Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

A flexible and stable zinc-ion hybrid capacitor with polysaccharide-reinforced cross-linked hydrogel electrolyte and binder-free carbon cathode

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1. Experimental section

1.1 Materials

Xanthan gum (XG), acrylamide (AM), zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$), and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone were purchased from Aladdin Industrial Corporation. Carboxymethyl cellulose (CMC, viscosity: 3500~5000) was purchased from Hefei Kejing Material Technology Co., Ltd., Ltd. *N*,*N*-methylenebisacrylamide (MBAA) was bought from Baishi Chemical Co., Ltd. The polyacrylonitrile (PAN, M_W = 150 000) was purchased from J&K Scientific Co., Ltd. *N*,*N*-dimethylformamide (DMF) and potassium hydroxide (KOH) were obtained from Beilian Chemical Co., Ltd. All chemical reagents were of analytical grade and obtained commercially.

1.2 Synthesis of PAM/CMC/XG/$Zn(CF_3SO_3)_2$ hydrogel electrolyte

Firstly, 2 g AM and 100 mg XG powder were dissolved in 20 mL aqueous solution containing 0.2 g CMC and stirred for 1 h at room temperature. Then, 30 mg 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (as the initiator) and 3 mg MBAA (as the crosslinker) were added successively. Afterward, the solution was stirred vigorously until its was completely homogeneous, and sonicated for 30 min to remove bubbles. Next, the mixture was subjected to a UV lamp (wavelength of 365 nm and intensity of 8 W) for 1 h to form the PAM/CMC/XG hydrogel. Finally, the as-synthesized hydrogel was soaked in 1 M $Zn(CF_3SO_3)_2$ aqueous solution for 12 h to obtain PAM/CMC/XG/$Zn(CF_3SO_3)_2$ hydrogel electrolyte. Similarly, PAM/CMC/$Zn(CF_3SO_3)_2$ and PAM/$Zn(CF_3SO_3)_2$ hydrogel electrolytes were also synthesized.

1.3 Synthesis of GCNF

Graphene quantum dots (GQDs) and GCNF were prepared according to the previous work.[1-3] For the preparation of GCNF, 0.4 g PAN was thoroughly dissolved in 5 mL GQD-containing DMF to obtain a homogeneous viscous suspension (0.4 g GQDs). Then, the above mixture was electrospun into the fabric and then pre-oxidized at 280 °C in air for 2 h with a heating rate of 1 °C min^{-1} to obtain PO-NF. Afterward, PO-NF was carbonized at 500 °C for 1 h in N_2 atmosphere with a heating rate of 2 °C min^{-1}. Finally, the carbonized sample treated with the KOH solutiom (the mass ratio of the carbonized sample to KOH was 1:2) was placed at 800 °C for 1 h in N_2 atmosphere with a heating rate of 5 °C min^{-1}. The activated sample was immersed and washed by 1 M HCl aqueous solution and deionized water successively to obtain GCNF.

1.4 Materials characterization

The samples were analyzed by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, F200X), high-resolution TEM (HRTEM, JEM-2100F) equipped with the selected area electron diffractometer (SAED, FEI Tecnai G2 F30), X-ray diffraction (XRD, Brüker D8 Advance), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi and Thermo Scientific K-Alpha), and Raman spectroscopy (Brüker SENTERRA). The tensile test of hydrogel electrolytes ($40 \times 10 \times 2$ mm^3) was tested by a universal testing machine (ZQ-990LB) at an extension rate of 100 mm min^{-1}. A piece of the PAM/CMC/XG/Zn(CF_3SO_3)$_2$ hydrogel electrolyte (25×20×2 mm^3) was sandwiched between two substrates that were fixed to a glass slide using double-side adhesive tape for the shear adhesive test with a rate of 10 mm min^{-1}. The specific surface area and pore size distribution of GCNF were measured by a volumetric adsorption apparatus (ASAP 2020, Micromeritics). The ionic conductivity (σ, S m^{-1}) of the hydrogel electrolyte was derived from the electrochemical impedance spectroscopy (EIS) according to the equation:

$$\sigma = l/AR \tag{S1}$$

where l, R, and A are the thickness (m), resistance (Ω), and test area (m^2) of the hydrogel electrolyte, respectively.

