Electronic Supplementary Information

Robust Fluorine-Rich YF_3 Artificial Interfacial Layer for Providing Uniform Zn^{2+} Flux and Enhancing Cycling Stability of Zn Anodes

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Experimental Section

Material characterization. The microstructure and elemental distribution of the samples were analyzed by scanning electron microscopy (SEM, Merlin compact, Zeiss, Germany) and energy dispersive spectrometer (EDS). The phase and structure of the samples were characterized by X-ray diffraction (XRD, Rigaku Ultima IV) in the Cu Kα wavelength range of 10° to 90° with a scanning rate of 10° min^{-1}. The surface chemical composition of the electrode was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The contact angle between the Zn sheet and YF_3@Zn was measured by a contact angle meter (OCA200, Beijing Data Instrument Co., Ltd.), with the contact angle ranging from 0° to 180°.The specific surface area and pore distribution were calculated by Barrett-Joyner-Halenda (BJH) method.

Assembly processes of electrochemical devices. The assembly process of the Zn//Zn symmetric cell: First, the commercial Zn foil with a thickness of 200 um is ultrasonically cleaned with ethanol and deionized water, followed by drying in a nitrogen atmosphere to obtain the treated Zn electrode. Two pieces of treated Zn electrode with a diameter of 8 mm are selected as electrodes, with Whatman GF/C glass fiber paper serving as the separator and a 2 M $ZnSO_4$ aqueous solution as the electrolyte to assemble a CR2032-type Zn//Zn symmetric coin cell.

The assembly process of the Zn//Cu half-cell: A Cu sheet with a diameter of 8 mm is employed as the working electrode, while a Zn electrode with a diameter of 8 mm is selected as a counter electrode. Whatman GF/C glass fiber paper is used as the separator, and a 2 M $ZnSO_4$ aqueous solution serves as the electrolyte to assemble a CR2032-type Zn//Cu half-cell coin cell.

The preparation process of the activated carbon (AC) electrode: The electrode slurry is prepared by mixing AC powder with polytetrafluoroethylene (PTFE) in a mass ratio of 8:2. This slurry is then coated onto a titanium (Ti) foil current collector. After drying at 60 oC overnight, the dried Ti foil coated with AC is cut into AC electrode sheets with a diameter of 8 mm.

The assembly process for Zn//AC zinc-ion capacitors: The AC electrode is utilized as the cathode, while the treated Zn electrode is selected as an anode. Whatman GF/C glass fiber paper is used as the separator, and a 2 M $ZnSO_4$ aqueous solution serves as the electrolyte to assemble a CR2032-type Zn//AC coin zinc ion capacitor.

Electrochemical Measurements. Zn//Zn symmetrical cells, Zn//Ti half cells and Zn//AC zinc-ion capacitors were assembled using CR2023 coin batteries and tested on a LAND battery testing system (CT2001A model battery tester from Wuhan Lantian Electronics Co., Ltd.). At room temperature, 2 M $ZnSO_4$ solution was used as the electrolyte. The cycling stability of the zinc anode was tested at current densities of 5 mA cm^{-2} and 2 mA cm^{-2} using Zn//Zn (YF_3@Zn// YF_3@Zn) cells. AC impedance spectroscopy (EIS), cyclic voltammetry (CV), and chronopotentiometry (C) tests were conducted on a CHI600E electrochemical workstation. Zinc sheets and platinum electrodes were used as the working and counter electrodes, respectively, with an Ag/AgCl electrode as the reference electrode for linear polarization curve and linear sweep voltammetry (LSV) measurements. LSV tests were carried out at a scan rate of 2 mV s^{-1} and a scan range of -1.4 to -2.0 V to evaluate the hydrogen evolution reaction of different electrode sheets. Linear polarization curves were measured at a scan rate of 1 mV s-1 between -0.2 and -1.2 V (versus Ag/AgCl electrode). Zn//AC zinc-ion capacitors were assembled using AC as the positive electrode and pure zinc or SYF_3-Zn as the negative electrode with $ZnSO_4$ electrolyte. The positive electrode slurry was prepared by mixing activated carbon powder and polyvinylidene fluoride (PVDF) at a mass ratio of 8:2 in N-methyl-2-pyrrolidone (NMP) solution. The slurry was then coated onto titanium foil and dried in a vacuum oven at 70°C for 12 hours to obtain an AC cathode (Φ = 8 mm) with a surface loading of approximately 1-2 mg cm^{-2}. All zinc foils used in the experiments had a thickness of 0.1 mm and a diameter of 8 mm.

