

Supporting Information

Polyaniline surface-modified Prussian blue analogue cathode for flexible aqueous Zn-ion battery

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Experimental Section

Preparation of ZnHCF/PANI:

The precipitation was obtained by mixing 0.05 M potassium ferricyanide ($K_3Fe(CN)_6$) aqueous solution and 0.1 M zinc sulfate ($ZnSO_4$) aqueous solution at 60 °C. ZnHCF powder was obtained after centrifugation and drying. Then, ZnHCF electrode was obtained by applying the prepared ZnHCF slurry to carbon cloth using the conventional coating method. The ZnHCF electrode was immersed in a 1 M HCl solution which contained aniline monomer at 0 °C. After soaking for 1 h, 1 M HCl solution containing ammonium persulfate was used for the polymerization reaction. After continuing the reaction for 1 h, the electrode was obtained after washing and drying. By measuring the mass of the electrode during the process, the loading of ZnHCF is about 1 mg cm⁻² and the loading of PANI is about 1.5 mg cm⁻². It is known that the density of ZnHCF is 1.85 g cm⁻³ and the density of PANI is 1.36 g cm⁻³, and it can be deduced that the thickness of ZnHCF is 5.4 μm and the thickness of PANI is 11 μm.

Preparation of PAM hydrogel electrolyte:

A mixed solution with 7.5 M $ZnCl_2$ and 4 M NaCl was prepared, in which acrylamide monomer and ammonium persulfate initiator were successively added. After the solution was completely dissolved, the PAM hydrogel electrolyte was finally obtained by polymerization at 60 °C for 40 min.

Materials characterization:

The structural information of the as-prepared electrode materials was collected by X-ray diffraction (XRD, Bruker D2 Phaser diffractometer with Cu K α irradiation ($\lambda = 1.54 \text{ \AA}$)) and Raman (Renishaw Invia Reflex system (UK), with an excitation wavelength of 514 nm). The morphology of powder active samples and deposited zinc was characterized by field scanning electron microscope (FE-SEM, FEI/Philips XL30). The polymer structure analysis was employed by Fourier transform infrared spectroscopy.

Electrochemical measurement:

For electrochemical testing, electrochemical impedance spectroscopy (10 kHz to

0.01 Hz), cyclic voltammetry, and galvanostatic charge/discharge measurements in gradient current density were obtained via an electrochemical workstation (CHI 760e). The electrochemical cycling test was carried out by battery testing system (LANHE, CT2001A).

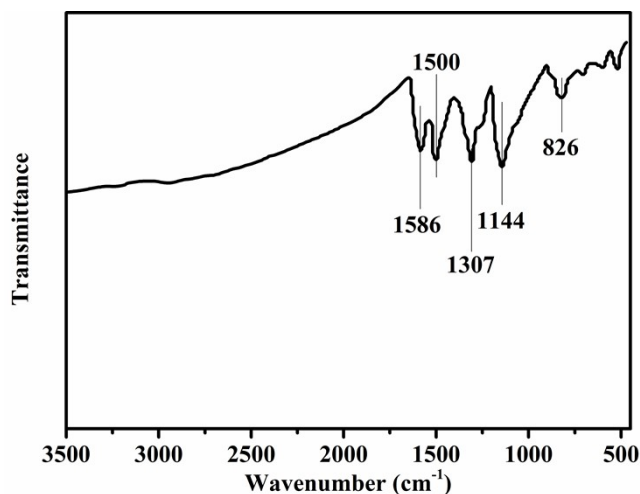


Figure S1. FTIR spectroscopy of ZnHCF/PANI.

The characteristic peaks at approximately 1586 cm⁻¹, 1500 cm⁻¹ and 1307 cm⁻¹ corresponded to the C=C stretching in the quinoid ring, the C=C stretching vibration mode for benzenoid rings and C-N absorption in the secondary aromatic amine. The peaks of 1144 cm⁻¹ and 826 cm⁻¹ are the in-plane and out-of-plane vibrational characteristic absorption bands of benzene ring, respectively.

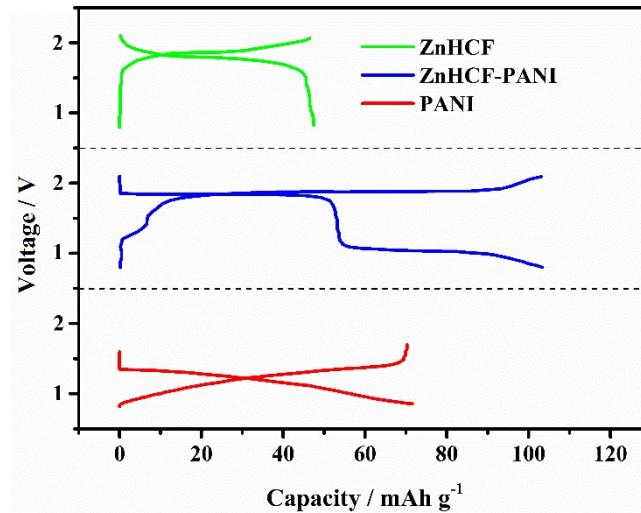


Figure S2. Comparison of GCD curves of ZnHCF, ZnHCF/PANI and PANI at 0.2 A g⁻¹.

