

Long-life Aqueous Zinc-iodine Flow Batteries Enabled by Selectively Intercepting Hydrated Ions

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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)

Development of low-cost and efficient energy storage technologies are of key importance for realizing the energy transition towards a clean model based on renewable sources. Among the various emerging technologies, aqueous zinc-iodine flow batteries (Zn-I FBs) holds great promising due to its low cost and the independent scalability of power and energy. However, there are several issues that prevent practical implementation of this promising technology. Namely, regulating the transport behaviors of water/hydrated ion clusters to avoid water unbalancing and preventing polyiodide cross-over. The strategy, i.e. the implementation of membranes having size-tailored pores with sub-nanochannels, tackles these two major challenges.

The scientific hypothesis is sound, and the findings reported in the manuscript seem to support the hypothesis. The performances achieved by implementing the proposed strategy are excellent, which will additionally bring technological interest. The manuscript well written and properly structured. A number of analytical techniques are used to support the hypothesis. Technically, the manuscript is very solid and major issue are not found. Beyond the figure of merit achieved in this work, the strategy demonstrated here paves the way for bring this important technology closer to commercialization. It should be noted that, although the membrane used here may not be the best choice from cost perspective, it certainly shows that these two major challenges can be addressed following the proposed strategy opening a new scientific direction in the field.

This referee considers that the topic is of high interest for the community of materials science and energy. The hypothesis is novel and the findings reported are relevant. Therefore, I recommend the publication of this work in Nature Communication.

Reviewer #2

(Remarks to the Author)

The manuscript discusses membrane modifications aimed at mitigating iodide crossover in Zn-I2 flow batteries. However, I find the reported results to be potentially exaggerated. Existing literature (Nat Energy 6, 517–528 (2021).

<https://doi.org/10.1038/s41560-021-00804-x>), already shows that coating a Nafion membrane with carbon paste effectively prevents electrolyte crossover. Simply replacing carbon with Zn-MOF might not justify publication in such a prestigious journal.

Additionally, several concerns need to be addressed:

Ion Permeability Calculation: The ion permeability is assessed using an H-type cell with the feed reservoir containing 2 M KI3, and the permeate side filled with deionized water. It is unclear how the authors address the osmotic pressure that could affect the results. Please provide clarification on this aspect.

Diffusion Through Zn-MOF: The authors claim that ion diffusion occurs through the pores of the Zn-MOF. However, in a solvent casting method using PVDF as a binder, a non-porous structure is often generated. This may hinder the diffusion of iodide ions, although diffusion of other cations, such as Zn²⁺, could still occur. Please comment on this potential issue and provide supporting documentation.

Transport Number Calculation: Please verify the formula used for calculating the transport number of bivalent ions by the membrane potential method. Ensure that it is correct and clearly described.

Reviewer #3

(Remarks to the Author)

The manuscript presents the development of the Zn-MOF-CJ3 tailoring ionic-molecular sieve (ZMC-IMS) membrane, representing a significant advancement in Zn-I flow batteries. The authors successfully address challenges related to ion transport and polyiodide crossover through precisely tuned subnanometer pore sizes, enhancing the selectivity for large-hydrated ion clusters and facilitating a reversible charge/discharge process. The systematic investigation of membrane properties supports the effectiveness of the ZMC-IMS design, demonstrating cycling stability under high-capacity conditions. The low self-discharge rate and high Coulombic efficiency further underscore its suitability for long-life energy storage. Additionally, the techno-economic analysis highlights the competitive cost-effectiveness of this system. Overall, the manuscript meets high standards with enough advancement in innovation and performance for publication in Nature Communications. The reviewer has raised some comments regarding this study, which could improve the quality of the manuscript. After a careful and complete review,

1: The presence of CNTs in the ZMC-IMS membrane should be clearly explained. This will help to highlight the contributions of the ZMC component and its overall effectiveness.

2: The coating method employed for the ZMC-IMS is a crucial aspect that may influence the rate performance of the battery. It is essential that this point is clarified in the manuscript to ensure a comprehensive understanding of the research.

3: Some of the Figures, particularly Fig. 5 (Techno-economic cost analysis), could benefit from more explicit labeling and a clearer distinction between the E-Cost, O&M, and Investment results. This would help readers follow the discussion more easily.

