nature portfolio

Peer Review File

A Parts-per-Million Scale Electrolyte Additive for Durable Aqueous Zinc Batteries

Corresponding Author: Professor Chunyi Zhi

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)
Zhi et al. proposed an electrolyte additive strategy with a feeding amount down to parts-per-million-scale to manipulate the Zn chemistry and eventually realized symmetric Zn deposition near 1 year. The ppm-scale additive, PPGA, was further verified effective in both Zn||ZnVO batteries and Zn||Br2 redox flow batteries. The work is impressive; in particular, it makes an additive a real additive instead of a major component in the electrolyte. This has been long neglected, although researchers always know it is important but never mention it. However, the following issues should be addressed before its acceptance.
1. The appearance of the O-H bond: is it from the zinc hydroxyl complex for the control sample in Fig. 2e? This should be clarified and discussed.
2. The "burnt-out" SEM images in Fig. 2d correspond to undesired charge accumulation on the insulative zinc hydroxyl complex covering the zinc anode. This kind of charging usually occurs while electrons accumulate on the surface of an insulating material, leading to imaging artifacts. The observation can highlight the drawbacks of such byproducts on zinc anode, which should be mentioned in the manuscript.
3. Considering that PPGA can remove zinc hydroxyl complex and impurities on the Zn surface, would it benefit the charge transfer process? The EIS spectra of Zn||Zn symmetric cells with and without PPGA should be provided in this regard.
4. The effectiveness of PPGA was examined in both static Zn||ZnVO batteries and Zn||Br2 redox flow batteries, and it showed a high capability to optimize Zn deposition/stripping. However, the adsorption ability of PPGA on zinc surfaces should be rigorously compared with water molecules. Theoretical calculation is recommended to evaluate their adsorption energy on the Zn surface.
Minor points:
5. Some guidelines are missing in Fig. 2a. Please double-check this issue.
6. The spectrum color of BZS in Fig. 4d should be consistent with that in other figures. The authors should examine all related figures in this regard.
7. Please double-check the clerical errors in Fig. S2 and Fig. S5b. Similar issues in the article should also be resolved.

Reviewer #2

(Remarks to the Author)
The author introduced a ppm-scale electrolyte additive, PPGA, directly into aqueous electrolytes to regulate Zn deposition and stripping, eventually enabling durable zinc chemistry in Zn||ZnVO batteries, Zn||Br2 redox flow batteries and their half cells. It is a commendable effort to examine the concept of scale inhibitors (that generally work in ppm levels) in Zn battery studies; however, the following issues need to be properly addressed before further evaluation.

(1) The loss of crystallized water in basic zinc sulfates caused a certain degree of lattice shrinkage. Would Raman result at "0 min" and "10 min" provide additional evidence to confirm the phase changes of the byproducts, to further support the observation in Fig. 2b?

(2) The crystal size of Zn somehow reduces after PPGA treatment in Fig. 2c. Does it relate to the so-called in-situ surface modification in Fig. 4c echoing the manipulation of Zn stripping?

(3) Nucleation on fresh Zn surface needs additional energy to pass through specific energy barriers after the transport of the ingredients from the electrolyte to the anode surface. The reduced initial nucleation overpotential of batteries with PPGA in Fig. S10 is suggested to discuss as an indicator of improved Zn deposition.

(4) Do the widely dispersed glass fibers observed on the stripped Zn anode in Fig. S6 result from the presence of Zn dendrites and the heterogeneous crystallization of Zn?

(5) Was the zinc acetate used for the synthesis of $Zn_{0.25}V_2O_5$ anhydrous? Please clarify to avoid any misunderstanding with "hydrated zinc acetate", as this would significantly affect the required feeding amount.

(6) The language discussing Fig. 1a should be revised as "…with a high average bond energy…". Similar errors in the article should also be resolved.

(7) The contrast in SEM-mapping images is not clear; the format of figures such as Fig. 2a, Fig. 4b, and Fig. 5f should be improved.

Reviewer #3

(Remarks to the Author)
The author conducted a study investigating the effect of phosphonoglycolic acid as an additive at ppm levels on the stability of aqueous Zinc batteries. The research includes both the physicochemical characterization of the electrolyte and its performance in these batteries. The findings indicate that even small amounts of the additive can significantly enhance battery performance.

However, a paper published online on June 29, 2024 (https://doi.org/10.1016/j.ensm.2024.103601), features a similar electrolyte composition. It seems likely that this research was conducted in parallel with the study submitted to Nature Communications, and the authors may not be aware of the overlap. The published paper uses an additive concentration of 30 mg/L, equivalent to 30 ppm. Therefore, the authors should highlight the differences between using 5 ppm and 30 ppm of the additive. It's unclear whether the lower concentration of 5 ppm will outperform the 30 ppm. Addressing this question is crucial, and if the authors respond to this and my other comments, I recommend considering a second revision.

1. What is the water-to-(salt+additive) ratio?
2. The authors should include more details about the PPGA, put references on its uses in corrosion suppression and also include the chemical and thermal stability of PPGA.
3. I recommend rephrasing the end of the introduction to focus on the techniques and methodologies used to investigate your system, rather than summarizing the results. This approach will make it easier for readers to grasp the novelty of your study.

4. What BZS is referred to?
5. In Fig1, it is difficult to understand why the peak intensity of water is increasing while adding the additive. Is it possible to normalize the peak intensity to the peak of SO4 around 1100 cm-1 wavenumbers? Also please include the full spectra in the SI.
6. What is the resolution of NMR used in this study? 0.07 ppm shift in NMR is too low to be considered.
7. The statement: “due to reduced mass of water molecule and decreased O-H bond length” is hard to believe. What does the author mean by reduced water molecules? The amount of the additive is quite low compared to water molecules. How many water molecules can PPGA interact with? What is the ratio between water and PPGA?

8. “The crystal size study derived from the Scherrer formula verified the above argument.” Please explain how the Scherrer formula verifies the stated argument.

9. In Fig.3b, it is necessary to include the initial potential around 0 V vs Ag/AgCl.
10. It would be beneficial to measure the fD after 50 cycles, similar to what was done in BZS. This measurement is crucial for understanding the impact of the additive, especially since Figure 4c indicates that the cell undergoes stabilization during the initial cycles.

11. After how many cycles the Zn foil was recovered in Fig. 4b.

12. I suggest to include SEM images at lower magnification to see the homogeneity of the deposition.

13. I don’t understand what the author meant by in-situ stripping optimization
14. The authors should give more details regarding the symmetric cell stripping/plating analysis: the diameter of Zn electrodes and the amount of the electrolyte.
15. For comparison with the literature, I suggest including the plating stripping of Zn at 0.5mA/cm2 current density.

16. Please give more details regarding the calculation of the capacity retention including current densities in the following statement: “Operation in PZS enabled the coin cell with a reasonably high capacity retention of 87.8% but dropped to 70.6% in BZS (Fig. 5d and Supplementary Fig. S14)

17. Is there an excess of electrolyte volume in the pouch cell configuration?

18. I don’t understand why the authors chose polyolefin membrane which is waterproof.

19. Could the authors explain why they chose the electrolyte with 10ppm additive in the redox flow battery?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Authors have addressed my concerns. This manuscript is acceptable after careful revision.

Reviewer #2

(Remarks to the Author)
The authors have addressed my comments. I recommend publication of this manuscript.

Reviewer #3

(Remarks to the Author)

The authors addressed most of the questions, and the revised version provides better clarity. However, the positioning of this work in comparison to Y. Yu et al.'s research in Energy Storage Materials journal remains unclear.

1. Y. Yu et al. also investigated the effect of the additive at concentrations ranging from 15 ppm to 45 ppm, with their best results observed at 30 ppm.
2. When comparing the Zn plating/stripping data from this paper at 5 ppm with Y. Yu et al.'s results at 30 ppm, the cycling stability at 10 mA/cm² with 10 mAh/cm² is quite similar—both studies report 500 hours of cycling with an overpotential of 0.1V. The only difference is that this study at 5 ppm shows longer cycling at 10 mA/cm² with 1 mAh/cm². In my view, it's difficult to conclude that 5 ppm outperforms 30 ppm; the results may be comparable and influenced by experimental errors.
3. The authors should also include Y. Yu et al.'s results in Figure 4f to properly position this work in relation to existing studies.
4. In the revised manuscript, the authors state, “Herein, we proposed a ppm-scale effective inhibitor, phosphonoglycolic acid (PPGA), as a new additive to the ZnSO4 electrolyte.” Unfortunately, this is no longer novel, as it has already been published.
Other comments
5. Please also specify in the caption of Fig. 1b that the BZS has been subtracted in the spectra with additives.
6. Please clarify how Fig. 3b was obtained, including the range and direction of the sweeping potentials used. It seems unlikely that this curve could be obtained in a single sweep.

