigma 300), energy dispersive spectroscopy (EDS, JSM-7610 FPLUS), transmission electron microscopy (TEM, JEM-2100F), X-ray diffraction (XRD, Br ü ker D8 Advance), X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi), and fully

automated surface area and porosity analyzer (Microelectronics ASAP 2460). Fourier transform infrared spectroscopy (FTIR) measurements were conducted on the VERTEX 70 spectrometer in the range of 550-4000 cm^{-1} . The tensile and compression tests of the hydrogel electrolytes were carried out at room temperature on the ZQ-990LB machine. The tensile measurement of hydrogel electrolyte (with the sample size of $40.0 \times 10 \times 1.5 \text{ mm}^3$) was conducted at a stretching rate of 50 mm min^{-1} . The compression test was carried out on a cylindrical hydrogel electrolyte (10 mm in height and 12 mm in diameter) with a compression rate of 30 mm min^{-1} .

3 Preparation of G/PAAm/AG/Zn(CF₃SO₃)₂ hydrogel electrolyte

First, 0.1 g of agarose was added in 10 mL deionized water under heating and stirring at 90°C for 30 minutes to form a transparent solution. Next, 1 g of gelatin and 4 g of acrylamide, 0.13 g of 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylphenylacetone (initiator), and 2.7 mg of N, N'-methylenebisacrylamide (MBAA, crosslinking agent) were added to a beaker, and continue stirring to form a transparent solution. Transferred the transparent solution to a glass mold and cooling it down to room temperature. After the cooling process is completed, the mold was exposed to ultraviolet light for 1h to form the G/PAAm/AG hydrogel. Finally, the G/PAAm/AG hydrogel was immersed in 1 M Zn(CF₃SO₃)₂ aqueous solution for 12 h to form the G/PAAm/AG/Zn(CF₃SO₃)₂ hydrogel electrolyte. Additionally, for revealing the effect of the multiple polymeric network on the mechanical properties and ionic conductivity, PAAm/AG/Zn(CF₃SO₃)₂ (without the gelatin component), G/PAAm/Zn(CF₃SO₃)₂ (without the agarose component) and

G/AG/Zn(CF₃SO₃)₂ (without the PAAm component) were also prepared under the same procedure except that the corresponding polymer chain was not added.

4 Preparation of HSSPC

After 1 g of coal tar asphalt was poured into the crusher for crushing, 4.5 g of KCl and 6.5 g of KOH were mixed and crushed in the crusher. Then, 1 g coal tar asphalt was further poured into the crusher for further mixing and crushing. After crushing, the mixture was transferred to a tube furnace. After that, the crushed mixture was calcined at 800°C at a rate of 5°C min⁻¹ 2 hours under the N₂ atmosphere. Finally, the obtained black product was repeatedly washed with 1 M dilute hydrochloric acid solution to remove excess impurities. After drying, a porous carbon with high specific surface area was obtained, named as HSSPC.

5. Fabrication of aqueous and quasi-solid-state ZHSC cells.

The activated carbon material HSSPC (80wt%), acetylene black conductive agent (10wt%), and polytetrafluoroethylene adhesive (PTFE, 10wt%) was mixed in an appropriate amount of ethanol, and then mix them evenly using an ultrasound. Subsequently, it was dried in a constant temperature drying oven at 70°C for half an hour, and the resulting mixture powder was pressed into uniform circular flakes (with an active substance mass of approximately 2 mg cm⁻²). Using HSSPC as the positive electrode, Whatman GF/D (Glass Microfiber Filters) as the separator, 1 M Zn(CF₃SO₃)₂ as the liquid electrolyte, and zinc sheet (with a thickness of 0.1 mm) as the negative electrode, aqueous ZHSC was assembled using a button cell (CR2032 type). quasi-solid-state ZHSC was assembled with HSSPC as positive electrode,

G/PAAm/AG/Zn(CF₃SO₃)₂ hydrogel electrolyte as separator and electrolyte, zinc sheet as negative electrode and graphite paper as collector.