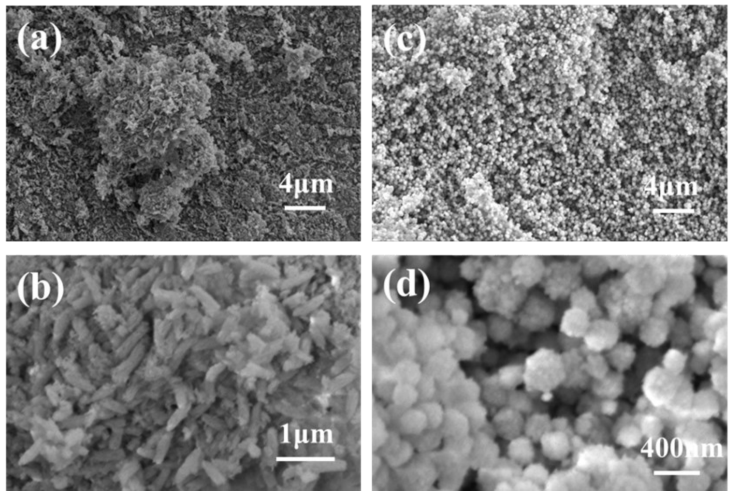

Fig. S1. (a-b) SEM images of CYF_3 at different magnifications and (c-d) SEM images of SYF_3 at different magnifications

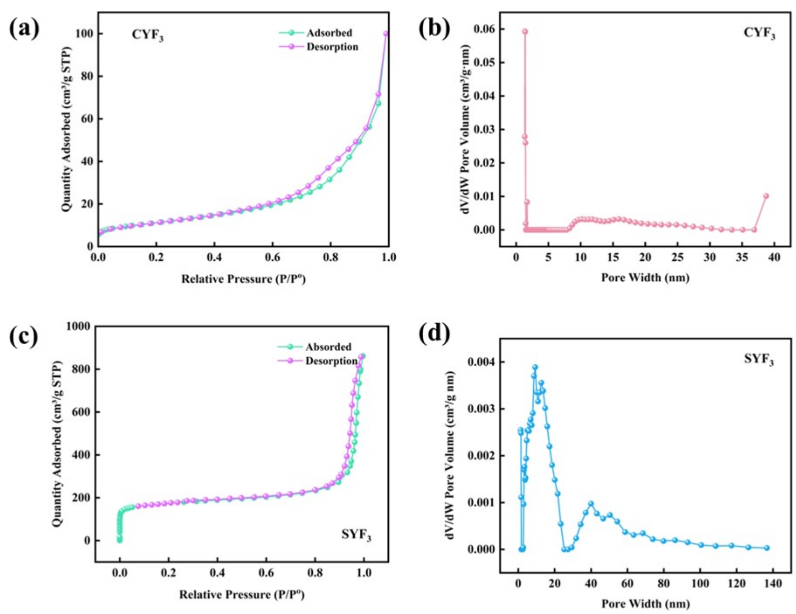

Fig. S2. The adsorption-desorption isotherm of CYF_3 (a)and SYF_3(c), pore distribution curves of CYF_3(b) and SYF_3(d)

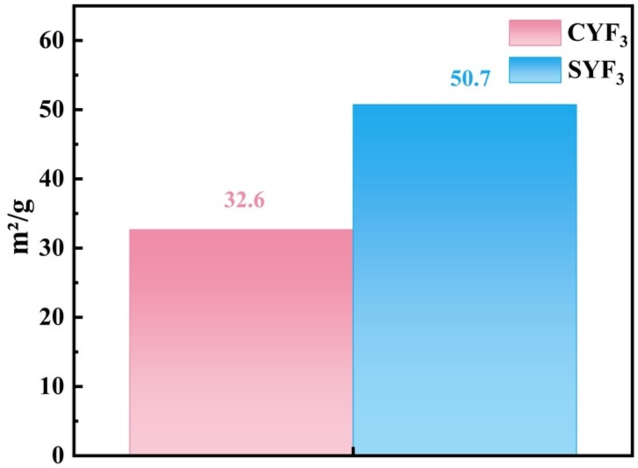

Fig. S3. Comparison chart of corresponding specific surface areas of CYF_3 and SYF_3

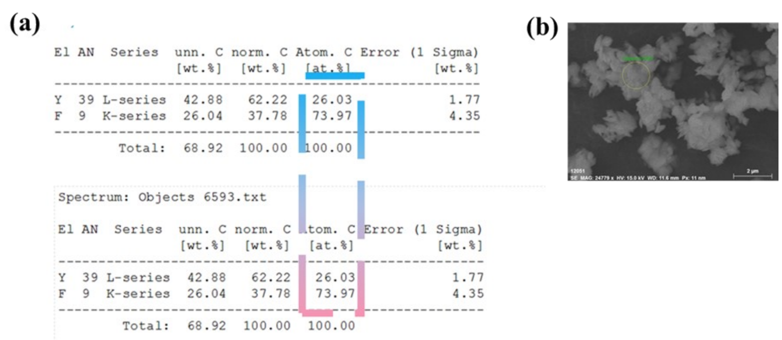

Fig. S4. The molar ration of Y:F (a) in CYF_3 measured by energy dispersive spectrometer within the selected area (b)