1.5 Assembly of aqueous and quasi-solid-state ZHCs

The GCNF cathode was cut into a discs (diameter: 1.2 cm). The coin-type aqueous Zn//GCNF ZHC was assembled by the GCNF cathode, Zn foil (thickness: 80 μm) anode, and a glass microfiber filter separator (Whatman GF/D) in 1 M Zn(CF_3SO_3)$_2$ aqueous electrolyte, whereas the quasi-solid-state device was fabricated by using the PAM/CMC/XG/Zn(CF_3SO_3)$_2$ as the hydrogel electrolyte and separator. To prevent the hydrogel electrolyte from losing moisture, the quasi-solid-state device was further encapsulated with polyimide tape.

1.6 Electrochemical characterization

The corrosion and hydrogen evolution were investigated by linear polarization and linear sweep voltammetry (LSV) measurements on three-electrode systems. The three-electrode system for linear polarization test included a saturated calomel electrode (SCE) (as the reference electrode) and Zn foils (as the working electrode and counter electrode). And the three-electrode system for LSV consisted of Pt plate working electrode, Zn counter electrode, and Ag/AgCl reference electrode. The cycling performance of Zn//Zn and Zn//Cu cells was measured on a M340A battery tester.

Galvanosatic charge-discharge (GCD) and cycle stability of aqueous and quasi-solid-state ZHCs were evaluated on a M340A battery tester. Cyclic voltammetry (CV) of aqueous ZHCs was measured on a CHI660D electrochemical instrument between 0.2 and 1.8 V at diffident scan rates from 1 to 50 mV s^{-1}. The EIS measurement was carried out in a frequency range of 10^5 to 10^{-2} Hz. The specific capacity (mA h g^{-1}) was read directly from the M340A battery tester. The power density (P, W kg^{-1}) based on the mass of the cathode was calculated from the following equation:

$$P = \frac{3600E}{t} \tag{S2}$$

where E (W h kg^{-1}) refers to the energy density from the tester and t (s) is the discharging time.

2. Supplementary figures

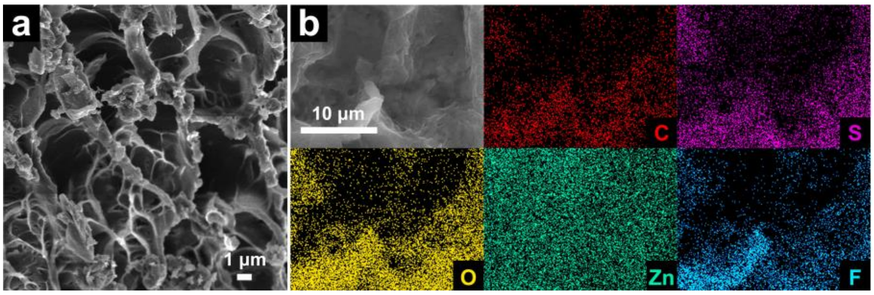

Fig. S1 (a) SEM image and (b) corresponding elemental mappings of the freeze-dried PAM/CMC/XG/Zn(CF_3SO_3)$_2$ hydrogel electrolyte.

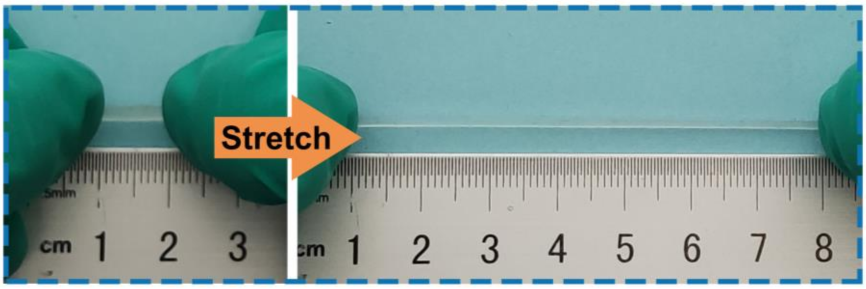

Fig. S2 Optical images demonstrating the stretching ability of the PAM/CMC/XG/$Zn(CF_3SO_3)_2$ hydrogel electrolyte.

