nature portfolio

Peer Review File

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

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This paper validates the method of loading Metal-Organic Framework (MOF) crystals into a fiber separator using a hot-pressing technique. The logical flow of the paper and the organization of the dataset are commendable. It is considered suitable for publication in Nature Communications, given its potential for large-scale applicability, outstanding stability, and performance. However, there are several unresolved questions and missing points that require further clarification and validation. Prior to publication, it is recommended that the authors address the following points.

1. The paper infers that two separators were utilized on either side of the Zn||Zn cell to highlight the effects of HTS. Was a similar approach adopted during full-cell testing? Additionally, how does the introduction of HTS on only one side affect the overall performance?

2. The chemical stability of the fabricated HTS within the electrolyte raises questions. Further verification is needed to determine whether residual components persist after repetitive cycles or if any leaching occurs in the electrolyte.

3. The evaluation of potential side reactions (such as XRD analysis and the hydrogen evolution reaction to identify Zn corrosion) at the Zn interface is lacking when using HTS. Could you investigate these aspects more thoroughly? It is crucial to examine closely which effects contribute to the increase in Coulombic Efficiency (CE) in both half-cells and full-cells.

4. It is interesting to determine whether the introduction of HTS addresses the self-discharge issue in full cells, a recent problem in aqueous Zn-metal batteries.

5. There are minor issues present that require rectification. These sections should be corrected (refer to page 2, line 32 of the main text and the numbering issue in Supplementary Fig. 3).

Reviewer #2 (Remarks to the Author):

This paper largely focuses on a new all-in-one processing approach necessary to incorporate MOFs into separator materials. The characterization of the separator and performance of the zinc cells is comprehensive and well-presented, but I don't feel the approach is suitably novel for the broad audience in Nature Communications. MOFs have previously been explored for aqueous zinc batteries, as discussed in the paper. And the synthesis routes for ZIF crystals appears to be fairly mature. Also it is unclear what the MOF loading is on the separator; if it is significant, then I don't see how this approach fits with the low cost advantages of aqueous zinc ion batteries. The performance data is impressive, but not

significantly better than previous papers (for instance, like those listed in a recent review on AZIB separators here: DOI j.enrev.2022.100005). In general, I see this as a high quality paper, but perhaps better suited in a more specialized journal for battery researchers.

Reviewer #3 (Remarks to the Author):

The authors developed an anti-dendrite hot-pressing separators (HTS), in which MOF precursors were firstly spread on nonwoven matrix, followed by a hot-pressing process. This method is indeed simple and mass-producible. Based on the HTS separators, the batteries performance also has an obviously improvement. Moreover, according to the test results, the authors put forward a new mechasim--"staged deposition". Nevertheless, I think the article quality is not up to the level of Nature Communications. The concerns are as follows:
Q1: As for how MOF plays a role in this work, the authors say that it mainly uses its rich nitrogen-containing functional group and high specific surface area, which has a strong attraction to zinc ions. On this point, MOFs and other nitrogen-containing compounds have also been mentioned to modulate Zn2+ ions in many articles, so this property is not new here. The author also mentions that this results in "staged deposition behavior" and presents the deposition curves shown in Figures 4i, 5c. But through what specific working mechanism does this HTS separators to form "staged deposition behavior"? It seems that only nitrogen-containing functional groups interact with zinc ions was referred in this paper, but if so, why don't other papers on MOFs or nitrogen-containing compounds show curves similar to Figure 4i or 5c?

Q2: According to the information provided in this paper, this "staged deposition behavior" seems to only occur under a small current. Similar information is also reflected in Fig.4i: When the current is 2 mA cm-2, the "staged deposition" phenomenon no longer exists. If only at a small current can have this effect, then its practical application is of little significance.

Q3: In this manuscript, the authors described that Zn anode tends to develop (002)Zn orientation under (0.1 ~ 1.0)iL, however, the test results show that with the HTS, the limit current is decreased from 109.9 mA to 14.3 mA. Although this is a significant drop, 14.3 is still a long way from the required 0.1-1.0. Therefore, this explanation of the HTS-induced (002)Zn is not appropriate. In addition, why is the limiting current greatly reduced in the presence of HTS? It is more hoped to explain the cause of (002)Zn from the most fundamental mechanism of action, rather than using one test performance to explain another.

Q4: Experiments on in-situ optical microscopes are not rigorous. Since the effect of the separator on zinc ion deposition is studied, the situation of the part covered by the separator should be observed. However, the images in the manuscript show that the separator is not aligned with the edge of the section but at a distance. As for Figure 3c, although uneven deposition is observed, it is distributed on the surface of the cross section or where there is no separator.

Q5: In this work, the author prepared a kind of MOF-modified nonwoven separator, but used

HTS||GF||HTS structure when testing symmetric batteries. This is not appropriate and only one piece of HTS should be used.

Q6: Although the THS-based symmetric battery has a significant increase in cycle life, its overpotential is too large, nearly 2-3 times the original. It is acceptable to increase some, but if increases too much, it is necessary to consider whether such modification is worthwhile.

Q7: The explanation that HTS improves the transference number of zinc ions is that a large number of zinc ions are attracted to nitrogen sites. If so, it should not be conducive to zinc ion transport, and how can the transference number be increased?

Q8: In Figure 2g, in addition to having peaks corresponding to ZIF-8, HTS also shows additional peaks. What do these peaks represent? Whether the battery performance is affected?

Q9: About the analysis of FTIR: The containment of water activity could be attributed to nitrogen sites in HTS that attract Zn2+ ions and reconfigure the solvation networks. What does the reconfigured solvation network look like? A little more detail is needed.

Q10: It is recommended that Figures 5c and 5d use data with the same number of cycles, which is more conducive to observing and comparing deposition condition in the same period.

Response to Reviewers' Comments

Dear Reviewers:

Thank you very much for reviewing this manuscript entitled "*Anti-dendrite separator enabling staged deposition behavior for highly-stable Zn anode*" (Manuscript ID: NCOMMS-24-05968). All these comments and advice are constructive and valuable to us for refining this research and improving the manuscript. We have added experimental data and textual corrections to solve those concerns point-by-point as follows. All the revisions are highlighted in the manuscript and supplementary information with a yellow background for supplemented text and a red box for replaced figures.

==========

Response to reviewers' comments

Reviewer #1:

This paper validates the method of loading Metal-Organic Framework (MOF) crystals into a fiber separator using a hot-pressing technique. The logical flow of the paper and the organization of the dataset are commendable. It is considered suitable for publication in Nature Communications, given its potential for large-scale applicability, outstanding stability, and performance. However, there are several unresolved questions and missing points that require further clarification and validation. Prior to publication, it is recommended that the authors address the following points.

Response: We appreciate Reviewer#1 for the valuable comments and constructive suggestions to improve the quality of our manuscript. We are trying to solve these concerns point-by-point as follows.

1. The paper infers that two separators were utilized on either side of the Zn||Zn cell to highlight the effects of HTS. Was a similar approach adopted during full-cell testing? Additionally, how does the introduction of HTS on only one side affect the overall performance?

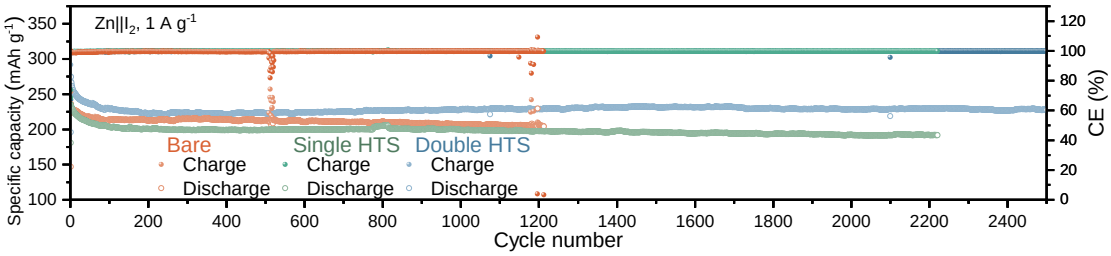
Response: We greatly appreciate the reviewer's valuable comments and suggestions.

Following the reviewer's suggestion, we supplemented the full-cell test with a single HTS on the anode side as shown in Supplementary Fig. 25. The result indicates that a single HTS near to anode also processes the function of anti-dendrite. However, the absence of HTS at the cathode side causes a larger capacity decrease. Quantitatively, the capacity retention ratios were calculated as represented in Supplementary Table 4, excluding the initial 100 cycles as the activation process. We

find higher capacity retention ratios in the double HTS group (99.6%) than that of single HTS (97.8%), and bare separator (96.7%). This phenomenon is attributed to the fact that MOF materials can inhibit the shuttle of iodine from the cathode (Adv. Mater., 2020, 32, e2004240). Therefore, two HTS were utilized on both sides in all the full-cell testing, achieving 15000 cycles in coin-cell and 840 cycles in pouch-cell with a high capacity of 120 mAh.

We have revised the manuscript accordingly. ***Revisions in the manuscript:***

"…In sharp contrast, the full-cell batteries with GF at the middle and double HTS separator close to both anode and cathode (marked as double HTS) exhibite an extended lifespan of over 15000 cycles, which can be attributed to the high stability of the anode. Full cells with single HTS close to the anode and GF close to the cathode (marked as single HTS) were tested to analyze the effect of HTS on the I_2 cathode, 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 MOFs[53]."



Supplementary Fig. 25 | Cycling performance of Zn||I_2 cells with double HTS, single HTS, and bare separator.

Supplementary Table 4 | Charge capacity after 100 cycles/1000 cycles, and capacity retention ratio after 1000 cycles of full-cell batteries with double HTS, single HTS, and bare separator, respectively

Separator	Charge capacity of 100th (mAh g^{-1})	Charge capacity of 1000^{th} (mAh g^{-1})	Capacity retention ratios after 1000 cycles
Double HTS	229.6	228.6	99.6%
Single HTS	203.8	199.3	97.8%
bare	214.3	207.2	96.7%

Reference added in manuscript:

53. Yang H, Qiao Y, Chang Z, Deng H, He P, Zhou H. A Metal-Organic Framework as a Multifunctional Ionic Sieve Membrane for Long-Life Aqueous Zinc-Iodide Batteries. *Adv. Mater.* **32**, 2004240 (2020).