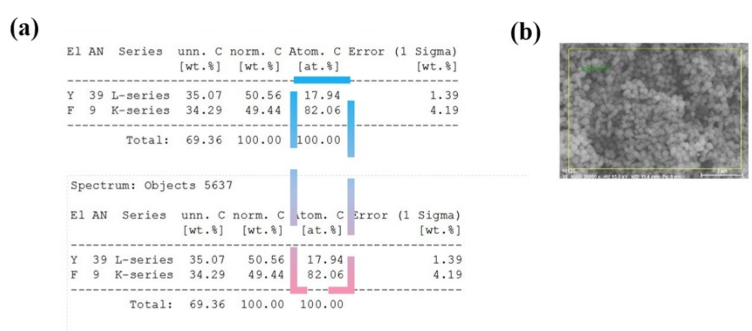

Fig. S5. (a) The molar ration of Y:F in SYF_3 measured by energy dispersive spectrometer within the selected area (b).

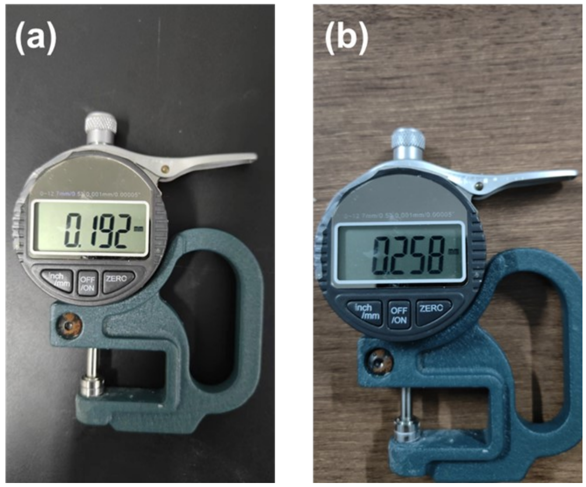

Fig. S6. Thickness of Zn electrode sheet before (a) and after (b) coated with SYF_3

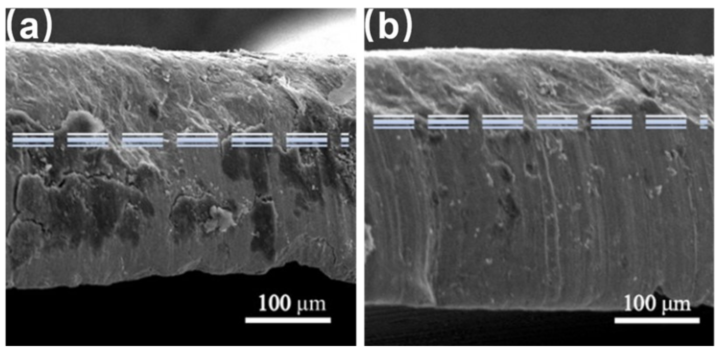

Fig. S7. SEM images of the cross-section of CYF_3@Zn (a) and SYF_3@Zn (b)

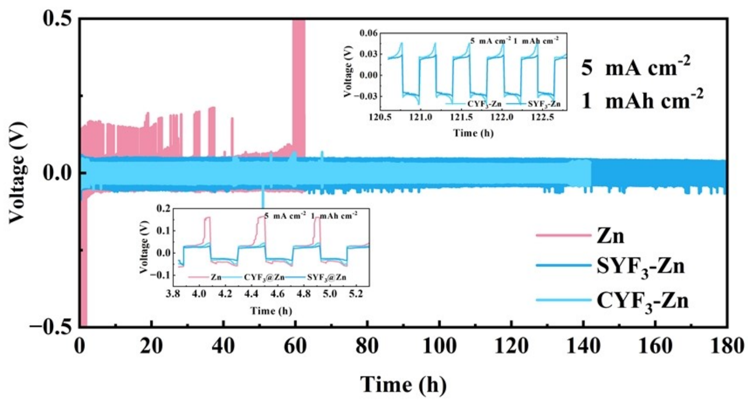

Fig. S8. The cycle performance of Zn//Zn, CYF_3@Zn//CYF_3@Zn and SYF_3@Zn//SYF_3@Zn symmetric batteries under a high-temperature condition (55 °C)