6. Electrochemical Characterizations.

This experiment used cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to test the electrochemical performance of aqueous Zn//HPCs ZHSC and the quasi-solid-state ZHSC on an electrochemical workstation (CHI 660E). Test the magnification, constant current charge discharge curve, self-discharge, and long cycle performance of the above two devices on a the Lanhe Battery Testing System (M340A). The specific capacity (C , mAh g⁻¹) and energy density (E , Wh kg⁻¹) were directly obtained from the M340A testing system. The ionic conductivity of G/PAAm/AG/Zn(CF₃SO₃)₂ hydrogel electrolyte is tested by using the alternating impedance spectroscopy (EIS). According to the EIS results, the ionic conductivity of G/PAAm/AG/Zn(CF₃SO₃)₂ can be calculated by the following formula:¹

$$\sigma = \frac{L}{AR} \quad (S1)$$

Where, L is the thickness of the hydrogel electrolyte (m), R is the ohmic resistance (Ω), A is the test area (m²), σ Is the ionic conductivity (S m⁻¹). The mass specific capacity (C_m , mAh g⁻¹) can be directly read on the Blue Electric testing system. The area capacity (C_a , mAh cm⁻²) is calculated by the following formula:²

$$C_a = \frac{mC_m}{S} \quad (S2)$$

Among them, C_m is the mass specific capacity, m (g) is the mass, and S (cm⁻²) is the electrode area. The S value used in this study is 0.785 cm⁻². The energy density (E ,

Wh kg^{-1}) can also be directly read on the Blue Electric testing system. In addition, the power density (P , W kg^{-1}) is calculated by the following formula:³

$$P = \frac{3600E}{t} \quad (\text{S3})$$

In the formula, E (Wh kg^{-1}) and t (s) represent energy density and discharge time, respectively.

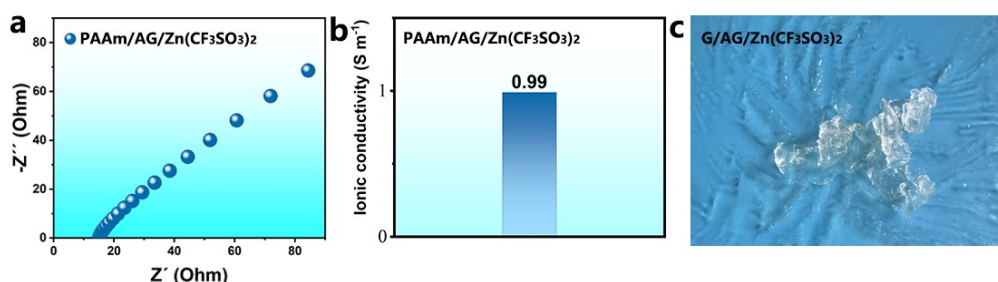


Fig. S1 (a) EIS testing and (b) the corresponding ionic conductivity of PAAm/AG/Zn(CF₃SO₃)₂.

(c) The optical photograph of G/AG/Zn(CF₃SO₃)₂.

As shown in Fig. S1c, G/AG/Zn(CF₃SO₃)₂ without the PAAm component exhibits poor mechanical strength and even is unable to maintain a fixed shape. While PAAm/AG/Zn(CF₃SO₃)₂ (without the gelatin component) and G/PAAm/Zn(CF₃SO₃)₂ (without the agarose component) exhibit inferior mechanical strength and ionic conductivity compared with the G/PAAm/AG/Zn(CF₃SO₃)₂ hydrogel electrolyte (Fig. 1e, Fig. 1j, and Fig. S1a-b). The tested results clearly show the advantage in constructing of the multiple crosslinked networks of the hydrogel electrolyte for enhancing the mechanical properties, ion transport behavior, and electrochemical properties.

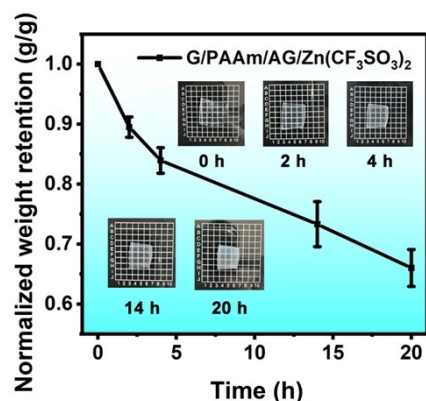


Fig. S2 Normalized weight retention ($W/W_0 = \text{current weight}/\text{initial weight}$) of G/PAAm/AG/Zn(CF₃SO₃)₂ after storage at 25°C, 25.0% RH for 20 h.

The water-retaining capacity of the G/PAAm/AG/Zn(CF₃SO₃)₂ hydrogel electrolyte was revealing by a weighting method. As shown in Fig. S2, the G/PAAm/AG/Zn(CF₃SO₃)₂ hydrogel electrolyte retained 65.1% of their initial weights after exposure for 20 h at 25°C within an extremely low 25.0% relative humidity (RH). Additionally, as shown in the inset of Fig. S2, the shape of the initial hydrogel electrolyte was well maintained under this condition, demonstrating its satisfactory chemical stability.

