

Bilateral in-situ functionalization towards Ah-scale aqueous zinc metal batteries

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript reported a bilateral in-situ functionalization strategy to achieve Ah-scale aqueous zinc metal batteries. The addition of PMS molecules as electrolyte additive enables a gradient interlayer formed on Zn anode for large-capacity plating/stripping and an in-situ modification interlayer into cathode lattice for high-loading stability. This work provides a practical route for achieving Ah-scale pouch cells in aqueous zinc metal batteries. The manuscript is well organized and the experiments have been soundly performed. I suggest its publication on Nature Communications after addressing the following issues.

1. In Figure 2h and 2i, the authors still didn't provide the most intuitive results and the discussion about the mechanism of PMS was not clear. What did the shift of SO₃ and H-O-H mean? How did SO₄²⁻ work?
2. In Figure 3b and c, how did the authors distinguish between the overpotential in the nucleation stage and the overpotential in the growth stage? How to read the overpotential in the growth stage? What did I_m and t_m stand for?
3. The authors mentioned that "The -SO₃- on the surface could attract and bind with Zn²⁺ in electrolyte, playing the role of active sites for promoting zinc plating/stripping". In addition to guide the Zn²⁺-deposition, can the PMS affect the diffusion kinetics of Zn²⁺? The authors need to supplement the measurements about reaction kinetics.
4. In Figure 3i and 3j, it seems that there is negligible change in the XRD peaks. The authors need to provide an explanation and supplement the XRD patterns for Ti and Cu foil.
5. The PMS treatment can activate and stabilize the cathode through modifying the interlayer lattice. However, in-situ XRD only offers cathode phase diffraction data from the initial cycles. The authors are suggested to provide additional details regarding the cathode behavior in post-cycling?
6. In Figure S18, there seemed to be errors in the annotation of SEM images corresponding to NVO of different cycle stages.
7. The authors stated that "A stack of four Zn||NH₄V₄O₁₀ single layer cells in series successfully power a toy car model to run with a voltage of 3.8 V (Figure S31; Video, Supporting Information)". However, according to Figure S31, it can be observed that the battery assembly depends on the clamp plate, which may lead to an increase in the whole weight of the battery. Furthermore, a video of the toy car is suggested to be provided.

Reviewer #2

(Remarks to the Author)

Comments for "Bilateral in-situ functionalization towards Ah-scale aqueous zinc metal batteries":

This manuscript introduces PMS as a bifunctional additive for both Zn anode and V-based cathodes. Improved anode and full cell performance were demonstrated, which were ascribed to the adsorption effect of PMS at the Zn anode and the pillar effect of PMS intercalated into NH₄V₄O₁₀ cathode. Although good performance of Ah-level pouch cells is achieved, most of the scientific aspects are wrongly understood and explained in this article. It is thus not recommended to publish in its current format:

1. "Unlike other organic electrolyte additives, PMS does not affect the Zn²⁺ solvation structure". Please use direct and more sensitive techniques to confirm this point, for example, XAS.
2. The concept of gradient adsorption layer of PMS on the Zn surface is mostly based on XPS. However, the author

analyzed their XPS data in a very superficial and wrong way: 1. The atomic concentration at different depths should be presented. 2. The fitting of S2p is completely wrong, the author even did not fit each component with 2p $\frac{1}{2}$ and 2p $\frac{3}{2}$. So does for the Zn 2p. All XPS data in this article needs to be re-analyzed. This is an often-to-see but pathetic phenomenon in this area, that XPS is overwhelmingly used without a strict understanding of it. Please also consider using 3D TOF-SIMS to visualize this proposed gradient adsorption layer, which should provide more sensitive results.

3. Authors claimed that PMS adsorption is chemical adsorption, but the calculation was based on physical electrostatic attraction. This is weird. Please explain.

4. For reaction " $\text{Zn-S-C}_3\text{H}_6\text{-SO}_3^- + 6\text{H}^+ + \text{Zn} + 4\text{e}^- = \text{Zn-S-C}_3\text{H}_6 + \text{Zn}^{2+} + \text{S}_2^- + 3\text{H}_2\text{O}$ ", it is hard to image such a 4-electron reaction can happen at ambient condition without any driving force. If the reaction happens in such an acidic environment, H^+ should directly react with Zn to form H_2 .

5. For Fig3b, it is very unusual to see the plating overpotential continuously goes up even after 1 mA h cm⁻², which is normally at a level of 0.1-0.2 mA h cm⁻² where the nucleation process ends. I suspect that a poorly polished Zn is used for PE whereas a well-polished Zn is used for SH. Please check.

6. The SEM images at 1 mA h cm⁻² can not well show the nucleation density as the growth behavior has already started for a period of time. Please do this at 0.1 mA h cm⁻² or below.

7. The concept of "PMS molecules can electrochemically in situ modify the interlayered lattice of $\text{NH}_4\text{V}_4\text{O}_{10}$ during the cycles" is not supported by any direct experimental results and mostly likely wrong due to the following points:

a. The author assumes Zn^{2+} intercalation dominates the discharge process, which is wrong. Many previous studies have already confirmed the presence of dominant proton interaction in both Mn and V-based cathodes. Therefore, the explanation about lattice shrinkage/expansion is not true.

b. "ZHS is due to the proton intercalation rather than the V dissolution. So does the pH vibration the reversible appearance/disappearance of ZSH and the absence of by-products could be observed in the SH, confirming the enhanced stability of lattice framework". ZHS only forms on the surface of cathodes, its reversible appearance/disappearance has nothing to do with the stability of the lattice framework of the cathode.

c. Again, the authors used XPS to propose the so-called lattice PMS, which is wrongly analyzed. In addition, XPS is only a surface technique, and cannot provide lattice information even with Ar sputtering. Please do not overanalyze the data. Overall, although good performance is demonstrated, the authors' claims in terms of understanding PMS functionality are based on XPS and simulations. The former technique is used in an unprofessional and unscientific way with too many assumptions. For the latter, with respect to all theoretical efforts, most calculations in this area are more likely designed to match what has been observed, and their reliability (especially at the interface) needs to be accompanied to more rigorous experimental results.

Reviewer #3

(Remarks to the Author)

In this manuscript, Song et al. emphasized the effect of dual modification at both cathode and anode interfaces on the electrochemical performances, contributing to the pouch cells with an Ah-level stability over 680 cycles and a cumulative capacity of 319.6 Ah. Unlike traditional electrolyte modifications, this manuscript proposes an interesting mechanism to explain the uniform deposition of zinc anode and the in-situ modification on the cathode, ultimately ensuring the overall stability of the battery. I think it is suitable for publication in Nature Communications after addressing several minor concerns.

(1) In Figure 4d-f, the authors mentioned that the in-situ modification introduced the PMS into the interlayer of cathode, which enhances the conductivity and structural stability of cathode. However, for the conductivity, more evidence should be provided to support this statement. What is the electronic structure of cathode with PMS?

(2) As is well known, vanadium-based cathodes in aqueous electrolyte exhibit severe capacity degradation at low current density. Solving this problem will play a key role in the development of Zn-V batteries. However, the Zn-V cell in this manuscript performs well only in a high current density (e.g. 2 A g⁻¹ in Figure 5g). Does PMS additive address the cycle stability of vanadium-based cathode at low current densities, such as 0.5 A g⁻¹?

(3) In the analysis of the nucleation mechanism, the author explained that PMS facilitates Zn nucleation, thereby resulting in a lower nucleation overpotential. However, in Figures 5d and e, it is evident that the hysteresis voltage of the SH electrolyte is higher than that of PE electrolyte at 10 mA cm⁻² and 20 mA cm⁻². Please explain this phenomenon.

(4) This manuscript demonstrates excellent cycling stability in high-capacity pouch cells. To date, many pouch cells with high capacity have been reported. The author should further elucidate the advancements and limitations of this work when compared to others.

(5) Some sentences are not clear. For example, in Page 2, "Compared to symmetrical cells, the situations in large-capacity pouch cells are more drastic and complex, especially the electrolyte composition fluctuations caused by the cathode reaction. Typically, cathode reactions in aqueous environments often lead to the pH fluctuation of electrolyte. Meanwhile, the dissolved metal ions may diffuse to Zn anode and lead to self-discharge." Does 'large-capacity pouch cells' refer to full cells rather than symmetric cells? Which type of ion is referred to as 'the dissolved metal ions'?

In Page 19, "The high areal specific capacity usually leads to more serious dendritic growth and corrosion issues, and consequently, the CE of the Zn||Cu cell with PE declined rapidly within 30 cycles." 'The high areal specific capacity' is not expressed appropriately and should be revised to 'The high areal capacity'.

(6) There are some errors and irregularities in the figures and tables that need to be corrected. For example, in

Supplementary Table S1, capacity should be corrected. The annotation text in Figure 3b is too light and I recommend using a darker color to enhance readability. Additionally, the enlarged view in Figure 4d and the inset in Figure 6a are blurry, making it difficult to discern detailed parts. To aid readers in better understanding this manuscript, the authors should provide higher-resolution images.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have fully addressed my concerns. This work proposes an important strategy for achieving high-loading and large-capacity zinc-vanadium batteries with superior stability, which is of great significance to the development of aqueous zinc metal batteries. It is recommended to publish it in Nature Communications in the present form.

Reviewer #2

(Remarks to the Author)

I appreciate the authors' effort to address my comments. These points need further consideration:

1. Nyquist plot should be drawn in a square format with the same xy scale, otherwise the shape of the semicircle is misleading to readers.
2. The authors indicate PMS participates in the Zn^{2+} solvation structure, which means the water- Zn^{2+} interaction is altered. In this case, the chemical environment of water molecules cannot remain unchanged. Please explain.
3. There is no intensity legend in 3D TOF-SIMS data, please add it. The complete profiles of each species are required to give a full view of SEI composition.
4. Point 7a, authors claim dominant Zn^{2+} (de)intercalation based on the comparison of lattice spacing with other different cathode materials. Even with similar Zn^{2+} intercalation, different cathode materials would have very different lattice change behavior, not to mention the amount of intercalated Zn^{2+} is also different based on the exhibited discharge capacity. This comparison is not scientific. In addition, the in-situ XRD in Figure 4b clearly shows the dominant presence of ZHS during the cycling, which is strong evidence of dominant proton intercalation.
5. I thank the authors' effort on reanalyzing the PMS functionality at NVO interface. This is more reasonable than PMS intercalated in NVO. I can see why the adsorbed PMS suppresses V dissolution, which is interesting. But how about the Zn^{2+} desolvation and Zn^{2+} diffusion at the PMS-cathode interface? Does the adsorbed PMS enhance Zn^{2+} transportation or suppress it? The formation of large amounts of porous ZSH at cathode surface also have huge impact on such an interface.

Reviewer #3

(Remarks to the Author)

My questions were well answered by the authors. This article reveals the mechanism of bilateral in-situ modification, achieving stable operation of Ah-level pouch batteries and providing good guidance for the development of aqueous zinc vanadium batteries. I recommend it to publish in Nature Communications.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors addressed all my questions well. I appreciate their efforts in solving these issues for the manuscript. I am now happy to recommend its publication on Nat Commun.

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Point-by-Point Response to Referee Reports

We sincerely appreciate the invaluable comments and insightful suggestions provided by the reviewers for our manuscript. Taking into consideration of these comments, we have revised the manuscript carefully and make the necessary changes and improvements in revised manuscript to improve the manuscript's overall content and central focus. The main changes are summarized below following a point-by-point response letter addressed to reviewers' comments.

Reviewer #1: This manuscript reported a bilateral in-situ functionalization strategy to implement Ah-scale aqueous zinc metal batteries. A gradient interface of Zn anode was proposed for large-capacity plating/stripping and an in-situ modification of cathode interlayer lattice enables high-loading stability. This work provides a good route for achieving practical Ah-scale pouch cells in aqueous zinc metal batteries. Therefore, I recommend its publication on Nature Communications after addressing the following minor issues.

Response: Thanks to the **Reviewer #1** for the valuable comments and suggestions. We also thank the reviewer for recognizing our work that provides a good route for achieving practical Ah-scale pouch cells in aqueous zinc metal batteries. In this revised version, we have addressed the issues with corrections and additional explanations to improve the logical coherence and scientific rigor of the manuscript. We will strive to improve the quality of this manuscript to meet the standards of *Nature Communications*.

1. In **Figures 2h and 2i**, the authors still didn't provide the most intuitive results and the discussion about the mechanism of PMS was not clear. What did the shift of SO₃ and H-O-H mean? How did SO₄²⁻ work?

Response: Thanks for pointing out the issue about the mechanism of PMS at Zn anode interface. We apologize for the insufficient explanation in **Figures 2h and 2i**. Hence, we further elaborated on the reasons for peak shift in SERS, including both the H-O-H bending and S-O stretching modes shifting towards high wavenumbers during cycling, respectively. According to the reports (*Nature*, 2021, 600(7887): 81-85; *J. Raman Spectrosc.*, 1990, 21(9): 563-567; *J. Raman Spectrosc.*, 2009, 40(8):972-981), the blue shift of H-O-H bending and S-O stretching modes indicates that the

adsorption and accumulation of water molecules on the surface of Zn metal led to enhanced hydrogen bonding interactions at the interface. Such abundant water molecule contributes to the formation and diffusion kinetics of solvated Zn^{2+} . Meanwhile, the potential side reactions caused by abundant water molecules will also be blocked by the interfacial layer.

Due to the outermost $-\text{SO}_3^-$ in the PMS derived interface gradient layer, which was proved by the supplemented 3D TOF-SIMS (**Figure 2e**), the SO_4^{2-} in the electrolyte will be repelled, thereby inhibiting the formation of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$ (ZSH). According to SEM images (**Figure S15**), XRD patterns (**Figure S33**) and etc., it can be found that the production of ZSH is significantly inhibited.

Changes:

Several distinct peaks at ~ 120 , ~ 630 , ~ 1120 and $\sim 1660 \text{ cm}^{-1}$ correspond to $\nu(\text{Zn-S})$, $\nu(\text{C-S})$, $-\text{SO}_3^-$ and $\delta(\text{H-O-H})$, respectively (**Figure 2g**)^{29,34,35}. Due to the statistical nature of SERS results for the vibration modes of $\text{Zn-S-C}_3\text{H}_6\text{-SO}_3^-$, it is challenging to observe the electrochemical behaviors of individual molecules within a cycle. **Figure 2h** displays the Raman shift statistics for the corresponding groups. And during the whole process, the wavenumbers of $\nu(\text{Zn-S})$ and $\nu(\text{C-S})$ were kept unchanged, indicating that the innermost self-assembled layer in direct contact with Zn did not experience significant electrochemical environmental changes and inner self-assembled layer keep stable. However, the blue-shift of $-\text{SO}_3^-$ peak, of which the scale is $\sim 2 \text{ cm}^{-1}$, indicated the ordered arrangement and contraction of the $-\text{SO}_3^-$ within the self-assembled layer, suggesting interactions with Zn^{2+} . The $-\text{SO}_3^-$ on the surface could attract and bind with Zn^{2+} in the electrolyte, serving as active sites for promoting Zn plating.

As illustrated in **Figure 2i**, these findings suggest that PMS molecules tend to adsorb on the Zn anode surface through $-\text{S-Zn}$ bonds by deprotonated $-\text{SH}$, forming thin self-assembled molecular layers that gradually evolve into a composition gradient film with $-\text{SO}_3^-$ at the outermost layer. As mentioned above, the $-\text{SO}_3^-$ groups on the surface could attract and bind with Zn^{2+} in the electrolyte, serving as active sites for promoting Zn plating. Meanwhile, the potential side reactions caused by abundant water molecules will also be blocked by the interface gradient layer induced by PMS³⁶. (in

Results-Directional adsorption of additives and gradient interface at the Zn anode)

2. In **Figures 3b and c**, how did the authors distinguish between the overpotential in the nucleation stage and the overpotential in the growth stage? How to read the overpotential in the growth stage?

What did I_m and t_m stand for?

Response: Thanks to the **Reviewer #1** for this valuable comment, and we also apologize for not specifying “ I_m ” and “ t_m ”. It is generally accepted that the overpotential during nucleation is the lowest point of the voltage at the beginning of deposition, as zinc metal deposition nucleation requires a certain overpotential. However, in this study, the deposition curve of the SH electrolyte did not follow this phenomenon. Therefore, we chose the potential at the beginning of deposition (η_n) as the nucleation overpotential. The overpotential for the growth stage is clear, which corresponds to the plateau voltage during deposition, indicating that the deposition process is dominated by growth. In addition, the I_m and t_m in equation (1) and equation (2) correspond to the current with maximum value and corresponding time in the I-t curve in **Figure 3d**, respectively.

Changes:

Regarding the behavior of instantaneous nucleation, nucleation occurs immediately, leading to a rapid increase in the number of nuclei followed by a decrease. In contrast, progressive nucleation involves a gradual increase in the number of nuclei, which slowly rises and then reaches saturation. I_m and t_m correspond to the current and time when the current maximum value occurs in the I-t curve, respectively. (in **Results-Uniform Zn deposition under high areal capacity**)

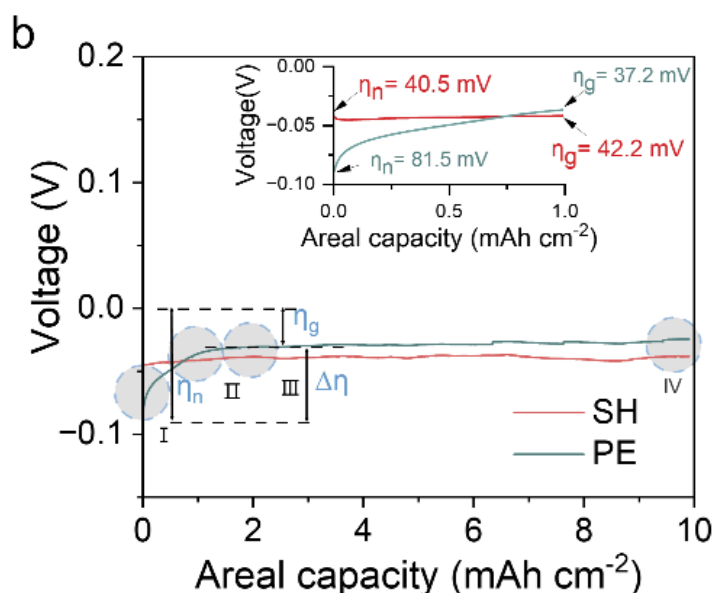


Figure 3. (b) Nucleation overpotential curves in PE and SH. (in Results-Uniform Zn deposition under high areal capacity)

3. The authors mentioned that “The $-\text{SO}_3^-$ on the surface could attract and bind with Zn^{2+} in electrolyte, playing the role of active sites for promoting zinc plating/stripping”. In addition to guide the Zn^{2+}

deposition, can the PMS affect the diffusion kinetics of Zn^{2+} ? The authors need to supplement the measurments about reaction kinetics.