Response Letter

Thank you very much for your message pertaining to our submission. We have studied the comments and suggestions. In our point-by-point responses, the Reviewer's comments are presented in black, our responses are provided in Blue. The modifications implemented during the revision are indicated in both the revised manuscript and the Supporting Information, highlighted in Red. The following is a summary of our revisions and responses to referees.

Reply to Reviewer #1:

Zhi et al. proposed an electrolyte additive strategy with a feeding amount down to parts-per-million-scale to manipulate the Zn chemistry and eventually realized symmetric Zn deposition near 1 year. The ppm-scale additive, PPGA, was further verified effective in both Zn||ZnVO batteries and Zn||Br_2 redox flow batteries. The work is impressive; in particular, it makes an additive a real additive instead of a major component in the electrolyte. This has been long neglected, although researchers always know it is important but never mention it. However, the following issues should be addressed before its acceptance.

Reply: We greatly appreciate your professional evaluation of our research. We've provided the following responses to your comments.

(1) The appearance of the O-H bond: is it from the zinc hydroxyl complex for the control sample in Fig. 2e? This should be clarified and discussed.

Reply: Yes, the O-H bond which only appeared in "0 min" should be attributed to the byproducts on the zinc surface. We've added further explanation as below.

Instead, the sample lacking adsorbed PPGA exhibited a minor O-H bond at around 526 eV, stemming from the zinc hydroxyl complex presented on the zinc surface. (Page 7)

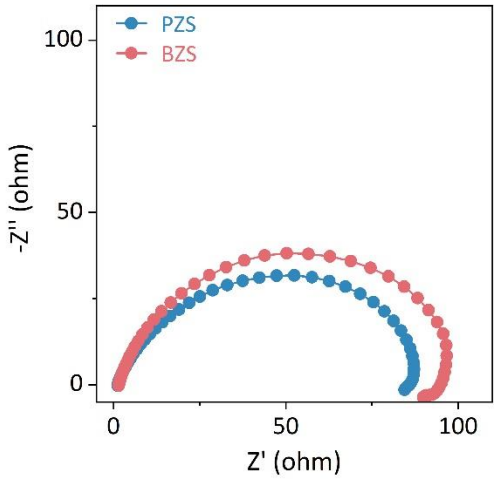
(2) The "burnt-out" SEM images in Fig. 2d correspond to undesired charge accumulation on the insulative zinc hydroxyl complex covering the zinc anode. This kind of charging usually occurs while electrons accumulate on the surface of an insulating material, leading to imaging artifacts. The observation can highlight the drawbacks of such byproducts on zinc anode, which should be mentioned in the manuscript.

Reply: Thank you for your suggestions. We've included the discussion in the main text.

Massive bulk crystals clustered on the zinc surface in the control sample, leading to substantial electron accumulation and imaging artifacts. However, these insulating byproducts greatly decreased after a 10-min treatment in the proposed mixed solution. (Page 7)

(3) Considering that PPGA can remove zinc hydroxyl complex and impurities on the Zn surface, would it benefit the charge transfer process? The EIS spectra of Zn||Zn symmetric cells with and without PPGA should be provided in this regard.

Reply: Thank you for your constructive suggestions. The addition of PPGA in the Zn||Zn cell exhibited a lightly reduced charge transfer resistance. We have added the following discussion to the manuscript.

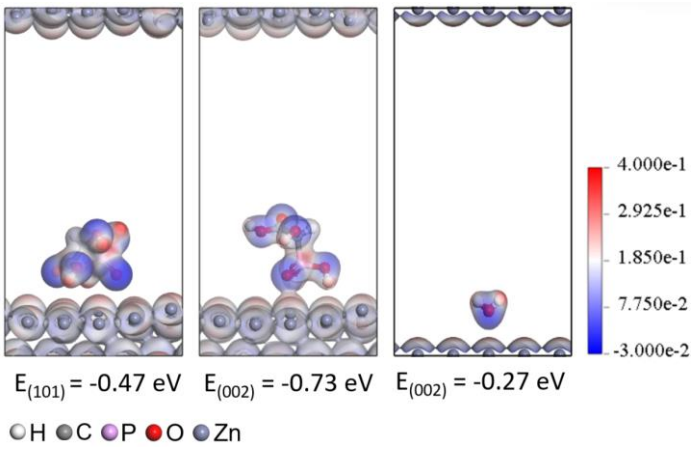


Supplementary Fig. 20 | EIS result of Zn||Zn symmetric cells. EIS spectra of cells based on BZS and PZS, respectively.

Similar to Zn||Zn symmetric cells, the charge transfer resistance on the anode (R_{ct1}) and the cathode (R_{ct2}) of the two cases showed mild differences except for the slightly dropped polarization of Zn||PZS||$Zn_{0.25}V_2O_5 \cdot nH_2O$, supporting no detectable adverse effect of the ppm-scale additive to this specific storage system. (Page 11)\

(4) The effectiveness of PPGA was examined in both static Zn||ZnVO batteries and Zn||Br_2 redox flow batteries, and it showed a high capability to optimize Zn deposition/stripping. However, the adsorption ability of PPGA on zinc surfaces should be rigorously compared with water molecules. Theoretical calculation is recommended to evaluate their adsorption energy on the Zn surface.

Reply: Thanks for your constructive suggestions. We have conducted the DFT calculation on the absorption of water molecules. The corresponding revision has been provided below.



Supplementary Fig. 3 | Molecular adsorption on the zinc surface. The adsorption of PPGA on the (101) and (002) lattice plane of zinc (left), and the interaction between water and zinc metal (right), with electrostatic potential mapped on the surface of the electron density.

Although wandered away from performing as a hydrogen bond acceptor, the electronegative oxygen atom of PPGA exhibited high responsibility for the adsorption on the zinc surface, particularly along the (002) lattice plane of zinc (Supplementary Fig. 3). This resulted in a considerable binding energy of -0.73 eV, surpassing that of H_2O molecules (-0.27 eV). (Page 6)

(5) Some guidelines are missing in Fig. 2a. Please double-check this issue.

Reply: Thank you for the reminder. The image has been revised below.

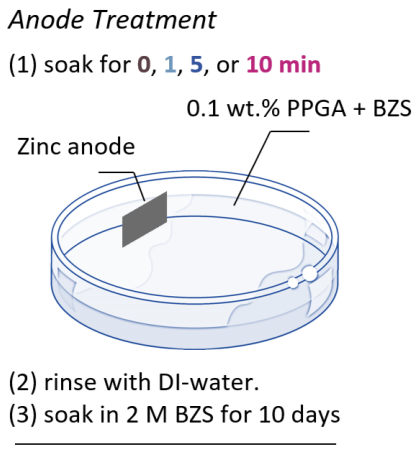


Fig. 2a. A method designed to evaluate the function of PPGA on the zinc surface.

(6) The spectrum color of BZS in Fig. 4d should be consistent with that in other figures. The authors should examine all related figures in this regard.

Reply: The color has been revised accordingly. Similar issues have been double-checked and revised.

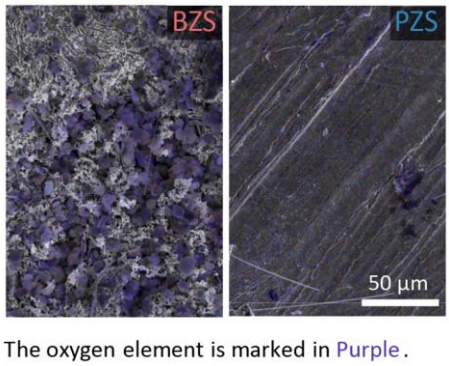


Fig. 4b. The SEM images of the plated side of Zn||Zn symmetric cells .

(7) Please double-check the clerical errors in Fig. S2 and Fig. S5b. Similar issues in the article should also be resolved.

Reply: Thank you for your reminders. We have gone through the manuscript and revised the clerical errors.

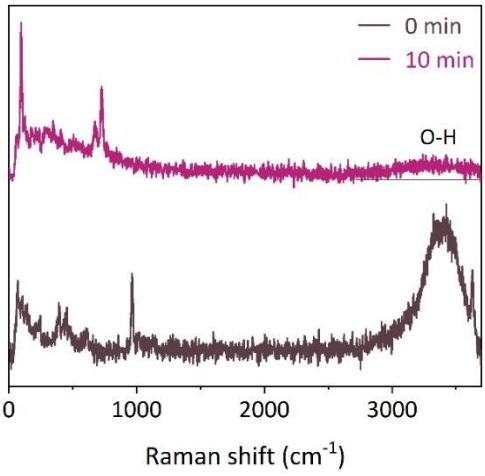
Reply to Reviewer #2:

The author introduced a ppm-scale electrolyte additive, PPGA, directly into aqueous electrolytes to regulate Zn deposition and stripping, eventually enabling durable zinc chemistry in Zn||ZnVO batteries, Zn||Br_2 redox flow batteries and their half cells. It is a commendable effort to examine the concept of scale inhibitors (that generally work in ppm levels) in Zn battery studies; however, the following issues need to be properly addressed before further evaluation.