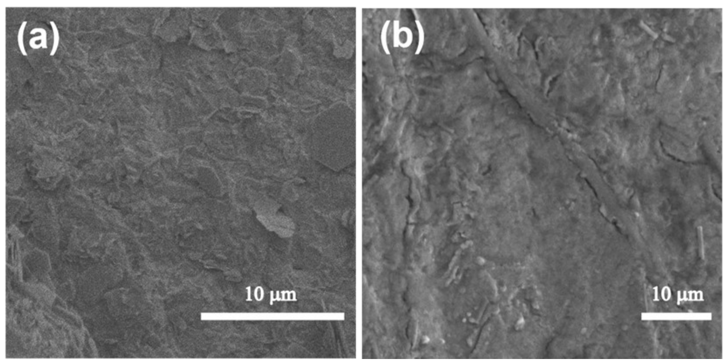

Fig. S9. SEM image of Zn deposits on Cu side in Zn-Cu half-cell after 200 cycles before and after introducing SYF_3 interlayer: (a) pure Zn, (b) SYF_3@Zn

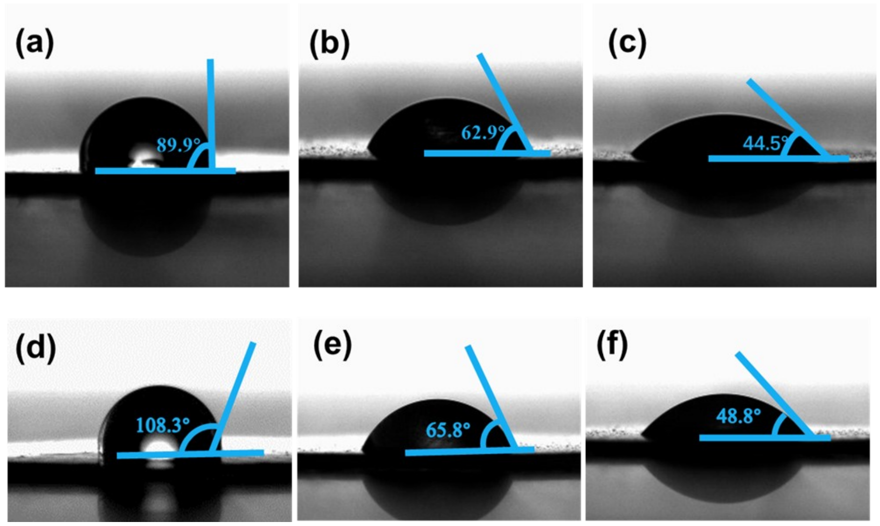

Fig. S10. Contact angles of 2M $ZnSO_4$ electrolyte on (a) pure Zn electrode sheet, (b) CYF_3@Zn electrode sheet, and (c) SYF_3@Zn electrode sheet.

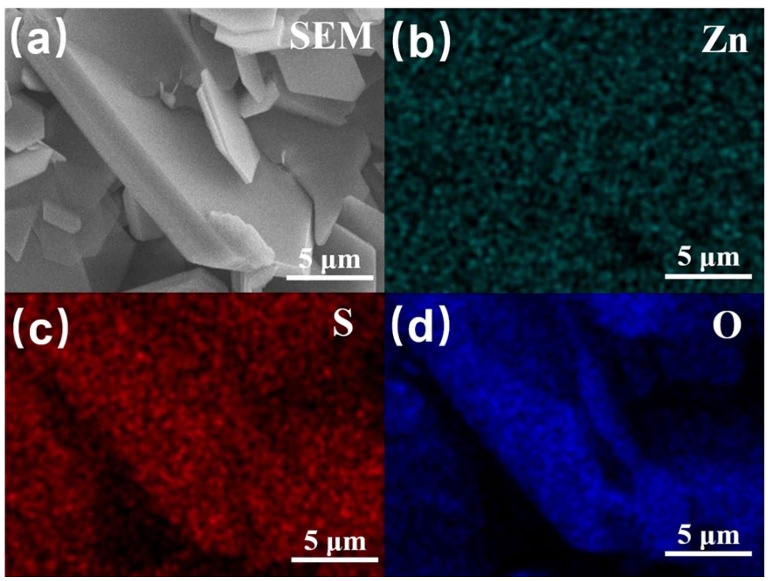

Fig. S11. SEM images (a) and EDS element mappings (b-d) of Zn, S and O of pure Zn sheet after immersion in 2M $ZnSO_4$ electrolyte for 7 days