4: In progress, Zn-based flow batteries also face issues with Zn metal anodes, such as uneven deposition and dendrite formation. Could the authors clarify how the issues are addressed in this work?

5: There are a few grammatical errors and instances of awkward phrasing that could be improved. Additionally, some language in the manuscript may come across as hyperbolic. Consider more precise and measured wording.

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The manuscript had been thoroughly revised, it is suitable for its publication in the current form.

Reviewer #4

(Remarks to the Author)

The authors present a study showing how using a Nafion membrane modified with CNT-MOF layers can improve the performance of a Zn-I flow battery. While the authors have presented rigorous work characterizing and testing this concept, the idea of modifying a current commercial membrane with a size excluding layer is not new (<https://doi.org/10.1002/ange.201510849> as one of many examples). I acknowledge that MOFs are getting a lot of attention in recent years as researchers expand their uses past the traditional catalyst field, but, in terms of a "Nature worthy" revelation, they are simply just another material used to modify a membrane in this work. Another big issue that prevents me from accepting publication of this work in this journal is the fact that the authors use Nafion 117 as the support. Ever since Nafion was invented, a major focus of the flow battery and fuel cell fields has been to find cheaper, less environmentally challenging replacements for Nafion. Without demonstrating a replacement for Nafion, I do not feel this work is impactful enough to be published in this journal.

The authors have put a lot of time and effort into the characterization, analysis and presentation of this work. I think it is worthy of publication in another journal within the field. However, there are still some major issues that should be addressed:

- 1) Page 7 – the authors need to mention in the main text that this is a layer being placed on Nafion 117. This is important because the fact that it still uses Nafion 117 means it will still be expensive and use environmentally challenging materials.
- 2) Page 8, line 173 – the comment that "there are few differences" between the CNT-Nafion and pristine Nafion membranes is misleading. According to the authors' own data there is an order of magnitude difference between the permeability with (3E-6) and without (2E-5) the CNT.
- 3) The claims about the MOFs absorbing I₃⁻ and preventing I₃⁻ crossover due to a high concentration are unsupported. The absorption experiment was only done in a KI solution. Please repeat in the actual flow battery electrolyte, where both Br⁻ and Cl⁻ are competing anions that could also uptake into the MOF. Or better yet, run the characterization after cycling.
- 4) SI Figure 2 – wrong caption
- 5) SI Figures 14 and 15 – wrong membrane label in Figure c.
- 6) The authors are clearly overselling their work. This type of salesmanship should be kept out of research publications. For instance, the term "high-energy" flow battery is used throughout the publication even though any flow battery can be high-energy by simply adding more electrolyte. If they mean "high energy density" that is also misleading because, although they have high concentrations of electrolytes, they operate at low current densities, with a 50% OCV of 1.35 V, and a DoD of

50%. Those are hardly “high energy dense” conditions.

7) Same comment as above, but with the term “harsh conditions” Their most harsh conditions are a 20 mA/cm² operation for 50% DoD for 3 hours. Those are not harsh.

8) In the same vein as the previous two comments, Page 11, Line 256 – the authors refer to the hydrated potassium clusters as small and large even though one is 2.7 nm and the other 3.5 nm. Just be quantitative and give the numbers.

9) Page 12, line 269 – authors claim more hydrophobic properties even though contact angles were quite similar (88.2 vs. 92.6 degrees). These are very similar values and could even be the same depending on the repeatability of the experiment.

10) Page 8, line 184 – the language makes it seem like you used XRD to determine thickness as opposed to just confirming the material is there. Please fix.

11) Figure 3 analysis – 4.5 V/nm is a very high electric field. Please justify that selection.

12) For all electrochemical data, please make clear what is meant by 20% and 50% SOC in the text and figures. Does that mean cycling from 0-20% and 0-50%?

13) The electrolyte in the FB experiments is highly concentrated. What are the saturation limit and viscosity with respect to temperature? These are important to know whether we can expect crash-out and/or excessive pumping issues in this system.

14) Page 14, line 304 – 10-50 mA/cm² is not a wide range. V/V can be run up to 200 mA/cm². Please be more quantitative with less excess adjectives that make it feel like this work is being oversold.