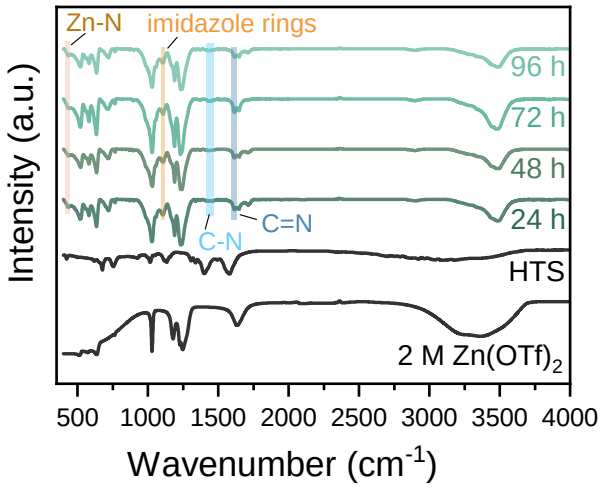
2. The chemical stability of the fabricated HTS within the electrolyte raises questions. Further verification is needed to determine whether residual components persist after repetitive cycles or if any leaching occurs in the electrolyte.

Response: We greatly appreciate the reviewer's professional insight.

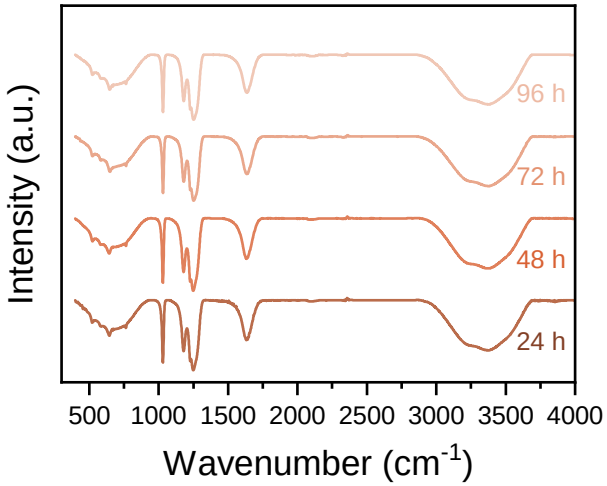
Following the reviewer's advice, further experimentally verification is discussed as follows. To verify the stability of MOF materials on HTS, the HTS was tested using FTIR spectrum after cycling in Zn||Zn cells for 24 ~ 96 hours under 1 mA cm^{-2} and 1 mAh cm^{-2}, as shown in Supplementary Fig. 12. HTS after different cycle times exhibits the same chemical structure, which considered as the combination spectrum of initial HTS and 2 M $Zn(OTf)_2$, which is attributed to the electrolyte residue in the separator. The key transmission peaks of Zn−N, C−N, C=N bonds, and imidazole rings well remained after cycling for 96 hours. For the possible leaching of MOF in the electrolyte, we tested the FTIR spectra of the electrolytes with the HTS immersed for 24 ~ 96 hours, as shown in Supplementary Fig. 13. The FTIR spectra reveal no additional peaks during this period, suggesting that there is no leaching occurring within the electrolyte. Consequently, the HTS possesses good chemical stability during repetitive cycles and the MOFs loaded on HTS are stable for a long time in the electrolyte environment without dissolution and leaching.

We have revised the manuscript accordingly. Revisions in the manuscript:

"…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."



Supplementary Fig. 12 | FTIR spectra of 2 M $Zn(OTf)_2$, initial HTS, and HTS after cycles for 24 ~ 96 hours at 5 mA cm^{-2} and 5 mAh cm^{-2}.



Supplementary Fig. 13 | FTIR spectra of 2 M $Zn(OTf)_2$ electrolytes with HTS immersing for 24 ~ 96 hours.

3. The evaluation of potential side reactions (such as XRD analysis and the hydrogen evolution reaction to identify Zn corrosion) at the Zn interface is lacking when using HTS. Could you investigate these aspects more thoroughly? It is crucial to examine closely which effects contribute to the increase in Coulombic Efficiency (CE) in both half-cells and full-cells.

Response: Thanks for the reviewer's constructive suggestion.

Following the reviewer's reminder, we have analyzed the by-product diffraction signal and HER potential of the LSV curves, as shown in Supplementary Figs. 9, and 10.

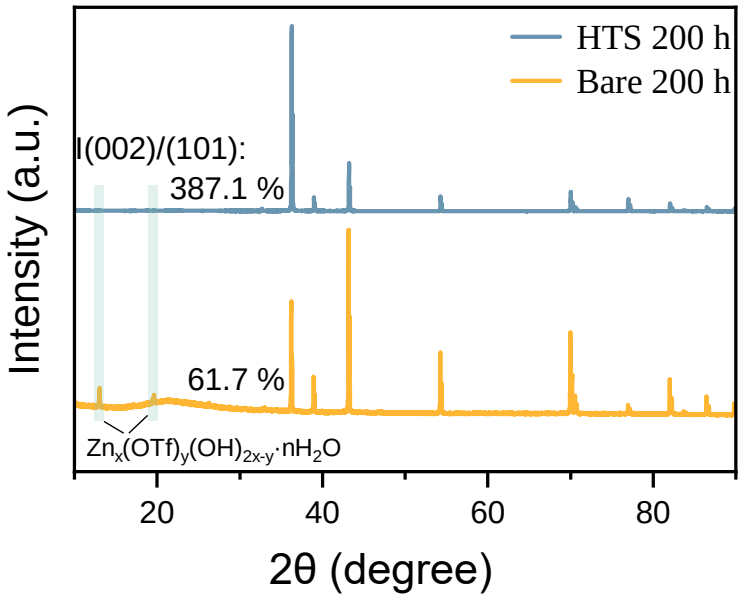
(1) To explore the by-products on the Zn interface, we supplemented the XRD data of the Zn anode after cycling for 200 h as shown in Supplementary Fig. 9. As the cycle time increased, significant peaks of by-products were found on the surface of Zn anode when using the bare separator. In sharp contrast, the Zn interface remained pure Zn peaks after 200 h of cycling when HTS was employed as the separator. More appealingly, it is found the intensity ratio of $(002)_{Zn}/(101)_{Zn}$ 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.

(2) For the hydrogen evolution reaction (HER) analysis, we conducted an LSV test in a 1 M Na_2SO_4 electrolyte to evaluate the HER potential on the anode side. As shown in Supplementary Fig. 10, the Zn anode 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.

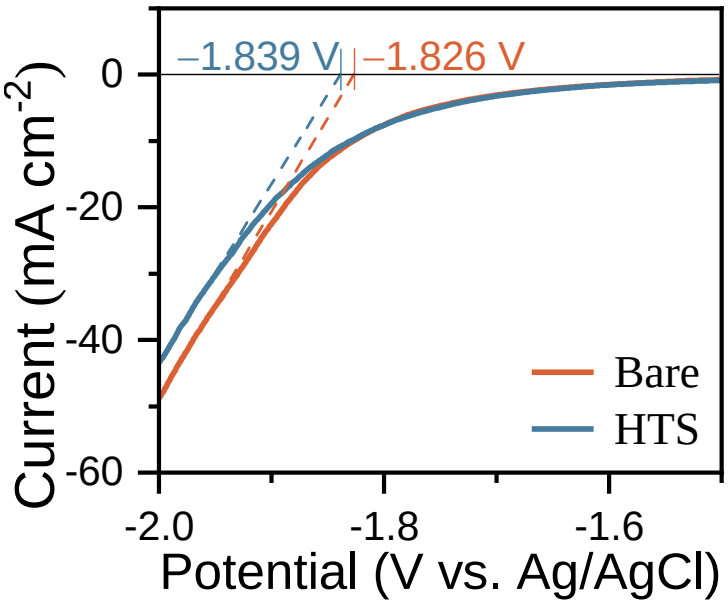
We have added the description and dataset in the manuscript. ***Revisions in the manuscript:***

"The side reactions on the anode were explored through Zn surface phase analysis and hydrogen evolution reaction (HER) test. As shown in Supplementary Fig. 9, after a long cycle time of 200 hours at 1 mA cm^{-2}, 1 mAh cm^{-2}, the surface compositions of Zn with HTS exhibit significant differences, compare 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 $Zn_x(OTf)_y(OH)_{(2x-y)}$[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 $(002)_{Zn}/(101)_{Zn}$ 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 LSV test in a 1 M Na_2SO_4 electrolyte to evaluate the HER potential on the anode side, as shown in Supplementary Fig. 10. The Zn anode 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."



Supplementary Fig. 9 | XRD patterns of Zn anode with HTS and bare separator after 100 cycles at 1 mA cm^{-2}, 1 mAh cm^{-2}.



Supplementary Fig. 10 | LSV plots of Zn anode with HTS and bare separator in 1 M Na_2SO_4 electrolyte at scanning speed of 1 mV s^{-1}, using Zn foil as the working electrode, Pt foil as the

counter electrode, Ag/AgCl electrode as the reference electrode.

References added in manuscript:

45. Liu Z, *et al.* Interfacial Engineering of Zn Metal via a Localized Conjugated Layer for Highly Reversible Aqueous Zinc Ion Battery. *Angew. Chem. Int. Ed.* **63**, e202319091 (2024).