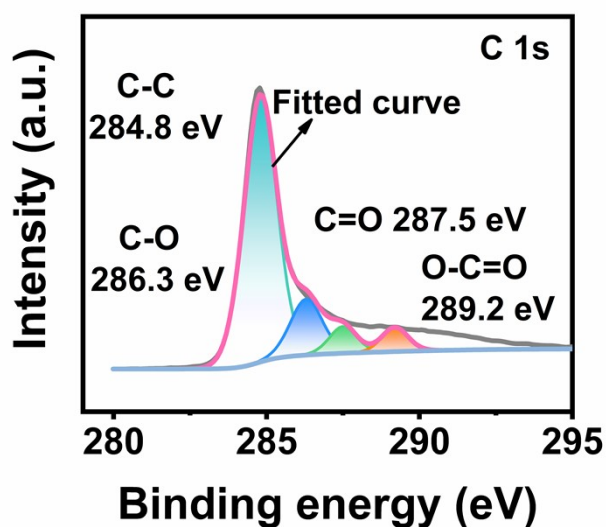


Fig. S3 XPS spectra of the C 1s region.

The high-resolution C 1s spectrum exhibits four distinct characteristic peaks (Fig. 2-7e), namely the C-C bond at 284.8 eV, the C=O bond at 286.3 eV, the C-O bond at 287.5 eV, and the adsorbed O-C=O bond at 289.2 eV.⁴

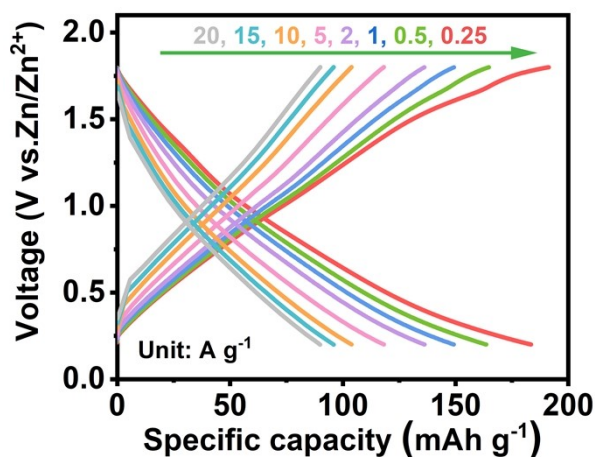


Fig. S4 GCD curves of the aqueous ZHSC.

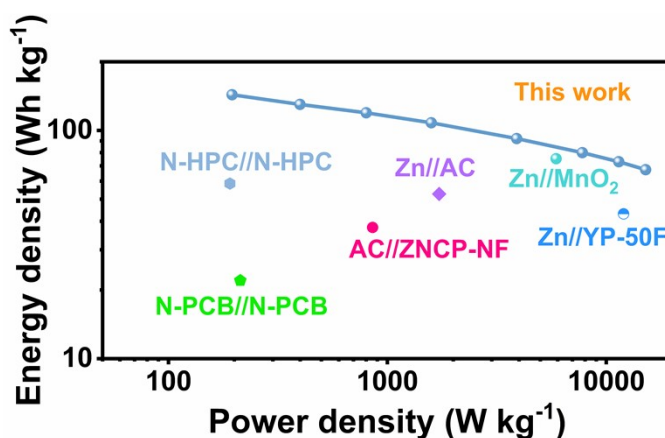


Fig. S5 Comparison of energy/power densities between Zn//Zn(CF₃SO₃)₂//HSSPC ZHSC and other reported devices.

The energy/power density graph in Fig. S5 reveals that the energy density of ZHSC can reach a maximum of 143.4 Wh kg⁻¹ (power density of 195.3 W kg⁻¹), and the power density can reach a maximum of 15.1 kW kg⁻¹ (energy density of 67.3 Wh kg⁻¹). Higher than previously reported quasi-solid-state devices, such as AC//ZNCP-NF (37.59 Wh kg⁻¹, 856.52 W kg⁻¹),⁵ Zn//AC (52.7 Wh kg⁻¹, 1725 W kg⁻¹),⁶ Zn//YP-50F (43.1 Wh kg⁻¹, 12.0 kW kg⁻¹),⁷ Zn//MnO₂ (75.2 Wh kg⁻¹, 5910.0 W kg⁻¹),⁸ N-PCB//N-PCB (22 Wh kg⁻¹, 213 kW kg⁻¹),⁹ Zn//N-HPC (191 W kg⁻¹, 58.5 Wh kg⁻¹).¹⁰

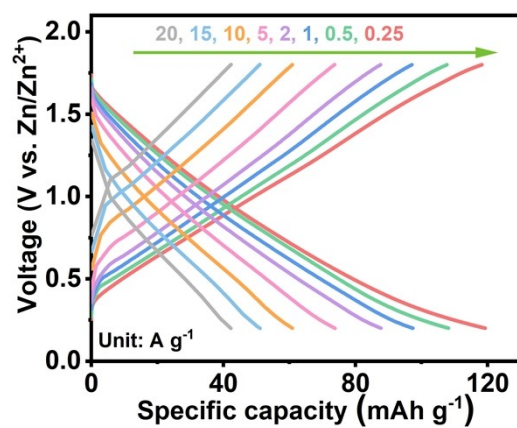


Fig. S6 GCD curves of the quasi-solid-state ZHSC.