Response: Thank **Reviewer #1** for the suggestion regarding the testing of diffusion kinetics. In the revised version, we have concluded the Nyquist plots data in **Figure S29** and calculated the activation energy (E_a) using the Arrhenius equation ($\frac{1}{R_{ct}} = A \exp(-\frac{E_a}{RT})$). In **Figure S29**, the E_a decreases from 31.17 kJ mol⁻¹ in PE to 26.69 kJ mol⁻¹ in SH, further supporting the role of PMS in improving Zn^{2+} deposition kinetic. This effectiveness in enhancing Zn^{2+} desolvation and promoting rapid ion transport is attributed to the role of the outer-layer $-\text{SO}_3^-$ in the self-assembled layer, which bind with Zn^{2+} and promote their deposition on the anode.

Changes:

Furthermore, the activation energy (E_a) calculated by the Arrhenius equation ($\frac{1}{R_{ct}} = A \exp(-\frac{E_a}{RT})$) decreases from 31.17 kJ mol⁻¹ in PE to 26.69 kJ mol⁻¹ in SH, further supporting the role of PMS in improving Zn^{2+} deposition (**Figure S29**). This effectiveness in enhancing Zn^{2+} desolvation and promoting rapid ion transport is attributed to the role of the outer-layer $-\text{SO}_3^-$ in the self-assembled layer, which bind with Zn^{2+} and promote their deposition on the anode. (in **Results-Electrochemical performances of coin cells**)

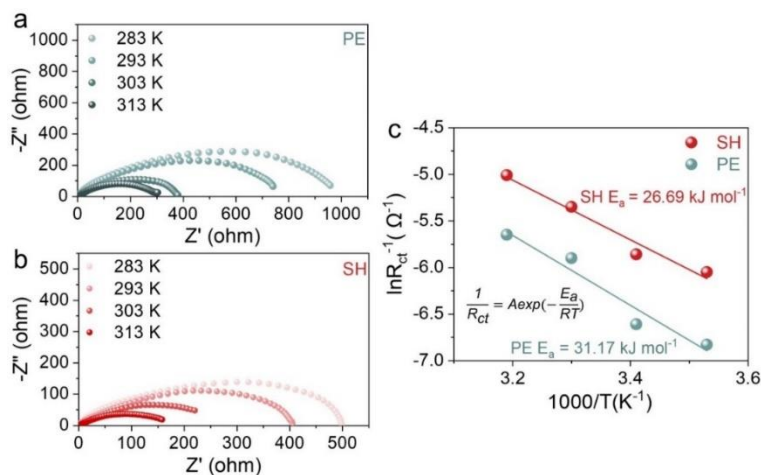


Figure S29. Nyquist plots of symmetric cells at different temperatures in (a) PE and (b) SH. (c) Corresponding Arrhenius curves and comparison of activation energies. (in **Supporting information**)

4. In Figure 3i and 3j, it seems that there is negligible change in the XRD peaks. The authors need to provide an explanation and supplement the XRD patterns for Ti and Cu foil.

Response: Thank to the **Reviewer #1** for the valuable comment. We apologize for not marking the diffraction peaks including Cu foil and Ti foil. In **Figures 3i and j**, we specifically focused on the changes in the diffraction peak intensities of Zn (002), (100), and (101) planes during the deposition process, without providing adequate explanations for other diffraction peaks. In order to clarify this issue, we performed XRD diffraction tests on both Ti and Cu foils as shown in **Figure S19**, and revised the corresponding content. Since the deposition process occurs on Ti foil, the intensity of the substrate peaks remains consistent, resulting in no observable changes in the XRD diffraction peak intensity. It is observed that the (111) diffraction peak of Cu near the (101) peak of Zn, while the (002) peak of Ti almost coincides with the (100) peak of Zn. We have revised the corresponding description in the original manuscript to make it more recognizable and scientific.

Changes:

The crystal orientation and reversibility of electrodeposited Zn can be revealed *in-situ* and *ex-situ* XRD (**Figure S18**). **Figure S19** shows a comparison of diffraction peaks between Ti foil, Cu foil, and Zn foil. It was found that the Zn (100) facet slightly overlaps with the Ti (002) facet, and the Cu (111) facet and Zn (101) facet also overlap in their diffraction angles. However, the high intensity of the diffraction peaks in Cu foil makes it difficult to accurately discern the deposition intensity of Zn. (in **Results-Uniform Zn deposition under high areal capacity**)

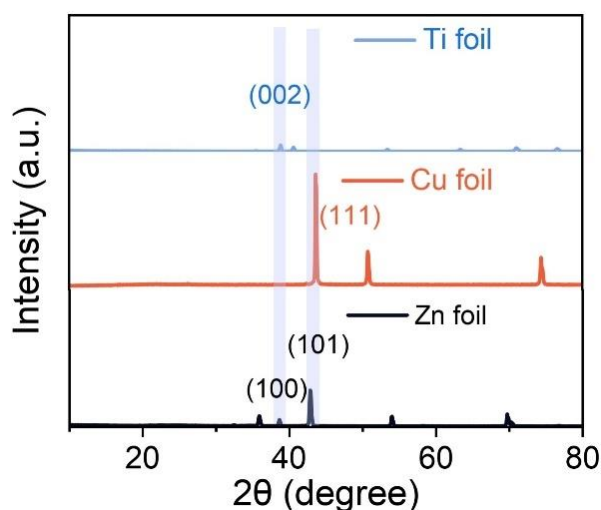


Figure S19. XRD patterns of Ti foil, Cu foil and Zn foil. (in **Supporting information**)

5. The PMS treatment can activate and stabilize the cathode through modifying the interlayer lattice. However, *in-situ* XRD only offers cathode phase diffraction data from the initial cycles. The authors

are suggested to provide additional details regarding the cathode behavior in post-cycling?

Response: Thanks to **Reviewer #1** for the attention on cathode evolution. To further illustrate the changes in the cathode after cycles, we supplemented *ex-situ* XRD patterns of NVO after 120 cycles. Similar to the results of *in-situ* XRD, the *ex-situ* XRD after 120 cycles exhibited obvious diffraction peaks in SH electrolyte and indicated the more stable lattice structure. The NVO exhibited indistinct diffraction peaks of the original phase, accompanied by the generation of a large amount of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, which may be due to the severe dissolution in PE during cycling.

Changes:

The phase composition of the cycled cathode was also analyzed by XRD patterns (**Figure S25c**). Similar to the *in-situ* XRD results, the *ex-situ* XRD pattern of NVO cathode after 120 cycles in SH electrolyte exhibited prominent diffraction peaks, indicating a more stable lattice structure. In contrast, the NVO cathode exhibited indistinct diffraction peaks of the original phase and the formation of a substantial amount of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, which may experience significant dissolution in the PE electrolyte during cycling. (in Electrochemically in-situ modification of cathode interlayer for high-loading stability)

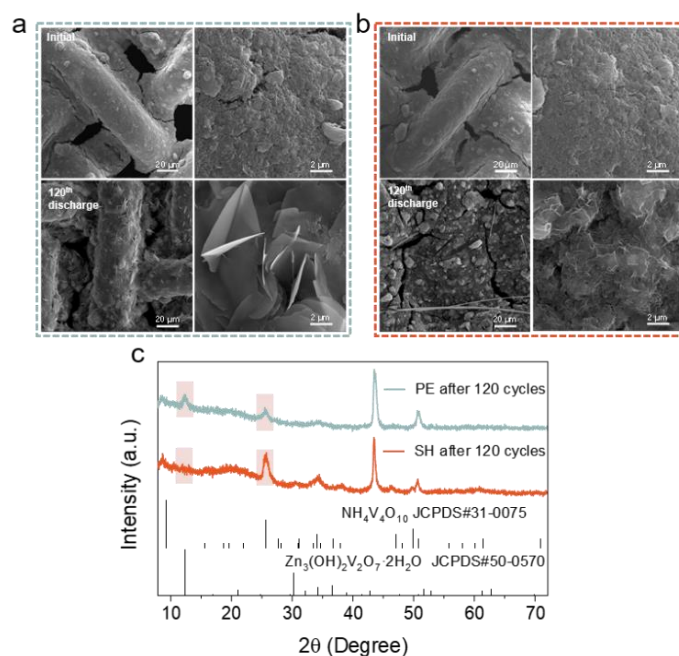


Figure S25. (c) *Ex-situ* XRD patterns of NVO in PE and SH electrolyte after 120 cycles. (in Supporting information)

6. In Figure S18, there seemed to be errors in the annotation of SEM images corresponding to NVO of different cycle stages.

Response: Thanks to **Reviewer #1** for your thorough review of the supplementary figures. Upon inspection, we discovered that a misplacement of text led to an inaccurate explanation of this figure. Consequently, we have redrawn **Figure S25** (original Figure S18) and included the XRD pattern after 120 cycles.

Changes:

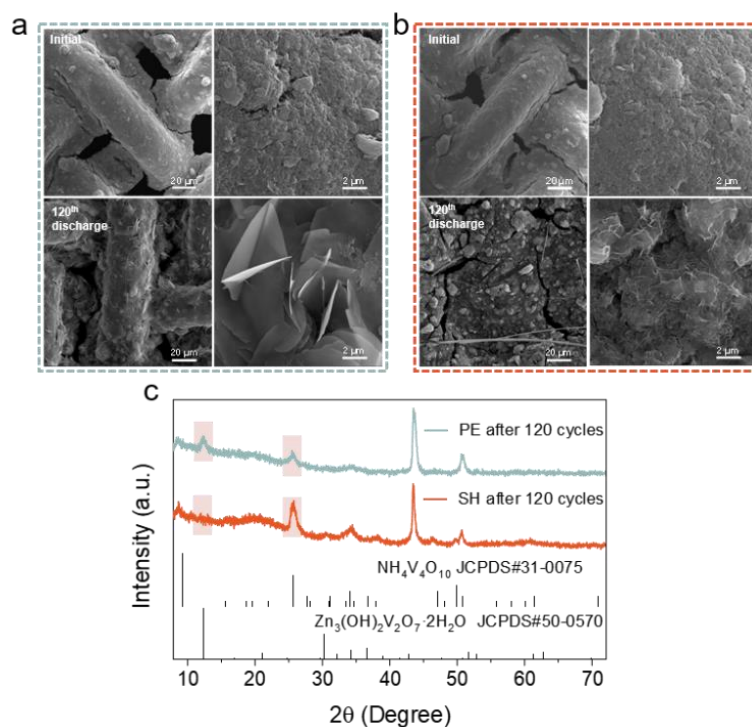


Figure S25. Surface morphology of NVO initial and after 120 cycles in (a) PE and (b) SH electrolyte. (c) *Ex-situ* XRD patterns of NVO in PE and SH electrolyte after 120 cycles. (in **Supporting information**)

7. The authors stated that “A stack of four $\text{Zn}||\text{NH}_4\text{V}_4\text{O}_{10}$ single layer cells in series successfully power a toy car model to run with a voltage of 3.8 V (Figure S31; Video, Supporting Information)”. However, according to Figure S31, it can be observed that the battery assembly depends on the clamp plate, which may lead to an increase in the whole weight of the battery. Furthermore, a video of the toy car is suggested to be provided.

Response: Thanks to **Reviewer #1** for your valuable suggestions. As observed in **Figure S41**, the pouch cell needs to be operated with an additional clamp, which is related to the limitations of our assembly process. Due to the inherent elasticity of the carbon felt and to prevent poor contact between the electrodes caused by gas generation, we were compelled to use a clamp during testing. Despite this,

the battery still demonstrated practical performance, with the device operating under the external clamp load. The specific parameters of double-layer pouch battery (1.2 Ah) are described in detail in **Table S2**. We have explained in detail the use of clamps in "**Assembly and test methods for pouch cells**". In addition, due to our negligence, the upload of the toy car running video is missing, and we are very sorry about this and now we have added it as the supplementary file.

Changes:

Assembly and test methods for pouch cells

Firstly, using polytetrafluoroethylene (PTFE) and carbon felt instead of PVDF and steel mesh as the binder and current collector, respectively. For a single-layer pouch cell ($6 \times 6 \text{ cm}^2$), the NVO loading was 25 mg cm^{-2} , while for the double-layer pouch cell ($9 \times 11 \text{ cm}^2$), the NVO loading was 20 mg cm^{-2} , respectively. A $100 \text{ }\mu\text{m}$ zinc foil, polished by 400, 800 and 1200 mesh and cleaned with water and ethanol, was used as the anode. The cells were assembled in a stacked configuration, with each separator containing $110 \text{ }\mu\text{L cm}^{-2}$ of electrolyte. And in the use of clamps, clamps were used at the four corners of the rectangle to apply 30 kg of pressure to ensure full contact between the positive and negative electrodes and the separators.

Testing procedure: In the tests of both single-layer and double-layer pouch cells, a constant areal current (3 mA cm^{-2}) was used. For the high-current double-layer pouch cell test (5 mA cm^{-2}), a lower current (3 mA cm^{-2}) was applied for the first two cycles to ensure proper activation and subsequent cycling performance. (in **Supporting information**)

Reviewer #2: This manuscript introduces PMS as a bifunctional additive for both Zn anode and V-based cathodes. Improved anode and full cell performance were demonstrated, which were ascribed to the adsorption effect of PMS at the Zn anode and the pillar effect of PMS intercalated into $\text{NH}_4\text{V}_4\text{O}_{10}$ cathode. Although good performance of Ah-level pouch cells is achieved, most of the scientific aspects are wrongly understood and explained in this article. It is thus not recommended to publish in its current format:

Response: Thanks to **Reviewer #2** for carefully examining the manuscript and providing insightful suggestions and comments, which are very helpful in improving the scientificity of our manuscript. In order to solve the issues proposed by Reviewer, more experiments and characterizations such as 3D TOF-SIMS, NMR, QCM, TEM, EDS mapping, ζ potential and theoretical calculations, etc. were supplemented. We have fully considered these comments, and have conducted in-depth analysis and adjustments on the corresponding content to make a comprehensive revision. We are trying our best to enhance the quality of our manuscript in order to meeting the *Nature Communications*. The detailed discussion and in-depth analysis are listed in point-by-point response below.

1. “Unlike other organic electrolyte additives, PMS does not affect the Zn^{2+} solvation structure”. Please use direct and more sensitive techniques to confirm this point, for example, XAS.

Response: Thank for this valuable comment. We apologize for the previous imprecise explanation that “PMS does not affect the Zn^{2+} solvation structure”. The FTIR results only suggest the weak interactions between PMS and water molecules, but in fact, through more sensitive characterization, we have found that PMS has an impact on the Zn^{2+} solvation structure.

Due to the lack of direct or indirect resources and channels for XAS characterization currently for us, we adopted ^1H NMR, which is also sensitive to solvation structure, to illustrate this point. As shown in **Figure 2a**, the ^1H of $-\text{CH}_2-$ (c, b, a) in PMS molecules shifts to a high field with increasing Zn^{2+} content, indicating that PMS participates in the Zn^{2+} solvation structure (*J. Electrochem. Soc.* 2011, 158, D143; *Angew. Chem.*, 2023, 135, e202309594).

Changes:

To clarify the Zn^{2+} solvation structure in the SH, ^1H nuclear magnetic resonance (NMR) spectra were carried out for SH electrolytes with different Zn^{2+} concentrations, as shown in **Figure 2a**. The ^1H of $-\text{CH}_2-$ (c, b, a) in PMS molecules shifts to a high field with increasing Zn^{2+} content, indicating that

PMS participates in the Zn^{2+} solvation structure^{22,23}. This bonding is due to the interaction between SO_3^- groups and zinc ions, which will be explained in more detail in subsequent tests. The ^1H of H_2O is approximately 4.8 ppm in the 20 mM PMS electrolyte. With increasing Zn^{2+} concentration, its chemical shift does not exhibit a significant change, indicating that the chemical environment of water molecules remains unchanged. This result is consistent with the FTIR (3000 cm^{-1} – 3600 cm^{-1}), suggesting weak interactions between PMS and water molecules (**Figure S2**).

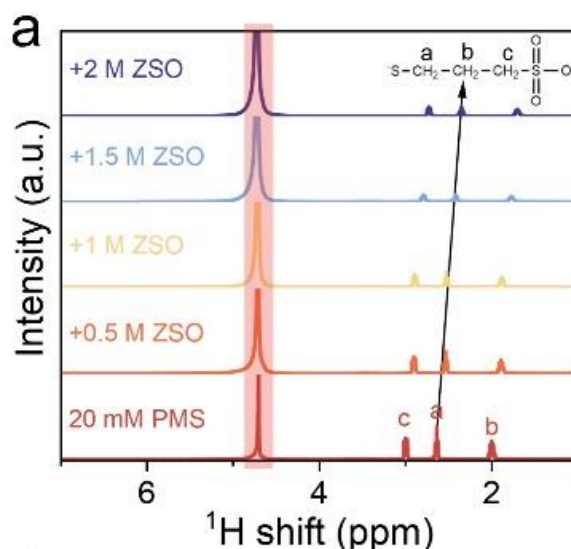


Figure 2. (a) The ^1H NMR spectra of PMS in the electrolytes with different ZnSO_4 salt concentrations. (in **Results-Directional adsorption of additives and gradient interface at the Zn anode**)

2. The concept of gradient adsorption layer of PMS on the Zn surface is mostly based on XPS. However, the author analyzed their XPS data in a very superficial and wrong way: 1. The atomic concentration at different depths should be presented. 2. The fitting of S 2p is completely wrong, the author even did not fit each component with 2p 1/2 and 2p 3/2. So does for the Zn 2p. All XPS data in this article needs to be re-analyzed. This is an often-to-see but pathetic phenomenon in this area, that XPS is overwhelmingly used without a strict understanding of it. Please also consider using 3D TOF-SIMS to visualize this proposed gradient adsorption layer, which should provide more sensitive results.

Response: Thanks to **Reviewer #2** for the valuable suggestions. Following your suggestions, we have conducted 3D TOF-SIMS tests and provided information on the atomic concentrations at different etching times, as well as re-fitted and analyzed the XPS peaks.

According to the 3D TOF-SIMS results (**Figure 2e**), the organic molecular layer represented by

CH_2^- and CH_2SO_3^- is distributed only on the surface, while the inorganic layer represented by ZnS^- and ZnS_2^- is distributed deeper. So, the interfacial self-assembled molecular layer is not a single molecular layer in the traditional sense, but an ordered thin film structure composed of multiple molecular layers with their derivative. It indicates that the outer layer is dominated by $-\text{SO}_3^-$, and the inner layer is dominated by Zn-S , forming a gradient molecular layer. The corresponding contents was supplemented and modified in the revised manuscript and Supporting Information.