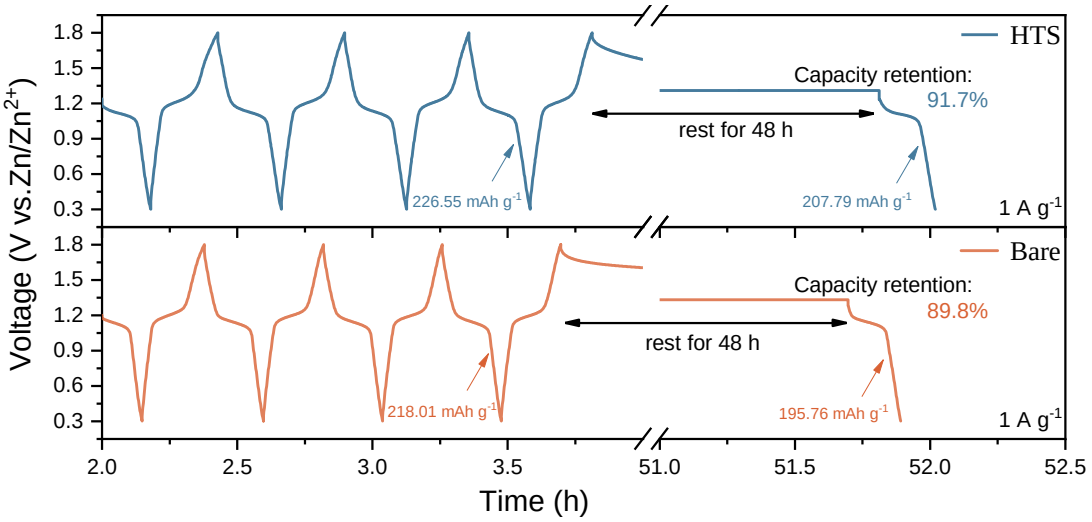
4. It is interesting to determine whether the introduction of HTS addresses the self-discharge issue in full cells, a recent problem in aqueous Zn-metal batteries.

Response: We sincerely appreciate the insightful question raised by the reviewer.

We agree with the reviewer that the self-discharge issue is more prominent in aqueous batteries. Following the reviewer's suggestion, we explored the self-discharge issue by setting a long rest step (48 h) after a fully charged step. After resting, the batteries were fully discharged to 0.3 V and compared their discharge capacity. As shown in Supplementary Fig. 27, the discharged capacity retention ratio of Zn||I_2 battery after a 48-hour rest is 91.7% with an HTS, which is higher than the capacity retention ratio (89.8%) in the full-cell battery with bare separator. Therefore, the introduction of HTS slightly suppresses the self-discharge issue in aqueous Zn-based full-cells.

We have revised the manuscript accordingly. Revisions in the manuscript:

"...To verify the capacity retention and self-discharge problem, Zn||I_2 cells were fully charged to 1.8 V and rested for 48 hours, then fully discharged to 0.3 V (The charged and discharged curves are shown in Supplementary Fig. 27). The capacity retention ratio of Zn||I_2 cell with HTS is 91%, higher than that of the cell with bare separator."



Supplementary Fig. 27 | Voltage-time profiles of Zn||I_2 full-cell batteries with HTS and bare separator at a current of 1 A g^{-1}. Both of the tests have set a 48-hour rest step between the charge and discharge processes.

5. There are minor issues present that require rectification. These sections should be corrected (refer to page 2, line 32 of the main text and the numbering issue in Supplementary Fig. 3).

Response: We greatly appreciate the reminder and sincerely apologize for these oversights.

Following the reviewer's suggestion, we have carefully rechecked all the content for the format error, listed as follows.

(1) Page 2, line 32: "120 mAh"

(2) Supplementary Fig. 3: "EDS energy spectra of HTS (a), Co-HTS (b), and bare separator (c)."

(3) Page 13, Same Y-axis titles of Fig. 4g, h: "Current density (mA cm^{-2})"

(4) Page 21, Same Y-axis titles of Fig. 6b, c: "Voltage (V vs. Zn/Zn^{2+})"

(5) Page 23, line 454: "32 × 28 cm"

(6) All the format of "bare separator" in text have been corrected to all lowercase.

(7) All the equations have been cited as "Equation (x)", following the format standard of *Nature Communications*.

(8) All the description of Zn||Zn cells test conditions have been corrected to the same format: "x mA cm^{-2}, x mAh cm^{-2}"

The manuscript has been revised accordingly.

Reviewer #2:

This paper largely focuses on a new all-in-one processing approach necessary to incorporate MOFs into separator materials. The characterization of the separator and performance of the zinc cells is comprehensive and well-presented, but I don't feel the approach is suitably novel for the broad audience in Nature Communications. MOFs have previously been explored for aqueous zinc batteries, as discussed in the paper. And the synthesis routes for ZIF crystals appears to be fairly mature. Also it is unclear what the MOF loading is on the separator; if it is significant, then I don't see how this approach fits with the low cost advantages of aqueous zinc ion batteries. The performance data is impressive, but not significantly better than previous papers (for instance, like those listed in a recent review on AZIB separators here: DOI j.enrev.2022.100005). In general, I see this as a high quality paper, but perhaps better suited in a more specialized journal for battery researchers.

Response: We sincerely appreciate Reviewer#2 for his/her confirmation that "the characterization of the separator and performance of the zinc cells is comprehensive and well-presented". We also thank the reviewer's valuable comments and constructive suggestions to improve the quality of our manuscript. We carefully divide the reviewer's concerns into three points and try to address these concerns point-by-point as follows:

1. MOFs have previously been explored for aqueous zinc batteries, as discussed in the paper. And the synthesis routes for ZIF crystals appears to be fairly mature.

Response: We greatly appreciate the reviewer's comment and apologize for not making the novelty of this HTS separator clear.

We agree with the reviewer that the synthesis routes of pure ZIF materials have been reported, which provides reliable reaction methods and raw materials for the scalable synthesis of MOF material. Furthermore, in previous research, the main ways to utilize MOF materials is by simply slurry coating, wherever the MOFs were loaded on the Zn surface or one side of a separator within a limited thickness, for example, 1 μm (Adv. Sci. 2020, 7, 2002173). This thin MOF coating takes the role to homogenize Zn^{2+} flux distribution. Moreover, the slurry coating strategy is limited in coating thickness, otherwise will cause an unacceptable increase of overpotential and detachment of the coating layer during repeated cycling.

In comparison, we developed a hot-pressing strategy as a cheaper and more efficient way to modify ZIFs in zinc ion battery separator. By using this hot-pressing strategy, we enlarged the distribution of MOFs in a ~160 μm thick space, making the functional groups of MOF contact with the electrolyte extensively and playing a significant regulatory role (1μm vs. ~160 μm). Leveraging the long-distance distribution, the high active surface area, and nitrogen-containing functional groups of MOFs, the hot-press separator (HTS) achieves staged deposition behavior by dynamic concentration control. The concentration control process induce the uniform deposition of Zn anode through a series of characterization tests and theoretical derivation. More importantly, we use ZIF-8 material as a typical example to verify the application of the hot-pressing solution. By changing the raw material, we can successfully load ZIF-67 MOF on the nonwoven substrate (Co-HTS, Supplementary Figs. 4−6), demonstrating its simple, universal, and mass-producible properties.

The mentioned key differences are signaled in Fig. R1, to further visually demonstrate the novelty of HTS.

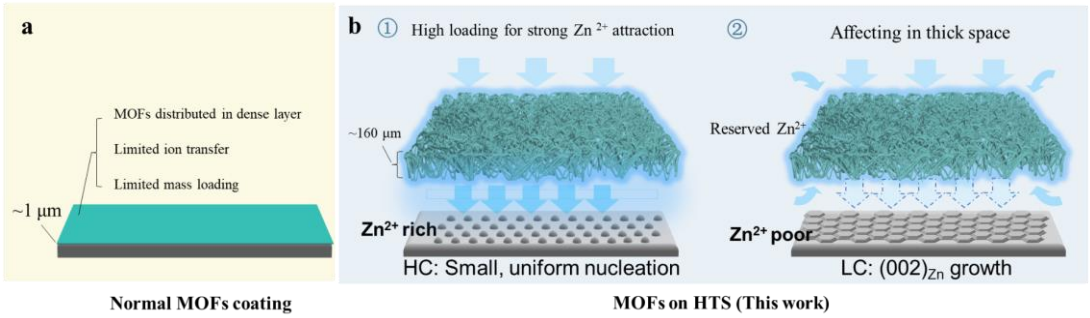


Fig. R1 | The key differences between previous MOFs coating (**a**) and HTS (**b**) in AZIBs.

Following the reviewer's suggestion, we have further highlighted the main idea and novelty of this work in the introduction section. ***Revisions in the manuscript:***

"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 the thick loading, the hot-press separator (HTS) achieves staged deposition behavior by dynamic concentration control."

2. Also it is unclear what the MOF loading is on the separator; if it is significant, then I don't see how this approach fits with the low cost advantages of aqueous zinc ion batteries.

Response: We sincerely thank the reviewer for the valuable suggestion.

Following the reviewer's suggestion, we conducted XRD measurement and revealed that the MOF materials on the separator are ZIF-8 (zinc 2-methylimidazole) (Fig. 2g). The mass loading of ZIF-8 is ~4 mg cm^{-2}. It is worth mentioning that all the raw materials to synthesize HTS are low-cost and readily available as shown in Supplementary Table 1. In addition, the matrix separator where MOFs are loaded is just a kind of normal nonwoven for wiping, with a price of only 5.3 CNY m^{-2}. The calculated cost of HTS and GF are shown in Supplementary Fig. 8. The price of glass fiber can be as high as 2257 CNY m^{-2} (Cytiva, Whatman GF/B 1821-150), which is ~16 times higher than that of HTS. These data suggest that as-prepared HTS fits with the low-cost advantage of the aqueous zinc ion batteries.

More importantly, we use ZIF-8 material as a typical example to verify the application of the hot-pressing solution. By changing the raw material, we can successfully load ZIF-67 MOF on the nonwoven substrate (Co-HTS, Supplementary Figs. 4–6) , demonstrating its' simple, universal, and mass-producible properties.

We have supplemented this information accordingly. ***Revision in manuscript:***

"...In addition, the unit prices of HTS was evaluated. 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."