ZnHCF and PANI have different discharge plateaus, ZnHCF is 1.8 V and that of PANI is about 1 V. The discharge curves of ZnHCF/PANI maintain two discharge plateaus, and the discharge voltage plateau of ZnHCF remains stable without decay during the discharge process. This indicates that ZnHCF is involved in the electrode reaction.

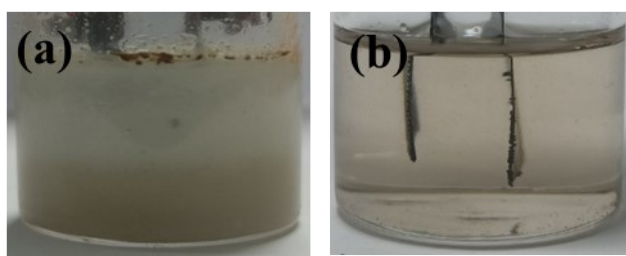


Figure S3. Picture of solution after cycle. (a) ZnHCF after 100 cycles of charge and discharge; (b) ZnHCF/PANI after 300 cycles of charge and discharge.

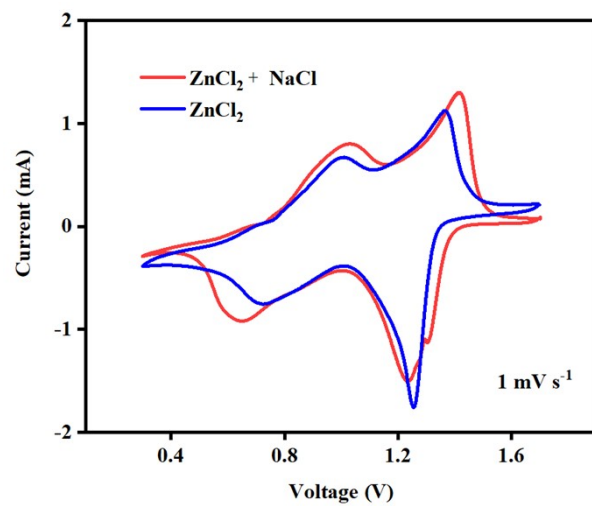


Figure S4. Cyclic voltammetry curves of PANI in different electrolytes.

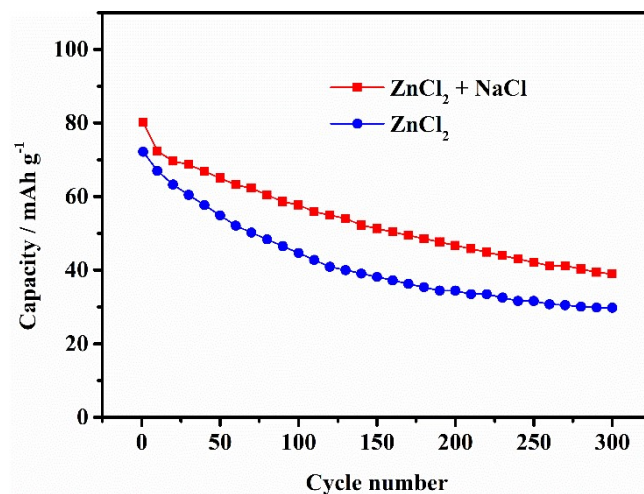


Figure S5. Cycling ability of PANI in different electrolytes.

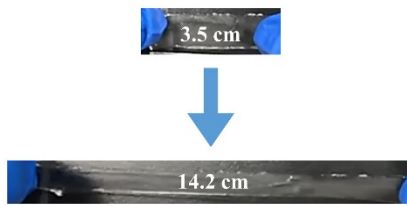


Figure S6. Images of pristine and stretched PAM hydrogel electrolyte.

The PAM hydrogel electrolyte has so excellent mechanical property that can be easily stretched by hand.