Reply: Thank you for your positive and professional evaluation of our work. We have provided explanations and experimental results to address your comments.

(1) The loss of crystallized water in basic zinc sulfates caused a certain degree of lattice shrinkage. Would Raman result at "0 min" and "10 min" provide additional evidence to confirm the phase changes of the byproducts, to further support the observation in Fig. 2b?

Reply: Thank you for your constructive suggestions. Raman measurement of the electrodes indeed presented a varying intensity from water, highlighting the role of PPGA in restraining the crystallization of basic zinc sulfates. The corresponding revised has been provided below.



Supplementary Fig. 6 | Raman result. Raman spectra of the "0 min" and "10 min" samples demonstrated in Fig. 2.

As shown in the X-ray diffraction (XRD) spectra in **Fig. 2**b and Supplementary Fig. 5, the zinc hydroxyl complex crystallized with a decreasing hydration number from 5 ($3Zn(OH)_2 \cdot ZnSO_4 \cdot 5H_2O$) to 4 ($3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$) and 3 ($3Zn(OH)_2 \cdot ZnSO_4 \cdot 3H_2O$) with prolonged treatment time. This process was accompanied by a reduction in Raman intensity of the O-H vibration and suppressed crystallization peaks, indicating its ability to impede the nucleation and growth of the zinc hydroxyl complex (Supplementary Fig. 6). (Page 7)

(2) The crystal size of Zn somehow reduces after PPGA treatment in Fig. 2c. Does it relate to the so-called *in-situ* surface modification in Fig. 4c echoing the manipulation of Zn stripping?

Reply: Thanks for the suggestion. And yes, the reduced crystal size of Zn was related to the *in-situ* surface modification. We have revised the text and added further explanation in the main text as below.

Notably, during the initial cycling stages, a significant stripping optimization (an autonomous reduction of stripping overpotential) of the Zn||PZS||Zn cell occurred without external intervention despite the initially high stripping overpotential resulting from an uneven zinc surface or insufficient polishing treatment (**Fig. 4**c). This validates the gradual modification of the zinc surface by PPGA, corroborated by the decreased crystallite size of bulk zinc as indicated in the XRD results presented in **Fig. 2**c (Page 9)

(3) Nucleation on fresh Zn surface needs additional energy to pass through specific energy barriers after the transport of the ingredients from the electrolyte to the anode surface. The reduced initial nucleation overpotential of batteries with PPGA in Fig. S10 is suggested to discuss as an indicator of improved Zn deposition.

Reply: Thanks for the suggestions. We have included the discussion below.

The reduced nucleation overpotential observed in Supplementary Fig. 16 somewhat indicates an optimized zinc deposition process, aligning with PPGA's function in modifying the zinc surface. (Page 10)

(4) Do the widely dispersed glass fibers observed on the stripped Zn anode in Fig. S6 result from the presence of Zn dendrites and the heterogeneous crystallization of Zn?

Reply: Yes, thank you for your suggestions. We have added the explanation below.

The widespread dispersion of glass fibers in "BZS-S" can be attributed to the existence of Zn dendrites and the heterogeneous crystallization of Zn that extended to the separator, leading to undesired Zn stripping/plating. (Page 8, SI)

(5) Was the zinc acetate used for the synthesis of $Zn_{0.25}V_2O_5$ anhydrous? Please clarify to avoid any misunderstanding with "hydrated zinc acetate", as this would significantly affect the required feeding amount.

Reply: We have clarified it in the "Chemicals and reagents" and stated the use of anhydrous zinc acetate.

Specifically, 4 mmol V_2O_5 and 2.6 mmol anhydrous zinc acetate were dissolved in a mixture of H_2O and acetate (94:6 % v/v) and subsequently transferred to a sealed Teflon vessel and heated to 200 ^oC for 72h. (page 2, SI)

(6) The language discussing Fig. 1a should be revised as "…with a high average bond energy…". Similar errors in the article should also be resolved.

Reply: Thanks for the reminders. The language in the article has been double-checked with proper revisions.

(7) The contrast in SEM-mapping images is not clear; the format of figures such as Fig. 2a, Fig. 4b, and Fig. 5f should be improved.

Reply: Thank you for your suggestions. We have revised those figures in our manuscript.

Reply to Reviewer #3:

The author conducted a study investigating the effect of phosphonoglycolic acid as an additive at ppm levels on the stability of aqueous Zinc batteries. The research includes both the physicochemical characterization of the electrolyte and its performance in these batteries. The findings indicate that even small amounts of the additive can significantly enhance battery performance.

However, a paper published online on June 29, 2024 (https://doi.org/10.1016/j.ensm.2024.103601), features a similar electrolyte composition. It seems likely that this research was conducted in parallel with the study submitted to Nature Communications, and the authors may not be aware of the overlap. The published paper uses an additive concentration of 30 mg/L, equivalent to 30 ppm. Therefore, the authors should highlight the differences between using 5 ppm and 30 ppm of the additive. It's unclear whether the lower concentration of 5 ppm will outperform the 30 ppm. Addressing this question is crucial, and if the authors respond to this and my other comments, I recommend considering a second revision.

Thank you for your recommendation and valuable suggestions. We aim to address your concerns in the following areas.

a. As you kindly noted, we indeed were not aware of the overlap. We submitted a patent for PPGA in April 2024 to the University, and this patent was filed on June 7, 2024, which preceded the aforementioned reference. However, this action inadvertently caused a delay in paper submission, along with the cycling measurement of symmetric Zn cells lasting for one year. Now, we have referenced this source (which used 30 mg/L PPGA as ref. 37) and enhanced our arguments through additional evaluation of the additive concentration. (https://scholars.cityu.edu.hk/en/publications/untitled(2ffcfe99-845d-4876-a697-9dc7597204a8).html).

b. Conventional additive studies typically concentrate on functional chemicals and assess their efficacy through electrochemical investigations in half and full batteries. However, these studies often overlook in-depth discussions regarding the dosage of the additives and their associated impacts**. In contrast, our study uncovered a counterintuitive**

discovery regarding the dosage of additives for the first time, demonstrating the efficacy of PPGA at the 5-ppm scale with favorable outcomes for Zn chemistry while showing decreased effectiveness at higher concentrations.

We wish to arouse the attention of the community to low-dosage additives instead of simply blending organic molecules into aqueous solutions. The low dosage of additives is of primary importance to low cost, high safety, and delicate mechanism studies, which are the core advantages of aqueous electrolyte batteries.

c. Considering the limitations of available measurement equipment for detecting ppm-scale additives, we introduced a novel immersion treatment for zinc metals in PPGA solution, unveiling a progressive transformation of the basic zinc sulfate byproducts in terms of phase structure (reduced number of crystalline waters), crystallinity, and quantity generated with increasing treatment time (Fig. 2). On the other hand, theoretical predictions in Fig. 1 indicated that the additive was inclined to adhere to the surface of zinc metal in 240 ps and interact with circumambient water molecules as a proton donor to regulate zinc deposition and restrain side effects. **The abovementioned efforts validated the efficacy of 5 ppm PPGA experimentally and theoretically.** On the contrary, relying solely on 30 ppm PPGA would overlook its genuine operational principles during Zn stripping/plating, merely revolving around battery cycling results and surface studies of cycled zinc.

