

Anti-dendrite separator interlayer enabling staged zinc deposition for enhanced cycling stability of aqueous zinc batteries

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Aqueous zinc ion batteries exhibit great prospects due to their low cost and high safety, while their lifespan is limited by severe dendritic growth problems. Herein, we develop an anti-dendrite hot-pressing separator interlayer through a mass-producible hot-pressing strategy, by spreading metal-organic framework (MOF) precursor on nonwoven matrix followed by a simple hot-pressing process. The in situ modification of MOF crystals on fiber surface processes abundant nitrogenous functional groups and high specific surface area ($190.8 \text{ m}^2 \text{ g}^{-1}$) with a strong attraction to Zn^{2+} . These features contribute to a staged deposition behavior to promote uniform nucleation at high concentrations and two-dimensional grain growth at low concentrations. Consequently, $\text{Zn}||\text{Zn}$ symmetrical cells with hot-pressing separator interlayer demonstrate cycle lives of 3000 hours at 2 mA cm^{-2} , 2 mAh cm^{-2} . Moreover, $\text{Zn}||\text{Li}_2$ pouch batteries with hot-pressing separator interlayer realizes 840 cycles lifespan with a capacity retention of 90.9% and a final discharge capacity of 110.6 mAh at 25°C .

Aqueous zinc-ion batteries (AZIBs) are appealing options for large-scale electrochemical energy storage due to the distinctive advantages of zinc metal negative electrodes and aqueous electrolytes^{1–3}. Zinc is a high-abundance metal, as a negative electrode offers the advantages of intrinsic safety, low redox potential (-0.76 vs. SHE), and high theoretical and volumetric capacity (820 mAh g^{-1} , 5585 mAh cm^{-3})^{4,5}. Meanwhile, the aqueous electrolyte shows a lower price, higher ionic conductivity, and faster reaction kinetics than organic electrolytes⁶. Many solutions, such as innovative microstructure design have been proven as effective ways to increase the positive electrode performance in the past few years⁷. However, the widespread application of AZIBs is still hindered by the challenges including Zn dendrite formation and associated side reactions on negative electrode⁸. These issues can lead to dendrite puncture, dead zinc (i.e., zinc metal regions that are electronically disconnected from the current collector) spalling, and hydrogen evolution during the operation of the batteries,

resulting in rapid short-circuit failures and a notable decrease in the coulombic efficiency of the AZIBs⁹. To address these issues, extensive efforts have been conducted on the zinc-negative electrodes in recent years, focusing on various aspects such as surface modification^{10–13}, electrolyte component designs^{14–16}, alternative zinc powder negative electrodes^{17–19}, anode-free electrodes^{20–22}, rocking-chair negative electrodes^{23–25}, and innovative structural designs^{26–28}. Most of those strategies concentrate on the optimization of zinc surface structure and solid-electrolyte interface or changing the negative electrode reaction from metal deposition to ion embedding. It is not negligible that the separator, as an important component of batteries, also plays a vital role in improving the electrochemical performance of AZIBs²⁹.

As a typical example illustrated in Supplementary Fig. 1, the mostly used glass fiber (GF) separator is observed to have severe dendrite and dead zinc problems in the $\text{Zn}||\text{Zn}$ symmetry battery due to its inhomogeneous voids and low mechanical strength^{30,31}. Thus

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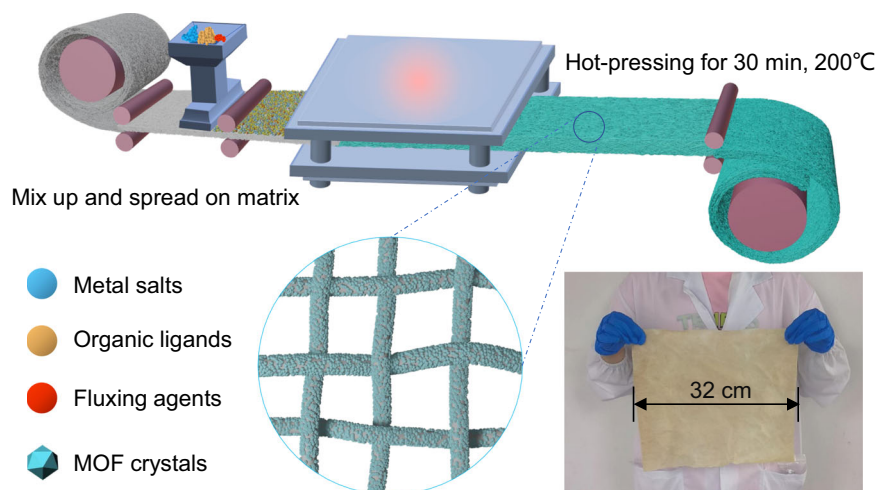


Fig. 1 | Preparation of HTS. The product of the HTS is a one-step hot-press strategy and graphic of finished Zn-based HTS.

searching for new separator materials or modifying the traditional separators to control the Zn deposition and improve the electrochemical properties of AZIBs are the two common strategies that have been reported in the past few years³². For the strategy to search for new separator materials, the reported materials mainly focus on polymers, such as Zn²⁺ substituted Nafion membrane³³, single-ion Zn²⁺-conducting nanocellulose membrane³⁴, mesoporous polypyrrole paper³⁵, and 3D long-range ordered polyacrylonitrile nanofiber^{30,34}. These materials tend to show high mechanical strength, anti-corrosion, and zincophilic/Zn-rich functional groups. By replacing the traditional GF separators with them, it is favorable to achieve homogenization of the electric field as well as the Zn interest channel, slow down active material loss, and improve the cycle life of AZIBs.

The second strategy is the modification of the GF separator by using functional supramolecules³⁶, MOF materials²⁹, or polymers^{37,38}. These modified separators also demonstrated superior affinity for zinc ions, due to the introduction of a large number of zincophilic groups, which could avoid the accumulation of zinc ions on the electrode surface, thereby regulating Zn deposition and improving the performance of AZIBs. Although the aforementioned methods are effective in the optimization of electrochemical performances for separators, the corresponding production techniques are mainly hydrothermal method^{29,36} or immersion method³³. The current fabrication techniques are time-consuming and complicated and suffer from the limited size of hydrothermal autoclave, which is not conducive to large-scale production. Moreover, the intrinsic mechanism of the regulation of deposition behavior and nucleation process by the separator has not been clarified clearly in the previous studies^{9,39}. Therefore, it is imperative to explore a more concise method for separator preparations accompanied by the mechanism elaboration for advancing the research in AZIBs.

Herein, we propose a one-step hot press strategy to prepare a functional separator interlayer, and mainly discuss the role of separators to influence the nucleation process with a unique staged behavior. This hot press method is to simply spreads all mixed raw materials on a nonwoven matrix, followed by the hot-pressing for 30 min. Based on the hot-pressing procedure, Metal-Organic Framework (MOF) crystals can be in situ modified on the fiber surface of the matrix membrane and preserve the original ion transport channels without physical obstruction. With this feature, MOF crystals can be introduced into the separator, distributed in a ~160 μm thick space as a carrier of functional groups in virtue of the high specific surface area of MOFs, making these functional groups contact with the electrolyte extensively and playing a significant regulatory role. Leveraging the high active surface area, nitrogen-containing functional groups of

MOFs, and thick loading, the hot-press separator (HTS) achieves staged deposition behavior by dynamic concentration control. Through this mechanism, HTS can facilitate the crystallization kinetics to induce the (002)_{Zn} orientation and significantly decrease the growth of dendrite. As a result, Zn||Zn symmetric cells utilizing the HTS demonstrate a cycling life of 4900 h at 1 mA cm⁻², 1 mAh cm⁻², and 3000 h at 2 mA cm⁻², 2 mAh cm⁻². In Zn||Cu cells, they exhibit 1650 cycles at 1 mA cm⁻², 1 mAh cm⁻². Moreover, the stability and high capacity of full-cell batteries with HTS are verified through a 120 mAh high loading capacity for 840 cycles in Zn||I₂ full pouch cells. This solution process the feature of low-cost, high-speed, and mass-producible, aims to extend the cycling life of AZIBs for the large-scale application.