For the re-analyzed XPS results: (i) **Figure S6b** shows the variations in the concentrations of C, O, S, and Zn atoms at different sputtering times. It demonstrates that with increasing sputtering time, the Zn element content increases while the O and C element contents decrease. This indicates the presence of a certain thickness and an organic-layer-dominated outer self-assembled molecular layer, which gradually transitions to a ZnS-dominated layer inward. (ii) We have fitted each component of S 2p spectrum with $2p_{1/2}$ and $2p_{3/2}$. In the fitting of the S 2p peaks, the energy difference between $2p_{1/2}$ and $2p_{3/2}$ is 1.2 eV. The peaks at 169-170 eV mainly correspond to $-\text{SO}_3^-$ at S $2p_{3/2}$ 168.9 eV and S $2p_{1/2}$ 170.1 eV (*Journal of Environmental Sciences*, 2025, 149: 254-267). The peaks between 162-163 eV represent several compound states, including ZnS (S $2p_{3/2}$ 161.6 eV and S $2p_{1/2}$ 162.8 eV), specific adsorbed $\text{C}_3\text{H}_6\text{-S}$ species (S $2p_{3/2}$ 162.4 eV and S $2p_{1/2}$ 163.6 eV, S $2p_{3/2}$ 164.3 eV and S $2p_{1/2}$ 165.5 eV) (*Journal of Crystal Growth*, 1988, 92(1-2): 128-142; *J. Phys. Chem. B* 2002, 106, 5438-5446). For Zn 2p, the energy difference between $2p_{1/2}$ and $2p_{3/2}$ is 23 eV, and the binding energy difference between elemental zinc and zinc oxide is approximately 0.3 eV. Therefore, we re-labeled the Zn 2p results. These results also show that the $-\text{SO}_3^-$ are located at the outermost part of the adsorption layer, and the $-\text{S-C}_3\text{H}_6-$ firmly binds to ZnS at the inner layer.

Changes:

Furthermore, the detailed adsorption configuration was studied by the 3D Time of flight secondary ion mass spectrometry (TOF-SIMS) of the Zn anode surface after soaking in PMS solution and then washing. In **Figure 2e**, the three-dimensional depth and intensity distribution of different functional groups are visually represented, showing that CH_2SO_3^- and CH_2^- , associated with SO_3^- , are only distributed in the outer layer. As the depth increases, the distribution shifts to ZnS_2^- and ZnS^- dominated. The interfacial self-assembled molecular layer is not a single molecular layer in the traditional sense, but an ordered thin film structure composed of multiple molecular layers with their derivative, which indicates that the outer layer is dominated by $-\text{SO}_3^-$, and the inner layer is dominated

by Zn–S, forming a gradient molecular layer. (in Results-Directional adsorption of additives and gradient interface at the Zn anode)

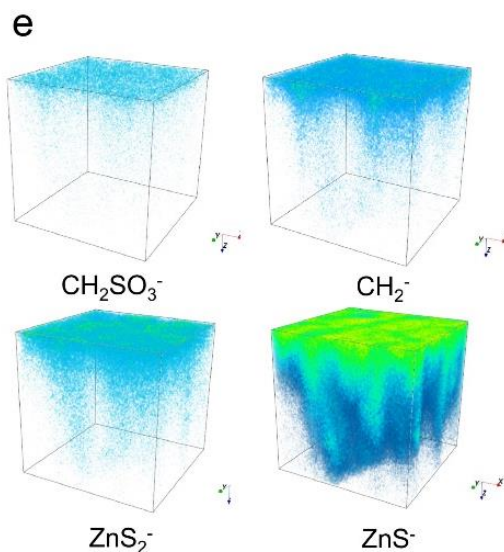


Figure 2. (e) Three-dimensional view of distributions for PMS on Zn anode in the negative TOF-SIMS sputtered volumes. (in Results-Directional adsorption of additives and gradient interface at the Zn anode)

And this result is also confirmed in X-ray photoelectron spectroscopy (XPS) depth profile (Figures S7 and S8). The increase in Zn intensity suggests that substances such as ZnS or Zn metal dominate the inner layer. And with increasing etching time, the $-\text{SO}_3^-$ peak³² intensity weakened, while the bond strength of $\text{C}_3\text{H}_6\text{--S}^{30,33}$ and Zn–S increased (Figure S7a). After etching for 480 seconds, the intensity of the $\text{C}_3\text{H}_6\text{--S/Zn--S}$ peaks significantly increased even the $-\text{SO}_3^-$ peak disappeared completely. Meanwhile, in the comparison between the $\text{C}_3\text{H}_6\text{--S}$ and Zn–S peaks, it was found that the intensity of the Zn–S peak and the $\text{C}_3\text{H}_6\text{--S}$ peak significantly increased after 90 s. Figure S7b also shows the variations in the concentrations of C, O, S, and Zn atoms at different sputtering times. The figure demonstrates that with increasing sputtering time, the Zn element content increases while the O and C element contents decrease. These results show that the $-\text{SO}_3^-$ are located at the outermost part of the adsorption layer, and the $-\text{S--C}_3\text{H}_6-$ firmly binds to ZnS at the inner layer, enabling the self-assembly process. (in Results-Directional adsorption of additives and gradient interface at the Zn anode)

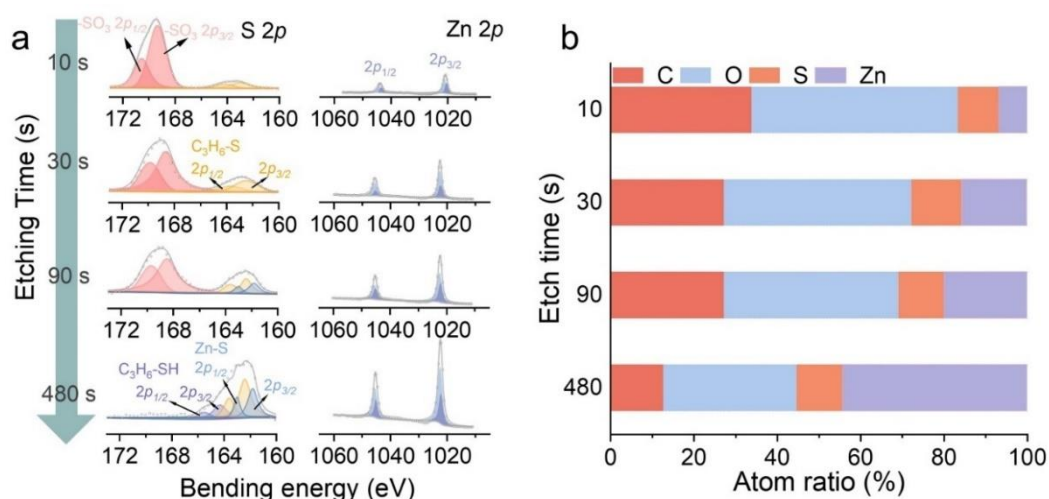


Figure S7. (a) XPS depth profiles of Zn foil surface after soaking in PMS solution. (b) The corresponding atom ratios. (in Supporting information)

3. Authors claimed that PMS adsorption is chemical adsorption, but the calculation was based on physical electrostatic attraction. This is weird. Please explain.

Response: Thank you for this comment. In fact, all calculations are performed using VASP, with PMS molecules involving charge transfer between functional groups and zinc metal atoms, as shown in **Figure 2d**. The key to distinguishing between chemisorption and physisorption lies in determining whether significant charge transfer occurs between the adsorbed atoms. On the one hand, the optimized interface structure shows that the distance between the sulfur atom in the thiol group is 2.0-2.4 Å, which is within the bonding range. On the other hand, according to the Bader charge density difference (**Figure S5a**), significant charge transfer occurs between Zn and the S/O atoms in the functional groups, which even exceeds that of the C-C or C-H bonds in PMS molecules. This could be observed from the more pronounced charge density difference between Zn-O/S in 2D plot as shown in **Figure S5b**. Therefore, the calculations in this study represent chemical bonding interactions rather than simple physical adsorption.

Changes:

Furthermore, the Bader charge density difference (**Figure S5**) further confirms the chemical adsorption effect. (in Results-Directional adsorption of additives and gradient interface at the Zn anode)

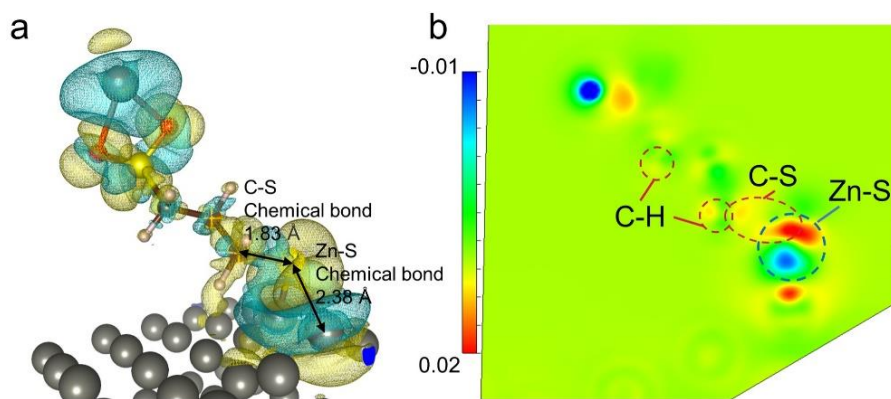
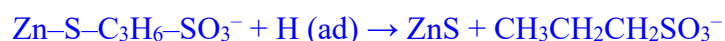
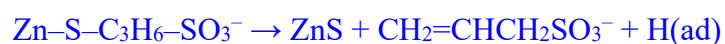


Figure S5. (a) Charge density difference of adsorbed PMS molecule at the interface of Zn. (b) 2D plot of interfacial charge densities. (in Supporting information)

4. For reaction “ $\text{Zn-S-C}_3\text{H}_6\text{-SO}_3^- + 6\text{H}^+ + \text{Zn} + 4\text{e}^- = \text{Zn-S-C}_3\text{H}_6^+ + \text{Zn}^{2+}\text{-S}^{2-} + 3\text{H}_2\text{O}$ ”, it is hard to image such a 4-electron reaction can happen at ambient condition without any driving force. If the reaction happens in such an acidic environment, H^+ should directly react with Zn to form H_2 .

Response: Thank you for pointing out this unreasonable equation. This reaction was originally referenced from the previous report (*Angew. Chem. Int. Ed.* 2023, 62, e202311988), but as mentioned by reviewer it is reasonable for the difficulty of such 4-electron reaction without any driving force. To provide a more rigorous and reasonable analysis of the interfacial reaction in our work, we have combined interfacial characterization such as 3D TOF-SIMS, etched XPS, theoretical calculation, etc., and revised this interfacial reaction based on our findings.

Based on LUMO/HOMO energy level calculations, PMS molecules may decompose on the zinc anode (**Figure 2f**). The adsorption and subsequent decomposition products can be verified through 3D TOF-SIMS (**Figure 2e**). As the etching time increases, the intensity of the CH_2SO_3^- and CH_2^- , associated with SO_3^- , are only distributed in the outer layer. With the depth increases, the distribution shifts to ZnS_2^- and ZnS^- dominated. The formation of ZnS suggests the cleavage of $\text{C}_3\text{H}_6\text{-S}$ bonds, as the electrons from Zn attack nucleophilically the C-S bond in the thiol group, forming the intermediate $-\text{C}_3\text{H}_6\text{-SO}_3^-$. This intermediate can undergo hydrogenation to produce $\text{CH}_3\text{CH}_2\text{CH}_2\text{SO}_3^-$ or a β -H elimination reaction to form $\text{CH}_2=\text{CHCH}_2\text{SO}_3^-$ (*J. Phys. Chem. B* 2002, 106, 5438-5446). Hence, the reaction formula can be concluded as follow:



After a layer of ZnS forms, no further C-S bond cleavage occurs due to the lack of excess electrons in ZnS. Therefore, subsequent PMS does not decompose but instead forms bonds with ZnS. This phenomenon can be observed in 3D TOF-SIMS, where the ZnS^- distribution is deeper, followed by a slightly lower intensity of ZnS_2^- , which indicates that PMS tends to adsorb onto ZnS, forming a product such as $\text{S-Zn-S-C}_3\text{H}_6\text{SO}_3^-$.

And this result is also confirmed in XPS. According to *J. Environ. Sci.*, 2025, 149: 254-267; *J. Cryst. Growth*, 1988, 92(1-2): 128-142; *J. Phys. Chem. B* 2002, 106, 5438-5446, we re-fitted the XPS results. As the etching time increases, the intensity of the $-\text{SO}_3^-$ peaks decreases, while the ZnS and specifically adsorbed $\text{C}_6\text{H}_7\text{-S}$ peaks increase, indicating the dominance of ZnS and $\text{C}_3\text{H}_6\text{-S}$ species (*J. Raman Spectrosc.* 2003; 34: 853-862). These results show that the $-\text{SO}_3^-$ are located at the outermost part of the adsorption layer, and the $-\text{S-C}_3\text{H}_6-$ firmly binds to ZnS at the inner layer, enabling the self-assembly process.

Changes:

Furthermore, the detailed adsorption configuration was studied by the 3D Time of flight secondary ion mass spectrometry (TOF-SIMS) of the Zn anode surface after soaking in PMS solution and then washing. In **Figure 2e**, the three-dimensional depth and intensity distribution of different functional groups are visually represented, showing that CH_2SO_3^- and CH_2^- , associated with SO_3^- , are only distributed in the outer layer. As the depth increases, the distribution shifts to ZnS_2^- and ZnS^- dominated. The interfacial self-assembled molecular layer is not a single molecular layer in the traditional sense, but an ordered thin film structure composed of multiple molecular layers with their derivative, which indicates that the outer layer is dominated by $-\text{SO}_3^-$, and the inner layer is dominated by Zn-S, forming a gradient molecular layer. (in **Results-Directional adsorption of additives and gradient interface at the Zn anode**)

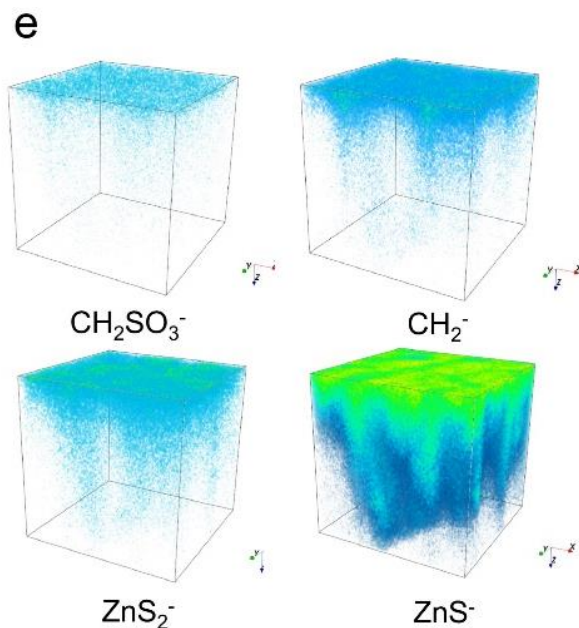
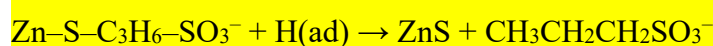
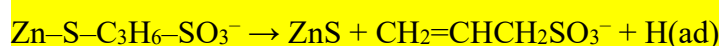


Figure 2. (e) Three-dimensional view of distributions for PMS on Zn anode in the negative TOF-SIMS sputtered volumes. (in Results-Directional adsorption of additives and gradient interface at the Zn anode)

The formation of ZnS suggests the cleavage of C-S bonds, as the electrons from Zn nucleophilically attack the C-S bond in the thiol group³⁴, forming the intermediate $-\text{C}_3\text{H}_6-\text{SO}_3^-$. This intermediate can undergo hydrogenation to produce $\text{CH}_3\text{CH}_2\text{CH}_2\text{SO}_3^-$ or a β -H elimination reaction to form $\text{CH}_2=\text{CHCH}_2\text{SO}_3^-$ ^{23,33}. On the other hand, the Zn-S exhibited lower adsorption energy with dehydrogenation -S- end ($-3.67 \text{ eV} < -2.93 \text{ eV}$ of $-\text{SO}_3^-$ in **Figure S6**), indicating that the $-\text{SO}_3^-$ of PMS anions, located at the outer self-assembled molecular layer, is also facing outward. Thus, the adsorbed $\text{Zn-S-C}_3\text{H}_6-\text{SO}_3^-$ preferentially receives electrons from Zn and is reduced, according to the equation:



After a layer of ZnS forms, no further C-S bond cleavage occurs due to the lack of excess electrons in ZnS. Therefore, subsequent PMS does not decompose but instead forms bonds with ZnS. This phenomenon can be observed in 3D TOF-SIMS, where the ZnS^- distribution is deeper, followed by a slightly lower intensity of ZnS_2^- , which indicates that PMS tends to adsorb onto ZnS, forming a product such as $\text{S-Zn-S-C}_3\text{H}_6\text{SO}_3^-$.

And this result is also confirmed in X-ray photoelectron spectroscopy (XPS) depth profile (Figures S7 and S8). The increase in Zn intensity suggests that substances such as ZnS or Zn metal dominate the inner layer. And with increasing etching time, the $-\text{SO}_3^-$ peak³¹ intensity weakened, while the bond strength of $\text{C}_3\text{H}_6-\text{S}$ ^{32,33} and Zn-S increased (Figure S7a). After etching for 480 seconds, the intensity of the $\text{C}_3\text{H}_6-\text{S}/\text{Zn-S}$ peaks significantly increased even the $-\text{SO}_3^-$ peak disappeared completely. Meanwhile, in the comparison between the $\text{C}_3\text{H}_6-\text{S}$ and Zn-S peaks, it was found that the intensity of the Zn-S peak and the $\text{C}_3\text{H}_6-\text{S}$ peak significantly increased after 90 s. Figure S7b also shows the variations in the concentrations of C, O, S, and Zn atoms at different sputtering times. The figure demonstrates that with increasing sputtering time, the Zn element content increases while the O and C element contents decrease. These results show that the $-\text{SO}_3^-$ are located at the outermost part of the adsorption layer, and the $-\text{S}-\text{C}_3\text{H}_6-$ firmly binds to ZnS at the inner layer, enabling the self-assembly process. (in Results-Directional adsorption of additives and gradient interface at the Zn anode)

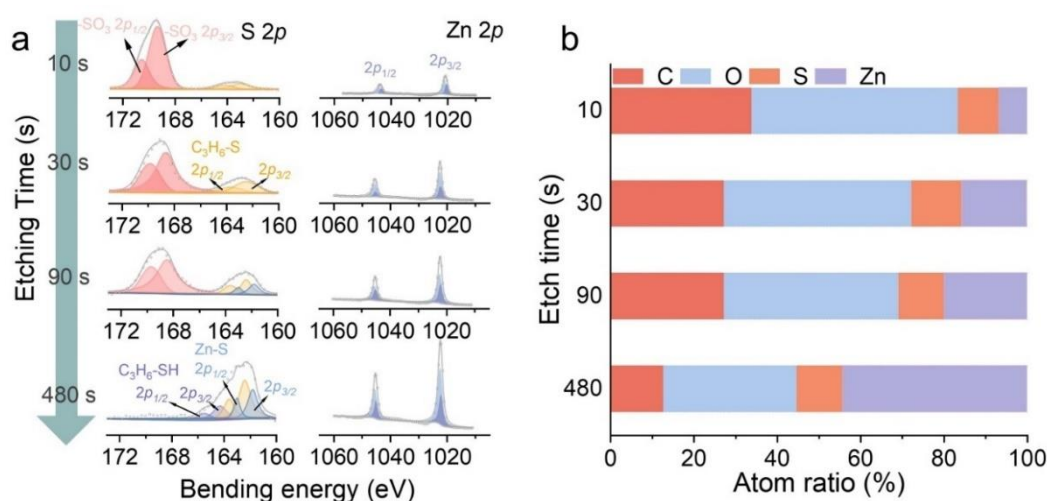


Figure S7. (a) XPS depth profiles of Zn foil surface after soaking in PMS solution. (b) The corresponding atom ratios. (in Supporting information)

5. For Fig3b, it is very unusual to see the plating overpotential continuously goes up even after 1 mAh cm⁻², which is normally at a level of 0.1-0.2 mAh cm⁻² where the nucleation process ends. I suspect that a poorly polished Zn is used for PE whereas a well-polished Zn is used for SH. Please check.