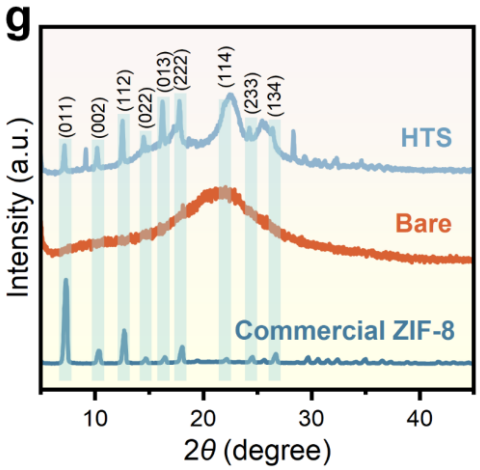
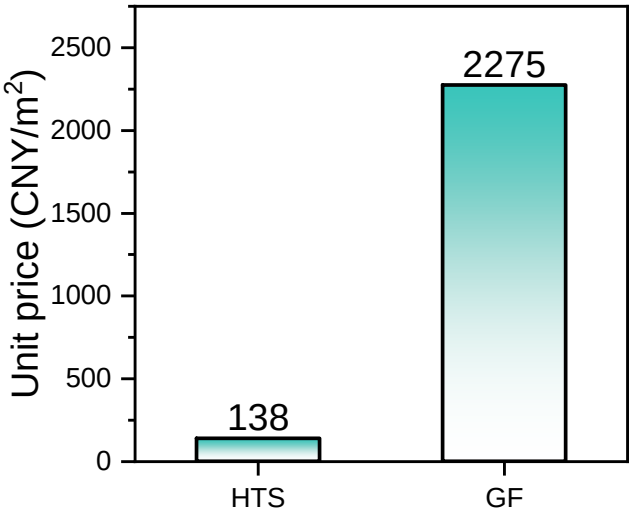


Fig. 2 | g XRD patterns of HTS, bare separator, and commercial ZIF-8.

Supplementary Table 1 | The unit prices of raw materials used in the synthesis of HTS

Raw materials	Stock No.	Unit price in bulk (CNY kg^{-1})	Addition (mg cm^{-2})	Unit price on HTS (CNY m^{-2})
2-methylimidazole (Aladdin, 98%)	M104839	143	53	75.8
Zinc acetate anhydrous (Aladdin, 99%)	Z111245	122	42	51.2
Polyethylene glycol (Aladdin, Mn 4000)	P103724	43	13	5.6
Nonwoven (Sontara)	LD-3	/	/	5.3



Supplementary Fig. 8 | Calculated unit price of HTS and GF separator.

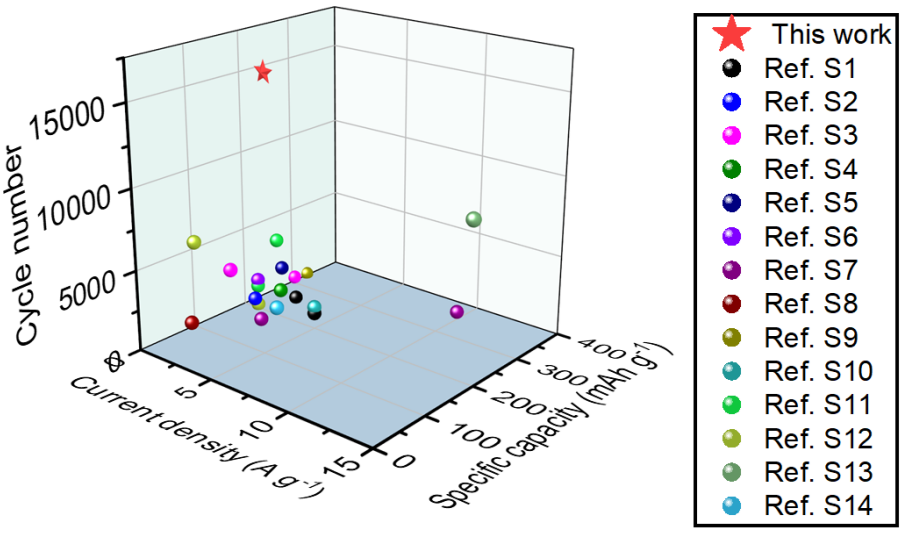
3. The performance data is impressive, but not significantly better than previous papers (for instance, like those listed in a recent review on AZIB separators here: DOI j.enrev.2022.100005).

Response: We sincerely thank the reviewer for pointing this out.

Following the reviewer's suggestion, we have carefully compared the Zn||Zn cell performance in the mentioned literature (DOI j.enrev.2022.100005). It is found that the longest cycle life under a current of 1 mA cm^{-2} is 2000 hours (Energy Storage Materials 44 (2022) 57–65) commented in the review. In our work, the cycle life is up to **4900 hours** (Supplementary Fig. 24), which is higher than the reported values. In addition, to illustrate the exceptional electrochemical properties of HTS, we also compared the cycle life of full-cell batteries with HTS and other reported typical works on separators used in AZIBs. The properties comparison is shown in Supplementary Fig. 28 and Supplementary Table 5. These results indicate that HTS processes ideal promotion on stable AZIBs.

We have supplemented the performance comparison in the manuscript. ***Revisions in the manuscript:***

"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."



Supplementary Fig. 28 | The comparison of cycling performance of full-cell batteries using HTS and other previous separator reports.

Supplementary Table 5 | The comparison of cycling performance of full-cell batteries using HTS and other previous separator reports.

Separator	Current density ($A\ g^{-1}$)	Specific capacity ($mAh\ g^{-1}$)	Cycle number	Ref.
HTS	1	220	15000	This work
PVDF@PDA	2	250	300	S1
	5	200	1000	
PNGF	1.5	180	1100	S2
NbN@GF	0.2	300	400	S3
	2	120	4000	
CCM	3	190	2000	S4
P/FS-Z	1	250	2000	S5
Sulfonic cellulose/graphene	1	200	1900	S6
AgNWs/BC Janus	3	150	700	S7
	10	350	500	
Bamboo cellulose membrane	1	70	1000	S8

BPE	0.1	330	200	S9
MXene/nanoporous NiO separator	5	200	1400	S10
Sulfonated cellulose	1	200	1500	S11
	1	240	4000	
Zr-CNF	1	200	250	S12
	1	80	6000	
SZ	15	190	10000	S13
HSOF	5	125	2500	S14

References added in Supplementary Information:

S1. Liu Y*, et al.* A functionalized separator enables dendrite-free Zn anode via metal-polydopamine coordination chemistry. *InfoMat* **5**, e12374 (2023).

S2. Zhang Y, Zeng Z, Yang S, Zhang Y, Ma Y, Wang Z. A nanocellulose-mediated, multiscale ion-sieving separator with selective Zn^{2+} channels for durable aqueous zinc-based batteries. *Energy Stor. Mater.* **57**, 557−567 (2023).

S3. Hu Q*, et al.* Redistributing zinc-ion flux by work function chemistry toward stabilized and durable Zn metal batteries. *Energy Environ. Sci.* **17**, 2554−2565 (2024).

S4. Zhang Y, Liu Z, Li X, Fan L, Shuai Y, Zhang N. Loosening Zinc Ions from separator boosts stable Zn plating/striping behavior for aqueous zinc ion batteries. *Advanced Energy Materials* **13**, 2302126 (2023).

S5. Yao L, Wang G, Zhang F, Chi X, Liu Y. Highly-reversible and recyclable zinc metal batteries achieved by inorganic/organic hybrid separators with finely tunable hydrophilic–hydrophobic balance. *Energy Environ. Sci.* **16**, 4432−4441 (2023).

S6. Zhang X*, et al.* An ion-sieving janus separator toward planar electrodeposition for deeply rechargeable Zn-metal anodes. *Adv Mater* **34**, e2205175 (2022).

S7. Zheng Z, Guo S, Yan M, Luo Y, Cao F. A functional Janus ag nanowires/bacterial cellulose separator for high-performance dendrite-free zinc anode under harsh conditions. *Adv. Mater.* **35**, 2304667 (2023).

S8. Fu J, Wang H, Xiao P, Zeng C, Sun Q, Li H. A high strength, anti-corrosion and sustainable separator for aqueous zinc-based battery by natural bamboo cellulose. *Energy Stor. Mater.* **48**, 191−191f (2022).

S9. Zhu J, Yang M, Hu Y, Yao M, Chen J, Niu Z. The construction of binary phase electrolyte interface for highly stable zinc anodes. *Adv. Mater.* **36**, 2304426 (2024).

S10. An Y*, et al.* Highly reversible Zn metal anodes enabled by freestanding, lightweight, and zincophilic mxene/nanoporous oxide heterostructure engineered separator for flexible Zn-MnO_2 batteries. *ACS Nano* **16**, 6755−6770 (2022).

S11. Zhou W*, et al.* Ion-sieving effect enabled by sulfonation of cellulose separator realizing dendrite-free Zn deposition. *Adv. Funct. Mater.* 2315444 (2024), doi:10.1002/adfm.202315444.

S12. Yang S*, et al.* Designing anti-swelling nanocellulose separators with stable and fast ion transport channels for efficient aqueous zinc-ion batteries. *Adv Funct. Mater.* **33**, 2304280 (2023).

S13. Qin Y, Wang X. Preventing dissolution of cathode active materials by ion-anchoring zeolite-based separators for durable aqueous zinc batteries. *Angew. Chem. Int. Ed.* **63**, e202315464 (2024).

S14. Fu M*, et al.* Global "interface-space" dual-modulation by functional supramolecules organic frameworks on aqueous zinc-ion batteries. *Adv. Funct Mater.* **34**, 2311680 (2024).

Reviewer #3:

The authors developed an anti-dendrite hot-pressing separators (HTS), in which MOF precursors were firstly spread on nonwoven matrix, followed by a hot-pressing process. This method is indeed simple and mass-producible. Based on the HTS separators, the batteries performance also has an obviously improvement. Moreover, according to the test results, the authors put forward a new mechanism--"staged deposition". Nevertheless, I think the article quality is not up to the level of Nature Communications. The concerns are as follows:

Response: We appreciate Reviewer#3 for his/her affirmative comments and the constructive suggestions to improve the quality of our manuscript. We are trying to solve these concerns point-by-point as follows.

1. As for how MOF plays a role in this work, the authors say that it mainly uses its rich nitrogen-containing functional group and high specific surface area, which has a strong attraction to zinc ions. On this point, MOFs and other nitrogen-containing compounds have also been mentioned to modulate Zn^{2+} ions in many articles, so this property is not new here. The author also mentions that this results in "staged deposition behavior" and presents the deposition curves shown in Figures 4i, 5c. But through what specific working mechanism does this HTS separators to form "staged deposition behavior"? It seems that only nitrogen-containing functional groups interact with zinc

ions was referred in this paper, but if so, why don't other papers on MOFs or nitrogen-containing compounds show curves similar to Figure 4i or 5c?

Response: We greatly appreciate your careful guidance and apologize for not making the novelty clear.