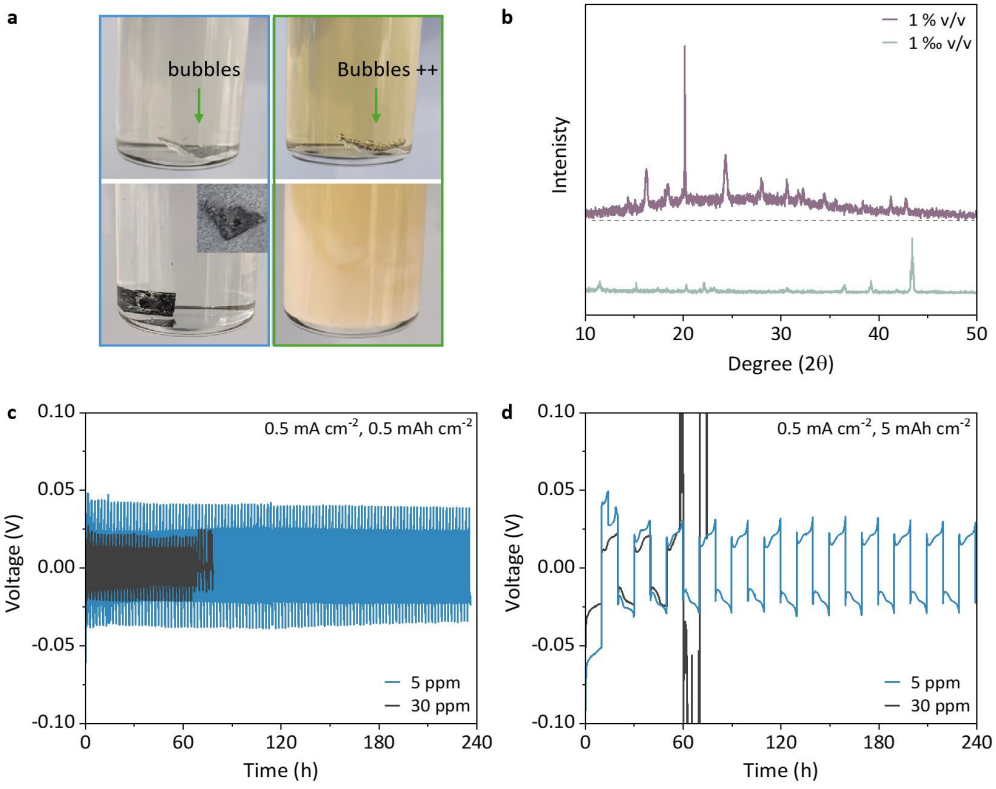
d. To further evaluate the interaction between zinc and concentrated PPGA, as shown in Fig. S4a and b, we submerged two pieces of zinc metals in 0.1% v/v and 1% v/v PPGA solutions and observed significant bubble accumulation on the metal surface, originating from a severe corrosion reaction between zinc and concentrated PPGA in water. After 8 days of storage, XRD diffractions from zinc were nearly imperceptible, and the zinc metal immersed in the 1% v/v PPGA solution completely transformed into unidentified white powders. **Given this, we could infer that augmenting the dosage of this threshold scale inhibitor may not be advantageous. This has been long ignored in additive studies.**

e. Further, long-term cycling measurement of Zn||Zn symmetric cells utilizing 5 ppm and 30 ppm PPGA additives underscored the importance of additive dosage even at a low concentration. As depicted in Fig. S4c and d, the Zn||Zn cell with 30 ppm PPGA ceased

functioning at approximately 60 hours at both 0.5 mA cm^{-2}, 0.5 mAh cm^{-2}, and 0.5 mA cm^{-2}, 5 mAh cm^{-2} (comparable to the values in the abovementioned reference). Instead, the Zn||PZS||Zn cell endured 240 hours under the same conditions. The observation emphasized the existence of (one or possibly multiple) critical dosages for the PPGA additive to achieve reversible Zn chemistry (due to PPGA's strong influence on the crystal size of Zn and could become more crucial during the stripping/plating process), among which 5 ppm was the optimal choice.

f. Still, we acknowledge that detailed studies of the additive's working mechanisms at such a low feed dosage, particularly with subtle differences in the feeding amount (5 and 30 ppm), require further investigation and the application of advanced analytical techniques moving forward. Nevertheless, our strategies to elucidate the impact of the ppm-scale additive could provide additional methodologies for monitoring the formation, growth, and types of byproducts, offering valuable insights into zinc anode research.

The related content in the manuscript has been revised as below.



Supplementary Fig. 4 | Impact of the PPGA concentration on zinc metal. Photograph showing the immersion of zinc metal into aqueous **a** 0.1 % v/v (blue wireframe) and 1 % v/v (green wireframe) PPGA solutions and stored for 8 days; **b** XRD patterns of the zinc metal in **a**; Zn||Zn symmetric cells cycled at **c** 0.5 mA cm^{-2}, 0.5 mAh cm^{-2} and **d** 0.5 mA cm^{-2}, 5 mAh cm^{-2}.

It is important to highlight that a high dosage of PPGA could be detrimental to the zinc electrodes and may have limited effectiveness in suppressing side effects (Supplementary Fig. 4). (Page 6)

The immersion treatment revealed ongoing corrosion of the zinc metal in a diluted aqueous PPGA solution. The 0.1% v/v PPGA solution partly dissolved the zinc metal and rendered it brittle after 8 days, as illustrated in the inset of Supplementary Fig. 4c. Remarkably, the zinc metal transformed into intricate white powders in the 1% v/v PPGA solution, unveiling the contrasting effect of concentrated PPGA on zinc. Subsequent cycling of Zn||Zn symmetric cells with 5 and 30 ppm PPGA indicated that a higher additive concentration may negatively impact battery performance. It could be attributed to the diminished crystal size of Zn post-PPGA treatment, as shown in Fig. 2b, c, and would become more crucial during the stripping/plating process, necessitating further comprehensive studies within the research community. (Page 7, SI)

(1) What is the water-to-(salt+additive) ratio?

Reply: The volume of $ZnSO_4$ salt = 2 mol * 161.47 $g \cdot mol^{-1}$ / (3.8 g mL^{-1}) = 84.98 mL

The volume of water = 1 L - 84.98 mL = 915.02 mL

The volume of additional PPGA = 5 ppm = 5 * 10^{-6} * (2 mol * 161.47 $g \cdot mol^{-1}$ + 915.02 mL * 1 g mL^{-1}) = 0.0061898 g / (1.3 g mL^{-1}) = 0.0047614 mL

So, the water-to-salt ratio is 10.76747 for BZS, and 10.76687 for PZS.

The corresponding test in has been revised accordingly.

The Zn||Zn symmetric coin cells were assembled by two Zn foils (100 μm, 1 cm^2) and an intermediate glassy fiber separator (Whatman, GF/C) with the addition of 60 μl electrolyte. 2 mol L^{-1} $ZnSO_4$ electrolyte (BZS) and the same electrolyte with an additional 5 ppm of PPGA (PZS) resulted in water-to-solute ratios of 10.76747 and 10.76687, respectively. (SI, page 3)

(2) The authors should include more details about the PPGA, put references on its uses in corrosion suppression and also include the chemical and thermal stability of PPGA.

Reply: Thanks for the suggestion. We've added further explanations on the properties of PPGA with proper citations (ref. 33-36), while academic investigations specifically focusing on its chemical and thermal stability are relatively scarce in the literature. Even so, such information is available on the product supplier's category page, where PPGA is characterized as "a good scale inhibitor", "can improve zinc solubility", "chemically stable", "hard to be hydrolyzed", "hard to be destroyed by acid or alkali", "widely used in industries of corrosion inhibition", etc.:

(a) https://www.atamanchemicals.com/2-hydroxyphosphonocarboxylic-acid_u26333/#:~:text=2%2DHydroxyphosphonocarboxylic%20Acid%27s%20appearance%20is,inhibitor%20with%20low%20phosphorus%20content
(b) http://www.xintaiwater.com/en/ArticleShow.asp?ArticleID=74
(c) https://aquapharm-india.com/hydroxyphosphono-acetic-acid-hpaa/#:~:text=HPAA%20is%20a%20powerful%20mild,regulated%20at%20very%20low%20levels
(d) https://www.irowater.com/products/hpaa/
(e) https://baike.molbase.cn/cidian/25232/

The main text has been revised below.

The water-soluble PPGA is widely employed in industries as a cathodic corrosion inhibitor, effectively halting scale formation at substoichiometric level by intervening in one or more steps of the scale formation processes, such as aggregation, nucleation, crystal growth and agglomeration.[33-36] It is a chemically stable organophosphorus compound featuring a

carboxyl group, a phosphono group, and a hydroxyl group covalently bonded to a carbon atom, as depicted in Fig. 1a. (Page 5)

(3) I recommend rephrasing the end of the introduction to focus on the techniques and methodologies used to investigate your system, rather than summarizing the results. This approach will make it easier for readers to grasp the novelty of your study.

Reply: Thanks for your constructive suggestions. We have revised this paragraph below.