Results

The preparation and physicochemical properties of the HTS separator

The HTS is prepared as signaled in Fig. 1. Metal salt, organic ligand, and fluxing agent are blended evenly and spread on the fiber separator matrix. A 30-minute hot-press step is applied, during which the raw materials are converted to MOF crystal grains that wrap around the surface through an in situ coordination reaction. Through the hot-pressing solution, it is feasible to load MOF crystals on a fiber separator, which promotes the expansion of the production scale. To illustrate the potential for large-scale production, a representative wide-area HTS (32 cm × 28 cm) was also fabricated using the one-step hot-press solution.

The scanning electron microscope (SEM) shows a tight bond between MOF crystals and the fiber matrix on HTS (Fig. 2a, b). The pore structure of the separator is unaltered by MOF crystals, homologous with the surface morphology of untreated nonwoven (bare separator) (Fig. 2d, e). Energy dispersive spectroscopy (EDS) elemental mapping images (Fig. 2c, f and Supplementary Fig. 2a, c) and corresponding EDS energy spectra (Supplementary Fig. 3a, c) were utilized to characterize the elemental information of the HTS and bare separator. The results demonstrate a uniform distribution of zinc on the HTS, confirming the attachment of MOF crystals. To further investigate the structure of the attached crystals, X-ray diffraction (XRD) patterns (Fig. 2g) were obtained to compare the lattice plane between the HTS and commercial zeolitic imidazolate framework-8 (ZIF-8). The peaks were divided into specific crystal planes⁴⁰, and the results revealed that the crystalline phase in the HTS exhibited a consistent diffraction angle but with a more uniform diffraction intensity, indicating that the MOF crystals in the HTS possess diverse crystallographic orientations, efficiently reducing inhomogeneity across the separator fibers. Fourier

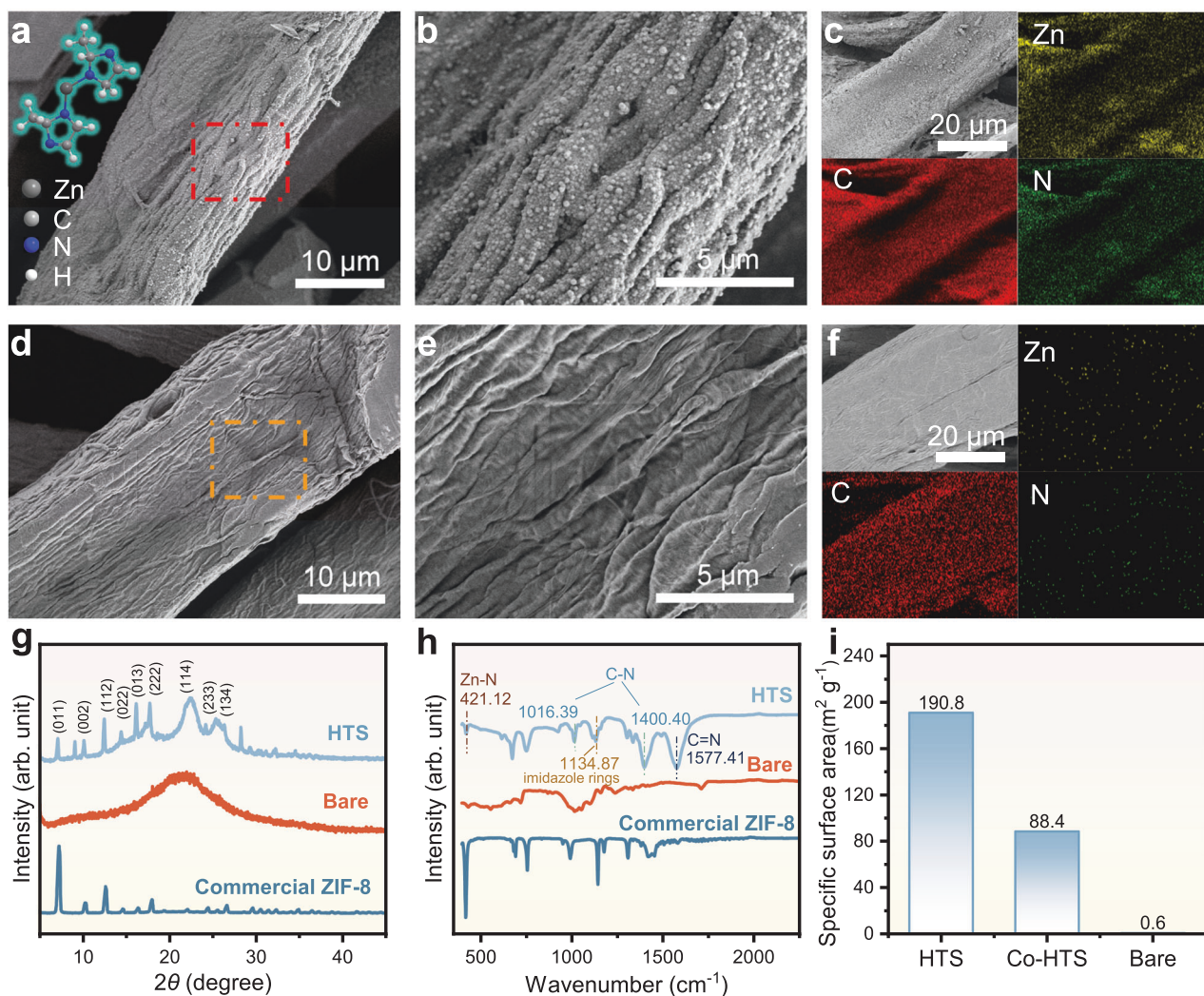


Fig. 2 | Characterization of HTS. **a–f** SEM image (**a**, **b**), and EDS mapping (**c**) of HTS. SEM image (**d**, **e**), and EDS mapping (**f**) of the bare separator. **g** XRD patterns of HTS, bare separator, and commercial ZIF-8. **h** FTIR spectrum of HTS, bare

separator, and commercial ZIF-8. **i** Specific surface area of HTS, Co-HTS, and bare separator, obtained from N₂ adsorption isotherms.

transform infrared (FTIR) spectra demonstrated the bonding structure of the HTS (Fig. 2h), and the results support that the HTS incorporates identical fingerprint areas. Notably, a peak at 421.1 cm⁻¹ is assigned to the vibrations of the Zn–N bond⁴¹. Stronger peaks observed at wave-numbers of 1577.4 cm⁻¹ are identified as C = N bond, while the peaks at 1016.4 cm⁻¹ and 1400.4 cm⁻¹ are indexed as C – N bond. Another peak at 1134.9 cm⁻¹ is attributed to imidazole rings^{42,43}. This suggests that HTS is rich in nitrogen-containing groups, which have potential as adsorption sites of Zn²⁺. In addition, a Co-based hot-press separator (Co-HTS) was also prepared to demonstrate the versatility of the hot-press method. From the EDS elemental mapping images (Supplementary Fig. 2b) and corresponding EDS energy spectra (Supplementary Fig. 3b), the Co-HTS shows a significant uniform distribution of cobalt. The SEM images (Supplementary Fig. 4) and XRD patterns (Supplementary Fig. 5) indicate that zeolitic imidazolate framework-67 (ZIF-67) crystal grains are attached to the surface of Co-HTS. The FTIR spectrums also proved the same peak position as the Zn-based HTS (Supplementary Fig. 6), attributed to the imidazole ring in their structure. N₂ adsorption isotherms were employed to provide further evidence for the existence of porous MOF materials, as shown in Fig. 2i and Supplementary Fig. 7. The relevant result illustrated that Zn-based HTS shows higher loading than that of Co-HTS, in good accordance with XRD diffraction intensity. In addition, a comparison is made

between the unit prices of HTS and the usually-used GF separator. As shown in Supplementary Table 1 and Supplementary Fig. 8, the cost for the unit price of HTS is only 138 CNY m⁻², significantly lower than that of a commercial GF separator (2275 CNY m⁻²), indicating that HTS possesses a enough cheap feature to fit the low-cost AZIBs. On the other side, as shown in Supplementary Table 2, the electrolyte absorption ratio of HTS is 205.7%, lower than that of the GF separator (745.0%). The limited electrolyte absorption ratio of HTS is attributed to the physical property of a nonwoven matrix. To address this issue, the interlayer structure (two pieces of HTS stacked on both sides of a piece of GF) is introduced in the following tests.