15) Page 14, line 325 – The EIS data is showing the opposite of the authors claims that the MOF membrane has better interfacial resistance. I understand the Arrhenius constant is lower for the MOF membrane, but the EIS data is showing that the MOF containing membrane has the highest charge transfer resistance at all temperatures. In addition, the presence of ZnO and ZnOH (SI Fig. 42) in the pristine membrane shows that the worse performance in the pristine membrane is likely due to a pH rise that causes the formation of passivating species, not because the MOF membrane has improved “Zn plating/stripping processes” as the authors claim.

16) Figure 4e – comparison only works if batteries are cycled at the same current density for the same amount of time. CE losses due to migration/drag are current dependent. CE loss due to diffusion is time dependent. I suggest limiting the comparison to as close to the same conditions as possible and including the current and time values in the SI table. Also, including Zn-Br is confusing. Your membrane works by excluding I³⁻ and some water crossover. I³⁻ is not present in Zn-Br. On a similar vein, it may also be useful to pick comparison cases with similar electrolyte compositions, assuming demonstrating the membrane effectiveness is the main goal. These should also be listed in the SI table.

17) Page 15, line 349 – please be quantitative about the water change and provide the numbers.

18) This is a major issue - For the technoeconomic analysis, the authors need to make sure they are running the comparison assuming a 20-year project life. It appears their Zn-I flow battery currently has a better LCOS because the authors assume a 40,000 cycle life vs. 20,000 for other FBs. At 180 cycles per year, 40,000 cycles corresponds to a project lifetime of 225 years, which is way too high for a LCOS analysis. Neither technology should have any replacement costs for a 20-year project under the current assumed cycle lives. Also, make sure you are discounting the energy from future cycles correctly. I would not expect your Zn-I to be so advantageous in your original analysis if you were doing this properly (the equations and references in <http://dx.doi.org/10.1149/2.0151816jes> can help). For instance, using the discount calculation of $1/(1+r)^t$ (t = time, r = discount rate of 8%), means that cycles at year 10, 20, and 50 are only worth 46%, 21%, and 2%, respectively, of a cycle in year 1. That would make any advantages of going past a 50-year lifetime relatively worthless.

19) Something is also wrong with the TEA because the Zn-I is NOT the most expensive option at short times in the authors' analysis even though it has 10x the power cost as competing technologies. Short times are dominated by power costs and I would expect the 10x higher power cost to cause a much higher LCOS at short times. I suspect it is related to the lifetime issues.

20) Zn-Br capital cost in SI Table 2 does not match the cost in SI table 5. It appears the cost in SI Table 2 is too high.

Version 2:

Reviewer comments:

Reviewer #4

(Remarks to the Author)

I thank the authors for their responses to my comments. While I think the authors and I will maintain differences in opinion of what constitutes a design paradigm for new flow battery membranes, I do acknowledge the novelty of a MOF coating and the rigorous characterization and testing done in this study. Therefore, I recommend the revised manuscript for publication after the following follow-up comments are addressed.

I want to re-iterate that I believe there is a high quality to the work conducted in this manuscript. My overall critique remains in some of the presentation and interpretation of this work that makes some of the conclusions feel oversold and under supported. It is OK to have uncertainties in a study because it provides motivation for the rest of the field. I also acknowledge that some of this “oversold” feeling comes from the pressures of publishing in a high-impact journal, and my frustration may be more with the system, which forces researches to feel like they have to invent something that has saved the world to publish in a journal like nature energy, and less with the individual authors. That said, I strongly advise the authors to please the following comments into consideration to help the readers understand, qualitatively, the conclusions and impact of this work.

Response to Comment 6: This type of calculation and comparison for the Wh/L would be very useful to include in the manuscript. It provides qualitative justification to the words “higher energy density.” I strongly suggest including this within

the work. That said, when presented in the text, can you please clarify the assumptions that went into the 71.82 Wh/L? Is that just the electrolyte? The energy density for V/V electrolyte at OCV is also ~70 Wh/L (1.8 M, 1.4 V). In table S5, you list the system at ~28 Wh/L. Please make sure you're either doing system to system or electrolyte to electrolyte.

Response to Comment 7: This justification for >50% being a harsh condition is an excellent qualitative explanation for why these conditions are "harsh." I suggest including this within the main text to provide the reader with this context. Just using the word "harsh," made me feel like you are trying to sell the invention, but if this information were included, I would fully understand that you were operating your system to the limits. While I consider myself a flow battery expert, I concede that I don't know the ins and outs of every chemistry.