We agree with the reviewer that MOFs and the attraction of nitrogen-containing groups with Zn^{2+} has been identified, which provides reliable reaction methods and raw materials for the scalable synthesis of MOF. Furthermore, in previous research, the main ways to utilize MOF materials is by simply slurry coating, wherever the MOFs were loaded on the Zn surface or one side of a separator within a limited thickness, for example, 1 μm (Adv. Sci. 2020, 7, 2002173). This thin MOF coating takes the role to homogenize Zn^{2+} flux distribution. Moreover, the slurry coating strategy is limited in coating thickness, otherwise will cause an unacceptable increase of overpotential and detachment of the coating layer during repeated cycling.

In comparison, we developed a hot-pressing strategy as a cheaper and more efficient way to modify ZIFs in zinc ion battery separator. By using this hot-pressing strategy, we enlarged the distribution of MOFs in a ~160 μm thick space, making the functional groups of MOF contact with the electrolyte extensively (1μm vs. ~160 μm) and playing a significant regulatory role. The mass loading of ZIF-8 is ~4 mg/cm^{-2}. Leveraging the long-distance distribution (~160 μm), the high active surface area, and the nitrogen-containing functional groups of MOFs, the hot-press separator (HTS) achieves staged deposition behavior by dynamic concentration control. The concentration control process induces the uniform deposition of Zn anode through a series of characterization tests and theoretical derivation. More importantly, we use ZIF-8 material as a typical example to verify the application of the hot-pressing solution. By changing the raw material, we can successfully load ZIF-67 MOF on the nonwoven substrate (Supplementary Figs. 4−6), demonstrating its simple, universal, and mass-producible properties.

The mentioned key differences are signaled in Fig. R1, to further visually demonstrate the novelty of HTS.

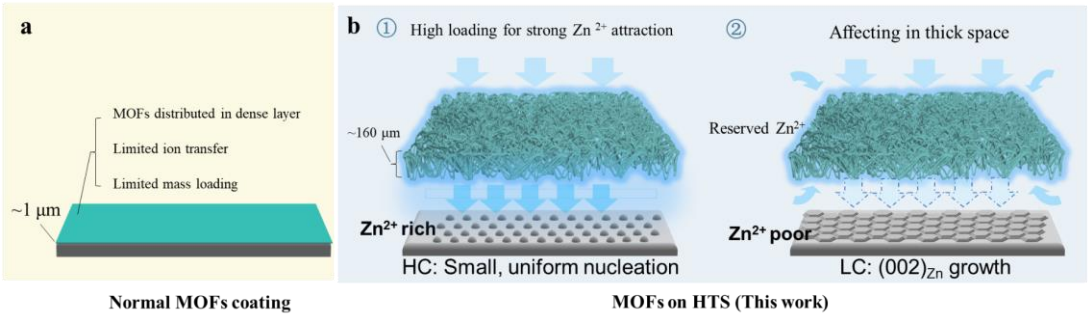


Fig. R1 | The key differences between previous MOFs coating (**a**) and HTS (**b**) in AZIBs.

Following the reviewer's suggestion, we have further highlighted the main idea and novelty of this work in the introduction section. ***Revisions in the manuscript:***

"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 the thick loading, the hot-press separator (HTS) achieves staged deposition behavior by dynamic concentration control."

2. According to the information provided in this paper, this "staged deposition behavior" seems to only occur under a small current. Similar information is also reflected in Fig.4i: When the current is 2 mA cm^{-2}, the "staged deposition" phenomenon no longer exists. If only at a small current can have this effect, then its practical application is of little significance.

Response: We sincerely thank the reviewer for the insightful comments.

We agree with the point that available current is important in batteries. Firstly, based on the enhanced Zn–N peak in FTIR results (Fig. 4a) and higher transference number of Zn^{2+} (more detailed discussion about t(Zn^{2+}) are supplemented in following Q7), we consider that the initial state with HTS is high concentration state of Zn^{2+} due to the strong attraction of nitrogen-containing groups with Zn^{2+}. Secondly, after the first stage under 1 mA cm^{-2} with the depletion of Zn^{2+}, the second stage is attributed to the densely growth of Zn crystal. As the electrodeposition current increases, the nucleation overpotential increases, and the consumption of zinc ion concentration

accelerates, thus shortening the nucleation stage (i.e., the HC stage). Therefore, the first stage of high concentration (HC) is shortened and replaced with a longer low concentration (LC) stage, as shown in following Fig. R2. From Equation (7), we propose that lower concentration is related to a larger critical nucleus radius. Thus, under the large current conditions, the long LC stage stands for a dense deposition of Zn, which is beneficial for the anti-dendrite effect.

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

To further prove this point, further morphology information under different currents is supplemented as follows:

(1) Morphology result: We add the SEM surface morphology of the Zn anode under different currents to support this conclusion as shown in Supplementary Fig. 20. Under the current density of 1 mA cm^{-2} conditions, it is observed that the deposition of Zn tends to small crystal grain, which consist with a long HC stage. When the current density increases to 2 mA cm^{-2}, the Zn grains start to grow bigger and denser morphology. Until at a current density of 5 mA cm^{-2}, the growth of Zn forms intact $(002)_{Zn}$ orientation (Fig. 3b).

(2) XRD result: The XRD results of the Zn anode under different currents also reveal the same pattern, as shown in Supplementary Fig. 21. The peak intensity ratio of $(002)_{Zn}$ and $(101)_{Zn}$ is gradually increased with the rise in current density, attributed to the longer LC stage under higher current.

Thus, 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.

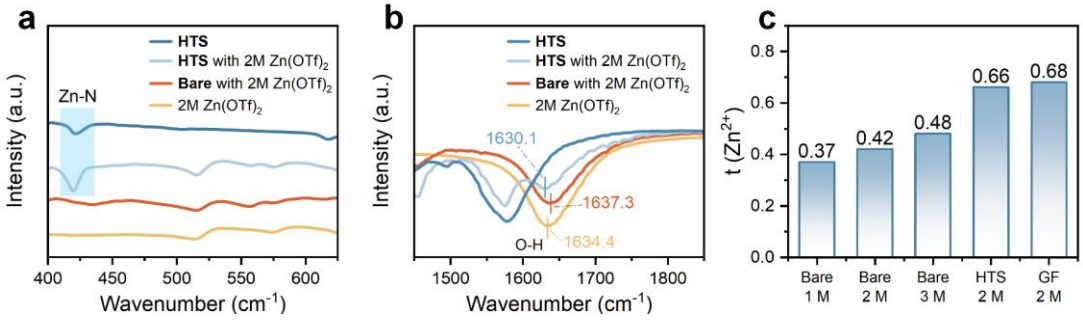


Fig. 4 | a, b FTIR spectra of HTS and bare separator immersed in 2M $Zn(OTf)_2$ electrolyte, dry HTS, and 2M $Zn(OTf)_2$ electrolyte. **c** The Zn^{2+} transference number of Zn||Zn batteries with HTS

and GF in 2 M $Zn(OTf)_2$, and with bare separator in 1, 2, 3 M $Zn(OTf)_2$.

Following your suggestion, we have revised the manuscript accordingly. ***Revisions in the manuscript:***

"…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."

"…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 $(002)_{Zn}$ crystal orientation. To verify the quantify component of Zn orientation, the XRD pattern of the Zn anode (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 $(002)_{Zn}$ to $(101)_{Zn}$ 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 Zn anode. These results consistent with the previous conclusion, indicate the long LC stage corresponds to the formation of $(002)_{Zn}$ orientation."

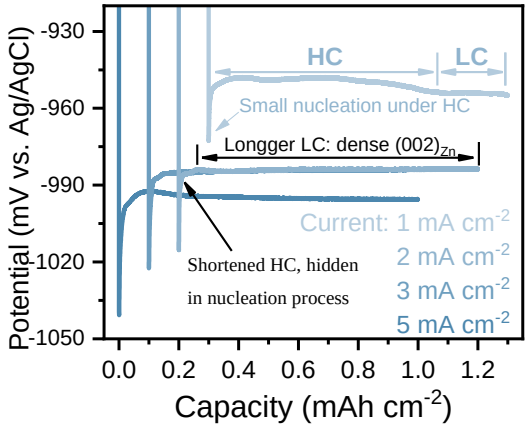
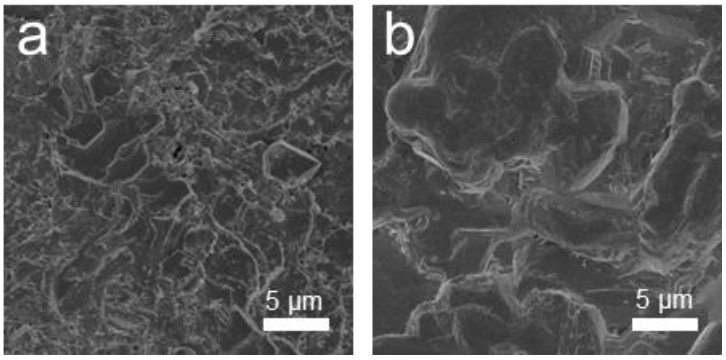
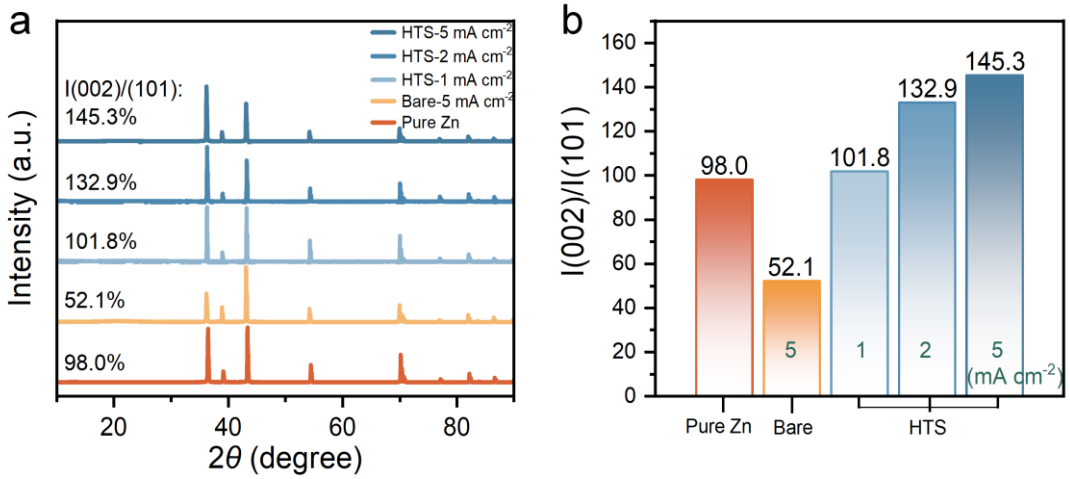


Fig. 4 | i Potential-capacity curves during Zn nucleation and deposition at the current density of 1 ~ 5 mA cm^{-2} using Zn foil as the working and counter electrode, Ag/AgCl electrode as the reference electrode.