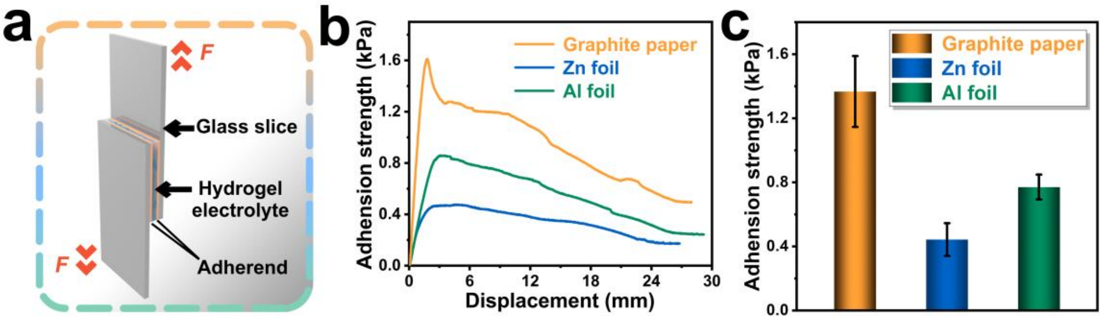

Fig. S3 (a) Diagram of shear adhesion measurement. (b) Lap shear curves and (c) shear adhesion strengths of the PAM/CMC/XG hydrogel electrolyte on various substrates.

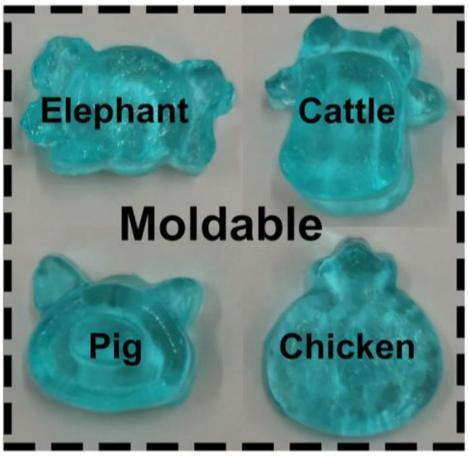

Fig. S4 Moldability of the PAM/CMC/XG/$Zn(CF_3SO_3)_2$ hydrogel electrolyte.

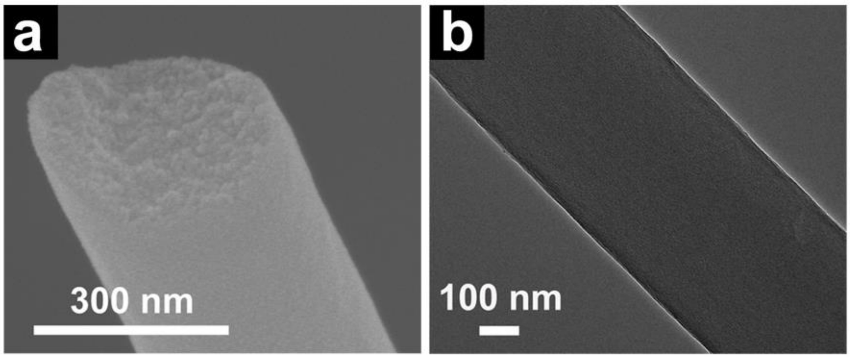

Fig. S5 (a) SEM and (b) TEM images of GCNF.

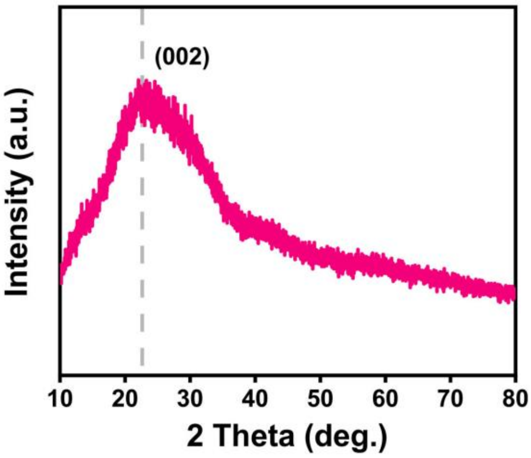

Fig. S6 XRD pattern of GCNF.