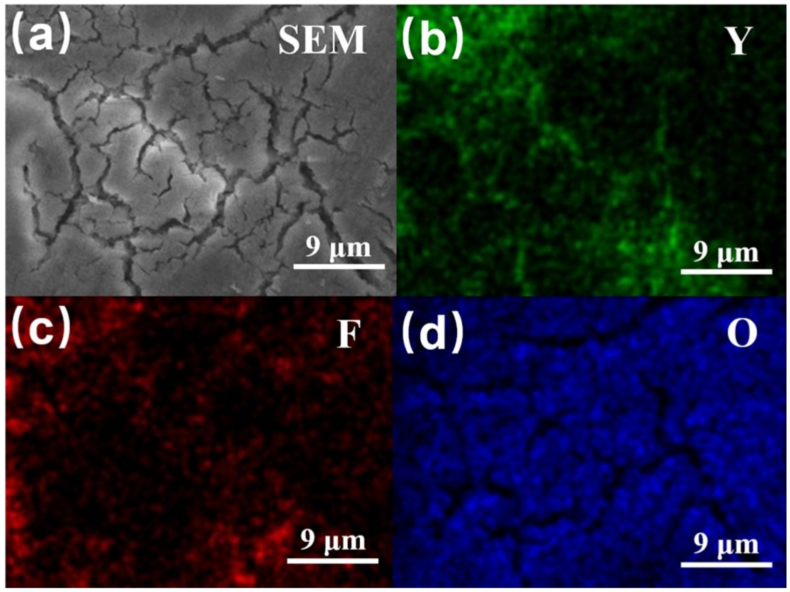

Fig. S12. SEM images (a) and EDS elemental mappings (b-d) of Y, F and O of CYF_3@Zn sheet after immersion in a 2 M $ZnSO_4$ electrolyte for 7 days

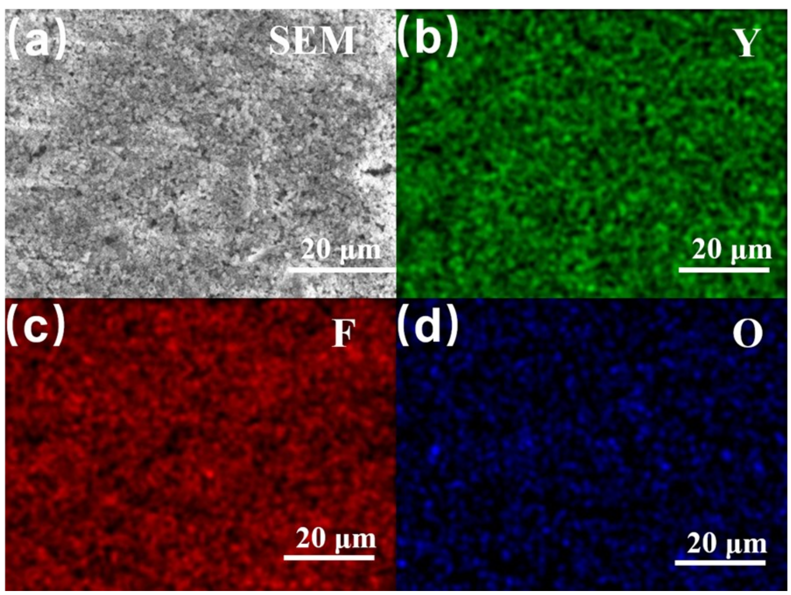

Fig. S13. SEM images (a) and EDS elemental mappings (b-d) of Y, F and O of SYF_3@Zn sheet after immersion in a 2 M $ZnSO_4$ electrolyte for 7 days

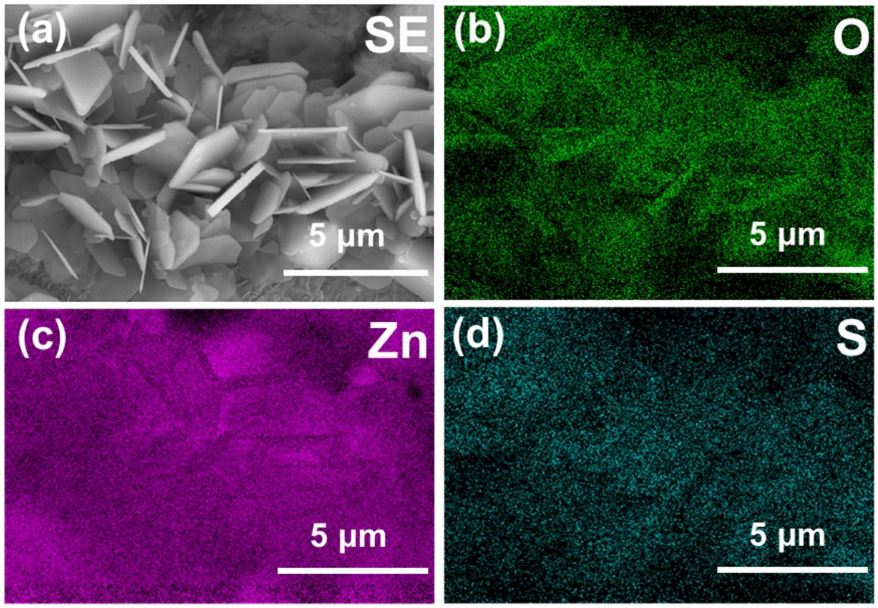

Fig. S14. SEM images (a) and EDS elemental mappings (b-d) of O, Zn and S of pure Zn sheet after 200 cycles at 5 mA cm^{-2}, 1 mAh cm^{-2}.