Supplementary Fig. 20 | SEM images of Zn foil anode with HTS after 20 cycles at (a) 1 mA cm^{-2}, 1 mAh cm^{-2}, and (b) 2 mA cm^{-2}, 2 mAh cm^{-2}.



Supplementary Fig. 21 | (a) XRD patterns of Zn anode after 20 cycles with HTS at 1 mA cm^{-2}, 1 mAh cm^{-2} , 2 mA cm^{-2}, 2 mAh cm^{-2} and 5 mA cm^{-2}, 5 mAh cm^{-2}, bare separator at 5 mA cm^{-2}, 5 mAh cm^{-2} and pure Zn foil without cycles. (b) Corresponding intensity ratio of $(002)_{Zn}/(101)_{Zn}$.

3. In this manuscript, the authors described that Zn anode tends to develop (002)Zn orientation under (0.1 ~ 1.0)iL, however, the test results show that with the HTS, the limit current is decreased from 109.9 mA to 14.3 mA. Although this is a significant drop, 14.3 is still a long way from the required 0.1-1.0. Therefore, this explanation of the HTS-induced (002)Zn is not appropriate. In addition, why is the limiting current greatly reduced in the presence of HTS? It is more hoped to explain the cause of (002)Zn from the most fundamental mechanism of action, rather than using one test performance to explain another.

Response: We greatly appreciate the reviewer's comment and apologize for these unclear

expressions. With your considerate reminder, we have revised and further discussed this part in more depth.

Firstly, we apologize for the confusing expression of "(0.1 ~ 1.0)i_L", and we have amended it to "0.1i_L ~ i_L". We should elucidate the differences in the conditions required for the formation of Zn(002) orientation in zinc anodes between HTS and bare separator systems. As the LSV plots shown in Fig. 4g–h, the limit current densities of HTS and bare separator systems are 14.3 mA cm^{-2} and 109.9 mA cm^{-2}, respectively. This indicates that within the HTS system, the anode tends to develop $(002)_{Zn}$ orientation when the current density lies between 1.43 ($0.1i_L$ = 0.1×14.3 = 1.43) and 14.3 mA cm^{-2} (Advanced Materials, 2023, 35(21): 2300073). Consequently, when the test conditions are 2, 3, and 5 mA cm^{-2}, the anode of the HTS system will tend to develop (002)Zn orientation.

In addition, we also sincerely agree with the reviewer of using mechanisms to explain the phenomenon. We suggest explaining the fundamental mechanism by combining the classic Butler-Volmer formula with the different stages of the LSV curve. The classic Butler-Volmer formula is shown as Equation (2) in the manuscript:

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

According to this equation, we consider the following two cases:

(I) When the overpotential ($E–E^0$) is small enough, the formula can be transformed into a linear form as Equation (4):

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

Then, it can be seen that the linear region on the left of Fig. 4g–h corresponds to Equation (4). In the linear area, the mass transfer at the interface is considered sufficient. Besides, the rate-controlling step during the linear interval is surface electrochemical activation.

(II) When the overpotential becomes larger, the rate-controlling step changes to mass transfer by the depletion of ions. The nonlinear regions in Fig. 4g–h indicates the formation of concentration polarization, corresponding to the LC stage we mentioned above.

Consequently, we use the critical value of linear regions "i_L" to measure the speed of state transitions in different systems. The critical value of linear regions for the anode with HTS is much smaller than that of linear regions for the anode with a bare separator, which means the former

system is more sensitive to the changes in charge density. Our test conditions are 1, 2, 3, and 5 mA cm^{-2} for the Zn anode with HTS and bare separator, but they show different potential-capacity curves. **For the anode with a bare separator**, its limit current density is 109.9 mA cm^{-2}, which means the anode will not develop $(002)_{Zn}$ orientation when the test current density is under 10.99 mA cm^{-2} ($0.1i_L$ for bare separator). So we can see the potential capacity curves in Supplementary Fig. 18 are always on the HC stage. **For the anode with HTS**, the results are different due to its smaller limit current density (14.3 mA cm^{-2}). When the test current densities are 2, 3, or 5 mA cm^{-2}, the anode will tend to develop $(002)_{Zn}$ orientation (the current density is greater than 1.43 mA cm^{-2}, $0.1i_L$ for HTS), and our SEM/XRD test have also proved this phenomenon (see the detailed discussion in question 2). Moreover, because of the rapid movement of current at the interface, the potential capacity curves only show the LC stage. When the test current density is 1 mA cm^{-2}, the anode will not develop $(002)_{Zn}$ orientation. However, due to the current density being near 1.43 mA cm^{-2}, the potential capacity curve clearly shows two steps, i,e, the "stage deposition behavior".

We have revised the description of LSV curves and limit current accordingly, following your important suggestion.

Revisions in the manuscript:

"…as Zn anode tends to develop $(002)_{Zn}$ orientation under $0.1i_L \sim 1.0i_L$[28]. 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 anode deposition tends to the $(002)_{Zn}$ orientation under current conditions of 1.43 ~ 14.3 mA cm^{-2}."

"…Furthermore, the shorter linear area of LSV curves at Fig. 4g can also be understood through Eq.2. When the overpotential ($E-E_0$) is small enough, the Equation (2) can be approximately equivalent to Equation (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 Zn^{2+} 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 Equation (5)…"

4. Experiments on in-situ optical microscopes are not rigorous. Since the effect of the separator on zinc ion deposition is studied, the situation of the part covered by the separator should be observed. However, the images in the manuscript show that the separator is not aligned with the edge of the section but at a distance. As for Figure 3c, although uneven deposition is observed, it is distributed on the surface of the cross section or where there is no separator.

Response: We thank the reviewer for the insightful comments.

Following the reviewer's comments, in-situ optical microscope observation was retested to make sure the separators contact tightly with the Zn anode and align with it.

The optical image has been replaced in Fig 3a, c. It can be seen that the Zn anode with HTS exhibits a uniform layered deposition in the cross-section after a 50-minute growth, while the Zn anode with bare demonstrate dendrites stab into the bare separator. Moreover, these results is consistent with those in the CT test, proving the anti-dendrite effect of HTS.

The retested results and description have been revised. ***Revision in manuscript:***

"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). "

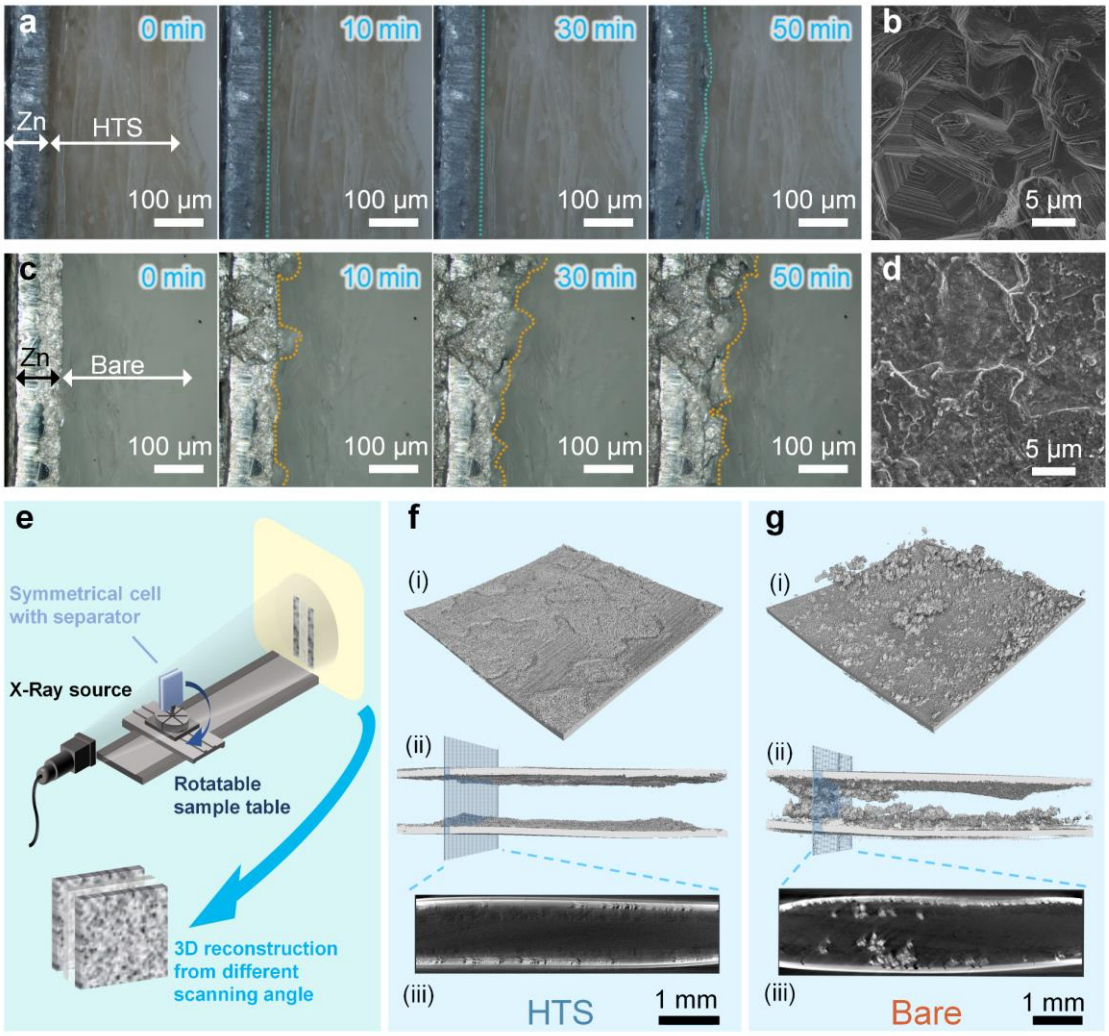


Fig. 3 | Morphology characterization of Zn anode with HTS. **a, c** In-situ optical observation of Zn anode after plating 0, 10, 30, 50 min at a current density of 5 mA cm^{-2} using the HTS (**a**) and bare separator (**c**). **b, d** SEM images of Zn foil anode after 20 cycles at 5 mA cm^{-2}, 5 mAh cm^{-2} using the HTS (**b**) and bare GF (**d**). **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}: **(i)** front view of anode 3D reconstruction, **(ii)** Side view of battery 3D reconstruction, **(iii)** Side X-CT view of battery cross-section.