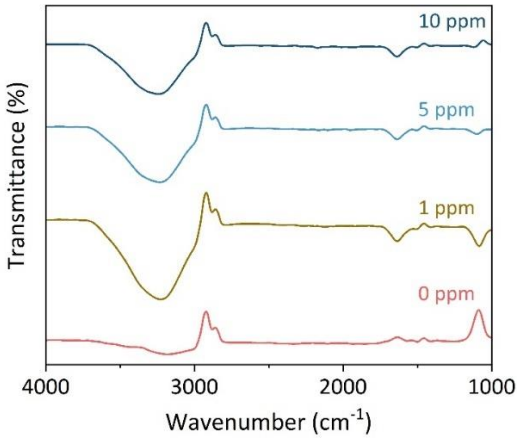
Herein, we proposed a ppm-scale effective inhibitor, phosphonoglycolic acid (PPGA), as a new additive to the $ZnSO_4$ electrolyte. Considering the low dosage and the necessity to understand the operational mechanism of the threshold scale inhibitor, we exposed zinc electrodes to a sub-ppm-level PPGA solution (0.1 wt.%) for various durations, leading to a progressive evolution of the byproducts in terms of phase structure, crystallinity, and quantity produced. In line with theoretical predictions, the findings demonstrated that PPGA was inclined to adhere to the surface of zinc metal and interact with circumambient water molecules to regulate zinc deposition and restrain side effects in both pouch cells and redox flow batteries. In addition to comprehending the ppm-scale additive, our methodologies for monitoring the formation, growth, and types of byproducts could offer valuable insights into zinc anode studies. (Page 4)

(4) What BZS is referred to?

Reply: BZS is the 2 M $ZnSO_4$ electrolyte. The corresponding description is provided on Page 5: "2 M $ZnSO_4$ electrolyte was referred to as BZS for the subsequent additive study".

(5) In Fig1, it is difficult to understand why the peak intensity of water is increasing while adding the additive. Is it possible to normalize the peak intensity to the peak of SO_4 around 1100 cm^{-1} wavenumbers? Also please include the full spectra in the SI.

Reply: BZS and HZS have the same composition except for the PPGA additive. A common practice involves scanning the air as the background to eliminate FTIR signals from CO_2 and humidity. However, this approach could lead to the loss of crucial information from the two samples. Hence, we opted to use BZS as the background to selectively track the FTIR signals originating from the difference of HZS, thereby generating a very low peak intensity of water for BZS. Additional explanations, including the full spectra, have been provided accordingly.



Supplementary Fig. 2 | FTIR result. FTIR spectra of BZS with a varying amount of PPGA (0, 1, 5, or 10 ppm).

Fourier transform infrared (FTIR) spectra in **Fig. 1**b and Supplementary Fig. 2 confirmed the strong interaction between PPGA and H_2O, with BZS utilized as the background to specifically analyze the signals originating from HZS. (Page 5)

(6) What is the resolution of NMR used in this study? 0.07 ppm shift in NMR is too low to be considered.

Reply: The resolution of Bruker 300MHz "AVANCE III HD" NMR is down to 0.24 Hz, though shimming, sampling, and processing may influence the resolution to some extent. The shift of 0.07 ppm corresponds to a change of 28 Hz, which is above the resolution. For comparison, a simplified micro-NMR spectrometer (Thermo Scientific picoSpin), which was introduced in 2009 and weighed 4.76 kg, could also give a resolution over 1.48 Hz. (https://www.thermofisher.com/hk/en/home/industrial/spectroscopy-elemental-isotope-

analysis/spectroscopy-elemental-isotope-analysis-learning-center/molecular-spectroscopy-information/nmr-information.html).

The "ppm" in NMR measurement represents a relative unit of frequency accurate to two decimal places, calculated as follows: "ppm" = (actual frequency - reference frequency) / reference frequency. For instance, if the reference sample, which is considered as 0 ppm is at 400.13 MHz and our sample's signal is at 400.132 MHZ and then gives a frequency of (400.132 - 400.13) / 400.13 = 4.998 ppm (an example posed by Dr. Clemens Anklin, Vice president at Bruker Corporation, on ResearchGate:

https://www.researchgate.net/post/How_to_convert_ppm_to_Hz_or_MHz#:~:text=If%20you%20want%20MHz%2C%20just%20devide%20your%20Hz,instrument%20would%20be%202500%20Hz%20i.e.%200.0025%20MHz.

Also, standard ^{1}H NMR chemical shift parameters are commonly reported with a Bruker value accurate to two decimal places (0.01 ppm), including the ^{1}H NMR shift table:

(a) https://www.carlroth.com/medias/INT-NMR-Shift-2022.pdf?context=bWFzdGVyfGRvY3VtZW50c3wxMzExMDl8YXBwbGljYXRpb24vcGRmfGRvY3VtZW50cy9oZmEvaGEyLzkwODQ0OTE3OTI0MTQucGRmfGYzNmM3ZWEzYWUxNDhhMjg0OTU0MTBkMTA2NGIwZmVhZDEwMTE1ZTQ1ODlmYmUwYzRlZTU3MTU5MDQyYmU4NDQ

(b) https://www1.udel.edu/chem/fox/H_NMR_Tables.pdf

(c) https://www.sigmaaldrich.com/HK/zh/technical-documents/technical-article/analytical-chemistry/nuclear-magnetic-resonance/1h-nmr-and-13c-nmr-chemical-shifts-of-impurities-chart

References like 10.1002/mrc.1801 also mentioned an NMR accuracy of 0.02 ppm for their study on the specific deuterium chemical. The mild shift in NMR (including the broad full-width half maximum) usually is also seen from a change of hydrogen bonds, which shifts from 8.31 ppm for C-H…DMSO to 8.34 ppm for C-H…Br (10.1002/adfm.202102182) or from 3.94 ppm for O-H…O to 4.32 ppm for O-H…Br (10.1021/acs.chemmater.1c01581s). The chemical shift, in our case, may indicate a dynamic breakage of intermolecular hydrogen bonds of water as the movement of PPGA molecules is consistent with the DFT

and MS results. The signal from deuterated DMSO at 2.50 ppm, which was used for calibration, has also been double-checked (Fig. R1).

Therefore, we may suggest retaining the NMR result.

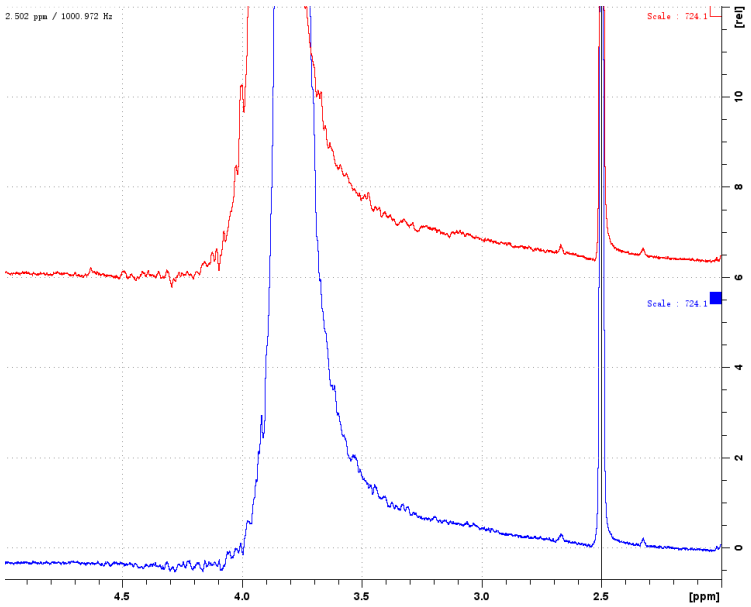


Fig. R1 | NMR spectra. A close-up view of the record spectra in Fig. 1c. Red and blue curves represent "BZS" and "5 ppm", respectively.

The related test has been revised below to enhance clarity.

Proton nuclear magnetic resonance (1H NMR) measurement in Fig. 1c demonstrated an upfield chemical shift with the inclusion of PPGA (5 ppm) due to increased electron density and reduced number of deshielded protons, convincing the disruption of intermolecular water hydrogen bond network. (Page 5)

The NMR measurement was conducted using the Bruker 300MHz "AVANCE III HD" Nuclear Magnetic Resonance System (NMR-300), which was equipped with an auto-sampler. (Page 2, SI)

(7) The statement: "due to reduced mass of water molecule and decreased O-H bond length" is hard to believe. What does the author mean by reduced water molecules? The

amount of the additive is quite low compared to water molecules. How many water molecules can PPGA interact with? What is the ratio between water and PPGA?

Reply: We are sorry for the misunderstanding caused, and thanks for your insightful comments.

As mentioned in Q5, instead of using the air as the reference, we employed BZS as the background in the FTIR measurement and thus the results could provide additional insights into the O-H bond vibrations of water in close proximity to PPGA molecules. When a hydrogen bond is established between H_2O and PPGA, the electrons around the oxygen atom of H_2O will partially share with the protons of PPGA (resulting in a light weight of the bonded H_2O). The process will cause a faster vibration frequency of this H_2O because the frequency of vibration is inversely proportional to the mass of the vibrating molecule. Therefore, the lighter the molecule, the higher the vibration frequency and the higher the wave numbers in FTIR spectra.

In our case, the O-H stretching vibration experienced a shift toward higher wave numbers after the inclusion of PPGA (Fig. 1b). This shift suggests the disruption of intermolecular water hydrogen bond network due to the interaction between PPGA and water, a conclusion supported by NMR findings.