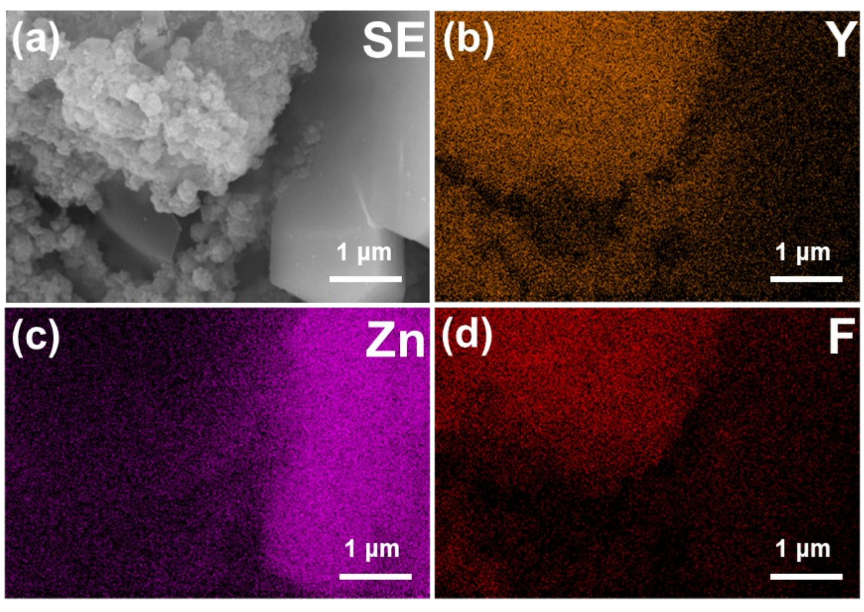

Fig. S15. SEM images (a) and EDS elemental mappings (b-d) of F, Zn and Y of CYF_3@Zn sheet after 200 cycles at 5 mA cm^{-2}, 1 mAh cm^{-2}.

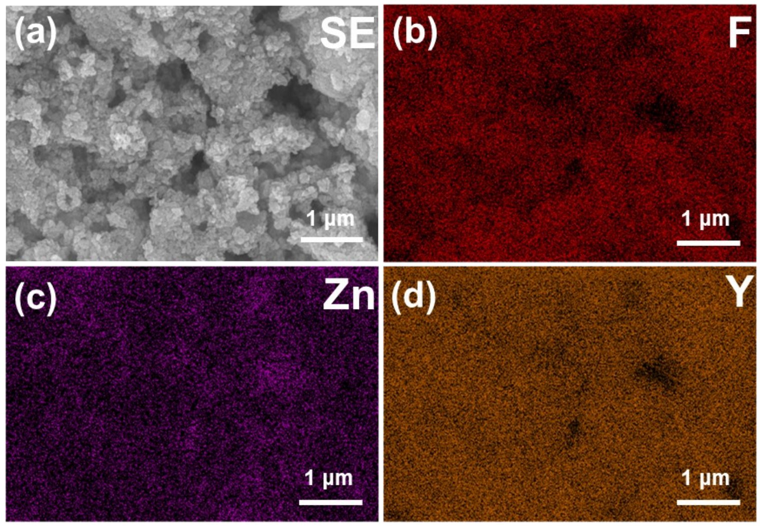

Fig. S16. SEM images (a) and EDS elemental mappings (b-d) of F, Zn and Y of SYF_3@Zn sheet after 200 cycles at 5 mA cm^{-2}, 1 mAh cm^{-2}.

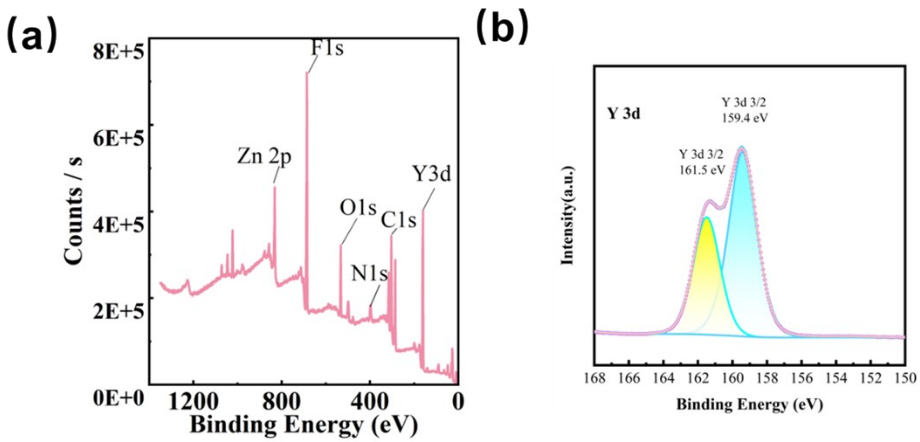

Fig. S17. XPS full spectrum (a) and high-resolution spectrum of Y element (b) of SYF_3@Zn electrode after 200 cycles in Zn-based symmetrical battery