Morphology evolution of the HTS separator/Zn negative electrode interface

To analyze the effect of the HTS on the negative electrode, Zn||Zn symmetrical cells were assembled using the interlayer structure. In situ optical observation was used to intuitively display the deposition of Zn metal on the negative electrode. The battery combined with HTS exhibits a uniform layered deposition in the cross-sectional morphology (Fig. 3a). Meanwhile, the SEM of the Zn negative electrode after 20 cycles at 5 mA cm⁻², 5 mAh cm⁻² (Fig. 3b) also shows the typical stacking shape of hexagonal grains, which is attributed to both the electro-crystalline orientation (ECO) of (002)_{Zn} and the exposed crystal face

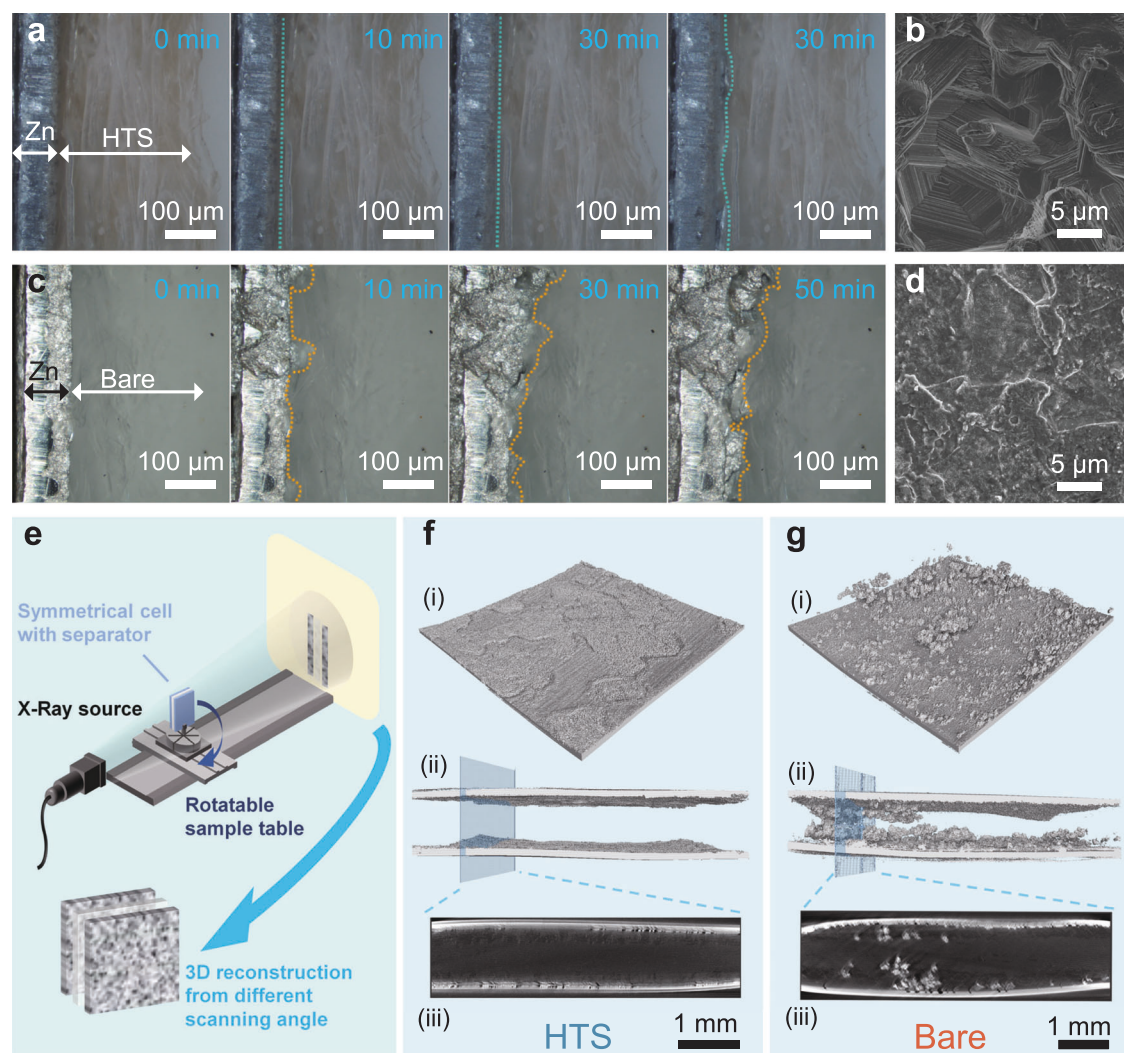


Fig. 3 | Morphology characterization of Zn negative electrode with HTS. a, c In situ optical observation of Zn negative electrode after plating 0, 10, 30, 50 min at a current density of 5 mA cm^{-2} using the HTS (a) and bare separator (c) at the temperature of 25°C . **b, d** SEM images of Zn foil negative electrode after 20 cycles at 5 mA cm^{-2} , 5 mAh cm^{-2} using the HTS (b) and bare GF (d) at the temperature of

25°C . **e** X-CT equipment structure and principle schema. **f, g** X-CT result of Zn || Zn symmetrical batteries using the HTS (f) and bare separator (g) after 20 cycles at 5 mA cm^{-2} , 5 mAh cm^{-2} and temperature of 25°C : (i) front view of negative electrode 3D reconstruction, (ii) Side view of battery 3D reconstruction, (iii) Side X-CT view of battery cross-section.

(ECF)⁴⁴ of $[002]_{\text{Zn}}$. In contrast, in the case of a blank separator, the Zn negative electrode with bare GF only exhibits visible hemispherical and inhomogeneous zinc particles in the in situ optical observation image (Fig. 3c), and the corresponding SEM image also reveals a raised micro surface on the Zn negative electrode (Fig. 3d).

The side reactions on the negative electrode were explored through the Zn surface phase analysis and hydrogen evolution reaction (HER) test. As shown in Supplementary Fig. 9, after a long cycle time of 200 h at 1 mA cm^{-2} , 1 mAh cm^{-2} , the surface compositions of Zn with HTS exhibit significant differences compared with bare separator. XRD peaks at 13.0 and 19.6 degrees appeared on the Zn with the bare separator, attributed to the by-product of $\text{Zn}_x(\text{OTf})_y(\text{OH})_{(2x-y)}$ ⁴⁵. In contrast, the Zn interface remained pure Zn peaks after 200 h of cycling when HTS was employed as the separator, indicating the ability of HTS to inhibit side effects. More appealingly, it is found the intensity ratio of $(002)_{\text{Zn}}/(101)_{\text{Zn}}$ was up to 387.1% after cycling for 200 h, which is significantly higher than that of bare separator (61.7%). This phenomenon demonstrates the continuous optimization effect of HTS during long cycles. Furthermore, the linear sweep voltammetry (LSV) test in a $1 \text{ M Na}_2\text{SO}_4$ electrolyte to evaluate the HER potential on the negative electrode side, as shown in Supplementary Fig. 10. The Zn

negative electrode with HTS exhibits a HER potential of -1.839 V , which is 13 mV lower than that of the bare separator (-1.826 V). These results confirm the inhibition of hydrogen evolution in the presence of HTS.

In addition, X-ray computed tomography (X-CT) is utilized to further examine the surface structure of the negative electrode beneath the separator. The equipment structure and principle of X-CT are illustrated in Fig. 3e, the X-ray is emitted from a radiation source, penetrating the symmetrical battery samples. Graphic information is recorded from various viewing angles by rotating the sample, and the results are combined to generate a 3D reconstruction. Figure 3f, g presents the 3D model image and the cross-sectional CT image of the battery with HTS and bare separator, in which the transparent separator enables a clear view of the continuous macro morphology of the Zn electrode. The phenomena of the CT result reveal that the battery with HTS demonstrated a notable inhibition of dendrite growth, evident from the smooth surface of Zn foil and the absence of dendrites within the separator region (Fig. 3f(i-iii)). Conversely, it is clear to observe a significant expansion of dendrites, which implant into the bare separator turning to “death zinc”, as indicated by the connected and discrete white Shadow between the electrodes

(Fig. 3g(i–iii)). The full cross-sectional CT scanning and 3D model were shown in Supplementary Movie 1 (with HTS) and Supplementary Movie 2 (with bare separator).