Response: Thanks for the question proposed by Reviewer #2. We have re-examined the curve in Figure 3b. We confirm that the conditions for the zinc foil used in the experiments were consistent,

utilizing polished zinc foil, which was polished by 400, 800 and 1200 mesh and cleaned with water and ethanol. To ensure reproducibility, twice parallel tests were also conducted (**Figure R2-1**), which are consistent with those presented in the original manuscript.

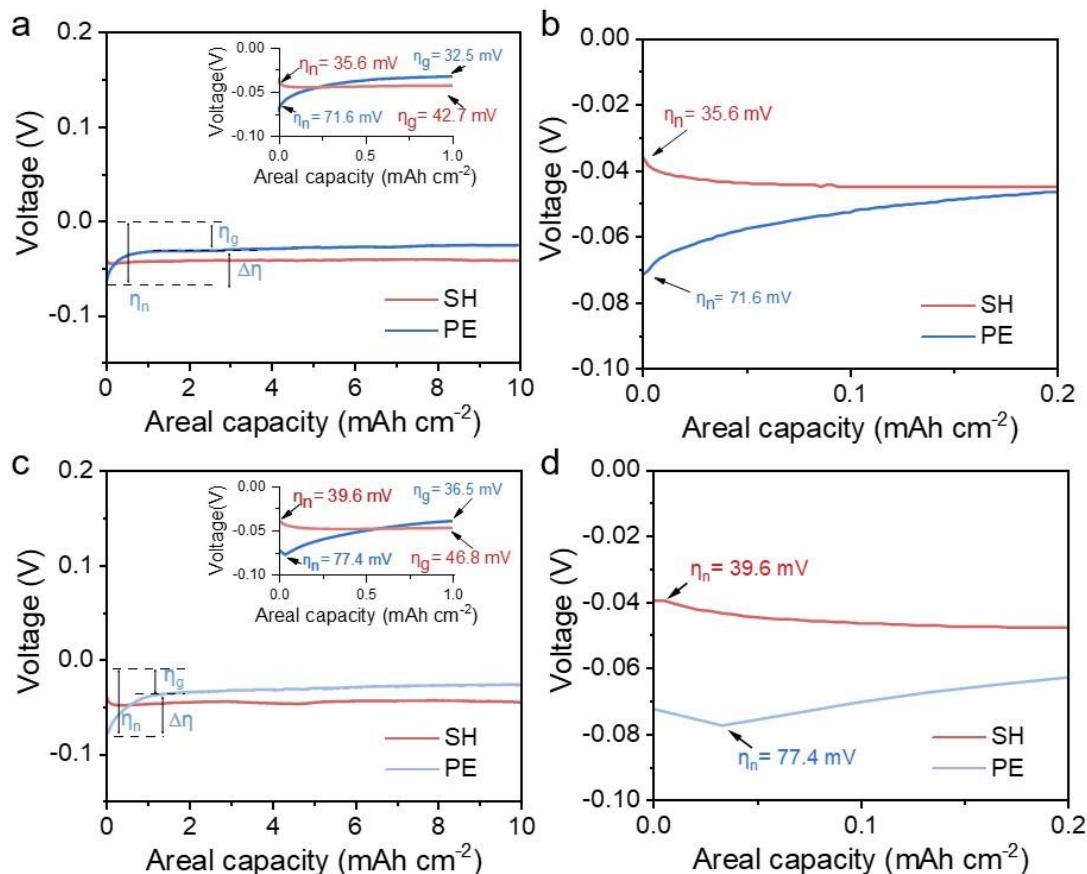


Figure R2-1. Two parallel experiments of deposition curves in SH and PE electrolytes at 2 mA cm⁻²–10 mAh cm⁻². (a) Supplementary Experiment 1, and (b) Corresponding magnified view of the areal capacity from 0 to 0.2 mAh cm⁻² in (a). (c) Supplementary Experiment 2, and (d) Corresponding magnified view of the areal capacity from 0 to 0.2 mAh cm⁻² in (c).

From **Figures R2-1 a and b**, it is evident that the deposition curve of the pure electrolyte still exhibits an increase at 0.1-0.2 mAh cm⁻², with a nucleation overpotential greater than that of the SH electrolyte. A similar trend is observed in another set of parallel experiments, where the deposition curve in the pure electrolyte also shows an upward trend (**Figures R2-1 c and d**). Moreover, the deposition curve in the PE electrolyte stabilized after 1 mAh cm⁻² deposition. The slight reduction in voltage may also be due to a decrease in the energy required for growth. This phenomenon is not unique. Similar observations have been reported in other studies, including *Joule*, 2023, 7, 1-31; *Adv. Energy Mater.* 2022, 2103231; *Adv. Mater.* 2024, 36, 2404140 (**Figure R2-2**). In fact, this change in

overpotential is due to the competitive advantage between nucleation and growth driving forces (*Joule*, 2023, 7, 1-31). Therefore, $\Delta\eta$ is an indicator used to evaluate the driving force difference between nucleation and growth, and we consider this curve behavior to be normal.

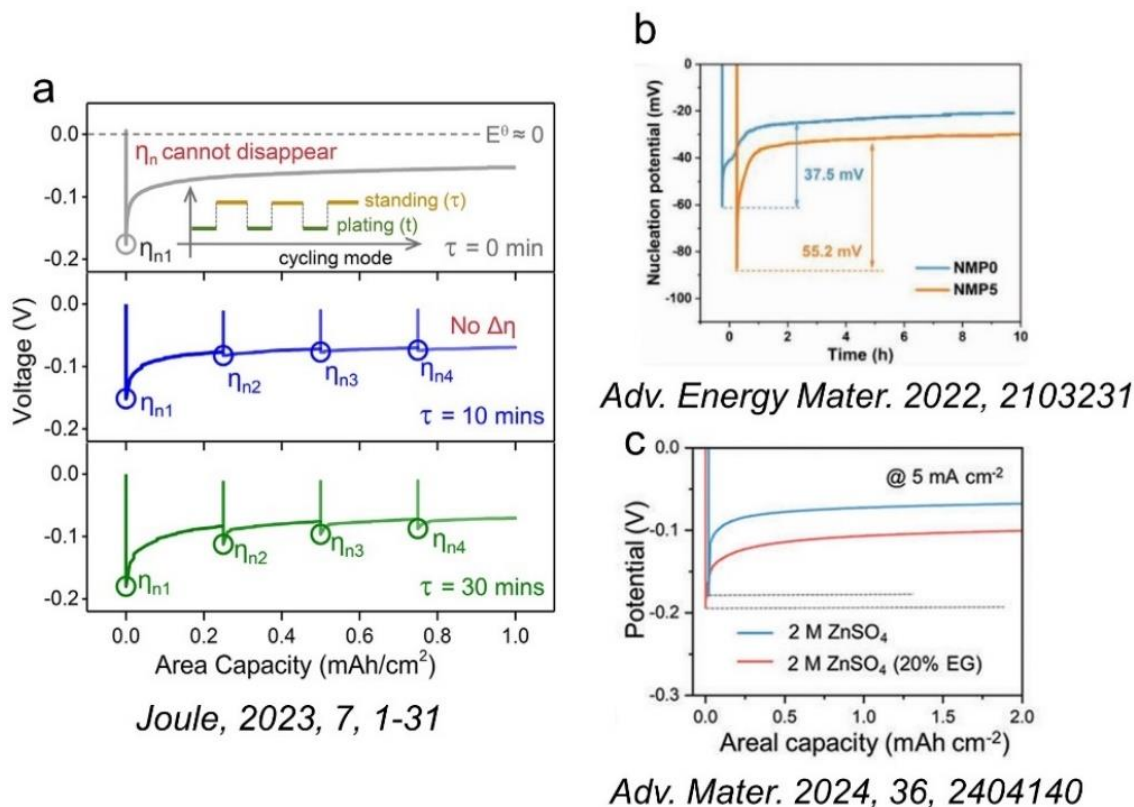


Figure R2-2. Deposition curves of (a) static test standing Zn/Zn cell for τ minutes after plating 0.25 mAh cm^{-2} at 1 mA cm^{-2} in the electrolyte of 2 M ZnSO_4 , (b) Zn/Ti cells at 1 mA cm^{-2} in the electrolyte of 2 M ZnSO_4 and 2 M ZnSO_4 with 5% N-Methylpyrrolidone, (c) On the Zn anode in the electrolyte of 2 M ZnSO_4 and $2 \text{ M ZnSO}_4 + 20\%$ ethylene glycol (EG) at 5 mA cm^{-2} .

Changes: None.

6. The SEM images at 1 mAh cm^{-2} cannot well show the nucleation density as the growth behavior has already started for a period of time. Please do this at 0.1 mAh cm^{-2} or below.

Response: We appreciate your comment regarding the SEM images. Our initial intention was to observe the differences at the onset of the nucleation stage after the termination of the nucleation, which led us to overlook the deposition stage of its nucleation. Following your suggestion, we have supplemented the SEM images at a deposition capacity of 0.1 mAh cm^{-2} and revised the original manuscript accordingly.

At a deposition capacity of 0.1 mAh cm^{-2} , the PE electrolyte exhibits a limited number of nucleation sites, leading to highly uneven nucleation concentrated at specific area (**Figure S13**). In contrast, the high nucleation density in the SH electrolyte results in uniform deposition on the substrate, making it difficult to observe exposed substrate areas (**Figure 3g**).

Furthermore, not only at the stage of 0.1 mAh cm^{-2} , but throughout the subsequent growth process, uniform Zn deposition was observed. Furthermore, in the PE electrolyte, the deposition of Zn clusters is evident from scans from 1 mAh cm^{-2} to 10 mAh cm^{-2} of deposited charge (**Figures 3g II, III and IV**), indicating a scarcity of nucleation sites, which results in the formation of clusters. Conversely, in the SH electrolyte, there is uniform deposition morphology with no significant Zn clusters (**Figures 3h and S15**), which is due to the presence of numerous nucleation sites.

Changes:

PMS significantly reduces the nucleation barrier of Zn^{2+} on the Zn anode. The results of the nucleation tests (**Figures 3d and e**), calculated using the relevant formula, reveal that the nucleation density of Zn in the SH electrolyte is significantly higher than in the PE electrolyte. The high nucleation density and derived uniform surface morphology were clarified by SEM images, and the different stages marked as I, II, III and IV in **Figure 3b** were selected. At a deposition capacity of 0.1 mAh cm^{-2} , the PE electrolyte exhibits a limited number of nucleation sites, leading to highly uneven nucleation concentrated at specific area (**Figures 3g I and S13**). In contrast, the high nucleation density in the SH electrolyte results in uniform deposition on the substrate, making it difficult to observe exposed substrate areas. (in **Results-Uniform Zn deposition under high areal capacity**)

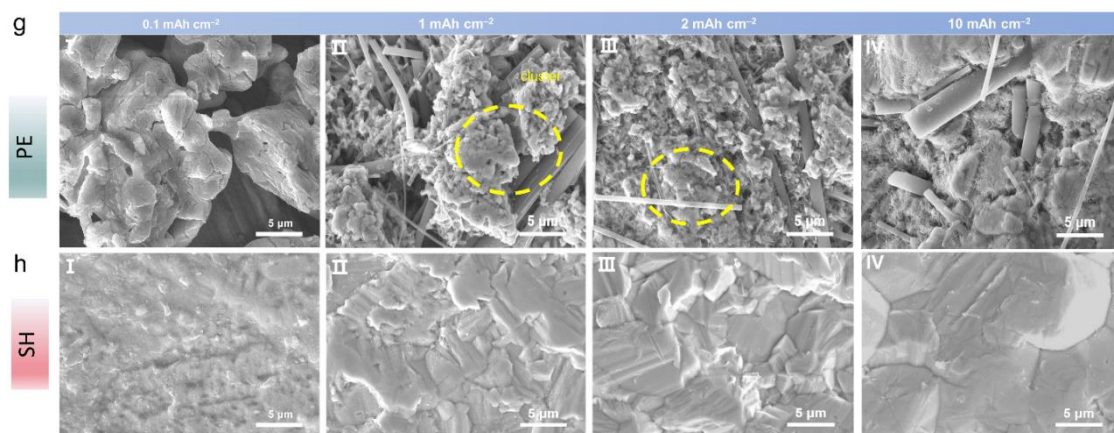


Figure 3. SEM images of Zn deposition with different capacity in (g) PE and (h) SH electrolytes. (in **Results-Uniform Zn deposition under high areal capacity**)

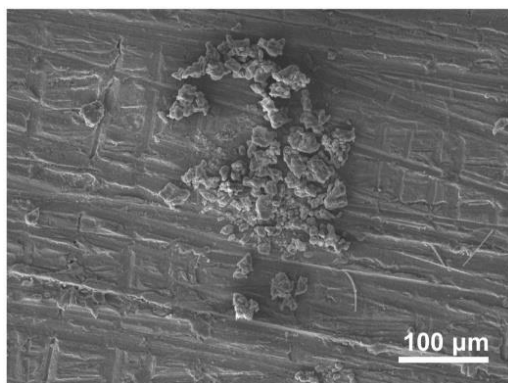


Figure S13. SEM image of Zn anode after 0.1 mAh cm^{-2} deposition in PE electrolyte. (in Supporting information)

7. The concept of “PMS molecules can electrochemically in situ modify the interlayered lattice of $\text{NH}_4\text{V}_4\text{O}_{10}$ during the cycles” is not supported by any direct experimental results and mostly likely wrong due to the following points:

a. The author assumes Zn^{2+} intercalation dominates the discharge process, which is wrong. Many previous studies have already confirmed the presence of dominant proton interaction in both Mn and V-based cathodes. Therefore, the explanation about lattice shrinkage/expansion is not true.

Response: Thanks for this valuable comment. We do agree with the reviewer that the presence of dominant proton interaction in both Mn-based (*Adv. Mater.* 2023, 35, 2300053; etc.) and V-based (*Nat. Commun.* 2018, 9, 1656; *Adv. Mater.* 2024, 36, 2310434; etc.) cathodes. In the original manuscript, we intended to demonstrate that the Zn^{2+} intercalation was occurred during the reaction process, without emphasizing its dominant role. Perhaps some expressions caused this misunderstanding, which have been modified in the revised manuscript.

We note that for vanadium-based cathodes, most works revealed a Zn^{2+} intercalation mechanism or a $\text{H}^+/\text{Zn}^{2+}$ co-intercalation mechanism, especially for layered materials. However, numerous works suggest that proton intercalation affects electrochemical behavior by enhancing reaction kinetics due to the relatively small volume of protons. It was reported the lattice changes induced by proton intercalation for the layered $\text{Na}_{0.12}\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot 2.5\text{H}_2\text{O}$ is very small (lattice spacing of $\sim 0.78\%$ in (001) plane), as evidenced in *Sci. Adv.* 2023, 9, eadf4589 (Figure R2-3a, b), which was analyzed by theoretical calculations and ex-situ XRD. While a report (*Nat. Commun.* 2023, 14, 3067, that proposed only Zn^{2+} intercalation mechanism) of similar layered cathode ($\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ as reported in *Nat.*

Energy 2016, 1, 16119, **Figure R2-3c**) has revealed that (003) diffraction peak variations of $\sim 1.3^\circ$ (lattice spacing of $\sim 4.5\%$ in (003) or (001) plane) was occurred based on *in-situ* XRD analysis (**Figure R2-3d**). These results indicate that the intercalation/de-intercalation of Zn^{2+} have a significant impact on the lattice shrinkage/expansion, while the effect of proton intercalation/de-intercalation on lattice shrinkage/expansion is relatively small. In our work, the lattice spacing variations of $\sim 2^\circ$ near 35° (lattice spacing of $\sim 5.00\%$ in (004) plane) and $\sim 2.5^\circ$ near 45° (lattice spacing of $\sim 5.90\%$ in (-205) plane) were observed by *in-situ* XRD (**Figure 4b**), which are highly similar to only Zn^{2+} intercalation mechanism. Therefore, we think that the lattice shrinkage/expansion is predominantly driven by the intercalation/de-intercalation of Zn^{2+} in NVO in our work.

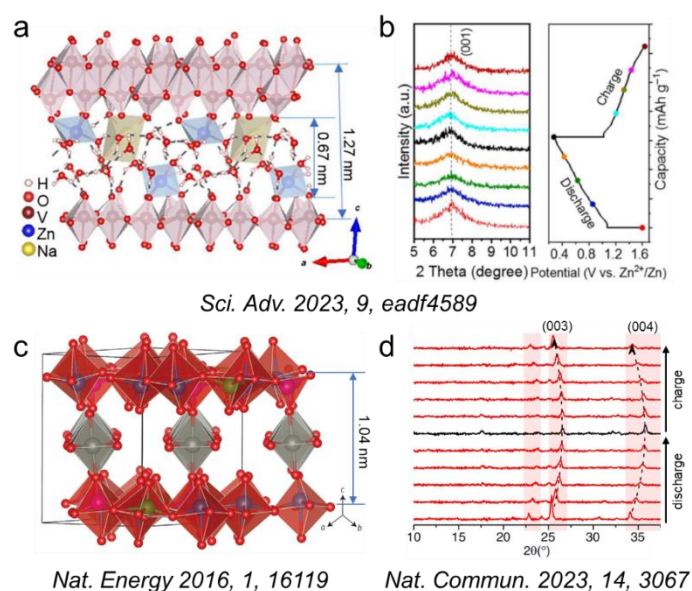
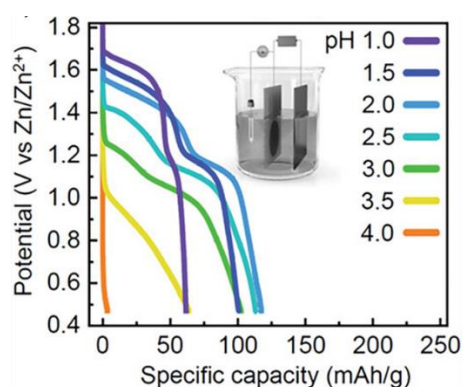


Figure R2-3. (a) Crystal structure of layered $\text{Na}_{0.12}\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot 2.5\text{H}_2\text{O}$, and (b) corresponding *ex-situ* XRD patterns with proton intercalation reaction mechanism and nearly unchanged (001) peaks (lattice spacing of $\sim 0.78\%$). (c) Crystal structure of layered $\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, and (d) corresponding *in-situ* XRD patterns in eutectic electrolyte with Zn^{2+} intercalation reaction mechanism and shifted (003)/(004) peaks (lattice spacing of $\sim 4.5\%$).