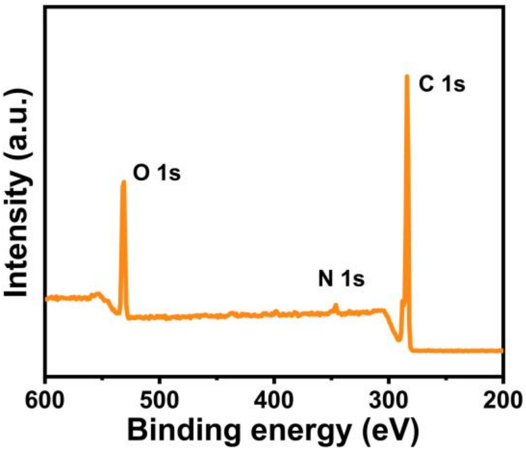

Fig. S7 The wide-scan XPS spectrum of GCNF.

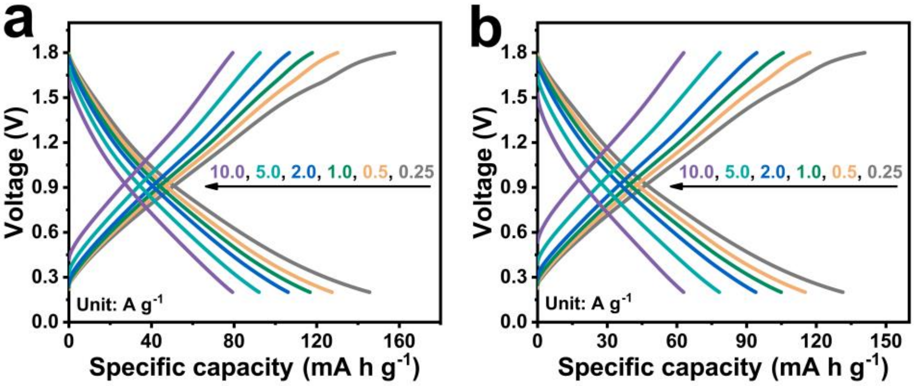

Fig. S8 GCD profiles of the aqueous Zn//GCNF ZHC with cathode loading of (a) 5.8 and (b) 8.8 mg cm^{-2} at various current densities.

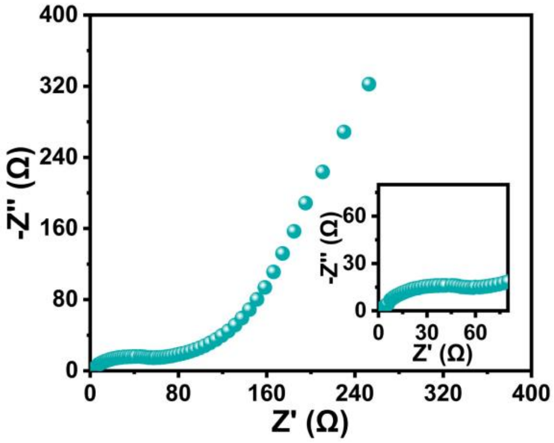

Fig. S9 Nyquist plot of the aqueous Zn//GCNF ZHC.

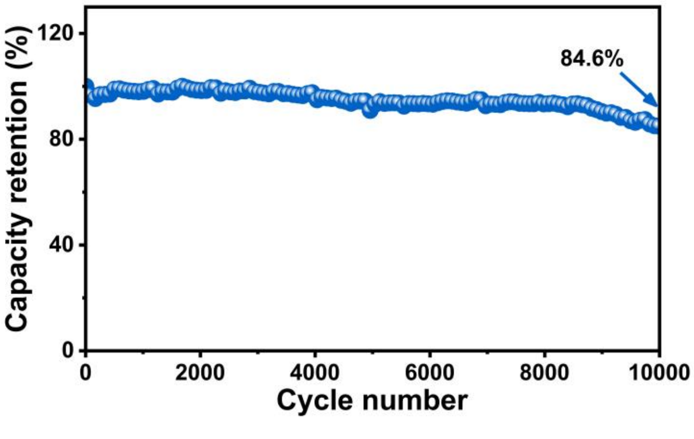

Fig. S10 Cycling stability the aqueous Zn//GCNF ZHC at 10 A g^{-1}.

References

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