Dynamic Zn²⁺ concentration regulation process of the HTS separator

To investigate the impact of HTS on the Zn deposition process, a comprehensive set of mechanistic characterizations was conducted. As shown in Fig. 4a, b, and Supplementary Fig. 11, FTIR spectra are provided to examine the solvent structure near the interface of the separator. The results indicate that the peak corresponding to Zn–N at 421.1 cm^{−1} is significantly enhanced when HTS is soaked in 2 M Zn(OTf)₂ (Fig. 4a), indicating the strong affinity between C–N, C=N groups and Zn²⁺. Moreover, the peak of electrolyte at 1634.4 cm^{−1}, which is recognized as O–H bending⁴⁶. Clearly, this peak is significantly reduced and redshifted to 1630.1 cm^{−1}, which proves that water activity is inhibited in the presence of HTS, which results in the inhibition of side reactions and the HER process. In contrast, the bare separator exhibits a blue shift to 1637.3 cm^{−1}. Equivalently, the peak at 3341.6 cm^{−1} (Supplementary Fig. 11), corresponding to O–H stretching⁴⁷, is prominently attenuated. Besides, to evidence the stability of HTS, the FTIR spectra of HTS after cycling are provided as shown in Supplementary Fig. 12. The spectra exhibit that the main peaks of HTS remain constant in intensity during long-time cycling. The corresponding test in electrolytes is shown in Supplementary Fig. 13, which indicates that the MOFs loaded on HTS are stable for a long time in the electrolyte environment without dissolution and leaching.

The results for transference numbers of Zn²⁺ ions (*t*(Zn²⁺)) are shown in Fig. 4c and Supplementary Figs. 14–16 (the corresponding digital are shown in Supplementary Table 3 and the calculation of *t*(Zn²⁺) is shown in Supplementary Note 1). In a 2 M Zn(OTf)₂ electrolyte, the HTS demonstrates a *t*(Zn²⁺) of 0.66, approaching the *t*(Zn²⁺) of GF (0.68) and higher than that of the bare separator (0.42). Regularly, the *t*(Zn²⁺) of the bare separator is found to increase following the concentration (from 0.37 in 1 M electrolyte to 0.48 in 3 M ones), showing a positive correlation. Thus, it is promoted that a high-concentration environment existed around the HTS, increasing its *t*(Zn²⁺). In addition, the HTS exhibits a buffer behavior in the CV curves of Zn||Cu, as shown in Fig. 4d, indicating a concentration state transition during deposition/stripping. Furthermore, exchange current density is calculated by the Tafel plot (Fig. 4e) and potential-current fitness (Fig. 4f), both of which confirmed a lower corrosion rate and ion transfer velocity in the presence of HTS. Notably, a transition stage was found over −0.95 ~ −0.90 mV in the Tafel plots of HTS, indicating a unique deposition process. Inspired by this observation, LSV curves were conducted under broad negative polarized conditions with different separators (Fig. 4g, h and Supplementary Fig. 17). The limiting current (*i*_L) of a linear area can explain the effect of current on deposition behavior, as Zn negative electrode tends to develop (002)_{Zn} orientation under 0.1*i*_L ~ 1.0*i*_L²⁸. In the presence of HTS, the limiting current is substantially decreased from 109.9 mA cm^{−2} for the bare separator to 14.3 mA cm^{−2} for HTS. This implies that within the HTS system, its negative electrode deposition tends to the (002)_{Zn} orientation under current conditions of 1.43 ~ 14.3 mA cm^{−2}. The unique deposition process can be more visually represented in the potential-capacity curves, as shown in Fig. 4i and Supplementary Fig. 18. We promote that the optimization effect of HTS on Zn deposition is maintained under different currents. At high current, the HC stage is shortened and mainly manifested as grain refinement, and the LC stage corresponds to the formation of (002)_{Zn} orientation. Obviously, the potential-capacity curves of the bare separator demonstrate much smaller difference values of potential between Zn nucleation and deposition (ΔE) than that of the bare separator at the same current density, and the ΔE values of the HTS and bare separator at 1 ~ 5 mA cm^{−2} were summarized as shown in Supplementary Fig. S19.

Meanwhile, the specific deposition curves corresponding to the unique deposition process were found in HTS, which is exhibited as a “stage behavior”.

It is worth noting that recent reports have highlighted the significance of concentration in determining deposition morphology^{48,49}. Then the “stage behavior” in the HTS from the point of view of concentration and deposition reaction are studied detailedly. By considering the simplified reaction as Eq. (1), we can derive the current-potential equation as Eq. (2) based on the kinetics of the electrode reaction⁵⁰:



$$i = FAK^0 [C_O e^{-\alpha F(E-E^0)} - C_R e^{(1-\alpha)F(E-E^0)}] \quad (2)$$

where *O* stands for oxidation state, *R* is the corresponding reduction product, *C*_O, *C*_R are the concentrations of oxide and reduction product, *k*⁰ is the standard rate constant. α is the transfer coefficient, *A* is the area of reaction, *F* is the Faraday constant, *E* and *E*⁰ are the electrode potentials.

In the case of Zn negative electrodes, where the concentration of the reduction product in the solid phase remains constant, *C*_R is counted as 1. Consequently, the relationship between oxide concentration, current, and potential can be expressed as Eq. (3):

$$C_O = \left(\frac{i e^{\alpha}}{FAK^0} + 1 \right) e^{F(E-E^0)} \quad (3)$$

This equation indicates a positive correlation between oxide concentration and potential under constant current conditions. Thus, it can be assumed that with HTS, the deposition process under low current density can be divided into two stages: a high Zn²⁺ concentration stage (HC) and a low Zn²⁺ concentration stage (LC), as depicted in Fig. 4i. As the current increases, the HC stage disappears and is replaced by the long LC stage, which is attributed to the fast depletion of Zn²⁺.

Furthermore, the shorter linear area of LSV curves in Fig. 4g can also be understood through Eq. (2). When the overpotential (*E* − *E*₀) is small enough, the Eq. (2) can be approximately equivalent to Eq. (4) as follows:

$$i = FAK^0 [-\alpha FC_O(E - E^0) - (1 - \alpha)FC_R(E - E^0)] \quad (4)$$

This equation corresponds to the linear area in LSV curves, attributed to enough Zn²⁺ ions at the first low overpotential stage. In linear area, the main rate control steps of reaction are surface area and activation. With the increasing overpotential, the curves turn to the nonlinear area and finally become the Tafel curve when the overpotential is high enough. The changes in the nonlinear area are attributed to the consumption of concentration, leading to the reconstruction of the equilibrium reaction. Thus, the *i*_L could be a parameter to measure the speed of concentration polarization construction. For HTS, the lower *i*_L indicates a faster concentration depletion rate and directly contributes to the creation of the LC stage.

As for how concentration affects the deposition process, this has been concluded from crystallization thermodynamics as shown in Eq. (5)⁵¹:

$$r_{crit} = \frac{2v_m \sigma}{ne|\eta|} \quad (5)$$

where the *r*_{crit} is the critical nucleus radius, *v*_m is the volume occupied by one atom in the crystal, σ is the specific surface energy, *n* is the electron transfer number, and η is the overpotential of the electrode.