5. In this work, the author prepared a kind of MOF-modified nonwoven separator, but used HTS||GF||HTS structure when testing symmetric batteries. This is not appropriate and only one piece of HTS should be used.

Response: Thanks for the insightful comments raised by the reviewer.

We agree with the reviewer's comment and have attempted to use only one piece of HTS or bare nonwoven to assemble the batteries. Unfortunately, it was found that the electrolyte is quickly depleted during cycling and causes a high overpotential. The main reason for this phenomenon is the insufficient uptake of electrolytes by the HTS separator. The data about electrolyte adsorption is added as shown in Supplementary Table 2. The dry weight of the same size separator (diameter of 16 mm) and wet weight after fully absorbing 2 M $Zn(OTf)_2$ electrolytes were weighted. The electrolyte absorption (compared with self-weight) amount of HTS (205.7%) is less than GF (745.0%), attributed to the physical property of a nonwoven matrix. Therefore, the HTS is not suitable to be used individually. Conversely, given that HTS is sufficiently thin, we suggest employing HTS with a GF interlayer structure to amalgamate the benefits of both. At the current stage, nonwoven is a matrix that is cheap enough and loadable. Also, we are following the reviewer's suggestion, trying to develop other high electrolyte adsorption matrices with heat-resisting performance to fit the hot-pressing process, aimed to use the HTS separator solely. We prospect the optimizing direction would be on hydrophilicity and porosity and hope to have breakthrough in our future work.

We have revised the manuscript accordingly. ***Revisions in the manuscript:***

"…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."

"To analyze the effect of the HTS on the anode, 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 anode. The battery combined with HTS exhibits a uniform layered deposition in the cross-sectional morphology (Fig. 3a)."

Supplementary Table 2 | The 2 M $Zn(OTf)_2$ absorption result of HTS and GF

Separator	Initial weight (mg)	Wet weight (mg)	Electrolyte absorption ratio
HTS	15.7	48.0	205.7%
GF	28.0	236.6	745.0%

6. Although the HTS-based symmetric battery has a significant increase in cycle life, its overpotential is too large, nearly 2-3 times the original. It is acceptable to increase some, but if increases too much, it is necessary to consider whether such modification is worthwhile.

Response: We sincerely thank the reviewer for the valuable suggestion.

We agree with the reviewer's view that too much increases in overpotential would affect the battery performance. Overpotential value needs to be evaluated from two aspects:

(I) For Zn anode, a larger overpotential during nucleation can promote Zn grain refining, as the Equation (5):

$$r_{crit} = \frac{2v_m\sigma}{ne|\eta|} \tag{5}$$

(II) For the full cells, a large overpotential would lead to a separation of charge and discharge platform voltage. This voltage change is directly related to the battery energy storage, as shown in Equation (8):

$$E_n = \int U(t)Idt = \sum U_t I\Delta t \tag{8}$$

Equation (5) indicates that an increased overpotential promotes grain refinement. A relatively large overpotential is advantageous for the uniform of zinc deposition. Equation (8) suggests that an increase in overpotential corresponds to a higher energy loss during charge/discharge processes. From this standpoint, the overpotential is considered detrimental. Therefore, the magnitude of overpotential has a dual nature.

Herein, we suggest to use energy efficiency (EE) to assess the effect of increased overpotential, as shown in Supplementary Fig. 26. In Zn||I_2 cells with double HTS and bare separator, their EE of both systems are significantly decreased, which is attribute to the influence of overpotential. These results are consistent with the law in Equation (8). Quantitatively, in early cycles the average EE of HTS is 84.4 %, only a little lower than that of the bare separator (85.3%). This suggests that the

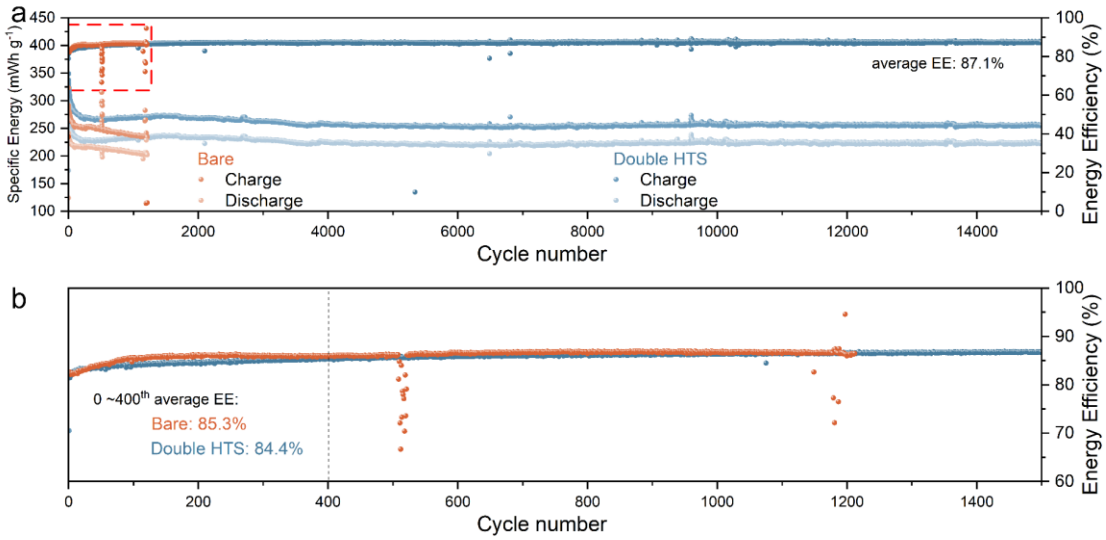
effect of overpotential in the Zn||I_2 cells with double HTS is comparable to that of Zn||I_2 cells with bare separator. Moreover, the average EE of Zn||I_2 cells with HTS is up to 87.1% in over 15000 cycles, better than that of the bare separator battery (85.9%). These evidences indicate that the overpotential in the HTS system remains within acceptable limits and will not cause a significant energy loss.

We have revised the manuscript accordingly. ***Revision in manuscript:***

"To evaluate the impact of overpotential on application level of batteries, the specific energy is introduced to measure the consolidated energy efficiency (EE), as the Equation (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 cycles test, the total average EE of full-cell with HTS is 87.1%, indicating a high reversibility of energy storage."



Supplementary Fig. 26 | (a) The specific energy and energy efficiency of Zn||I_2 cells with double HTS and bare separator. (b) The enlarged view of the marked area in (a).

7. The explanation that HTS improves the transference number of zinc ions is that a large number of zinc ions are attracted to nitrogen sites. If so, it should not be conducive to zinc ion transport, and how can the transference number be increased?

Response: We deeply appreciate the reviewer's insightful questions.

Firstly, we deeply apologize for calculating mistakes in the transference number of zinc ions ($t(Zn^{2+})$) in the first vision. We confused the current unit "μA" with "mV", leading to a unit mismatch. The right results and relevant parameters are listed in Supplementary Table 3. We agree with the reviewer's point that the obstructions in zinc ions transport would lead to the decrease of $t(Zn^{2+})$, and then we will carefully discuss this question as follows.

The definition of $t(Zn^{2+})$ is the proportion of Zn^{2+} ions transferred charge in the total ones. For an electrically neutral system, the transference numbers of positive and negative ions satisfy the relationship:

$$t^{+} + t^{-} = 1$$

On the one hand, the attraction to Zn^{2+} ions would inhibit transport and result in a reduction of the transference number. On the other hand, when Zn^{2+} are reactive ions in a zinc salt solution, the transfer process of Zn^{2+} is both affected by diffusion and reaction kinetics, thereby the $t(Zn^{2+})$ is also affected by the ion concentration in the solution. To simulate the effect of concentration, we supplemented the $t(Zn^{2+})$ under different concentrations with a bare separator, as shown in Fig. 4c. The result shows that the $t(Zn^{2+})$ exhibits a direct proportionality to the concentration of the electrolyte. Therefore, the high $t(Zn^{2+})$ in the HTS system is affected by both high concentration and low kinetics, in which the concentration is also an important factor.

Following your suggestion, the corresponding information has been revised. ***Revision in manuscript***:

"The results for transference numbers of Zn^{2+} ions ($t(Zn^{2+})$) are shown in Fig. 4c and Supplementary Figs. 14−16 (the corresponding digital are shown in Supplementary Table 3). In a 2 M $Zn(OTf)_2$ electrolyte, the HTS demonstrates a $t(Zn^{2+})$ of 0.66, approaching the $t(Zn^{2+})$ of GF (0.68) and higher than that of the bare separator (0.42). Regularly, the $t(Zn^{2+})$ 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(Zn^{2+}).”