Regarding the number of water molecules that PPGA can interact with, we can depend on the DFT findings in Fig. S1 for elucidation, revealing that at least six sites on PPGA could affect the hydrogen bond network of water. On the other hand, due to the highly soluble nature of PPGA, it will remain active and mobile in the aqueous solution, leading to a dynamic equilibrium involving the constant disruption of H_2O-H_2O hydrogen bonds and the establishment of "PPGA-H_2O" hydrogen bonds. Therefore, FTIR showed a shift from 3182 cm^{-1} (representing the initial water hydrogen bond network) to 3230 cm^{-1} (indicative of hydrogen bonds after the system reached equilibrium).

We have revised the relevant text to ensure clarity and precision.

Fourier transform infrared (FTIR) spectra in **Fig. 1**b and Supplementary Fig. 2 confirmed the strong interaction between PPGA and H_2O, with BZS utilized as the background to specifically analyze the signals originating from HZS. (Page 5)

(8) "The crystal size study derived from the Scherrer formula verified the above argument." Please explain how the Scherrer formula verifies the stated argument.

Reply: The Scherrer equation, in X-ray diffraction and crystallography, is a formula that relates the size of crystallites in a solid to the broadening of a peak in a diffraction pattern. It is used to determine the crystal size in the form of powder. The Scherrer equation can be written as $\tau = \frac{K\lambda}{\beta cos\theta}$, where τ is the mean size of the measured crystals, K is a dimensionless shape factor (typically equals to 0.9), λ is the X-ray wavelength (1.5406 Å, in our case), β is the line broadening at half the maximum intensity (FWHM), θ is the Bragg angle. Therefore, we can draw a general conclusion that the wider the FWHM, the smaller the crystal size.

The text in the manuscript has been revised accordingly.

The calculation of crystal size was determined using the Scherrer equation, expressed as $\tau = \frac{K\lambda}{\beta cos\theta}$, where τ is the mean size of the measured crystals, K is a dimensionless shape factor (typically equals to 0.9), λ is the X-ray wavelength (1.5406 Å), β is the line broadening at half the maximum intensity (FWHM), θ is the Bragg angle.[2] (Page 4, SI)

(9) In Fig.3b, it is necessary to include the initial potential around 0 V vs Ag/AgCl.

Reply: Thank you for your constructive suggestion. This figure has been revised as below.

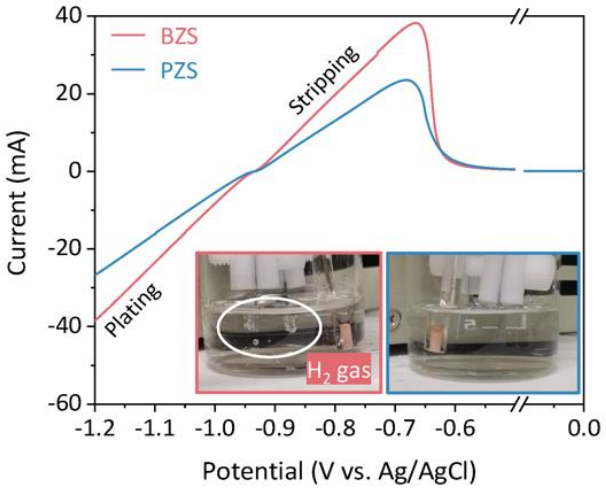
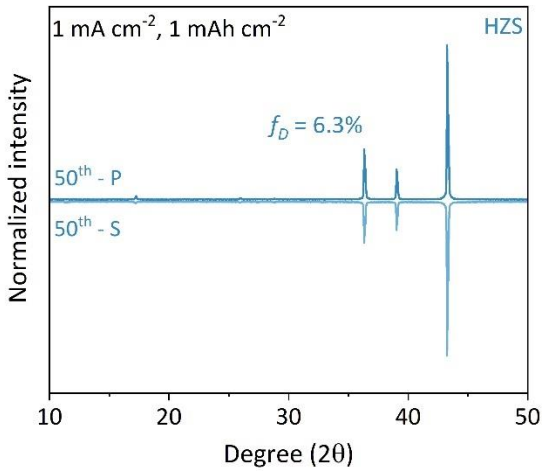


Fig. 3b The linear sweep voltammetry (LSV) of Zn||BZS||Ti and Zn||PZS||Ti cells.

(10) It would be beneficial to measure the f_D after 50 cycles, similar to what was done in BZS. This measurement is crucial for understanding the impact of the additive, especially since Figure 4c indicates that the cell undergoes stabilization during the initial cycles.

Reply: Thank you for your valuable suggestion. We found that the f_D value reduced from 6.3% after 50 cycles to 4.4% after 300 cycles, indicating a progressively optimized Zn plating/stripping process during cycling to some extent. The following description has been added to the main text accordingly.



Supplementary Fig. 9 | XRD result of cycled zinc electrodes. XRD pattern of stripped/plated zinc electrodes in the Zn||PZS||Zn cell.

Moreover, PZS facilitated a notably symmetrical and reversible deposition in the Zn||Zn cell, exhibiting a low f_D factor (following the equation $f_D = \left|I_{P(0\,0\,2)}/I_{P(1\,0\,1)} - I_{S(0\,0\,2)}/I_{S(1\,0\,1)}\right| \times 100\%$) of 6.3% (after 50 cycles) and 4.4% (after 300 cycles) at 1 mA cm^{-2}, 1 mAh cm^{-2},[39] suggesting a balanced and progressively improved stripping and deposition on the two symmetric Zn electrodes (**Fig. 4**a and Supplementary Fig. 9). (Page 9)

Notably, during the initial cycling stages, a significant *in-situ* stripping optimization of the Zn||PZS||Zn cell occurred without external intervention despite the initially high stripping overpotential caused by an uneven zinc surface or insufficient polishing treatment (**Fig. 4**c). This validates the gradual modification of the zinc surface by PPGA, corroborated by the decreased crystallite size of bulk zinc as indicated in the XRD results presented in **Fig. 2**c. (Page 9)

(11) After how many cycles the Zn foil was recovered in Fig. 4b.

Reply: We are sorry for the misunderstanding caused. Fig. 4b is the SEM images of cells in Fig. 4a, which demonstrated that PPGA enabled a smooth zinc surface after plating while the control sample underwent sever side reactions and dendrite growth. The process was not associated with surface recovery during the cycling stage.

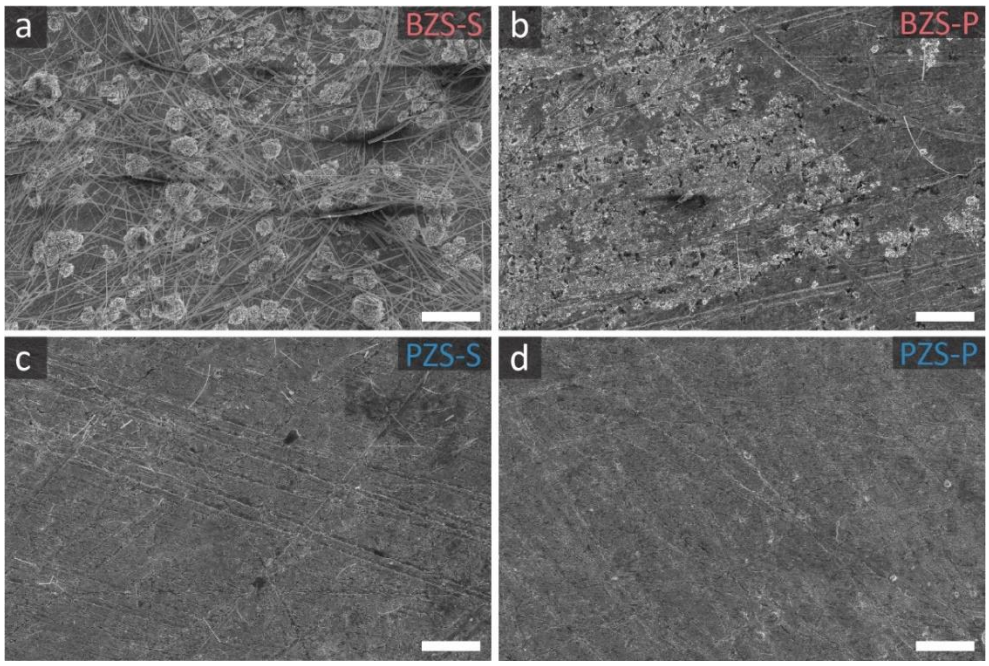
In case that you were alluding to the so-called "surface modification" in Fig. 4c, it is worth highlighting that the stripping overpotential gradually decreased over 8 cycles, eventually sustaining one year of operation. The finding supports an autonomous reduction of stripping overpotential due to the inclusion of PPGA. The corresponding sentence has been revised as below.