To further demonstrate the above viewpoint, the effect of proton intercalation on the lattice was revealed. The discharge test was carried out in 50 mM H_2SO_4 without Zn^{2+} . The discharge curve was obtained using a three-electrode system with Pt as a counter electrode and AgCl/Ag as reference electrode (0.226 V vs. SHE), setting the corresponding discharge cutoff voltage to -0.56 V (0.4 V vs. Zn/Zn^{2+}). As shown in **Figure S22a**, the characteristics of the discharge curve are highly consistent with the report (**Figure R2-4**, *Adv. Funct. Mater.* 2023, 33, 2303763). It should be noticed that the

capacity contributed by proton intercalation in NVO ($\sim 75 \text{ mAh g}^{-1}$) is obviously lower than that in normal ZnSO_4 electrolyte ($\sim 400 \text{ mAh g}^{-1}$ in **Figure 5f**), which highlighted the significance role of Zn^{2+} intercalation. Meanwhile, the XRD of cathode after the discharge reaction does not exhibit obvious diffraction peaks except for the stainless-steel mesh (SSM) current collector (**Figure S22b**). This indicates that the excessive proton intercalation can lead to a significant collapse of NVO cathode material, making the reaction difficult to reverse.

In order to make this part more scientific, the corresponding contents were modified in the revised manuscript.



Adv. Funct. Mater. 2023, 33, 2303763

Figure R2-4. First discharge curves in H_2SO_4 electrolytes with different pH values in three-electrode beaker-type cells with abundant electrolytes and proton intercalation reaction mechanism.

Changes:

As shown in **Figure 4a** and **Figure 4b**, the structural evolution was elucidated following the lattice modification according to *in-situ* XRD. Due to the electrostatic interaction between intercalated cations and lattice framework, the (001) diffraction peak of $\text{NH}_4\text{V}_4\text{O}_{10}$ shifted toward high angle during the discharging, being accompanied by the reversibly formation of hydrated hydroxyzinc sulfate ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$, ZSH) at 8.0° . Considering the interference of the ZSH (001) peak on the observation of the $\text{NH}_4\text{V}_4\text{O}_{10}$ (001) peak, the (004) and (-205) diffraction peaks were also marked with more obvious peak shift than (001) peak. Different from the nearly unchanged peaks (interlayered spacing of $< 1\%$) in the previous reported proton intercalation mechanism⁴⁰, the peak shift is larger and the change of interlayered spacing reaches $\sim 5\%$ in this work, which is consistent with the reported phenomenon of Zn^{2+} intercalation reaction⁴¹. Meanwhile, the NVO also exhibits lower specific capacity and collapsed lattice during the discharge in pure H_2SO_4 solution (**Figure S22**), which

indicates that the excessive proton intercalation can lead to a significant degradation of NVO structure and make the reaction difficult to reverse⁴². The NVO cathode exhibited that the (004) peak shifted from 34.1° to 36.0°, and (-205) peaks shifted from 43.0° to 45.8° during the discharge process, respectively. In contrary, the shift amplitude in SH electrolyte (34.1°-36.6° and 43.0°-46.1°) is lower than that in PE electrolyte, indicating weakened contraction caused by the Zn²⁺-lattice electrostatic effect. (in Results-Electrochemically in-situ modification of cathode interface for high-loading stability)

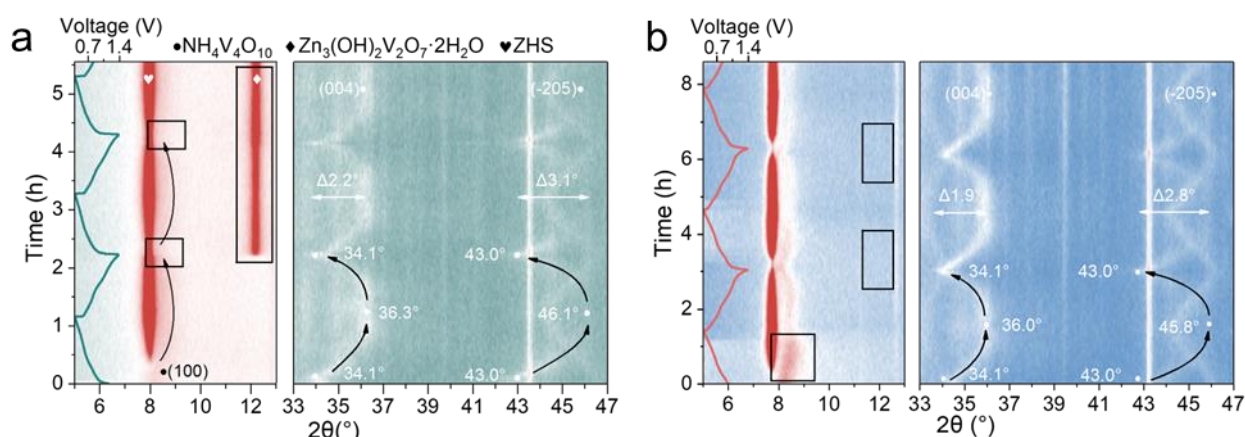


Figure 4. Enhanced stability of lattice framework by PMS adsorption. *In-situ* XRD pattern in (a) PE and (b) SH electrolytes. (in Results-Electrochemically in-situ modification of cathode interface for high-loading stability)

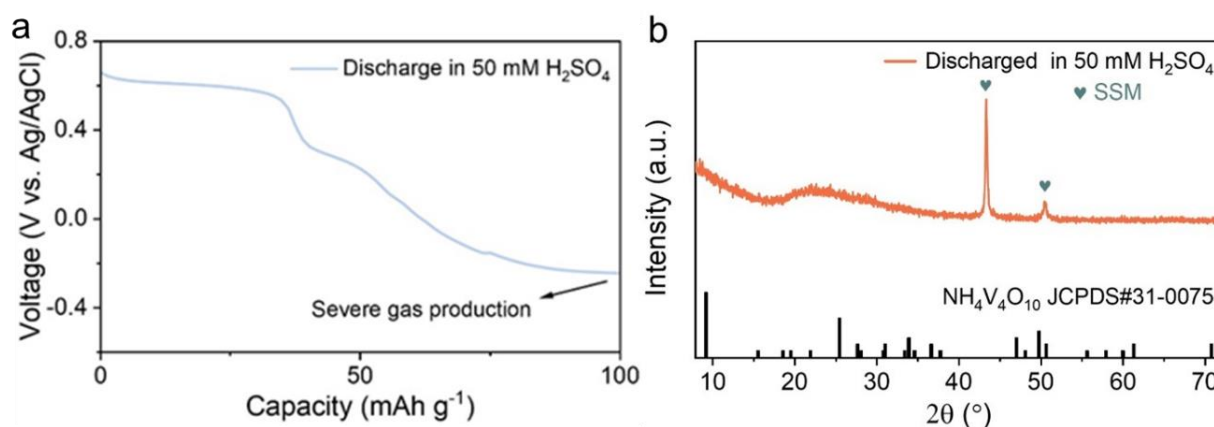


Figure S22. (a) Discharge curve of NVO cathode in a three-electrode battery system with 50 mM H₂SO₄ electrolyte. (b) XRD of cathode after discharge reaction. (in Supporting information)

b. “ZHS is due to the proton intercalation rather than the V dissolution. So does the pH vibration the reversible appearance/disappearance of ZSH and the absence of by-products could be observed in the

SH, confirming the enhanced stability of lattice framework". ZHS only forms on the surface of cathodes, its reversible appearance/disappearance has nothing to do with the stability of the lattice framework of the cathode.

Response: Thanks to **Reviewer #2** for pointing out this unclear description. We apologize for the previous imprecise explanation regarding the formation of ZSH. In fact, we would like to clarify that ZSH is reversibly present during the charge-discharge process, which ensures the stability of the electrode. The intercalation of Zn^{2+} induces lattice changes, leading to the V dissolution in normal ZnSO_4 electrolyte. The dissolved vanadium will partially deposit again as hydroxyvanadate when the electrolyte pH value increases during cycling, which could be found as the byproduct $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (JCPDS #50-0570) in *in-situ* XRD (**Figure 4a**). But in the SH electrolyte, the absence of by-products could be observed (**Figure 4b**), confirming the improved stability of NVO cathode. The corresponding content has been corrected in the revised version.

Changes:

From another point of view, there is still significant residual ZSH even after charging to 1.4 V in PE electrolyte. This residual ZSH is likely irreversible, as evidenced by the increase of electrolyte pH value with *in-situ* pH test (**Figures S23 and S24**) and SEM images (**Figure S25**). And this residual ZSH can occupy the electrochemical active sites of the cathode, preventing them from contributing to capacity, thereby leading to a decline in battery performance. In a complementary manner, the dissolved vanadium will partially deposit again as hydroxyvanadate when the electrolyte pH value increases during cycling. As a validation, the (001) peak disappeared and an obvious peak at 12.5° appeared after the first cycle and could be indexed as the byproduct $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (JCPDS #50-0570). On the contrary, the (001) peak and the absence of by-products could be observed in the SH electrolyte, confirming the improved stability of NVO cathode (**Figure 4b**). (in **Results-Electrochemically in-situ modification of cathode interlayer for high-loading stability**)

c. Again, the authors used XPS to propose the so-called lattice PMS, which is wrongly analyzed. In addition, XPS is only a surface technique, and cannot provide lattice information even with Ar sputtering. Please do not overanalyze the data.

Response: We really apologize for this misuse. We initially believed that PMS could be *in-situ* embedded in the NVO interlayer because during the first discharge process, the (100) plane of NVO

underwent significant changes (**Figure 4b**), and theoretical calculations also revealed that PMS molecules could stabilize in the NVO interlayer. However, as pointed out by the reviewer, it still lacks direct evidence. We have removed the incorrect results, and supplemented a series of data such as ζ potential (**Figure 4c**), QCM (**Figure 4d**), EDS mapping with TEM (**Figure 4e**), theoretical calculations (**Figure 4g** and **Figure 4h**) to reanalyze the effect of PMS on NVO cathode.

The ζ potential and QCM results indicate that PMS can easily adsorb at the NVO cathode interface and participate in the formation of electric double layer. The obvious C and S elements signals in the EDS mapping images of NVO cathode after cycles indicate the adsorption of PMS on interface of NVO, which suggest the *in-situ* modification of NVO surface during electrochemical reaction. The theoretical calculations of adsorption energy of PMS on NVO interface show that the O in $-\text{SO}_3^-$ can adsorb and coordinate with V on the cathode surface, ensuring the stability of $[\text{VO}_6]$ coordination octahedra. In the case of PMS adsorption, the ΔG of V atom dissolution is higher than that of bare surface, indicating that the *in-situ* modification of PMS can inhibit the vanadium dissolution in NVO cathode. ICP results (**Figure 6e**) also confirmed the significant effect of PMS in inhibiting vanadium dissolution, thus enabling the high-loading stability of NVO cathode and long-term Ah-scale pouch cell.

Changes:

In the subsequent cycles, the NVO lattice did not exhibit significant crystallographic changes. Combining the ζ potential of NVO powder in different solutions, PMS is mainly located at the cathode interface to inhibit vanadium dissolution and byproduct generation. The ζ potential represents the charge of particles with tightly adsorbed layers in specific solution. As shown in **Figure 4c**, the ζ potential in 2 M ZnSO_4 (PE, -19.27 mV) and 20 mM PMS solutions (-19.93 mV) is similar, indicating the similar interfacial electric double layer structure (inset in **Figure 4c**). After introducing Zn^{2+} into PMS solution (SH), the ζ potential significantly increased, indicating that the low valence ions such as H^+/Na^+ were replaced by Zn^{2+} . This is beneficial for the Zn^{2+} adsorption from bulk electrolyte and subsequent Zn^{2+} intercalation, avoiding the cathode dissolution caused by excessive H^+ intercalation as discussed above. The adsorption of PMS can also be verified by quartz crystal microbalance (QCM) as shown in **Figure 4d**. It can be observed that mass of the adsorbed species on NVO do not change significantly even after introducing 2 M ZnSO_4 into the solution, while the addition of 20 mM PMS could obviously improve the adsorption mass. This is similar to the phenomenon of the zinc metal

surface *in-situ* adsorption as shown in **Figure 2c**, indicating that the PMS anion- Zn^{2+} electric double layer was constructed and *in-situ* modified the NVO cathode interface.

Further analysis of the *in-situ* modification of NVO cathode interface is conducted through energy dispersive spectrum (EDS) mapping with transmission electron microscope (TEM). The cycled cathode was first thoroughly washed in dilute H_2SO_4 to eliminate the influence of ZSH. As shown in **Figure 4e**, the element mapping analysis of NVO material revealed the presence of C and S elements with atomic ratios of 7.07% and 0.11%, respectively (**Table S1**), confirming the adsorption of PMS on interface of NVO, which suggest the *in-situ* modification of NVO interface during electrochemical reaction. More importantly, the XPS analysis of V 2p in the NVO cathode under different states reveals that PMS combines with NVO cathode in the form of anions. As shown in **Figure 4f**, most V is kept at the valence of +5 in PE whether in charging or discharging state, while the V^{4+} peaks dominated in SH, which could be attributed to the electron brought by the adsorbed PMS anions. (in **Results-Electrochemically in-situ modification of cathode interface for high-loading stability**)

The *in-situ* modification of PMS anions at the interface was simulated by *ab-initio* molecular dynamics (AIMD). As shown in **Figure 4g**, the introduction of a single PMS anion resulted in the decreased Gibbs free energy of -1.36 eV and -2.31 eV for the whole system when the -S- and -SO_3^- adsorbed at the surface, respectively. This indicates that the PMS anions tend to adsorb on the NVO surface spontaneously with the configuration of -SO_3^- adsorption. This can also be predicted from the electrostatic potential (ESP) of PMS anions (**Figure S26**), and the lower potential results in tighter adsorption. Furthermore, according to the optimized configuration of interfacial adsorption, the -S- tends to bond with surface O and provide electrons, but there is no significant charge transfer between S and V. The -SO_3^- tends to coordinate with V atoms on the surface through O anions. Compared to the incomplete $[\text{VO}_5]$ pentahedron at the bare surface, the $[\text{VO}_6]$ octahedron formed by coordination with -SO_3^- exhibits more stable coordination preference and higher crystallographic stability.

As a result, the PMS anion *in-situ* modified cathode interface not only inhibits the direct contact between active water and $[\text{VO}_x]$ polyhedra to some extent, but also hinders the vanadium dissolution. As shown in **Figure 4h**, taking the -SO_3^- surface adsorption configuration with lower energy as an example, the vanadium dissolution and the formation of vanadium vacancies result in a significant increase in Gibbs free energy (18.66 eV) compared to the bare surface (13.13 eV). This represents a

stronger driving force required for vanadium dissolution with PMS adsorption. According to Bader differential charge density of V–O–O–V slice, an obvious charge transfer from adsorbed O to lattice V could be observed (**Figure 4g**), which is consistent with the decreased valence of vanadium as shown in **Figure 4f**. As a logical progression, the adsorbed PMS anions could hinder the vanadium dissolution into the electrolyte, it could also provide energy barriers for ion (de)intercalation. As a verification, we analyzed the energy efficiency over the initial three cycles (**Figure 4i**). In the SH electrolyte, statistical analysis reveals that the average energy efficiencies for the first three cycles are 71.4%, 69.2%, and 68.7%, respectively, all of which are lower than those observed in the PE electrolyte. The phase composition of the cycled cathode was also analyzed by XRD patterns (**Figure S25c**). Similar to the *in-situ* XRD results, the *ex-situ* XRD pattern of NVO cathode after 120 cycles in SH electrolyte exhibits prominent diffraction peaks, indicating a more stable lattice structure. In contrast, the NVO cathode exhibited indistinct diffraction peaks of the original phase and the formation of a substantial amount of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, which may experience significant dissolution in the PE electrolyte during cycling.

In summary, the charge transfer between the adsorbed PMS anions and the lattice vanadium ensures firm adsorption and electrochemical stability of the $[\text{VO}_x]$ lattice framework, and the *in-situ* modification of NVO cathode could prohibit vanadium dissolution even during the (de)intercalation process of a large amount of Zn^{2+} . This optimization of cathode can significantly improve the comprehensive electrochemical performances, paving the way for the practical application of efficient pouch cells. (in **Results-Electrochemically in-situ modification of cathode interface for high-loading stability**)

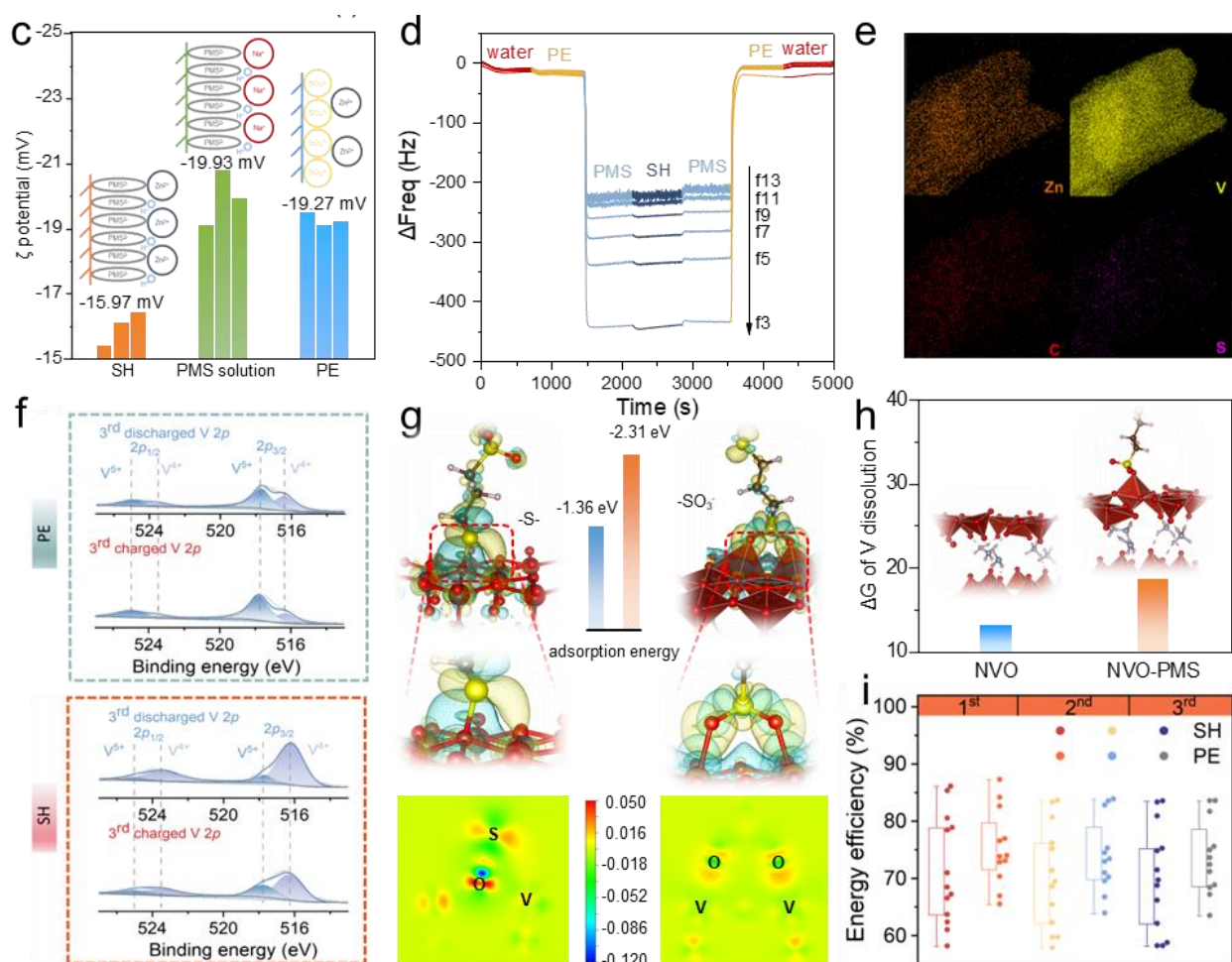


Figure 4. Enhanced stability of lattice framework by PMS adsorption. (c) ζ potential and (d) QCM-D of NVO powders in different solutions. (e) EDS results of NVO at discharged state in SH electrolyte (discharge to 0.4 V). (f) *Ex-situ* XPS V 2p spectra in PE and SH electrolytes. (g) Adsorption energy, configuration and Bader differential charge density of PMS at the NVO surface. (h) Δ G of V dissolution and formation of V defect. (i) Statistical energy efficiency at initial 3 cycles. (in **Results-Electrochemically in-situ modification of cathode interface for high-loading stability**)

Table S1. The atomic content of different elements of PMS-intercalated $\text{NH}_4\text{V}_4\text{O}_{10}$ at discharged state in TEM (discharge to 0.4 V).