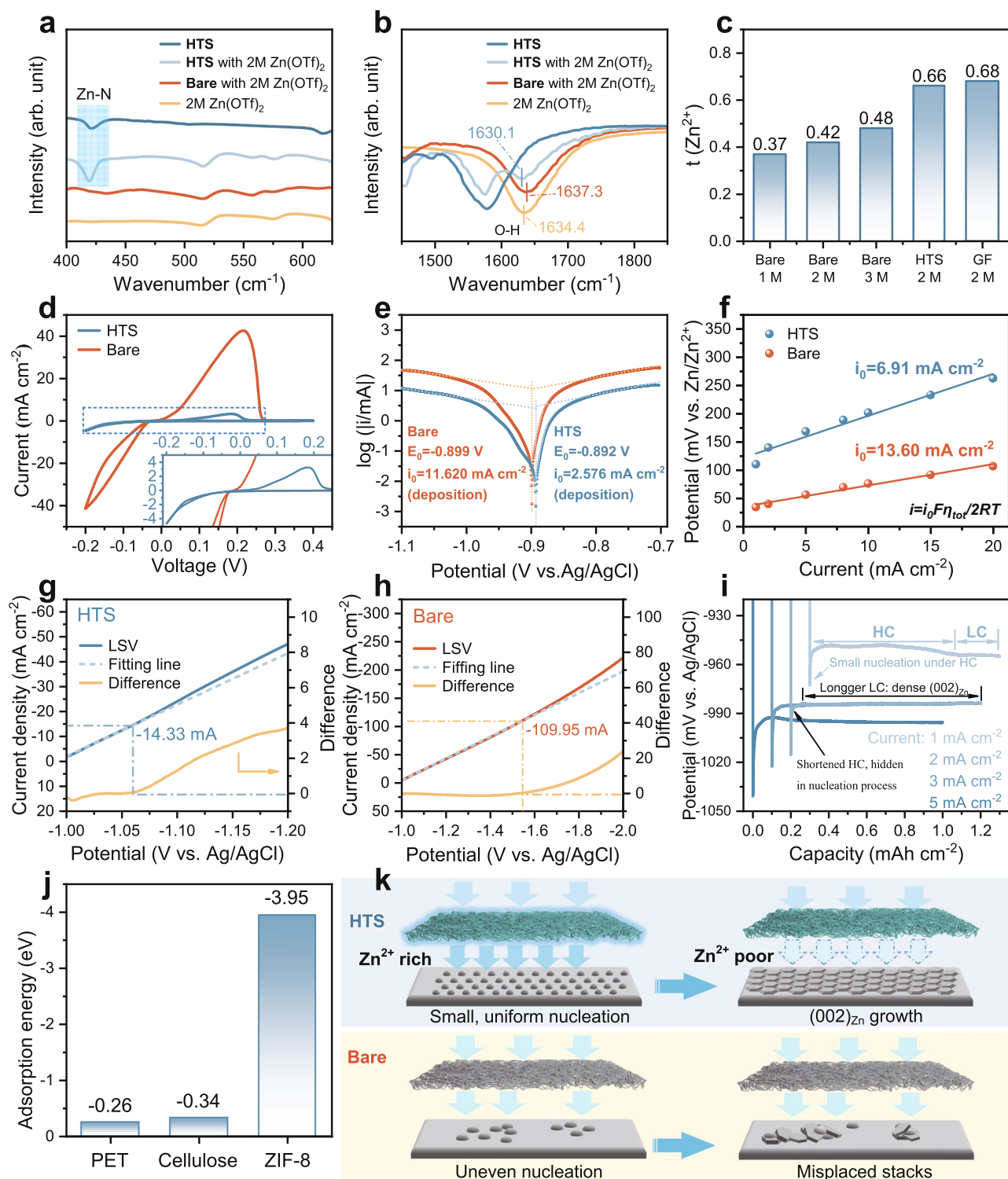


Fig. 4 | Electrochemical characterization and theoretical simulation of Zn negative electrode with HTS. a, b FTIR spectra of HTS and bare separator immersed in 2 M Zn(OTf)₂ electrolyte, dry HTS, and 2 M Zn(OTf)₂ electrolyte. **c** The Zn²⁺ transference number of Zn || Zn batteries with HTS and GF in 2 M Zn(OTf)₂, and with bare separator in 1, 2, 3 M Zn(OTf)₂. **d–f** CV curves (**d**), Tafel plots (**e**), and current-potential fitting line from rate performance tests (**f**) of Zn || Cu battery with HTS and bare separator. The insert in **d** is the enlarged part of the dashed box.

g, h LSV curves and linear regional analysis of HTS and bare separator without iR corrected. **i** potential-capacity curves during Zn nucleation and deposition at the current density of 1–5 mA cm⁻² using Zn foil as the working and counter electrode, Ag/AgCl electrode as the reference electrode, and without iR corrected. **j** Theoretical calculated adsorption energies of Zn atom on PET, cellulose, and ZIF-8 surface. **k** Schematic diagram of Zn ion deposition mechanism in the HTS and bare separator.

In the steady-state growth phase of a negative electrode, the Nernst equation (Eq. (6)) is introduced with a quasi-static perspective to derive Eq. (7):

$$E = E^0 + \frac{RT}{nF} \ln \frac{C_R}{C_O} = E^0 - \frac{RT}{nF} \ln C_O \quad (6)$$

$$r_{crit} = \frac{2v_m \sigma F}{eRT \ln C_O} \quad (7)$$

where the R is universal gas constant, and T is the temperature under the Kelvin scale.

Besides, the SEM results under lower current and capacity were provided as shown in Supplementary Fig. 20, the deposition of Zn with HTS tends to smaller crystal grain at 1 mA cm^{-2} , 1 mAh cm^{-2} . As the condition becomes 2 mA cm^{-2} , 2 mAh cm^{-2} , the crystals start to larger and denser, approaching the prototype of $(002)_{\text{Zn}}$ crystal orientation. To verify the quantified component of Zn orientation, the XRD pattern of the Zn negative electrode (Supplementary Fig. 21) was analyzed following the same treatment as the SEM sample. Notably, the XRD pattern shows a significant enhancement in the peak intensity ratio of $(002)_{\text{Zn}}$ to $(101)_{\text{Zn}}$ on the HTS. With the current and capacity turns higher, the peak intensity of the HTS group also increased (from 101.8% to 145.3%) all higher than that of pure Zn (98.0%), consistent with the SEM results. While on the bare separator, the intensity ratio decreased to 75.2%, attributed to the uneven deposition of the Zn negative electrode. These results are consistent with the previous conclusion, indicating the long LC stage corresponds to the formation of $(002)_{\text{Zn}}$ orientation.

Within this framework, the critical nucleus radius is negatively correlated to the Zn^{2+} concentration. Consequently, during the HC stage, the Zn negative electrode tends to form smaller nuclei with a lower critical nucleus radius and energy barrier. As the Zn^{2+} concentration decreases, owing to the depletion of Zn^{2+} and limited mass transfer dynamics, the deposition process translates into the LC stage. In this stage, a larger critical nucleation radius impedes the nucleation process, prompting the transformation of the Zn nucleus into the growth stage and characterized by 2D directional growth with $(002)_{\text{Zn}}$ orientation. To further determine the low kinetics of Zn^{2+} transport in HTS, the adsorption energies of Zn ions by HTS and bare separator were calculated using density functional theory (DFT) calculations. Due to the complex composition of HTS and bare separator, their main components are used for the modeling and calculation here. ZIF-8 is the main representative component of HTS, while polyethylene terephthalate (PET) and cellulose are the two main representatives of the bare separator. Based on these main components, the surface models (Supplementary Figs. 22, 23, and Supplementary Data 1) were established to calculate the adsorption energies of Zn ions, and the results are shown in Fig. 4j. It is evident the adsorption energy of Zn ion on the surface of ZIF-8 surface (-3.95 eV) is much larger than that on PET and cellulose (-0.26 eV and -0.34 eV), which indicates that the HTS can effectively block the transport of Zn^{2+} , thereby slowing down its kinetics.

Combined with the above experimental and theoretical analyses, we have proposed that this HTS separator exhibits a unique mechanism of dynamic concentration regulation, as depicted in Fig. 4k, which promotes dominantly oriented growth to reduce the formation of dendrites and dead zinc in AZIBs.

Long stability performance and high loading capacity application

To evaluate the stability of the negative electrode, $\text{Zn}||\text{Zn}$ symmetric cells and $\text{Zn}||\text{Cu}$ cells were employed to compare cycling performance while eliminating the influence of the positive electrode. Benefiting from the function of regulating the negative electrode deposition

process, the negative electrode with an HTS separator commands exceptional long-term cycling stability. $\text{Zn}||\text{Zn}$ cells with HTS exhibit a cycling life of 3000 h (Fig. 5a) at 2 mA cm^{-2} , 2 mAh cm^{-2} , and 4900 h at 1 mA cm^{-2} , 1 mAh cm^{-2} (Supplementary Fig. 24). On the other hand, $\text{Zn}||\text{Cu}$ cells, to decouple the Zn deposition/stripping behavior, are utilized in Coulombic efficiency (CE) plots to demonstrate significant optimization of the HTS separator for negative electrode reversibility, achieving 1650 cycles and 98.7% average CE (Fig. 5b). Further examination of deposition/stripping profiles as shown in Fig. 5c, d reveals a distinct stage that appears in both deposition and stripping processes, corresponding to HC and LC stages with different concentrations of nucleation and grain growth. At a higher current density, the HTS exhibits a cycling life span of 850 h at 5 mA cm^{-2} , 5 mAh cm^{-2} (Fig. 5e), with an 8.5% depth of discharge (DOD), and a 4210 mAh cm^{-2} cumulative charge/discharge capacity. Rate performance tests were conducted at current densities of $1\text{--}20 \text{ mA cm}^{-2}$ (Fig. 5f), where the HTS possesses better reversibility through the concentration control strategy employed by the HTS separator. Conversely, batteries with bare separators were short-circuited at high current, attributed to the uncontrolled dendrite growth.