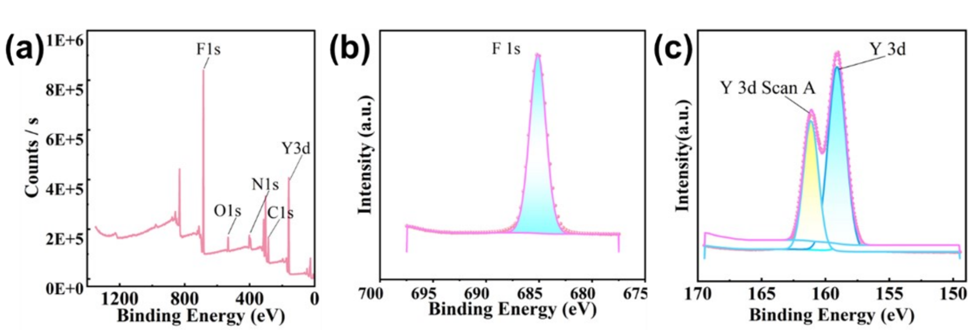

Fig. S18. XPS full spectrum (a), high-resolution spectrum of F element (b) and high-resolution spectrum of Y element (c) of CYF_3@Zn electrode after 200 cycles in Zn-based symmetrical battery

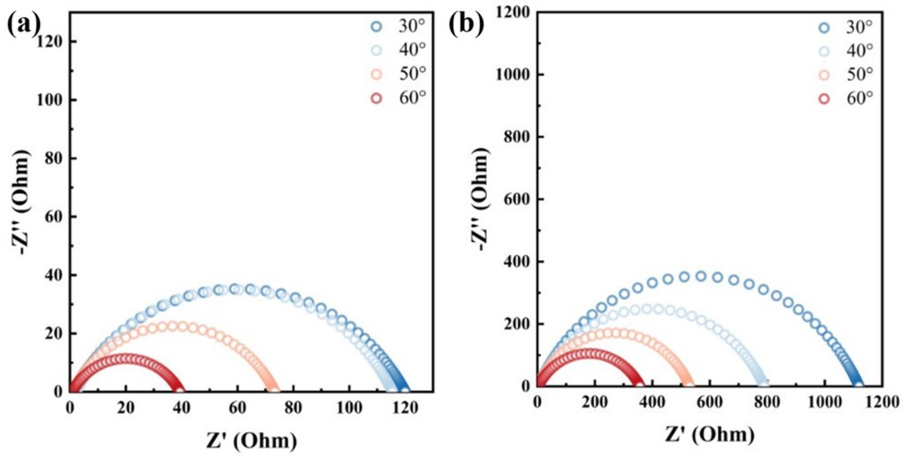

Fig. S19. EIS spectra of the Zn-based symmetrical batteries assembled by CYF_3@Zn (a) and bare Zn electrode (b) at different temperatures