Element	Line Type	Wt%	Wt% Sigma	Atomic %
C	K series	3.20	0.20	7.07
N	K series	2.20	0.23	4.16
O	K series	35.77	0.29	59.29
S	K series	0.13	0.04	0.11

V	K series	48.32	0.28	25.16
Zn	K series	10.38	0.16	4.21
Total:		100.00		100.00

(in **Supporting information**)

Overall, although good performance is demonstrated, the authors' claims in terms of understanding PMS functionality are based on XPS and simulations. The former technique is used in an unprofessional and unscientific way with too many assumptions. For the latter, with respect to all theoretical efforts, most calculations in this area are more likely designed to match what has been observed, and their reliability (especially at the interface) needs to be accompanied to more rigorous experimental results.

Response: We once again thank **Reviewer #2** for your valuable comments and suggestions. In the revised manuscript, we supplemented abundant characterization and analyses to prove the superiority of PMS. For instance, the differential capacitance, QCM, TOF-SIMS and *in-situ* SERS were employed to deeply investigate its mechanism at zinc anode surface, and the uniform and stable zinc plating/stripping could be observed according to CA and SEM. Additionally, the *in-situ* XRD, ζ potential, QCM, TEM and theoretical calculation were also carried out to demonstrate the benefits of adsorbed PMS at the NVO cathode interface, which constructs stable $[\text{VO}_6]$ coordination octahedron, thereby inhibiting vanadium dissolution. Overall, we hope this revised format can address the concerns of the reviewer and meet the requirements of *Nature Communications*. Finally, if the reviewer has any other questions, please feel free to raise them and we will do our best to make revisions.

Reviewer #3: In this manuscript, Song et al. emphasized the effect of dual modification at both cathode and anode interfaces on the electrochemical performances, contributing to the pouch cells with an Ah-level stability over 680 cycles and a cumulative capacity of 319.6 Ah. Unlike traditional electrolyte modifications, this manuscript proposes an interesting mechanism to explain the uniform deposition of zinc anode and the in-situ modification on the cathode, ultimately ensuring the overall stability of the battery. I think it is suitable for publication in Nature Communications after addressing several minor concerns.

Response: We appreciate the review's recognition of our work. These valuable feedbacks help us improve the quality of this manuscript. In response to these comments, we have revised and supplemented the manuscript, including evidence for *in-situ* modification of the PMS in cathode and its corresponding cycling performance. Additionally, we have addressed the concerns regarding the pouch cell. In brief, we are trying our best to improve the quality of this manuscript to meet the high standards of *Nature Communications*.

1. In Figure 4d-f, the authors mentioned that the in-situ modification introduced the PMS into the interlayer of cathode, which enhances the conductivity and structural stability of cathode. However, for the conductivity, more evidence should be provided to support this statement. What is the electronic structure of cathode with PMS?

Response: Thanks to **Reviewer #3** for proposing the valuable question. In previous version, we found that the NVO cathode exhibited different in-situ XRD peaks during the first discharge process in SH and PE electrolytes, indicating potential structural transitions. Theoretical calculations also indicate that PMS molecules can stably exist between the NVO interlayers. Hence, we proposed the co-intercalated interlayer PMS. However, further detailed research has found that PMS does not seem to modify the NVO lattice structure during subsequent cycles, which seems to be inconsistent with the assumption of PMS co-intercalation. We supplemented the characterization of ζ potential, TEM and quartz crystal microbalance (QCM), and found that PMS may be more inclined to adsorb at the NVO cathode surface. The O in $-\text{SO}_3^-$ can adsorb and coordinate with V on the NVO surface, creating a more stable coordination environment from $[\text{VO}_5]$ to $[\text{VO}_6]$ and thus inhibiting dissolution. The relevant calculation results can also prove the suppressed dissolution. Hence, most of the content in **Figure 4** has been changed to make the manuscript more scientific and rigorous.

Changes:

In the subsequent cycles, the NVO lattice did not exhibit significant crystallographic changes. Combining the ζ potential of NVO powder in different solutions, PMS is mainly located at the cathode interface to inhibit vanadium dissolution and byproduct generation. The ζ potential represents the charge of particles with tightly adsorbed layers in specific solution. As shown in **Figure 4c**, the ζ potential in 2 M ZnSO₄ (PE, -19.27 mV) and 20 mM PMS solutions (-19.93 mV) is similar, indicating the similar interfacial electric double layer structure (inset in **Figure 4c**). After introducing Zn²⁺ into PMS solution (SH), the ζ potential significantly increased, indicating that the H⁺/Na⁺ attracted by adsorbed interfacial PMS anions was replaced by Zn²⁺. This is beneficial for the Zn²⁺ adsorption from bulk electrolyte and subsequent Zn²⁺ intercalation, avoiding the cathode dissolution caused by excessive H⁺ intercalation as discussed above. The adsorption of PMS can also be verified by quartz crystal microbalance (QCM) as shown in **Figure 4d**. It can be observed that mass of the adsorbed species on NVO do not change significantly even after introducing 2 M ZnSO₄ into the solution, while the addition of 20 mM PMS could improve the adsorption obviously. This is similar to the phenomenon of the zinc metal surface *in-situ* adsorption as shown in **Figure 2c**, indicating that the PMS anion-Zn²⁺ electric double layer was constructed and *in-situ* modified the NVO cathode surface.

Further analysis of the modified interface is conducted through transmission electron microscope (TEM). The cycled cathode was first thoroughly washed in dilute H₂SO₄ to eliminate the influence of ZSH. As shown in **Figure 4e**, the element mapping analysis of NVO material revealed the presence of C and S elements with atomic ratios of 7.07% and 0.11%, respectively (**Table S1**), confirming the PMS *in-situ* modification. More importantly, the XPS analysis of V 2p in the NVO cathode under different states reveals that PMS combines with NVO cathode in the form of anions. As shown in **Figure 4f**, most V is kept at the valence of +5 in PE whether in charging or discharging state, while the V⁴⁺ peaks dominated in SH, which could be attributed to the electron brought by the adsorbed PMS anions. The peaks of V⁴⁺ are located at 523.4 and 517.6 eV for V 2p_{1/2} and V 2p_{3/2}, and V⁵⁺ are located at 524.9 and 517.7 eV for V 2p_{1/2} and V 2p_{3/2}⁴³. Compared with the obvious increased V⁴⁺ (517.6 eV) after discharging in SH, the changes in PE seemed negligible. This may be due to the low electrochemical activity of the thicker cathode with high mass loading in PE, and most vanadium did not participate in charge transfer. On the other hand, the decrease in valence of vanadium will result in its dissolution in PE in the form of VO²⁺, and the XPS results reflect the inner cathode materials with

lower reaction depth actually.

The *in-situ* modification of PMS anions at the interface was simulated by ab-initio molecular dynamics (AIMD). As shown in **Figure 4g**, the introduction of a single PMS anion resulted in the decreased Gibbs free energy of -1.36 eV and -2.31 eV for the whole system when the $-S-$ and $-SO_3^-$ adsorbed at the surface, respectively. This indicates that the PMS anions tend to adsorb on the NVO surface spontaneously with the configuration of $-SO_3^-$ adsorption. This can also be predicted from the electrostatic potential (ESP) of PMS anions, and the lower potential results in tighter adsorption (**Figure S26**). Furthermore, according to the optimized configuration of interfacial adsorption, the $-S-$ tend to bond with surface O and provide electrons, but there is no significant charge transfer between S and V. The $-SO_3^-$ tend to coordinate with V atoms on the surface through O anions. Compared to the incomplete $[VO_5]$ pentahedron at the bare surface, the $[VO_6]$ octahedron formed by coordination with $-SO_3^-$ exhibits more stable coordination preference and higher crystallographic stability.

As a result, the PMS anion *in-situ* modified cathode surface not only inhibits the direct contact between active water molecules and $[VO_x]$ polyhedra to some extent, but also hinders the vanadium dissolution. As shown in **Figure 4h**, taking the $-SO_3^-$ surface adsorption configuration with lower energy as an example, the vanadium dissolution and the formation of vanadium vacancies result in a significant increase in Gibbs free energy (18.66 eV) compared to the bare surface (13.13 eV). This represents a stronger driving force required for vanadium dissolution with PMS adsorption. According to Bader differential charge density of V–O–O–V slice, an obvious charge transfer from adsorbed O to lattice V could be observed (**Figure 4g**), which is consistent with the decreased valence of vanadium as shown in **Figure 4f**. As a logical progression, the adsorbed PMS anions could hinder the vanadium dissolution into the electrolyte, it could also provide energy barriers for ion (de)intercalation. As a verification, we analyzed the energy efficiency over the initial three cycles (**Figure 4i**). In the SH electrolyte, statistical analysis reveals that the average energy efficiencies for the first three cycles are 71.4%, 69.2%, and 68.7%, respectively, all of which are lower than those observed in the PE electrolyte. The phase composition of the cycled cathode was also analyzed by XRD patterns (**Figure S25c**). Similar to the *in-situ* XRD results, the *ex-situ* XRD pattern of NVO cathode after 120 cycles in SH electrolyte exhibited prominent diffraction peaks, indicating a more stable lattice structure. In contrast, the NVO cathode exhibited indistinct diffraction peaks of the original phase and the formation of a

substantial amount of $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, which may experience significant dissolution in the PE electrolyte during cycling.

In summary, the charge transfer between the adsorbed PMS anions and the lattice vanadium ensures firm adsorption and electrochemical stability of the $[\text{VO}_x]$ lattice framework, and the *in-situ* modified cathode could prohibit dissolution even during the (de)intercalation process of a large amount of Zn^{2+} . This optimization of cathode can significantly improve the comprehensive electrochemical performances, paving the way for the practical application of efficient pouch cells. (in **Results-Electrochemically in-situ modification of cathode interface for high-loading stability**)

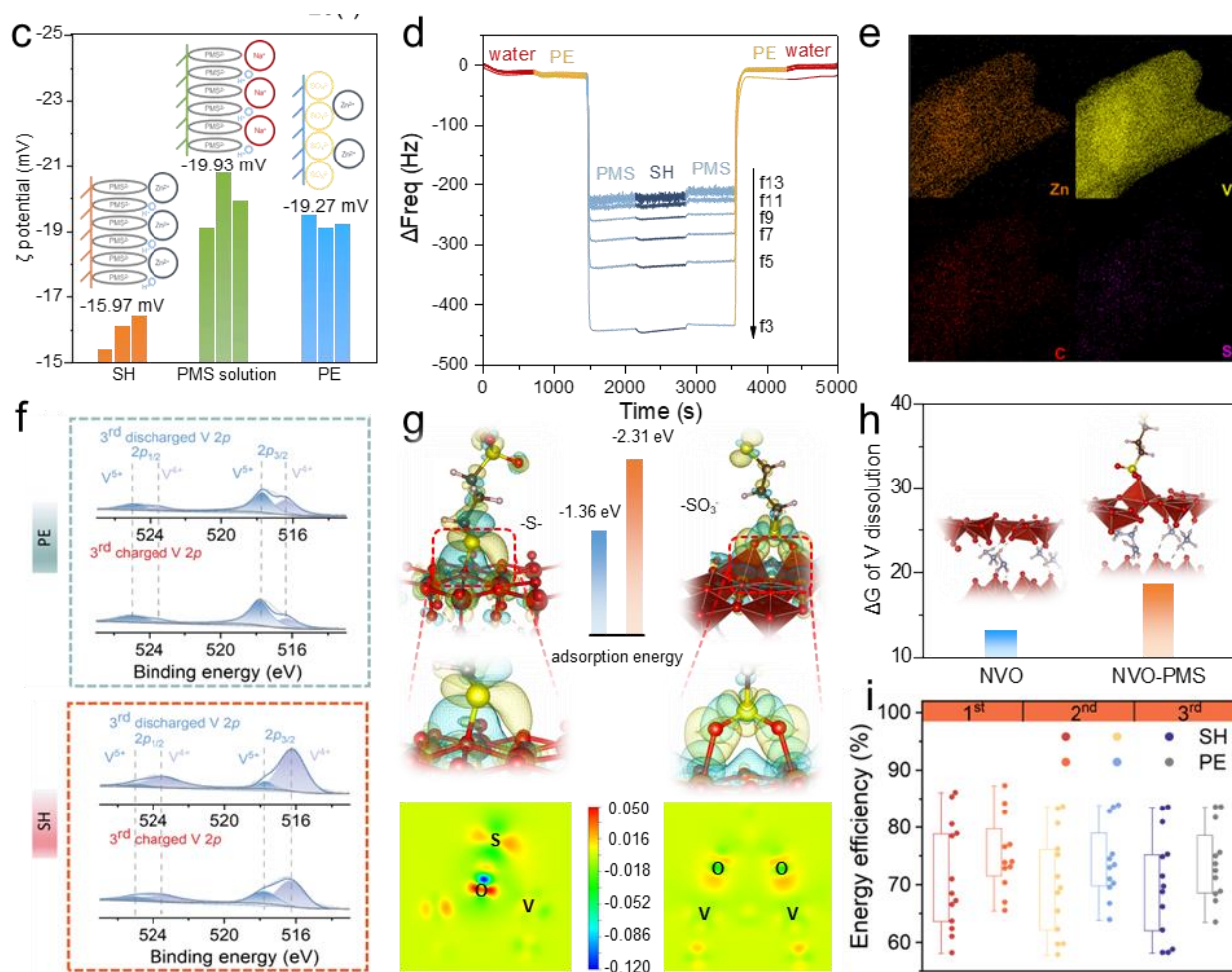


Figure 4. Enhanced stability of lattice framework by PMS adsorption. *In-situ* XRD pattern in (a) PE and (b) SH. (c) ζ potential and (d) QCM-D of NVO powders in different solutions. (e) EDS results of NVO at discharged state in SH (discharge to 0.4 V). (f) *Ex-situ* XPS V 2p spectra in PE and SH. (g) Adsorption energy, configuration and Bader differential charge density of PMS at the NVO surface. (h) ΔG of V dissolution and formation of V defect. (i) Statistical energy efficiency at initial 3 cycles.

(in **Results-Electrochemically in-situ modification of cathode interface for high-loading stability**)

2. As is well known, vanadium-based cathodes in aqueous electrolyte exhibit severe capacity degradation at low current density. Solving this problem will play a key role in the development of Zn-V batteries. However, the Zn-V cell in this manuscript performs well only in a high current density (e.g. 2 A g^{-1} in Figure 5g). Does PMS additive address the cycle stability of vanadium-based cathode at low current densities, such as 0.5 A g^{-1} ?

Response: We appreciate your suggestion regarding the cycling performance of vanadium-based cathodes at low current density. We also agree that testing vanadium-based cathodes under low current density is crucial. Therefore, we conducted long-cycle test at 0.5 A g^{-1} using coin cells. The test results demonstrate that the full cell with added PMS additive can stably cycle for 550 cycles at 0.5 A g^{-1} , with a cycling retention rate of 84.7% (**Figure S38**). Additionally, we converted the areal current densities for the single-layer and double-layer pouch cells tested. For the single-layer pouch cell in **Figure 6a**, 3 mA cm^{-2} corresponds to 0.12 A g^{-1} , while for the double-layer pouch cell in **Figure 6c**, 3 mA cm^{-2} corresponds to 0.15 A g^{-1} , respectively. Therefore, we have revised these informations including mass current density for better understanding and feedback. In future applications of fixed energy storage devices, the demand for charge/discharge times between 4-10 h will significantly increase (*Joule*, 2023, 7, 1415–1436). In our manuscript, the single-layer pouch cell cycles for 5 h per cycle, and the double-layer pouch cell cycles for 4 h per cycle, respectively. Therefore, this study on pouch cells is highly relevant to practical applications and offers significant reference value.

Changes:

Even after 4000 cycles, the exceptional long-term cycling stability of maintaining 162.8 mAh g^{-1} could be achieved. The cycling stability at low current density (0.5 A g^{-1}) also have been evaluated, with 84.7% retention after 550 cycles in **Figure S38**, which underscore the superior cycle stability induced by SH compared to the PE electrolyte. (in **Results-Electrochemical performances of coin cells**)

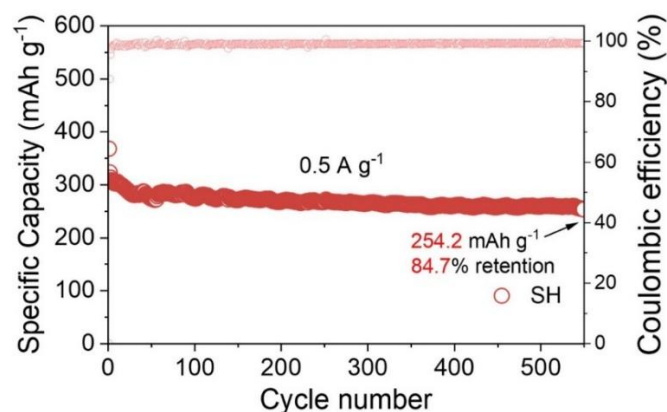


Figure S38. Cycle performance of $\text{NH}_4\text{V}_4\text{O}_{10}||\text{Zn}$ cells at 0.5 A g^{-1} in SH electrolytes. (in Supporting information)

3. In the analysis of the nucleation mechanism, the author explained that PMS facilitates Zn nucleation, thereby resulting in a lower nucleation overpotential. However, in Figures 5d and e, it is evident that the hysteresis voltage of the SH electrolyte is higher than that of PE electrolyte at 10 mA cm^{-2} and 20 mA cm^{-2} . Please explain this phenomenon.