Furthermore, the $\text{Zn}||\text{I}_2$ battery was utilized to assess the practical application of the HTS separator in a full-cell battery, using active carbon as the positive electrode current collector to adsorb iodine by electrolytic deposition solution. Figure 6a illustrates the cycling performance of $\text{Zn}||\text{I}_2$ full coin-type cells. When the bare separator was utilized, the cell exhibited soft short⁵² at cycle 450th and dead short circuits at cycle 1200th, due to the inhomogeneous deposition on the negative electrode. In sharp contrast, the full-cell batteries with GF at the middle and double HTS separator close to both the negative electrode and positive electrode (marked as double HTS) exhibited an extended lifespan of over 15000 cycles, which can be attributed to the high stability of the negative electrode. Full cells with single HTS close to the negative electrode and GF close to the positive electrode (marked as single HTS) were tested to analyze the effect of HTS on the I_2 positive electrode, as shown in the local magnification plot in Supplementary Fig. 25. The 1000 cycles capacity retention ratios were calculated as Supplementary Table 4, compare with the capacity at 100th cycle after activation. The result shows that the double HTS structure processes a significantly higher capacity retention ratio (99.6%) than that of the single HTS (97.8%) and bare separator (96.7%), which superior performance is attributed to the shuttle resistance function of MOFs⁵³. To evaluate the impact of overpotential on the application level of batteries, the specific energy of the I_2 positive electrode is introduced to measure the consolidated energy efficiency (EE), as Eq. (8):

$$E_n = \int U(t) I dt = \sum U_t I \Delta t \quad (8)$$

where E_n is the charge/discharge energy, $U(t)$ is the real-time voltage, U_t is the records real-time voltage in tests, I is the real-time current, and Δt is the interval of records in tests. The results of full-cell specific energy and energy efficiency are shown in Supplementary Fig. 26. The average EE of full-cell with HTS over the first 400 cycles is 84.4%, -0.9% lower than that of the full cell with a bare separator (85.3%). In the long term (400–1200 cycles), the EE of full-cell with HTS is comparable to that of the bare separator system. Notably, over the whole cycle test, the total average EE of full-cell with HTS is 87.1%, indicating a high reversibility of energy storage.

In addition, cells with the HTS demonstrated steady capacity retention throughout the charge/discharge profiles, as depicted in Fig. 6b, c. To verify the capacity retention and self-discharge problem, $\text{Zn}||\text{I}_2$ cells were fully charged to 1.8 V and rested for 48 h, then fully discharged to 0.3 V (The charged and discharged curves are shown in Supplementary Fig. 27). The discharged capacity retention ratio of

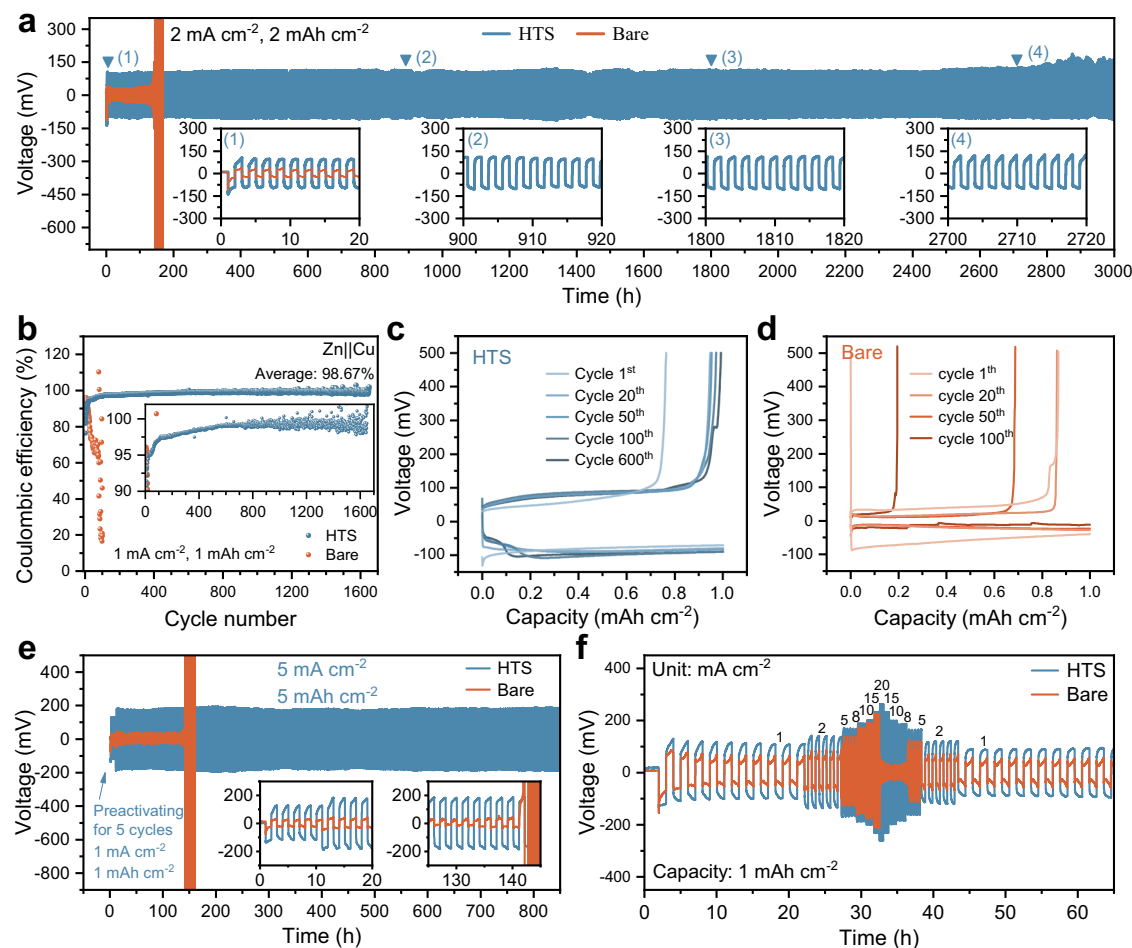


Fig. 5 | Electrochemical performance of Zn||Zn and Zn||Cu cells with HTS.

a Zn||Zn symmetric cell cycling performance with different separators at 2 mA cm⁻², 2 mAh cm⁻² and temperature of 25 °C. **b** Coulombic efficiency Zn||Cu cells with different separators at 1 mA cm⁻², 1 mAh cm⁻² discharge capacity, 0.5 V charge cut-off voltage, and temperature of 25 °C. **c, d** Corresponding charge/

discharge profiles of Zn||Cu cells. **e** Zn||Zn symmetric cell cycling performance with different separators at 5 mA cm⁻², 5 mAh cm⁻², and a temperature of 25 °C. **f** Rate performance of Zn||Zn symmetric cells with different separator at 1–20 mA cm⁻² and temperature of 25 °C.

Zn||I₂ cell with HTS is 91.7%, higher than that of the cell with a bare separator (89.8%). The electrochemical behavior with HTS and bare separator from the CV plot in Fig. 6d, e remained similar without the shift in peak position, suggesting that the HTS has no significant effect on the reaction process of the I₂ positive electrode. Analogously, the HTS and bare separator also had identical rate performance from Fig. 6f, g. Furthermore, a comparison of the cycling performance of full-cell batteries is presented in Supplementary Fig. 28 (The actual data is shown in Supplementary Table 5). These results demonstrate that the HTS exhibits significant performance optimization after 15,000 cycles, surpassing previous reports on AZIBs with different separators.

To evaluate the performance of the HTS under more challenging conditions and larger-scale applications, pouch cells were assembled as Fig. 6h, i, using a 5 cm × 5 cm Zn foil negative electrode and 5 cm × 5 cm I₂ positive electrode with a loading capacity of 120 mAh, resulting in an areal capacity of 4.8 mAh cm⁻² and current density of 5 mA cm⁻², was achieved over 840 cycles (Fig. 6i) and 98.0 Ah high cumulative capacity. For larger capacity, stratified pouch cells were assembled using overlapped 2 pieces of positive electrode and 3 pieces of negative electrode with a size of 5 cm × 5 cm achieving stable operation with 800 mAh total capacity at 800 mA current, demonstrating the application prospect feasibility of HTS for large-scale energy storage (Supplementary Fig. 29).