Notably, during the initial cycling stages, a significant stripping optimization (an autonomous reduction of stripping overpotential) of the Zn||PZS||Zn cell occurred without external intervention despite the initially high stripping overpotential resulting from an

uneven zinc surface or insufficient polishing treatment (**Fig. 4**c). This validates the gradual modification of the zinc surface by PPGA, corroborated by the decreased crystallite size of bulk zinc as indicated in the XRD results presented in **Fig. 2**c (Page 9)

(12) I suggest to include SEM images at lower magnification to see the homogeneity of the deposition.

Reply: Thank you for your suggestion. SEM images at low magnification have been provided below.



Supplementary Fig. 11 | Overall surface condition of cycled zinc electrodes. SEM images at a lower magnification showing stripped and plated electrodes in **a, b** Zn||BZS||Zn and **c, d** Zn||PZS||Zn symmetric cells. "-S" and "-P" denote the stripped and plated side in the last cycle, respectively. The scale bar measures 100 μm.

SEM and SEM-mapping images with a broader field of vision further convinced the uniform deposition/stripping of zinc in Zn||PZS||Zn cell without byproducts and corrosion spots (Supplementary Fig. 10-12). (Page 9)

(13) I don’t understand what the author meant by *in-situ* stripping optimization.

Reply: The fresh Zn electrodes can be considered as "bulk Zn", initially lacking sufficient energy to engage in the stripping process. Therefore, an initial stripping overpotential is required to activate this "bulk Zn." However, this stripping process may induce cracks on the zinc surface, promoting the formation of dendrite clusters. [*Nat. Commun.* 13, 3699 (2022)].

In our case, an unusual high stripping overpotential in the initial cycling stage of the Zn||PZS||Zn cell was observed (Fig. 4c), probably originating from an uneven zinc surface or inadequate polishing treatment. Nonetheless, with the presence of PPGA, the stripping process itself gradually became smoother and did not compromise the cycling performance, without any further modification of the Zn||PZS||Zn cell. Given that "*in situ*" is defined as "in the original place" in the dictionary, we interpreted the reduction of the stripping overpotential as an *in-situ* stripping optimization on the zinc surface. On the other hand, PPGA treatment caused reduced crystal size of zinc according to the XRD results (**Fig. 2**c), which would promote the stripping process.

To enhance the clarity of the description, the corresponding text has been revised as below.

Notably, during the initial cycling stages, a significant stripping optimization (an autonomous reduction of stripping overpotential) of the Zn||PZS||Zn cell occurred without external intervention despite the initially high stripping overpotential resulting from an uneven zinc surface or insufficient polishing treatment (**Fig. 4**c). This validates the gradual modification of the zinc surface by PPGA, corroborated by the decreased crystallite size of bulk zinc as indicated in the XRD results presented in **Fig. 2**c (Page 9)

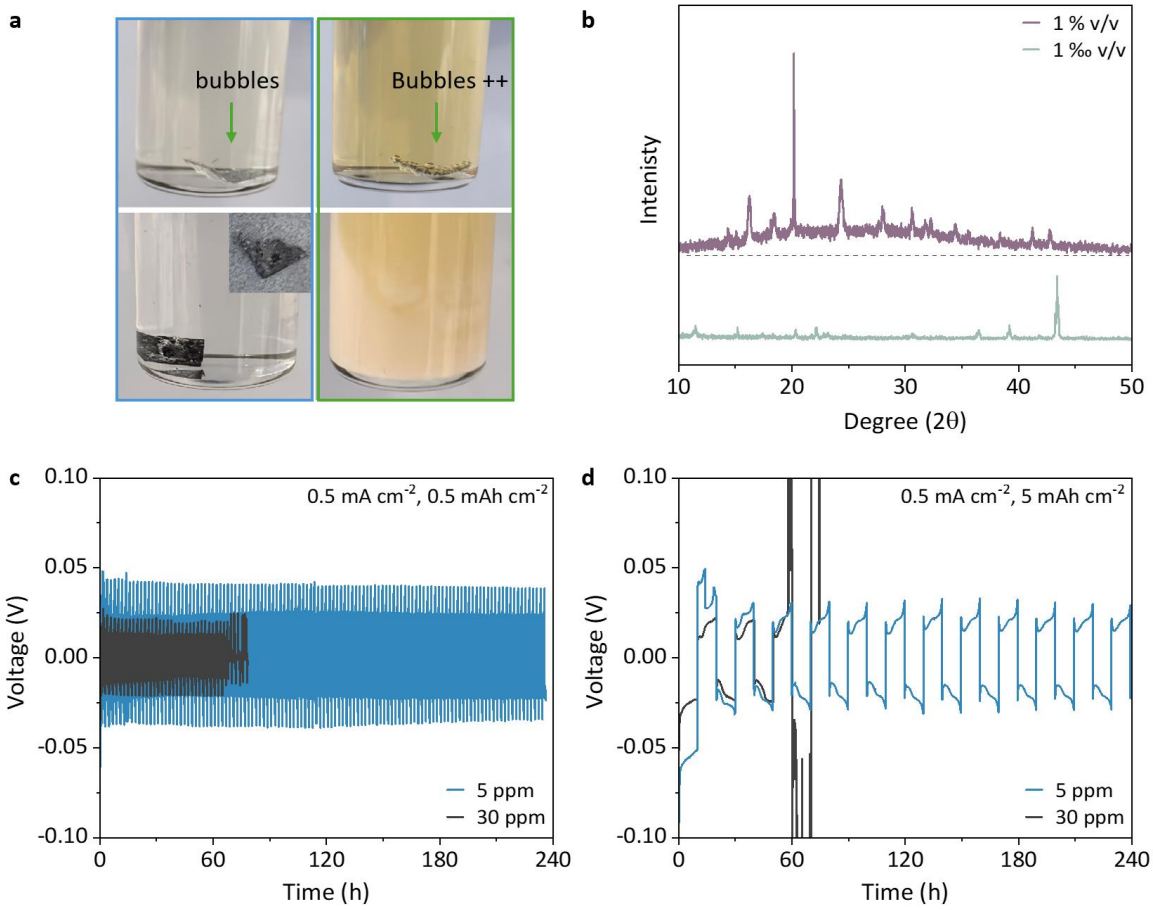
(14) The authors should give more details regarding the symmetric cell stripping/plating analysis: the diameter of Zn electrodes and the amount of the electrolyte.

Reply: Thank you for your suggestions. The details have been included in the experimental section below.

The Zn||Zn symmetric coin cells were assembled by two Zn foils (100 μm, 1 × 1 cm^2) and an intermediate glassy fiber separator (Whatman, GF/C) with the addition of 60 μl electrolyte. 2 mol L^{-1} $ZnSO_4$ electrolyte (BZS) and the same electrolyte with an additional 5 ppm of PPGA (PZS) resulted in water-to-solute ratios of 10.76747 and 10.76687, respectively. (Page 3, SI)

(15) For comparison with the literature, I suggest including the plating stripping of Zn at 0.5 mA/cm^2 current density.

Reply: Thank you for your valuable suggestion. As shown in Fig. S4, we have conducted a comparison based on Zn||Zn symmetric cells at 0.5 mA/cm^{-2} accordingly. We found that the control cell (which used 30 ppm PPGA) failed at around 60 hours at 0.5 mA cm^{-2} (comparable to the values in the above-mentioned reference) while the Zn||PZS||Zn cell endured 240 hours under the same conditions, regardless of the depth of discharge.



Supplementary Fig. 4 | Impact of the PPGA concentration on zinc metal. Photograph showing the immersion of zinc metal into aqueous **a** 0.1 % v/v (blue wireframe) and 1 % v/v (green wireframe) PPGA solutions and stored for 8 days; **b** XRD patterns of the zinc metal in **a**; Zn||Zn symmetric cells cycled at **c** 0.5 mA cm^{-2}, 0.5 mAh cm^{-2} and **d** 0.5 mA cm^{-2}, 5 mAh cm^{-2}.

The corresponding text has been revised as below.

It is important to highlight that a high dosage of PPGA could be detrimental to the zinc electrodes and may have limited effectiveness in suppressing side effects (Supplementary Fig. 4). (Page 6)

The immersion treatment revealed ongoing corrosion of the zinc metal in a diluted aqueous PPGA solution. The 0.1% v/v PPGA solution partly dissolved the zinc metal and rendered

it brittle after 8 days, as illustrated in the inset of Supplementary Fig. 4c. Remarkably, the zinc metal transformed into intricate white powders in the 1% v/v PPGA solution, unveiling the contrasting effect of concentrated PPGA on zinc. Subsequent cycling of Zn||Zn symmetric cells indicated that a higher PPGA concentration may negatively impact battery performance. It could be attributed to the diminished crystal size of Zn post-PPGA treatment as shown in Fig. 2b, c and would become more crucial during the stripping/plating process and necessitate further comprehensive studies within the research community. (Page 7, SI)

(16) Please give more details regarding the calculation of the capacity retention including current densities in the following statement: "Operation in PZS enabled the coin cell with a reasonably high capacity retention of 87.8% but dropped to 70.6% in BZS (Fig. 5d and Supplementary Fig. S14)."