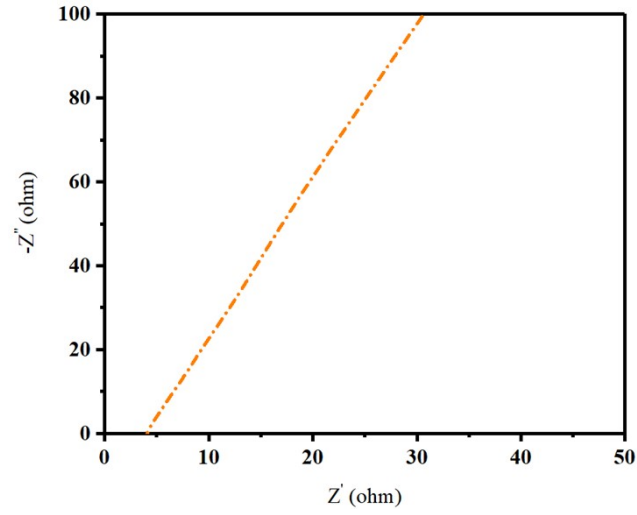


Figure S7. Electrochemical impedance spectroscopy (EIS) of PAM hydrogel electrolyte.

The ionic conductivity is calculated to be $6.1 \times 10^{-3} \text{ S cm}^{-1}$ according to the EIS plot.

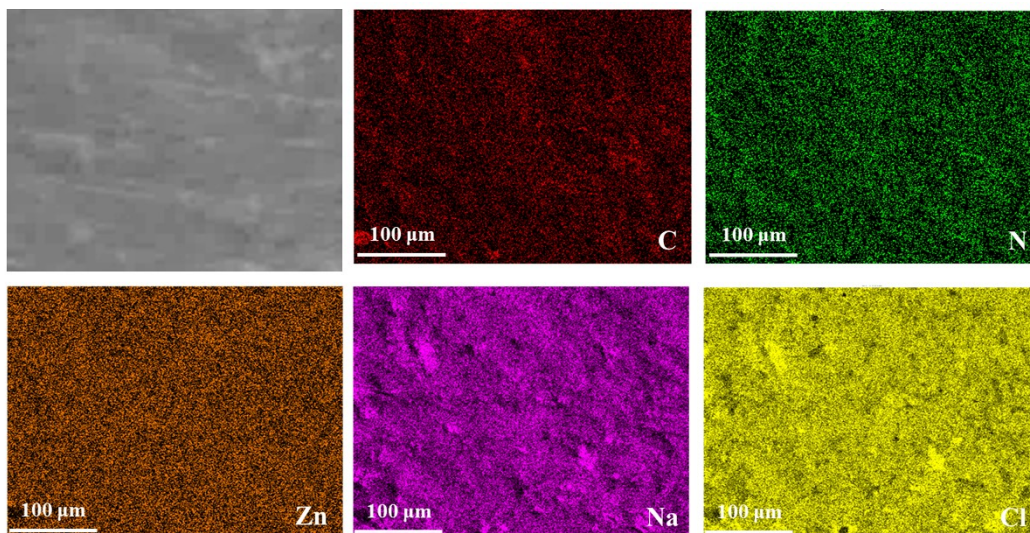


Figure S8. Elemental mapping of C, N, Zn, Na and Cl in PAM hydrogel electrolyte.

The presence of Zn, Na and Cl elements in mapping illustrates that ZnCl_2 and NaCl added in the synthesis process exist uniformly in the hydrogel, which provides a basis as an electrolyte.

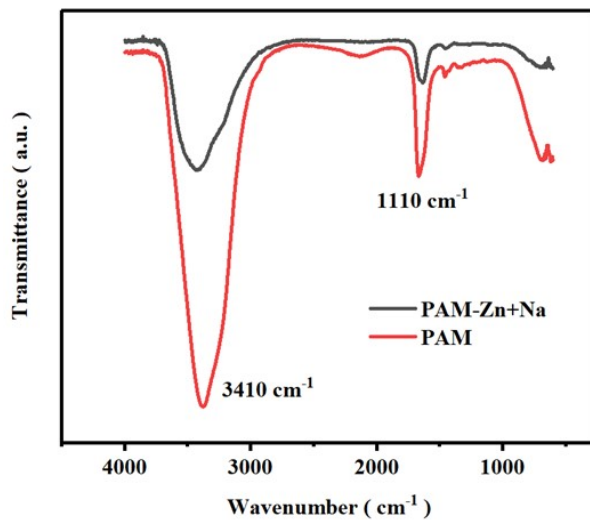


Figure S9. Infrared spectra of PAM hydrogel electrolyte and bare PAM hydrogel.

To further explore whether the addition of NaCl and ZnCl₂ would cause changes in the structure of PAM gel, the gel is tested by infrared spectroscopy (Figure S6). The peaks do not shift, indicating that the introduction of ZnCl₂ and NaCl would not cause a change in PAM structure.