Discussion

In summary, the hot-press solution is proposed as a versatile and cost-effective strategy for in situ modification of separators with various MOF materials to address dendrite-related issues in Zn negative electrodes. The HTS is turned to be modified by in situ MOF crystals on the fiber surface and without the obstruction of the original pore structure. On the Zn negative electrode, particularly the region obscured by the separator, dendrites, and dead zinc are effectively restrained by the HTS. Furthermore, the mechanisms of the dynamic concentration-regulation process were characterized by involving the guidance of homogeneous nucleation at high concentrations and the promotion of two-dimensional crystal growth at low concentrations attributed to interfacial high concentration and slow diffusion kinetic of HTS. Based on the aforementioned characteristics, the HTS enables a high stability of negative electrode accompanied with a long cycling life of 3000 hours at 2 mA cm⁻², 2 mAh cm⁻², 4900 h at 1 mA cm⁻², 1 mAh cm⁻². For the Zn||I₂ full-cell battery, the HTS allowed for a long cell life of 15000 cycles at 1 A g⁻¹. A 120 mAh Zn||I₂ pouch cell could also realize 840 cycles life and 80 cycles with 800 mAh high capacity, demonstrating the application prospect feasibility of HTS for large-scale energy storage. Through this work, we anticipated that a more efficient and in situ approach to separator modification with MOF materials could provide useful insights into designing low-cost and high-performance separators for AZIBs.

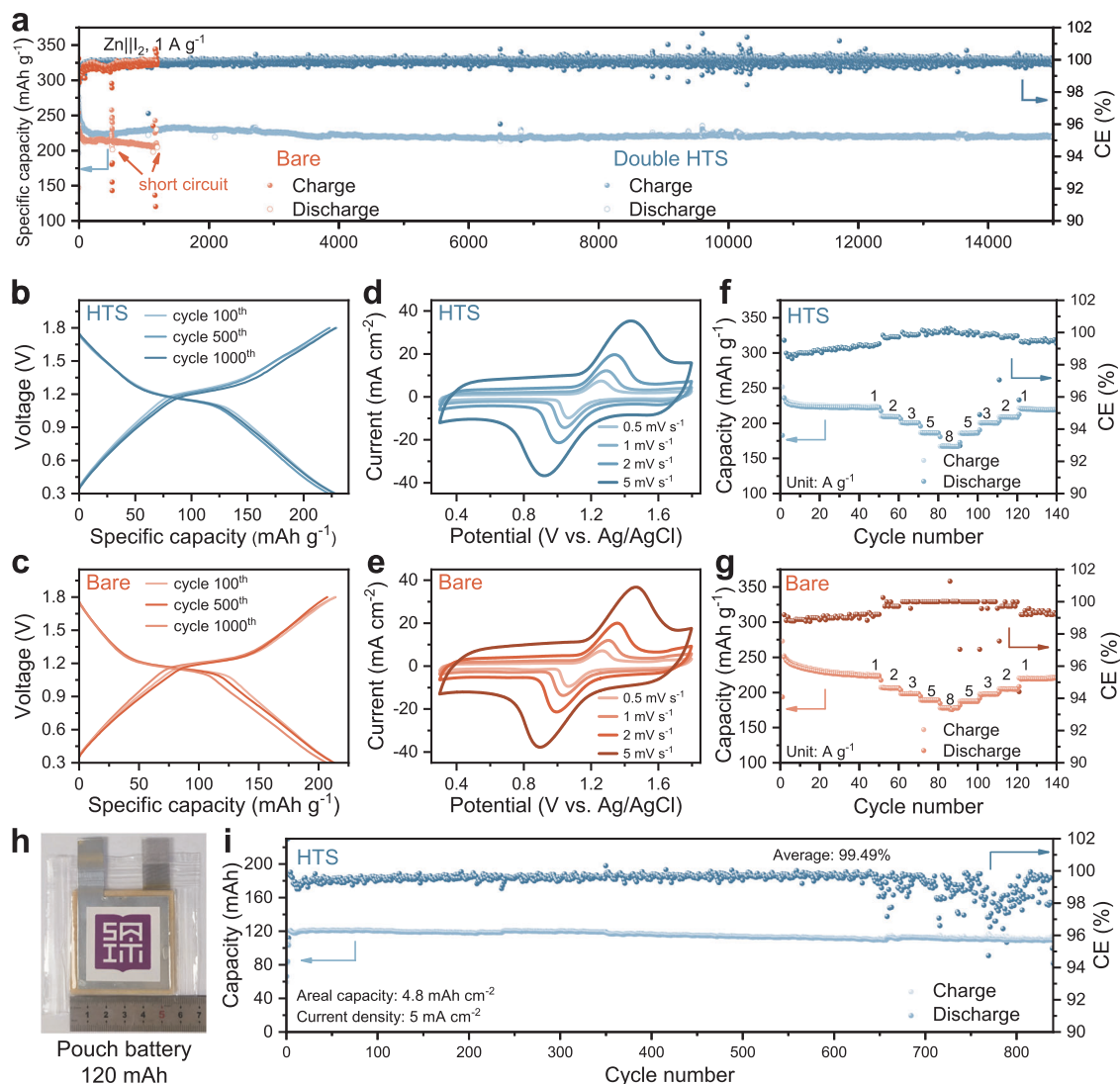


Fig. 6 | Electrochemical performance of Zn||I₂ batteries with HTS. a Cycling performance of Zn||I₂ cells with double HTS and bare separator at the temperature of 25 °C. **b, c** Charge-discharge profiles of Zn||I₂ cells with HTS and bare separator at temperature of 25 °C. **d, e** CV curves at 0.5 - 5 mV s⁻¹ of Zn||I₂ cell with HTS and

bare separator at temperature of 25 °C without iR corrected. **f, g** Rate performance of Zn||I₂ cell with HTS and bare separators at temperature of 25 °C. **h, i** Photograph and cycling performance of Zn||I₂ pouch cells at temperature of 25 °C.

Methods

Preparation of Zn-based hot-press separator (HTS)

37.5 g zinc acetate anhydrous (99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), 47.6 g 2-methylimidazole (98%, Shanghai Aladdin Biochemical Technology Co., Ltd.), and 11.9 g polyethylene glycol (average Mn 4000, Shanghai Aladdin Biochemical Technology Co., Ltd.) were weighted and put into the grinding jar. After mixing for 3 min on an SFM-7 vacuum mixer (Shenzhen Kejing Star Technology Co., Ltd.) at a rotation speed of 320 rpm/min, the uniform mixture was spread on a nonwoven fiber separator (LD-3, Sontara®), and pressed under 200 °C for 30 min. Before use, the nonwoven fiber separator was washed with ethanol (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd.). Then the modified separator was washed in ethanol and deionized water to remove unreacted raw material and finally dried at 60 °C.

Preparation of Co-based hot-press separator (Co-HTS)

37.5 g Co(OAc)₂ (99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), 47.6 g 2-methylimidazole (98%, Shanghai Aladdin Biochemical Technology Co., Ltd.), and 11.9 g polyethylene glycol

(average Mn 4000, Shanghai Aladdin Biochemical Technology Co., Ltd.) were weighted and put into grinding jar. After mixing of 3 min on SFM-7 vacuum mixer (Shenzhen Kejing Star Technology Co., Ltd.) at a rotation speed of 320 rpm/min, the uniform mixture was spread on a nonwoven fiber separator (LD-3, Sontara®), and pressed under 200 °C for 30 minutes. Before use, the nonwoven fiber separator was washed with ethanol (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd.). Then the modified separator was washed in ethanol and deionized water to remove unreacted raw material and finally dried at 60 °C.