Reply: Thanks for the reminder. The capacity retention was evaluated to be 325.6 / 371.7 × 100% = 87.6 % and 275.5 / 389.7 × 100% = 70.6%, for the cells operated in PZS and BZS, respectively. Further explanations have now been added to the main text.

As depicted in Fig. 5d and Supplementary Fig. 21, Zn||PZS||$Zn_{0.25}V_2O_5 \cdot nH_2O$ facilitated a high capacity of 371.7 mAh g^{-1} at 0.2 A g^{-1} with a reasonably high capacity retention of 87.6% (retained 325.6 mAh g^{-1} after the current reset). In contrast, the capacity retention of the battery operated in BZS decreased to 70.6%, maintaining 275.5 mAh g^{-1} out of 389.7 mAh g^{-1}. (Page11)

(17) Is there an excess of electrolyte volume in the pouch cell configuration?

Reply: Yes. The electrolyte for the pouch cell was 10% over the prescribed amount compared to that for the coin cell (60 µl per square centimeter).

We have added further explanation below.

Specifically, the $Zn_{0.25}V_2O_5$ cathode (~ 60 mg cm^{-2}) and Zn anode were both shaped to 10 cm × 10 cm and assembled with a slightly larger separator (10.4 cm × 10.4 cm) and a

suitable amount of PZS electrolyte (around 10% over the required dose), subjected to Al packaging bag. (Page 3, SI)

(18) I don’t understand why the authors chose polyolefin membrane which is waterproof.

Reply: The polyolefin membrane used for aqueous flow batteries is hydrophilic. The producer, Daramic (USA), is the global leader in supplying high-performance polyethylene battery separators to the lead acid battery industry. According to the product specification, it consists of ultrahigh molecular polyethylene and amorphous silica and possesses a porosity of 58% with a moisture content of 3%. As per the supplier's specifications, the membrane is hydrophilic; otherwise, the water droplet demonstrated below would exhibit a contact angle significantly greater than 90 degrees.

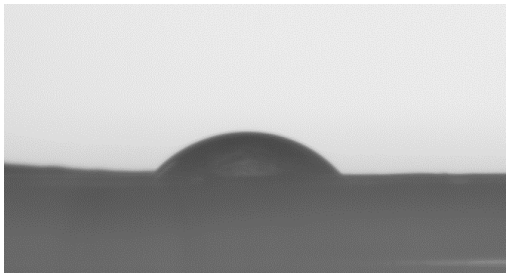


Fig. R2. The contact angle between the hydrophilic Daramic membrane and water.

Detailed parameters of the membrane have been added to the manuscript:

Hydrophilic Daramic membranes, approximately 900 μm thick, with an average pore size of around 0.1 μm and a porosity of about 58% (Polypore (Shanghai) Membrane Products Co., Ltd, China), were utilized as received. All electrolytes were prepared with deionized water. (Page 2, SI)

(19) Could the authors explain why they chose the electrolyte with 10 ppm additive in the redox flow battery?

Reply: The area of each electrode in a Zn||Zn symmetric cell is around 1 $cm^{2,}$ while the active area of carbon felt is 4 cm^2. Thus, we slightly increased the amount of PPGA in flow

batteries for a comparative assessment of the effectiveness of the additive in the two battery systems.

The corresponding text has been revised to clarify the treatment.

For the batteries with PPGA, an additional 10 ppm of PPGA was added to the anolyte considering the varied surface area of the cathode electrodes in flow batteries and coin cells. (Page 4, SI)

Reviewer #3 (Remarks to the Author):

The authors addressed most of the questions, and the revised version provides better clarity. However, the positioning of this work in comparison to Y. Yu et al.'s research in Energy Storage Materials journal remains unclear.

Reply: Thank you for your positive comments. We hope the following replies will address your concerns.

1) Y. Yu et al. also investigated the effect of the additive at concentrations ranging from 15 ppm to 45 ppm, with their best results observed at 30 ppm.

Reply: 30 ppm could outperform 15 and 45 ppm while we counterintuitively optimized it to 5 ppm. As explained in the previous response, PPGA has an impact on the crystal size of zinc and can even cause the dissolution of zinc metal at 0.1 % v/v, revealing the presence of one or several critical dosages to reach improved zinc chemistry.

The success stems from our introduction of a new immersion treatment for zinc metals in diluted PPGA solution to uncover its influence on zinc anode with varying exposure time, albeit constrained by the capability of available measurement equipment to detect ppm-scale additives (Fig. 2, Fig. S4, etc.).

2) When comparing the Zn plating/stripping data from this paper at 5 ppm with Y. Yu et al.'s results at 30 ppm, the cycling stability at 10 mA/cm² with 10 mAh/cm² is quite similar—both studies report 500 hours of cycling with an overpotential of 0.1V. The only difference is that this study at 5 ppm shows longer cycling at 10 mA/cm² with 1 mAh/cm². In my view, it's difficult to conclude that 5 ppm outperforms 30 ppm; the results may be comparable and influenced by experimental errors.

Reply: Our study at 5 ppm showed a much-improved cycling stability at 10 mA/cm², 1 mAh/cm² for 350 days (8400 h), whereas the referenced study only reached 1200 hours. Similarly, the 5-ppm additive endowed the Zn||Zn symmetric cell with high durability at 1 mA/cm², 1 mAh/cm² for 362 days (8688 h), while that in the referenced study was 2000 h. Such discrepancies can hardly be attributed to experimental errors.

3) The authors should also include Y. Yu et al.'s results in Figure 4f to properly position this work in relation to existing studies.

Reply: Thanks for the suggestion. We have added Y. Yu's results, accordingly, marking in light pink color in Fig. 4f (10.1016/j.ensm.2024.103601).

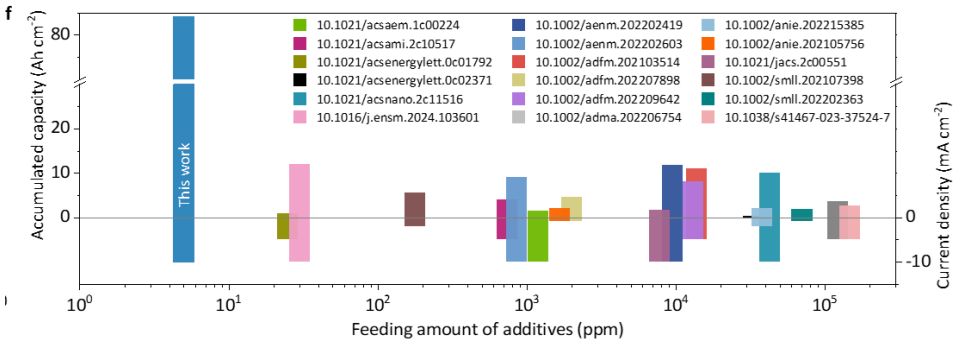


Fig. 4f Comparison of achieved cycling performance with values reported in the literature (estimated by simplified ex-post calculations).

4) In the revised manuscript, the authors state, “Herein, we proposed a ppm-scale effective inhibitor, phosphonoglycolic acid (PPGA), as a new additive to the ZnSO4 electrolyte.” Unfortunately, this is no longer novel, as it has already been published.

Reply: Thanks for the reminder. We have removed such descriptions from our manuscript. The corresponding text has been revised below.

Herein, we proposed a ppm-scale effective inhibitor, phosphonoglycolic acid (PPGA), as the additive to the $ZnSO_4$ electrolyte. (Page 4)

Other comments

5) Please also specify in the caption of Fig. 1b that the BZS has been subtracted in the spectra with additives.

Reply: Figure caption of Fig. 1b has been revised accordingly: **b** FTIR spectra of BZS with a varying amount of PPGA (0, 1, 5, or 10 ppm), where BZS was used to subtract the background. (Page 19)

6) Please clarify how Fig. 3b was obtained, including the range and direction of the sweeping potentials used. It seems unlikely that this curve could be obtained in a single sweep.

Reply: Such curves are commonly obtained in a single sweep for three-electrode Zn||Ti or Zn||Cu asymmetric cells. The test details are provided on Page 8 now.

Experimental observations shown in the inset of Fig. 3b witnessed the violent HER of a three-electrode Zn||BZS||Ti cell (swept from -1.25 V to 0 V with a scan rate of 5 mV/s).