Response: Thank you for your question regarding the hysteresis voltage. In the entire process of Zn^{2+} electroplating with corresponding deposition curve, overpotentials mainly include nucleation overpotential (η_n) and growth overpotential (η_g), as shown in **Figure 3b**. Due to the gradient interface formed by PMS guiding the Zn^{2+} electroplating, SH does exhibit lower η_n , which is not contradictory to the description in manuscript.

As for higher hysteresis voltage, it could be observed that this is mainly due to higher η_g in the subsequent reaction process. As a logical progression, the zinc tends to deposit in the form of dendrites in PE, and its tip effect can provide a stronger electric field to drive and attract more Zn^{2+} electroplating, thus leading to a gradual decrease in η_g in the short term. In the long run, more severe dendrites and tip effects will cause short circuits or gas production inevitably, which is not conducive to long cycle life. In contrast, the surface gradient layer in SH provides a stable reaction environment for subsequent Zn^{2+} electroplating, while it may also shield the tip electric field and thus slow down the subsequent growth kinetics. This indicates that a higher η_g does not necessarily represent deteriorated reaction kinetics, but rather represents stable interface state and suppressed side reactions to some extent.

More specifically, according to the enlarged view of **Figure 5d (Figure R3-1)**, the PE exhibits a higher η_n than the SH at the initial stage of each deposition cycle. However, the η_g is slightly lower

than that of the SH at the end of the deposition. For further verification, we supplemented the exchange current density tests for both SH and PE. We tested the nucleation potential under different currents and fitted the data through $i_0 = i \times \frac{F\eta}{2RT}$, resulting in **Figure S30**. In the SH, the super instantaneous nucleation mechanism leads to a higher exchange current density compared to the PE. This increased exchange current density indicates a significant improvement in the deposition kinetics of zinc, as the guiding effect of PMS on the anode accelerates the zinc deposition process.

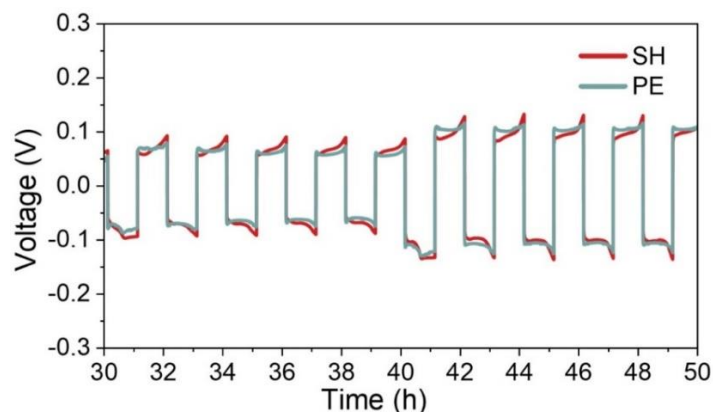


Figure R3-1. Enlarged view of the symmetric cell rate performance in **Figure 5d** (10 mA cm^{-2} to 20 mA cm^{-2}).

Changes:

The nucleation potential under different currents also fitted the data through $i_0 = i \times \frac{F\eta}{2RT}$, resulting in **Figure S30**. In the SH, the super instantaneous nucleation mechanism leads to a higher exchange current density compared to the PE, representing the faster zinc nucleation kinetics. (in **Results-Electrochemical performances of coin cells**)

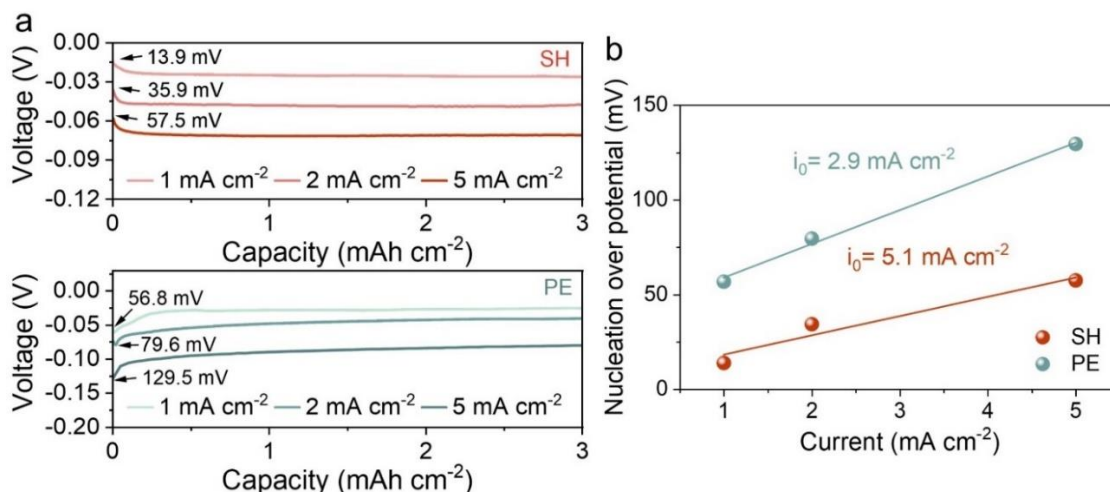


Figure S30. (a) Galvanostatic nucleation overpotential of Zn anode in the SH and PE electrolyte. (b) The calculated exchange current density. (in **Supporting information**)

4. This manuscript demonstrates excellent cycling stability in high-capacity pouch cells. To date, many pouch cells with high capacity have been reported. The author should further elucidate the advancements and limitations of this work when compared to others.

Response: Thank you for acknowledging and appreciating the performance of the pouch cells in this work. In this manuscript, we have focused on comparing the performance of several representative pouch cells from the perspective of cost, capacity, manufacturing simplicity, specific capacity and retention, as shown in **Figures 6g and h** and the reference in **Supporting information**.

Ref. 15 presents a strategy for alloying Zn anodes, where the assembled pouch cells demonstrated stable cycling at 34 mAh for over 500 cycles, with a capacity retention rate of 85%. Although this alloying process offers some advantage in capacity retention, it is relatively complex. **Ref. 18** employed an organic-based Zn salt, which does not offer a cost advantage compared to ZnSO₄. The anode modification process in **Ref. 19** is also relatively complex. Additionally, **Ref. 20** showcased a strategy for large-scale manufacturing of gel electrolyte that achieved Ah-scale cycling with low-cost, environmentally friendly raw materials. However, the preparation and storage of the gel pose some complexity for battery assembly. And our work demonstrates leading performance in terms of capacity, retention rate, and specific capacity, and we achieved a significant cost advantage due to the low manufacturing difficulty and cost.

However, there is still a gap between the assembled pouch cells and practical applications. Although the areal capacity can reach high levels (7 mAh cm⁻² or more), the corresponding N/P ratio and E/C ratio do not show outstanding advantages, limiting the overall energy density of the cells.

Changes:

The use of inexpensive sulfate-based salts and low-concentration additives is conducive to cost-effectiveness. Thus, under conditions where capacity and capacity retention rates are comparable, the incorporation of cost-effective electrolyte additive has further enhanced our strategy, achieving significant advantages in terms of cost-efficiency and manufacturing complexity at high loading (**Figure 6h**). Given the current level of development, further research and improvements in energy density are still required. (in **Results-Highly stable Ah-level pouch cells**)

5. Some sentences are not clear. For example, in Page 2, “Compared to symmetrical cells, the situations in large-capacity pouch cells are more drastic and complex, especially the electrolyte composition fluctuations caused by the cathode reaction. Typically, cathode reactions in aqueous environments often lead to the pH fluctuation of electrolyte. Meanwhile, the dissolved metal ions may diffuse to Zn anode and lead to self-discharge.” Does 'large-capacity pouch cells' refer to full cells rather than symmetric cells? Which type of ion is referred to as ‘the dissolved metal ions’?

In Page 19, “The high areal specific capacity usually leads to more serious dendritic growth and corrosion issues, and consequently, the CE of the Zn||Cu cell with PE declined rapidly within 30 cycles.” ‘The high areal specific capacity’ is not expressed appropriately and should be revised to ‘The high areal capacity’.

Response: Thank you for your valuable feedback on the writing issues in the manuscript. We sincerely apologize for the oversight that led to these errors.

Due to our oversight during the preparation of this manuscript, several errors were introduced, for which we deeply apologize. In Page 2, we intended to convey that, compared to symmetrical coin cells, the situation in large-capacity pouch cells is more severe and complex.

The dissolved metal ions mainly refer to VO^{2+} , VO_2^+ and etc. for vanadium-based cathode materials, as we introduced in manuscript that ‘*For instance, $\text{VO}^{2+}/\text{VO}_2^+$ generated by the dissolution of vanadium-based cathode will eventually deposit on the surface of Zn anode to form VO_x , causing severe corrosion of Zn anode²¹.*

Additionally, in Page 22, we overlooked the issue of inappropriate statements regarding high area-specific capacity, which has since been corrected. Other errors related to high area-specific capacity have also been addressed. And we have thoroughly re-examined the entire manuscript and made revisions to ambiguous sections to enhance the scientific accuracy and rigor of the manuscript.

Changes:

Compared to symmetrical coin cells, the situations in large-capacity pouch cells are more drastic and complex, especially the electrolyte composition fluctuations caused by the cathode reaction. (in Introduction)

The high areal capacity usually leads to more serious dendritic growth and corrosion issues, and

consequently, the CE of the Zn||Cu cell with PE declined rapidly within 30 cycles. (in **Results-Electrochemical performances of coin cells**)

6. There are some errors and irregularities in the figures and tables that need to be corrected. For example, in Supplementary Table S1, capacity should be corrected. The annotation text in Figure 3b is too light and I recommend using a darker color to enhance readability. Additionally, the enlarged view in Figure 4d and the inset in Figure 6a are blurry, making it difficult to discern detailed parts. To aid readers in better understanding this manuscript, the authors should provide higher-resolution images.

Response: Thank you for your valuable suggestions. We apologize for the issues related to labeling and descriptions. We have thoroughly reviewed the manuscript to correct unclear labels and descriptions. Additionally, we have replaced the low-resolution images with clearer ones to facilitate better reading and understanding for the readers. The unclear labels in **Table S2** and **Figure 3b** have been revised. Furthermore, we have changed the content of **Figure 4** and improved the resolution of **Figures 6a**, which could be helpful in clearer review and comprehension.

Changes:

Table S2. The parameters of every component in the ampere-hour Zn||NVO pouch cell.

Mass of the components	Values	Electrochemical parameter	Values
Cathode	5.657 g	Specific capacity	311.2 mAh g ⁻¹
Carbon felt (1 mm)	2.775 g	Cell average voltage	0.68 V
Electrolyte	30.520 g	Capacity	1.2 Ah
Separator	2.836 g	Energy	0.874 Wh
Package	4.317 g		
Zn anode (100 μm)	15.990 g		
Pouch-cell weight	62.113 g		

(in **Supporting information**)

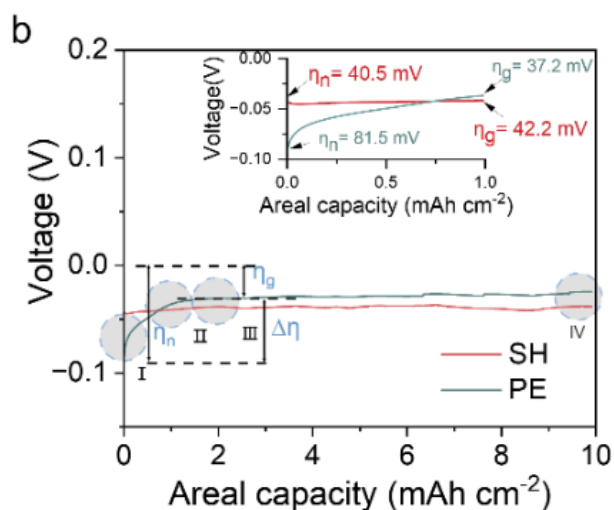


Figure 3. Highly uniform deposition morphology with abundant nucleation. (a) CLSM of surficial morphologies with Zn deposition capacity of 10 mAh cm⁻² and (b) nucleation overpotential curve in PE and SH. (in Results-Uniform Zn deposition under high areal capacity)

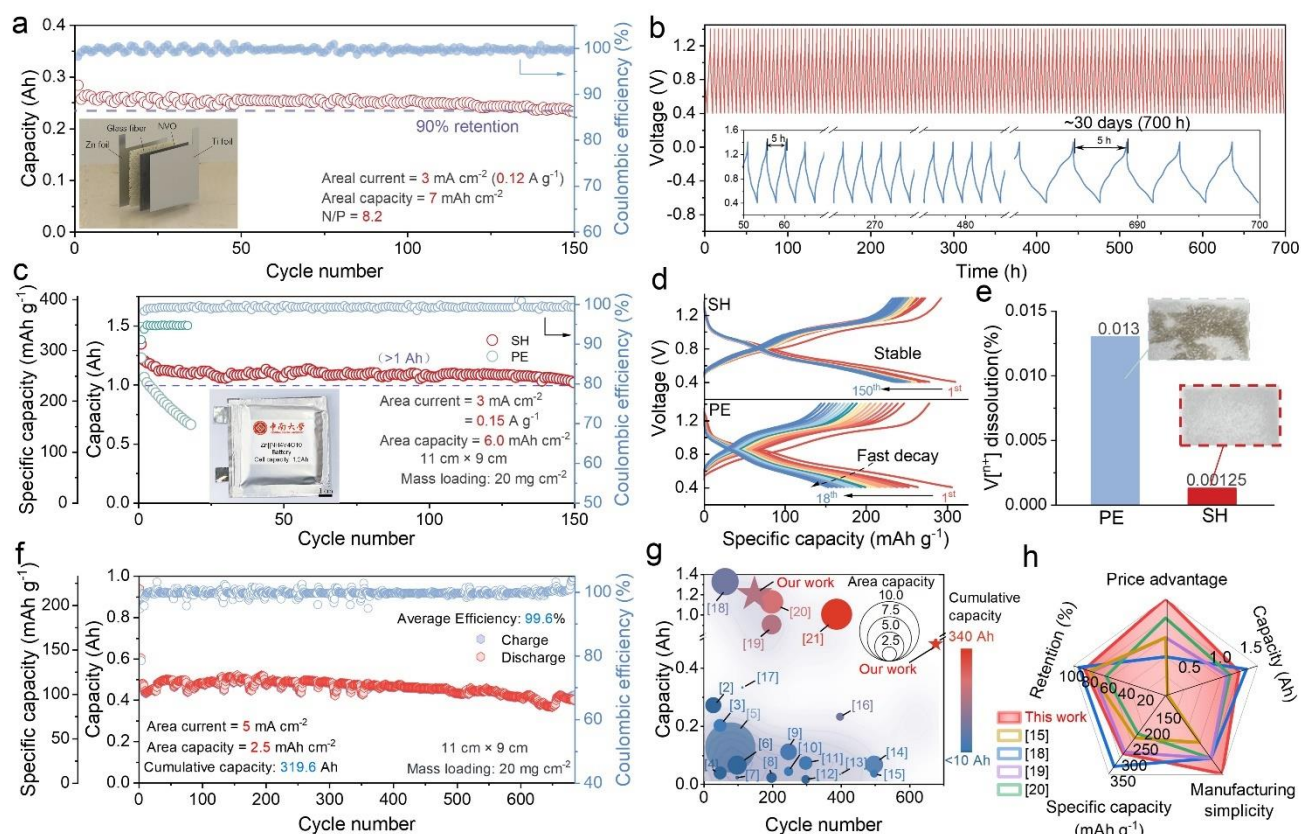


Figure 6. Electrochemical performances of practical Ah-level pouch cells. (a) Cycle performance of single-layer pouch cell with (b) corresponding charge-discharge curves. (c) Long-life cycle stability of double-layer battery in PE and SH, with (d) corresponding charge-discharge curves. (e) ICP results of vanadium dissolution in pouch cells. (f) Long-life cycle stability of double-layer pouch cell under high current density in SH. (g) Comparison of most pouch cells in cycle number and capacity and (h) comparison with typical reported pouch cells. (in Results-Highly stable Ah-level pouch cells)

Response to editor' comments:

*Please provide full details of all pouch cell assembly procedures in the Methods section, including the electrolyte volume; the electrolyte dosing should be stated in the main text. Please include any details on pressure applied or any clamping plates used, as well as any formation/activation procedures. Please provide details about all pouch cells, detailing both the single- and double-layer cells.

Response: Thanks for the editor's suggestions. We have provided detailed explanations of the preparation process and testing conditions of the pouch cell in the Supplementary Information.

Changes:

Assembly and test methods for pouch cells

Firstly, using polytetrafluoroethylene (PTFE) and carbon felt instead of PVDF and steel mesh as the binder and current collector, respectively. For a single-layer pouch cell ($6 \times 6 \text{ cm}^2$), the NVO loading was 25 mg cm^{-2} , while for the double-layer pouch cell ($9 \times 11 \text{ cm}^2$), the NVO loading was 20 mg cm^{-2} , respectively. A $100 \text{ }\mu\text{m}$ zinc foil, polished by 400, 800 and 1200 mesh and cleaned with water and ethanol, was used as the anode. The cells were assembled in a stacked configuration, with each separator containing $110 \text{ }\mu\text{L cm}^{-2}$ of electrolyte. And in the use of clamps, clamps were used at the four corners of the rectangle to apply 30 kg of pressure to ensure full contact between the positive and negative electrodes and the separators.

Testing procedure: In the tests of both single-layer and double-layer pouch cells, a constant areal current (3 mA cm^{-2}) was used. For the high-current double-layer pouch cell test (5 mA cm^{-2}), a lower current (3 mA cm^{-2}) was applied for the first two cycles to ensure proper activation and subsequent cycling performance. (in Supporting information)

*Please provide the chemical name and write out the abbreviation when introducing $\text{HSC}_3\text{H}_6\text{O}_3\text{Na}$ in the text. In the Methods section please provide a chemical identifier, such as the CAS number.

Response: Thanks for the editor's suggestions. The abbreviations in the text are defined in the Introduction. Additionally, we have included the CAS numbers in the Methods section.

Changes:

Materials: Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, sinopharm chemical reagent co., 99.5%), NH_4VO_3 (Aladdin, 99%), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aladdin, 99%), $\text{HSC}_3\text{H}_6\text{SO}_3\text{Na}$ (PMS, Aladdin, 90%, CAS: 17636-10-1), Na_2SO_4 (Aladdin, 99%).

*Please provide information about the contaminants of $\text{HSC}_3\text{H}_6\text{SO}_3\text{Na}$, as the purity is listed as 90%. If further purification was performed before any experimental tests, please provide details and give the resultant purity. Depending on the identity of the contaminant(s) and contaminant level, please provide additional controls and/or repeat experiments with higher purity $\text{HSC}_3\text{H}_6\text{SO}_3\text{Na}$ additives. Please include the discussion about contaminants in the point-by-point response to the reviewers.