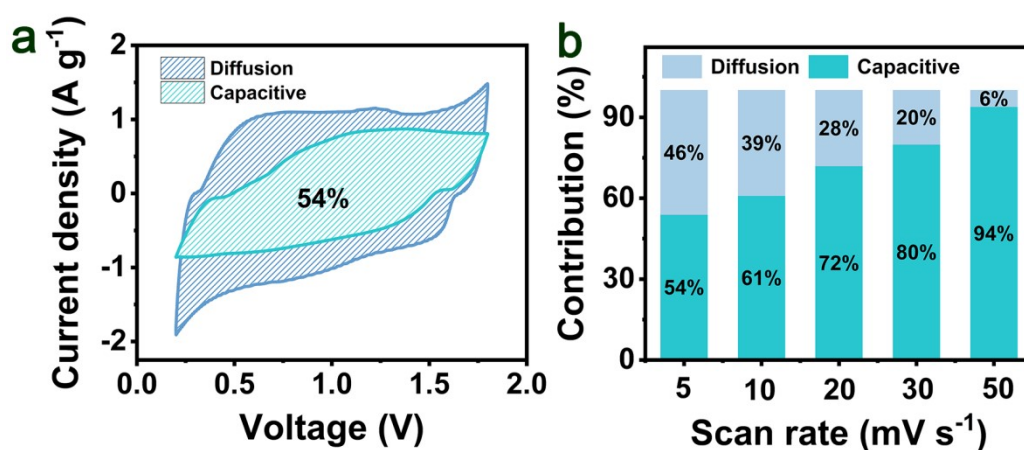


Fig. S7 (a) The capacitive contribution and diffusion contribution of the quasi-solid-state ZHSC at 5 mV s⁻¹. (b) Capacitive contribution and diffusion contribution at different scanning rates.

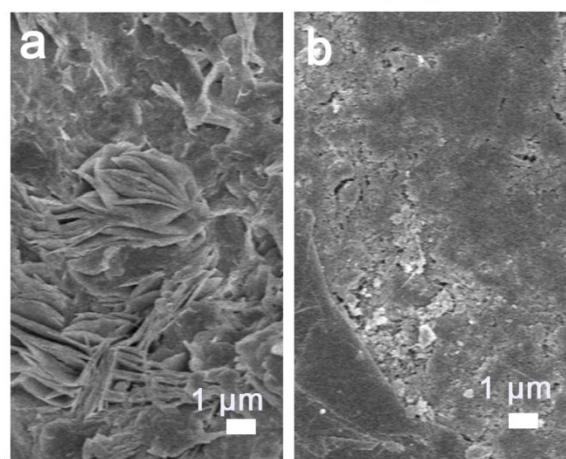


Fig. S8 SEM images of the Zn electrode after cycling from the (a) Zn//Zn(CF₃SO₃)₂//Zn battery and (b) Zn//G/PAAm/AG/Zn(CF₃SO₃)₂//Zn battery.

Table S1. Comparison of the ionic conductivity with recently reported hydrogel electrolytes.

Electrolytes	Ionic conductivity (S m ⁻¹ /mS cm ⁻¹)	Ref.

κ -CG/PAAm/Zn(CF ₃ SO ₃) ₂	2.3 S m ⁻¹	11
P(AMPS _{0.3} -co-AAM _{0.4})	0.82 S m ⁻¹ (-20°C) 1.12 S m ⁻¹ (100°C)	12
PAAm/agar/Zn(CF ₃ SO ₃) ₂	1.55 S m ⁻¹	13
PVA/glycerol/CaCl ₂	1 S m ⁻¹	14
P(AM-co-DMAEMA)-AMP/gelatin	~1.35 S m ⁻¹ (25°C) 0.43 S m ⁻¹ (-40°C)	15
AFHE	5.88 mS cm ⁻¹ (20°C)	16
cross-linked lignin hydrogel	10.35 mS cm ⁻¹ (25°C)	17
PAM-co-PAA/ k-CG/ZnSO ₄	1.76 S m ⁻¹	18
HPAAN/PDA	0.32 S m ⁻¹	19
G/PAAm/AG/Zn(CF ₃ SO ₃) ₂	2.64 S m ⁻¹	This work

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