Electrode and electrolyte preparation

Zinc trifluoromethanesulfonate (Zn(OTf)₂, 98%, Shanghai Aladdin Biochemical Technology Co., Ltd.) was dissolved in deionized water as 2 M Zn(OTf)₂ solution for the electrolyte in all batteries. Zn foil (100 μm, Wuhan Luojia Yanxin Technology Co., Ltd) was treated with a metal polishing agent (Nihon Maryo Kogyo Co., Ltd.) and soaked in ethanol, and sonicated for ten minutes as the negative electrode. Cu foil was cleaned by ethanol as the positive electrode in Zn||Cu cells. Activated carbon (YP-50, Kuraray Co., Ltd), Ketjen black (Suzhou

Sinero Technology Co., Ltd), and poly(tetrafluoroethylene) (PTFE) powder (Guangdong Canrd New Energy Technology Co., Ltd.) were mixed with a mass ratio of 8:1:1, made from dry film by hot rolling method, and loaded on titanium mesh (Hebei Mengshang Metal Mesh Industry Co., Ltd) as a current collector of positive electrode. I_2 on the current collector was prepared by electrodeposition method with 0.5 M $ZnSO_4$ and 1 M KI mixed solution as electrolyte and Zn foil as counter electrode.

Electrochemical measurements

$Zn||Zn$, $Zn||Cu$, and $Zn||I_2$ cells were assembled in CR-2032 coin-type cells (stainless steel, Guangdong Canrd New Energy Technology Co., Ltd.), using HTS|GF|HTS or bare|GF|bare as separator with 160–200 μ L electrolyte and ensure the separators were completely wetted. The size of the spring is 15.4×1.1 mm. The GF is brought from Whatman™ (1821–110). The cycling performance of negative electrode by galvanostatic charge/discharge tests, rate performance, and Zn^{2+} transference number was used $Zn||Zn$ coin cells with diameter 16 mm separator and 12 mm Zn foil. The electrochemical impedance spectroscopy (EIS) was conducted in a potentiostat mode, and the frequency was between 200 MHz and 100 kHz, and the recording condition was 10 points per decade. Before each test, the cells were rested for 30 min. The cyclic voltammetry (CV) curves (–0.2–0.4 V) and columbic efficiency of the negative electrode were tested in $Zn||Cu$ coin cells with a diameter 16 mm separator, 12 mm Zn foil, and 16 mm Cu foil. The Tafel plots, linear sweep voltammetry (LSV) plots, and potential-capacity curves during Zn nucleation and deposition were tested in a beaker cell with Zn foil as the working and counter electrode, Ag/AgCl electrode as the reference electrode (pre-soaked in 3 M KCl for 12 h for calibration), with 15 mL electrolyte. HTS, or bare separator was unfolded over the working electrode and secured on the backside with double-sided tape. To exhibit the direct results, iR -correction was not used in the 3-electrode cell test. Three tripartite electrode holes on the beaker cells were utilized to ensure the position of electrodes was the same in each test. The active size of working and counter electrodes was 1×1 cm. The cycling performance by galvanostatic charge/discharge tests, CV curves, and rate performance were measured with round zinc foil negative electrode (diameter: 12 mm) and square I_2 positive electrode ($1 \text{ cm} \times 1 \text{ cm}$), with a controlled $\sim 5 \text{ mg cm}^{-2}$ I_2 loading. $Zn||I_2$ full pouch cells were assembled from $5 \text{ cm} \times 5 \text{ cm}$ (or $8 \text{ cm} \times 8 \text{ cm}$) Zn foil negative electrode, $5 \text{ cm} \times 5 \text{ cm}$ (or $8 \text{ cm} \times 8 \text{ cm}$) I_2 positive electrode ($\sim 25 \text{ mg cm}^{-2}$ I_2 loading) with 80–120 μ L cm^{-2} electrolyte and ensure the separators were completely wetted. For coin cells, the positive electrode materials were loaded on a single face of titanium mesh close to the separator, and for pouch cells, those were loaded on a double face of titanium mesh for higher loading. All area-based current densities were calculated by the area of the negative electrode, and specific currents were calculated by the mass of iodine in the positive electrode. The cell assembling and electrochemical measurements were conducted in an air-conditioned room at $25 \pm 0.5^\circ\text{C}$. The cycling performance tests were carried out on the CT3002A LAND battery testing system. The CV, LSV, and EIS curves were tested on a VSP-3e multichannel electrochemical workstation.

Characterizations

X-ray Diffraction (XRD). X-ray diffraction measurements were conducted on a MiniFlex600 diffractometer fitted with Cu-K α X-rays ($\lambda = 1.5406 \text{ \AA}$) radiation at a scan rate of $10^\circ/\text{min}$. Commercial ZIF-8 powder (Shanghai Aladdin Biochemical Technology Co., Ltd.) and commercial ZIF-67 (Nanjing XFANO Materials Tech Co., Ltd) were measured to compare crystal structure.

N_2 adsorption isotherms. N_2 adsorption isotherms were tested on a MicrotracBEL BELSORP MINI X. For pretreatment, the separator

samples were cut into pieces smaller than 2 mm and vacuum degassed for 12 h under 60°C .

Scanning electron microscopy (SEM). The SEM measurements of separators were obtained from Thermo Fisher Scientific Apreo 2 S HiVac under the electron current of 13 pA and accelerating voltage of 2 kV to avoid the charged effect. The SEM results of the negative electrode were through Phenom Pharos G2 Desktop SEM, under 5 kV acceleration voltage. Negative electrodes after cycles were rinsed with deionized water and ethanol. Then the negative electrodes were fast air-drying at room temperature and carefully transferred into an SEM device. The separator and negative electrode samples were stable in the air and treated fast to protect their morphology.

In situ optical observation. The in situ optical image during the deposition process was carried out by DPX M6000-3D Digital Microscope (Deltapix) with MicroElab R-2-CS-TC Optical-electrochemical test cell (Cross-section). To demonstrate the morphology of the sample at a certain depth, an ultra-deep field image was formed from different depths.

X-ray Computed tomography (X-CT). The X-CT was measured by a Phoenix V|tome|x M300 under an accelerating voltage of 140 kV, a current of 180 μ A with a resolution of 3 μ m, and an exposure time of 334 ms. The 3D reconstruction model and cross CT-view were carried out by integrating the results of scans from different angles.

Fourier transform infrared (FTIR). The FTIR spectrums were carried out through an Invenio S FT-IR Spectrometer at reflex mode in the wavenumber range of 400–4000 cm^{-1} . The separator results were tested by directly pressing the separator against the viewing window. The results of the percolate separator were carried out by dropping enough electrolytes on the corresponding separator.

Computational methods. All the density functional theory (DFT) calculations were conducted using the projector-augmented wave (PAW) method within the Vienna Ab initio Simulation Package (VASP) software⁵⁴. The plane-wave cutoff energy of the geometry optimization and adsorption calculations was set to 500 eV. The generalized gradient approximation (GGA) method, specifically the Perdew-Burke-Ernzerhof (PBE)⁵⁵, was utilized as the exchange-correlation function. In addition, the DFT-D3 (Grimme)⁵⁶ was employed to account for the van der Waals interactions. The structure models of PET, cellulose, and ZIF-8 were established based on their chemical composition and previous literature⁵⁷. In the calculations for adsorption energy (E_a), slab models were constructed by using a $2 \times 4 \times 2$ supercell for PET, a $4 \times 3 \times 2$ supercell for cellulose, and a $1 \times 1 \times 1$ conventional cell for ZIF-8, respectively. A 20 $\text{\AA}$ vacuum layer was established along the z -direction of these models. The convergence criteria were set to 10^{-4} eV for total energy and $< 0.03 \text{ eV \AA}^{-1}$ for the force on each atom. Γ -only k -meshes were used for geometry relaxation, allowing all atoms to relax. The E_a was defined as:

$$E_a = E_{\text{slab} + \text{Zn}} - E_{\text{slab}} - E_{\text{Zn}}$$

where $E_{\text{slab} + \text{Zn}}$ represents the total energy of the slab model with an adsorbed Zn atom, E_{slab} is the energy of the free slab model, and E_{Zn} is the energy of a free Zn atom. Furthermore, the E_a calculations incorporated dipole corrections along the z -direction.

Data availability

The data that support the findings of this study are available within the text, including the Methods, and Supplemental information. Raw datasets related to the current work are available from the corresponding author upon request. Source data are provided in this paper.

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Author contributions

C.H. and J.Z. conceived the project. D.W., C.H., C.C., and S.L. designed the experiments. D.W., T.L., S.G., H.L., Q.L., and J.G. synthesized the materials. D.W., T.L., and S.L. did the materials characterizations. S.H. did the theoretical simulations. All authors contributed to the data analysis and discussions. S.H., D.W., and T.L. wrote the manuscript. C.H., J.Z., C.C., S.H., and D.W. revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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