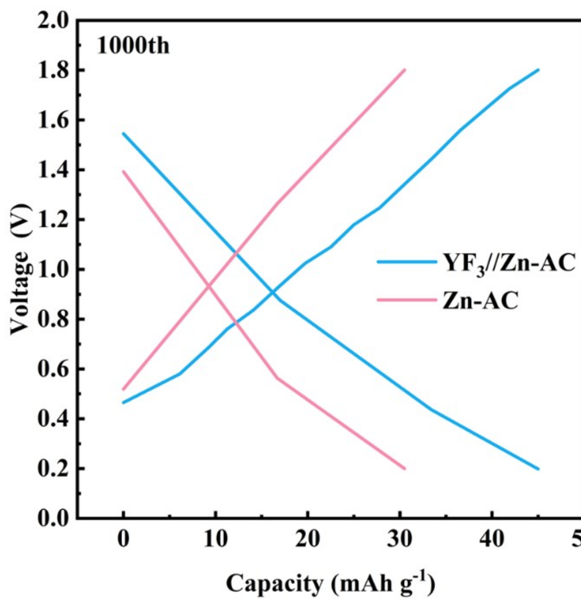

Fig. S20. The capacity-voltage curve of SYF_3@Zn//AC zinc ion capacitor

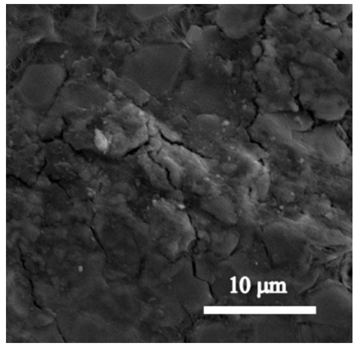

Fig. S21. SEM image of the Zn anode in CYF_3@Zn//AC after 2000 cycles

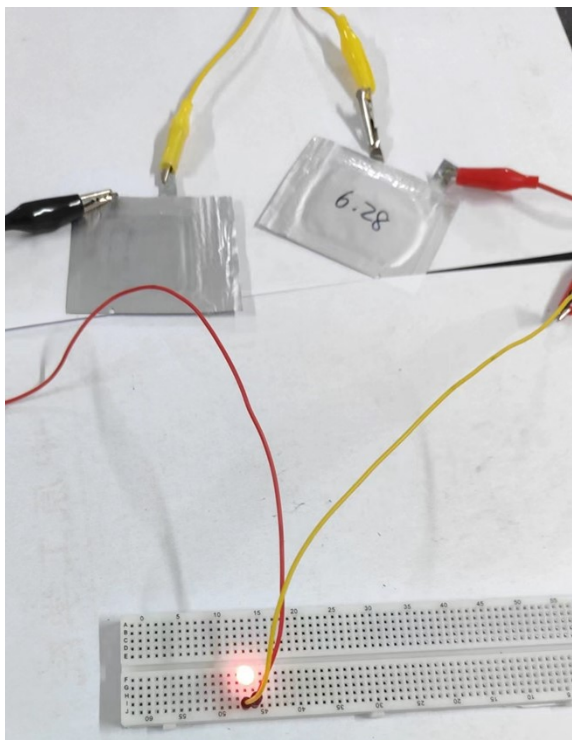

Fig. S22. A red LED lamp lit by pouch SYF_3@Zn//AC zinc ion capacitors

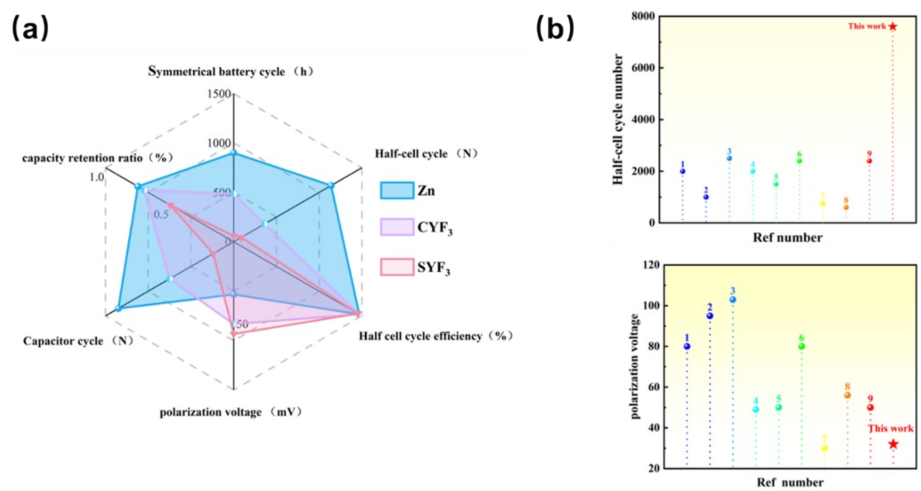

Fig. S23. (a) Radar chart for performance comparison of CYF_3, SYF_3 and Zn anodes, (b) performance comparison between CYF_3@Zn anode and other reported research results

Table S1. BET surface area and pore size of CYF_3 and SYF_3 powder according to the absorption-desorption curves

Thermophysical	CYF_3	SYF_3
BET surface area ($m^2\ g^{-1}$)	39.75 ± 0.12	50.7± 0.31
Q_m（cm^3/g）	9.13	11.20
Molecular cross-sectional area（nm^2）	0.16	0.16

Table S2. The Y:F atom ratio of CYF_3, SYF_3 powder according to EDS results

Sample	Y:F
SYF_3	18: 82
CYF_3	26 : 74

Table S3. Thickness of the electrode sheet as measured multiple times and the calculated average thickness

Number of tests	Zn	YF_3@Zn
1	0.192	0.258
2	0.205	0.278
3	0.202	0.246
average value	0.200	0.260

References

1. S. Gao, G. Chen, Y. Dall'Agnese, Y. Wei, Z. Gao and Y. Gao, *Chemistry - A European Journal*, 2018, **24**, 13535-13539.
2. X. Xu, H. Zeng, D. Han, K. Qiao, W. Xing, M. J. Rood and Z. Yan, *ACS Appl. Mater. Interfaces*, 2018, **10**, 37172-37180.