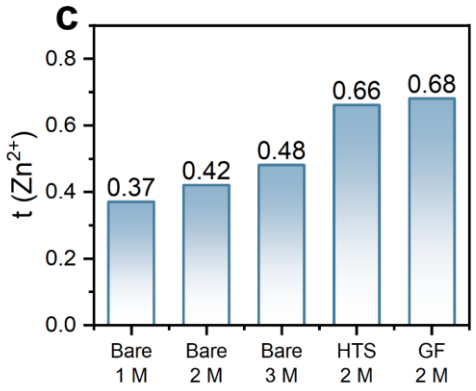
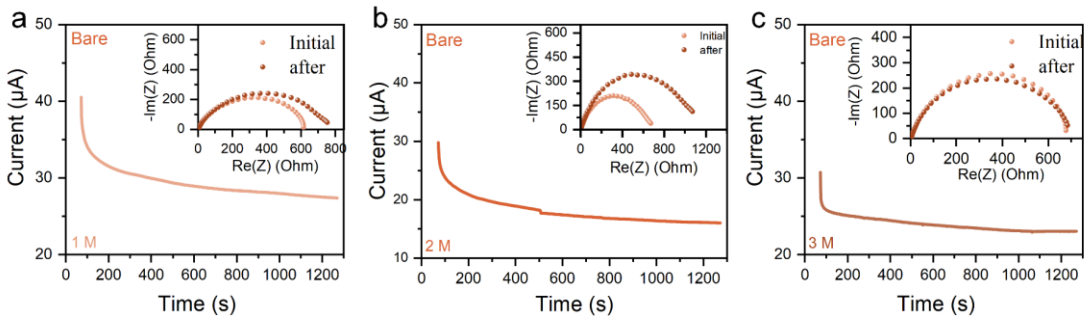
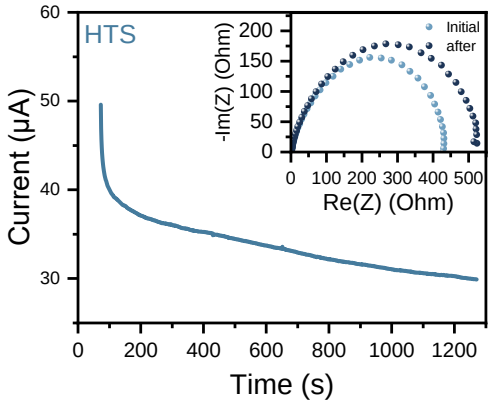


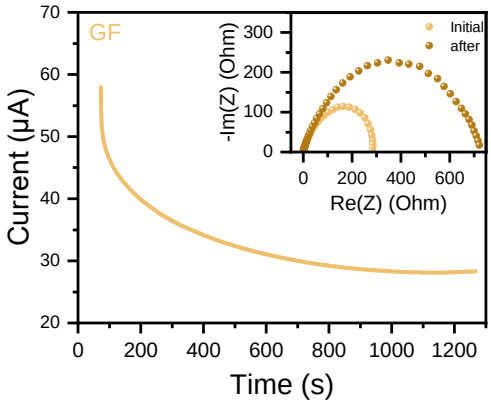
Fig. 4 | c The Zn^{2+} transference numbers of Zn||Zn batteries with HTS in 2 M $Zn(OTf)_2$, with GF in 2 M $Zn(OTf)_2$, and with a bare separator in 1, 2, 3 M $Zn(OTf)_2$.



Supplementary Fig. 14 | Chronoamperometry curves of bare separator in 1, 2 3 M $Zn(OTf)_2$ at 30 mV constant voltage. The insets are the corresponding in-situ EIS plots.



Supplementary Fig. 15 | Chronoamperometry curve of HTS in 2 M $Zn(OTf)_2$ at 30 mV constant voltage. The inset is the corresponding in-situ EIS plots.



Supplementary Fig. 16 | Chronoamperometry curve of GF in 2 M $Zn(OTf)_2$ at 30 mV constant voltage. The inset is the corresponding in-situ EIS plots.

Supplementary Table 3 | Corresponding parameters in calculation of Zn^{2+} transference number

	I_0 (mA)	I_s (mA)	R_0 (Ω)	R_s (Ω)	t(Zn^{2+})
bare-1 M	0.0405	0.0274	615.9	754.2	0.37
bare-2 M	0.0298	0.0160	672.5	1073.2	0.42
bare-3 M	0.0307	0.0230	677.6	684.3	0.48
HTS-2 M	0.0329	0.0247	479.7	560.1	0.66
GF-2 M	0.0582	0.0283	285.9	722.5	0.68

The t(Zn^{2+}) is calculated using the following formula:

$$t(Zn^{2+}) = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)}$$

where I_0 and I_s are the currents in the CA curve before and after polarization, and R_0 and R_s are the impedances of cells before and after polarization. ΔV is applied potential during the test, which is 30 mV in this work.

8. In Figure 2g, in addition to having peaks corresponding to ZIF-8, HTS also shows additional peaks. What do these peaks represent? Whether the battery performance is affected?

Response: We greatly appreciate this comment.

We carefully compared the XRD results and referenced literature to divide the attribution of peaks as shown in Fig. 2g. The two additional peaks at the degree of 9.2 and 28.3 were also found in the traditional hydrothermal method ZIF-8 (Carbohydrate Polymers 247, 116693 (2020)., Journal of Inorganic and Organometallic Polymers and Materials 27, 1317−1322 (2017).). Therefore, we

suggest that the additional peaks are not caused by the hot-pressing step and might be some derivative or different crystal type of MOFs.

The related mark of peaks has been revised following your suggestion. ***Revisions in the manuscript:***

"The peaks were divided into specific crystal planes[40] and the results revealed that…"

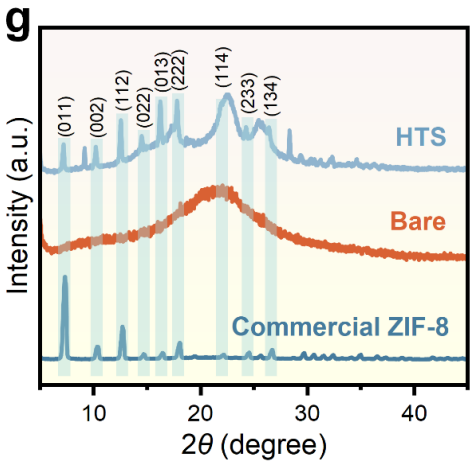


Fig. 2g XRD patterns of HTS, bare separator, and commercial ZIF-8.

References added in manuscript:

40. Venna SR, Carreon MA. Highly permeable zeolite imidazolate framework-8 membranes for CO_2/CH_4 separation. *J. Am. Chem. Soc.* **132**, 76−78 (2010).

9. About the analysis of FTIR: The containment of water activity could be attributed to nitrogen sites in HTS that attract Zn^{2+} ions and reconfigure the solvation networks. What does the reconfigured solvation network look like? A little more detail is needed.

Response: We greatly appreciate the reviewer for pointing this out.

With the attraction of nitrogen sites leading to a high Zn^{2+} concentration, more H_2O molecules would be involved in the solvation sheath of Zn^{2+}, and the free state H_2O would be lesser. The FTIR results in Fig. 4b evidenced the inhibited water activity, corresponding to the inhibition of side reactions. However, simulating a solvation network via Density Functional Theory (DFT) presents challenges due to the two-phase interface and an extra solid Metal-Organic Framework (MOF) phase. Moreover, methods for analyzing solvation interfaces are scarce and typically require testing with aqueous samples. Considering the difficulty in characterizing the solvation networks, the

descriptions about the solvation network have been deleted for accuracy.

The descriptions of the solvation network have been deleted. ***Revision in manuscript:***

"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 HER process."

10. It is recommended that Figures 5c and 5d use data with the same number of cycles, which is more conducive to observing and comparing deposition condition in the same period.

Response: We greatly appreciate the reviewer for this reminder.

Following the reviewer's suggestion, we updated the charge/discharge plot for both HTS and bare separator, to ensure a comparison under the same cycle number, as shown in Fig. 5b–d. For the charge/discharge test with a bare separator, we have extended the test time even when the cells had failed, to collect the data at the 100th cycle. In addition, the curves of the charge/discharge with HTS at cycles of 1st, 20th, and 50th were added in Fig. 5c. The results exhibit that the deposition profile of the bare separator had a short circuit at the 100th cycle. Conversely, during the same cycle durations (100th), the HTS processes a staged behavior. Notably, due to the phase differences between Zn and copper (Cu), the deposition/stripping of Zn on the Cu electrode process an activated process at first 20 cycles, leads to the staged behavior being unobvious. After 50 cycles, the staged profile with HTS becomes stable, while the deposition profile of the bare separator approximates a flat shape.

Following your suggestion, we have revised the manuscript accordingly. ***Revision in manuscript:***

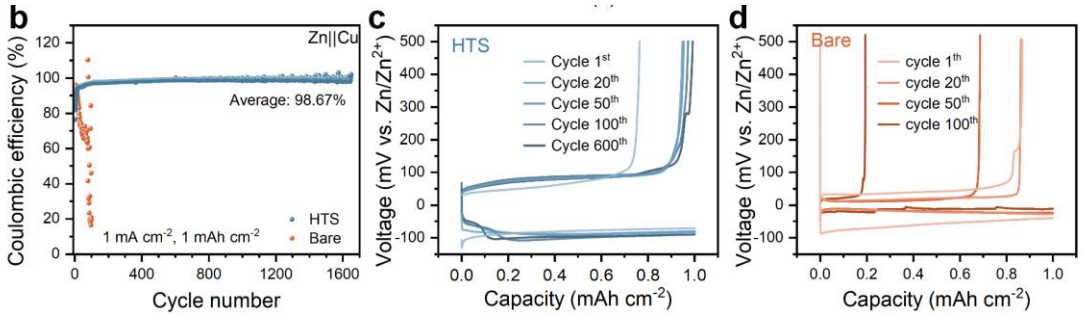


Fig. 5 | b Columbic efficiency of Zn||Cu cells with different separators at 1 mA cm^{-2}, 1 mAh cm^{-2} discharge capacity, and 0.5 mV charge cut-off voltage. **c, d** Corresponding charge/discharge profiles of Zn||Cu cells.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have addressed my concerns in this revision, and the current version looks suitable for publication. They further performed the experiments to fully address the chemical stability of MOF using XRD, LSV, and FTIR. Moreover, the bi-functionality of the separator (Zn dendrite suppression and prevention of chemical crossover) was also well explained. Before the publication, please do not miss some typos (exhibite -> exhibited).

Reviewer #2 (Remarks to the Author):

I appreciate the detailed response to the review and better understand the novelty and significance of the result. I now believe that this paper is sufficiently noteworthy for publication.

Reviewer #3 (Remarks to the Author):

The manuscript is well revised and answered all the questions, therefore it cna be accepted now.