Response: We appreciate the editor's suggestions regarding purity. The main NMR peaks of the electrolytes as shown in **Figure 2a** are consistent with J. Electrochem. Soc. 2011, 158.3: D143 (**Figure R4-1**), showing no additional ^1H peaks, which indicates the absence of other organic compounds. Furthermore, the presence of some water as an impurity is not problematic since the electrolyte itself is aqueous and thus does not affect our testing.

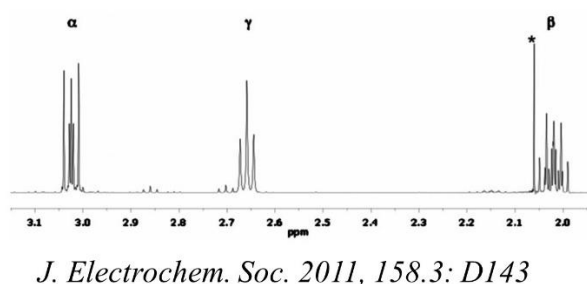


Figure R4-1. Proton NMR spectrum of PMS in 0.25 M D_2SO_4 .

Point-by-Point Response to Referee Reports

We sincerely appreciate the invaluable comments and insightful suggestions provided by the reviewers for our manuscript. Taking into consideration of these comments, we have revised the manuscript carefully and make the necessary changes and improvements in revised manuscript to improve the manuscript's overall content and central focus. The main changes are summarized below following a point-by-point response letter addressed to reviewers' comments.

Reviewer #1: The authors have fully addressed my concerns. This work proposes an important strategy for achieving high-loading and large-capacity zinc-vanadium batteries with superior stability, which is of great significance to the development of aqueous zinc metal batteries. It is recommended to publish it in Nature Communications in the present form.

Response: Thanks for the comments of **Reviewer #1**.

Reviewer #2: I appreciate the authors' effort to address my comments. These points need further consideration:

Response: Thanks for the further comments and suggestions from **Reviewer #2**. We do our best to address the issues to meet the high-level of *Nature Communications*.

1. Nyquist plot should be drawn in a square format with the same xy scale, otherwise the shape of the semicircle is misleading to readers.

Response: Thank for this valuable comment. We apologize for this error of Nyquist plot. Based on your suggestion, we have made the necessary corrections, as shown in Figure S32.

Changes:

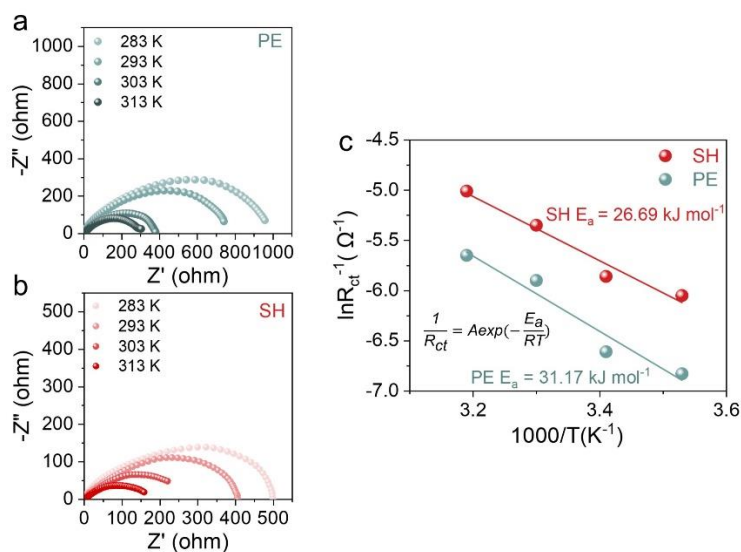


Figure S32. Nyquist plots of symmetric cells at different temperatures in (a) PE and (b) SH. (c) Corresponding Arrhenius curves and comparison of activation energies. (in Supporting information)

2. The authors indicate PMS participates in the Zn^{2+} solvation structure, which means the water- Zn^{2+} interaction is altered. In this case, the chemical environment of water molecules cannot remain unchanged. Please explain.

Response: Thanks to **Reviewer #2** for insightful comments regarding the changes in the chemical environment of water molecules. We apologize for the inaccurate statement that the water environment remained unchanged in the manuscript. In **Figure 2a**, we examined the chemical environment of PMS and H_2O by incrementally increasing the concentration of Zn^{2+} to observe any resultant shifts. As shown in **Figure S2a**, the gradual addition of Zn^{2+} led to a noticeable shift in the water molecule signal, a change (~ 0.02 ppm shift) that became prominent only when the Zn^{2+} concentration reached 2 M. In 2 M ZnSO_4 electrolyte ($\rho \approx 1.3 \text{ g ml}^{-1}$) (*Journal of Chemical & Engineering Data* 2021 66 (1), 38-44), the number ratio of Zn^{2+} and H_2O is approximately 1:54.3, meaning that even when Zn^{2+} exists as fully hydrated $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ complexes, a significant number of free water molecules remain. The NMR measurement reflects an average of all water molecules in the solution, and the concentration of PMS we used (20 mM) was insufficient to significantly alter the chemical environment of the water. **Figure S2b** further supports this observation, showing no significant shift in the water peak with increasing PMS concentration. To avoid misunderstandings, we have revised the relevant sections accordingly.

Changes:

The ^1H shift of H_2O is approximately 4.72 ppm in the PE electrolyte (Figure S2b). With increasing PMS concentration, its chemical shift does not exhibit a significant change (Figure S2b).

(in Results-Directional adsorption of additives and gradient interface at the Zn anode)

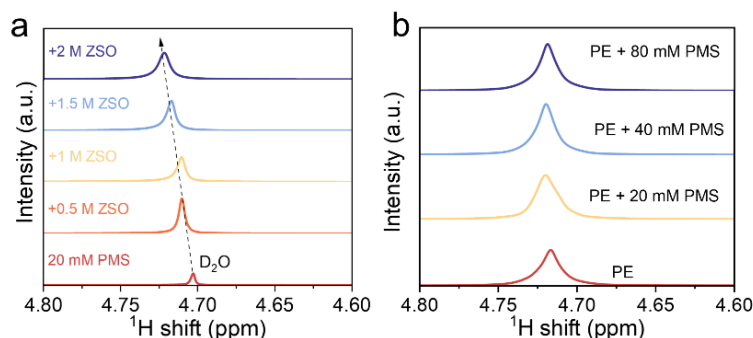


Figure S2. The ^1H shift of D_2O from 4.8 ppm to 4.6 ppm. (a) In the electrolytes with different ZnSO_4 salt concentrations and (b) in PE with different PMS concentration. (in Supporting information)

3. There is no intensity legend in 3D TOF-SIMS data, please add it. The complete profiles of each species are required to give a full view of SEI composition.

Response: Thank you for this valuable suggestion. We have added an intensity legend in the resubmitted manuscript and provided the sputtering depth and corresponding intensity information for each species in Figure S7.

Changes:

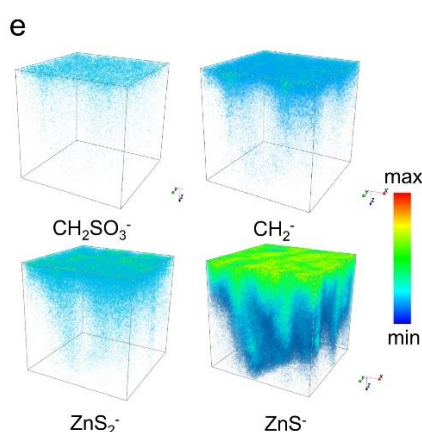


Figure 2. (e) Three-dimensional view of distributions for PMS on Zn anode in the negative TOF-SIMS sputtered volumes. (in Results-Directional adsorption of additives and gradient interface at the Zn anode)

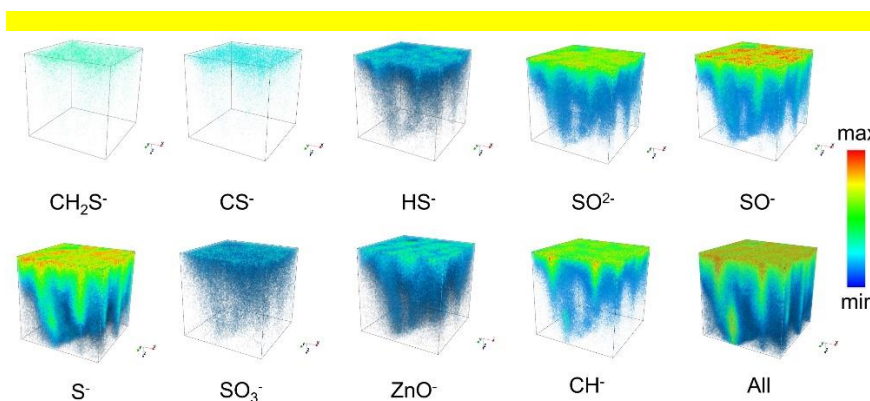


Figure S7. Different species in Three-dimensional view of distributions for PMS on Zn anode in the negative TOF-SIMS sputtered volumes. (in Supporting information)

4. Point 7a, authors claim dominant Zn^{2+} (de)intercalation based on the comparison of lattice spacing with other different cathode materials. Even with similar Zn^{2+} intercalation, different cathode materials would have very different lattice change behavior, not to mention the amount of intercalated Zn^{2+} is also different based on the exhibited discharge capacity. This comparison is not scientific. In addition, the *in-situ* XRD in Figure 4b clearly shows the dominant presence of ZHS during the cycling, which is strong evidence of dominant proton intercalation.

Response: Thanks to **Reviewer #2** for pointing out the issue that is not appropriate to compare the diffraction peak shift of different vanadium-based materials. Therefore, we focused on investigating the lattice parameter changes of the reported $\text{NH}_4\text{V}_4\text{O}_{10}$ (NVO) cathode materials. We found that most reported NVO cathode exhibit interlayer spacing shrinkage during discharge, including *Angew. Chem.* 2023, 62, e202310577, *Adv. Funct. Mater.* 2023, 33, 2306205, *Adv. Sci.* 2023, 10, 2206836, *Nano-Micro Lett.* 2021, 13, 116, etc., which is consistent with the phenomenon in this work. These reports attributed the shrinkage to the electrostatic attraction between lattice framework and intercalated cations. However, there is indeed insufficient evidence to suggest that only Zn^{2+} are intercalated, and the H^+ in electrolyte could also participate in ion (de)intercalation, as mentioned by reviewer. The change of lattice parameters may be the comprehensive result of co-(de)intercalation of various ions. However, we can see that the improvement in stability of the NVO cathode is mainly due to the addition of PMS, despite the presence of proton intercalation. To avoid this misleading, the relevant statements have been corrected.

Changes:

The reversibly formation of hydrated hydroxyzinc sulfate ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$, ZSH) at 8.0° suggests the presence of proton intercalation/(de)intercalation. Considering the interference of the ZSH (001) peak on the observation of the $\text{NH}_4\text{V}_4\text{O}_{10}$ (001) peak, the (004) and (-205) diffraction peaks were also marked with more obvious peak shift than (001) peak. The NVO cathode exhibited that the (004) peak shifted from 34.1° to 36.0° , and (-205) peaks shifted from 43.0° to 45.8° during the discharge process, respectively. In contrary, the shift amplitude in SH electrolyte (34.1° - 36.6° and 43.0° - 46.1°) is lower than that in PE electrolyte, indicating weakened contraction caused by the intercalated cations-lattice electrostatic effect. (in **Results-Electrochemically in-situ modification of cathode interface for high-loading stability**)

5. I thank the authors' effort on reanalyzing the PMS functionality at NVO interface. This is more reasonable than PMS intercalated in NVO. I can see why the adsorbed PMS suppresses V dissolution, which is interesting. But how about the Zn^{2+} desolvation and Zn^{2+} diffusion at the PMS-cathode interface? Does the adsorbed PMS enhance Zn^{2+} transportation or suppress it? The formation of large amounts of porous ZSH at cathode surface also have huge impact on such an interface.

Response: Thank you for this valuable question. We supplemented the adsorption calculation between NVO surface with $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ or H^+ under the condition of adsorbing interfacial PMS or H_2O molecules. The lower adsorption energy caused by interfacial PMS indicates that it can attract cations in the electrolyte effectively, and the optimized configuration of adsorbed Zn^{2+} with less solvated H_2O molecules also indicates that it could promote their desolvation. This is consistent with the ζ potential results in PMS solution and SH electrolyte (**Figure 4c**), and this may also be an important reason for adsorbed PMS enhancing ion desolvation and diffusion kinetics at the cathode interface. We also rechecked the changes in energy efficiency during long-life cycles and found that the energy efficiency was stabilized gradually in SH (**Figure 4i**), although the energy efficiency was slightly lower than that of PE in the initial three cycles. In contrast, the energy efficiency in PE is significantly reduced after initial several cycles. This may be due to the repulsion and isolation of H_2O molecules by the interfacial PMS of fresh cathode.

As for the impact of ZSH, with the increased amount of intercalated H^+ in the NVO cathode, the

ZSH will form at the surface to block the contact between the electrode and electrolyte, thus interrupting the reaction (*Energy Environ. Sci.* 2024, 17, 8904). This is no longer just an energy barrier for ions to diffuse across the interfacial electric double layer and then intercalate into the NVO lattice, but mainly the question of whether to allow the reaction to continue kinetically determined by covered ZSH. It can be regarded that a layer of insulating film was *in-situ* formed at the NVO cathode surface, and the adsorption of PMS or other ions cannot endow this film with electrochemical activity. Hence, it can be observed that ZSH irreversibly forms during the first discharge process in PE (**Figure 4a**), resulting in the lower specific capacity (**Figure 5f**) and degraded cycle stability (**Figure 5g**). On the contrary, the ZSH generated in SH can be gradually dissolved by the deintercalated H^+ during the charge process, exhibiting high reversibility. The relevant content has been supplemented in manuscript.

Changes:

From another point of view, there is still significant residual ZSH even after charging to 1.4 V in PE. This residual ZSH is likely irreversible, as evidenced by the increase of electrolyte pH value with *in-situ* pH test (**Figures S24 and S25**) and SEM images (**Figure S26**). The residual electrochemically inert ZSH can occupy the electrochemical active sites of the cathode, blocking the contact with electrolyte and interrupting the reaction⁴⁰. This blockage directly determines the absence of ion diffusion pathways and is independent of the cathode interfacial ion adsorption, thereby leading to a decline in battery performances.

The PMS anions could also attract the ions in electrolyte and promote intercalation. According to the calculated adsorption of $-S^-$ of interfacial PMS anions to H^+ or $Zn(H_2O)_6^{2+}$, as shown in **Figure S29**, it exhibits much lower adsorption energy (-5.02 eV for H^+ and -5.85 eV for $Zn(H_2O)_6^{2+}$) than that of interfacial H_2O molecules (-4.00 eV for H^+ and -0.46 eV for $Zn(H_2O)_6^{2+}$). More specifically, the complete $Zn(H_2O)_6^{2+}$ solvation will remove most of the solvated H_2O molecules spontaneously and coordinate with $-S^-$ to form the configuration with lower Gibbs free energy. This indicates that the $-S^-$ can not only attract interfacial cations, but also promote their desolvation and reduce the interfacial reaction energy barrier. As a verification, we analyzed the energy efficiency over the 500 cycles (**Figure 4i**). The NVO cathode exhibits higher energy efficiency in SH, although it is slightly lower than PE in the initial several cycles, which may be due to the interfacial PMS suppressing excessive

H₂O molecules from co-intercalating the NVO lattice interlayers.

In summary, in the case where excessive H⁺ intercalation leads to structural degradation of NVO (**Figure S27**), the interfacial PMS can not only promote the adsorption and intercalation of H⁺ and Zn²⁺, but also its coordination with surface [VO₆] octahedron can still ensure the electrochemical stability of lattice framework. (in **Results-Electrochemically in-situ modification of cathode interface for high-loading stability**)

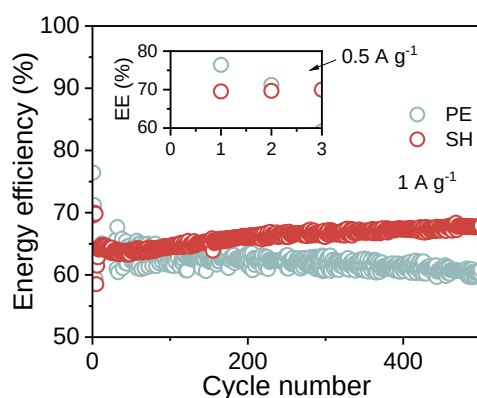


Figure 4. Enhanced stability of lattice framework by PMS adsorption. (i) Comparison of energy efficiency in PE and SH electrolytes.

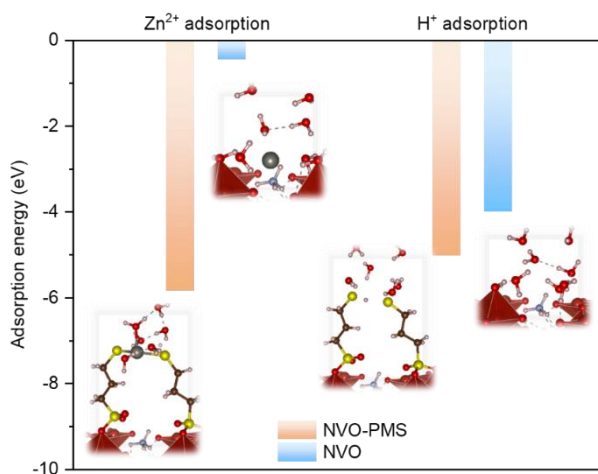


Figure S29. Adsorption energy with Zn²⁺ or H⁺ of the NVO cathode interface with adsorbed PMS or H₂O. (in Supporting information)

Reviewer #3: My questions were well answered by the authors. This article reveals the mechanism of bilateral in-situ modification, achieving stable operation of Ah-level pouch batteries and providing good guidance for the development of aqueous zinc vanadium batteries. I recommend it to publish in Nature Communications.

Response: Thanks for the comments of **Reviewer #3**.

Point-by-Point Response to Referee Reports

We sincerely appreciate the invaluable comments and insightful suggestions provided by the reviewers for our manuscript. Taking into consideration of these comments, we have revised the manuscript carefully and make the necessary changes and improvements in revised manuscript to improve the manuscript's overall content and central focus. The main changes are summarized below following a point-by-point response letter addressed to reviewers' comments.

Reviewer #2: The authors addressed all my questions well. I appreciate their efforts in solving these issues for the manuscript. I am now happy to recommend its publication on Nat Commun.

Response: We thank Reviewer #2 for the positive recommendation regarding the publication of our manuscript in Nature Communications. Your suggestions have been instrumental in enhancing the quality of our manuscript.

Response to editor' comments:

Response: We sincerely appreciate the substantial effort made by the editor to improve the quality of our manuscript. Following the suggestions provided in the author checklist, we have carefully reviewed and corrected the errors and issues in the manuscript, including the replacement of contrast colors, addressing the issues with the figures and resolving other related issues. Additionally, we have prepared all the necessary files.