Response to Comment 9: If the contact angles are reasonable and repeatable, I assume you did these experiments multiple times and should be able to provide error bars on the numbers provided. Please do so in the manuscript and also include information on the number of repetitions conducted (keeping all in SI is fine)

Response to Comment 12: Thank you for clarifying this point. Can you please make sure it is clear within the manuscript for future readers?

Response to Comment 15: I suggest being less definitive in the text that the improved deposition is from modulating the Zn desolvation energy. EIS is a very complicated technique, where the one definite conclusion you have is that the Arrhenius dependence of the charge transfer resistance is lower for the ZMC-IMS-GF membrane system. This could result from many things as the EIS charge transfer resistance depends on the morphology, local speciation, etc. Also, in a symmetric cell, you are getting a combined resistance from deposition and stripping, making interpretation of the results even less clear. I went into reference 55 hoping to find a rigorous study linking EIS temperature dependence to solvation, but could not find anything. As such, just mention that "the uniform deposition MAY BE due to a modulating of the Zn desolvation energy, as suggested by changes in the arrhenius dependency of the charger transfer resistance of the EIS of a symmetric cell. However, addition characterization is needed to confirm this hypothesis."

Response to Comment 16: Thank you for including more data. While working time is great, the metrics that provide me the most insight for comparison are the cycle time (i.e., time for a single charge and single discharge) and the applied current density. For instance, I would expect the CE to be lower in studies the use low current densities and long cycle times. Can you please include these numbers in the table?

Response to Comment 18: I agree that www.EnergyStorage.ninja is a great resource that provides a third party validation of LCOS costs. I also see that the tool does apply a discount rate. That said, as someone who conducts techno-economic analyses for industry and government (I work at a National Laboratory), I strongly suggest applying a project lifetime to these calculations. If you feel 20 years is too short for your technology, feel free to use a higher number (30, 40, 50?). Just be explicit in the text for what you assumed and keep in mind that LCOS is an economic benchmark for a technology and the assumed project lifetime is an important assumption when comparing technologies. I'm OK with you going as high as 50 years under the assumption this is a public works project like a hydro-electric dam.

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Responses to Reviewer's Comments

Reviewer #1:

Development of low-cost and efficient energy storage technologies are of key importance for realizing the energy transition towards a clean model based on renewable sources. Among the various emerging technologies, aqueous zinc-iodine flow batteries (Zn-I FBs) holds great promising due to its low cost and the independent scalability of power and energy. However, there are several issues that prevent practical implementation of this promising technology. Namely, regulating the transport behaviors of water/hydrated ion clusters to avoid water unbalancing and preventing polyiodide crossover. The strategy, i.e. the implementation of membranes having size-tailored pores with sub-nanochannels, tackles these two major challenges.

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This referee considers that the topic is of high interest for the community of materials science and energy. The hypothesis is novel and the findings reported are relevant. Therefore, I recommend the publication of this work in Nature Communication.

Response: We sincerely appreciate your positive and constructive comments regarding our manuscript. We appreciate your recognition that our strategy of using ZMC-IMS membranes with size-tailored pores and sub-nanochannels is vital for developing low-cost and efficient flow batteries (FBs)-based energy

storage technologies, effectively addressing the challenges in aqueous Zn-I FBs. Again, we appreciate your recognition of the structure of the manuscripts and the analytical techniques employed, which we believe strengthen our findings. We also acknowledge your point regarding the cost analysis of the membrane, and we are committed to exploring more cost-effective alternatives in future work. Finally, we have thoroughly reviewed our manuscript to eliminate any grammatical errors and typo mistakes. All revisions are highlighted in yellow in our revised manuscript.

Responses to Reviewer's Comments

Reviewer #2:

The manuscript discusses membrane modifications aimed at mitigating iodide crossover in Zn-I₂ flow batteries. However, I find the reported results to be potentially exaggerated. Existing literature (Nat Energy 6, 517–528 (2021). <https://doi.org/10.1038/s41560-021-00804-x>), already shows that coating a Nafion membrane with carbon paste effectively prevents electrolyte crossover. Simply replacing carbon with Zn-MOF might not justify publication in such a prestigious journal.

Additionally, several concerns need to be addressed:

Response: Thank you for your professional and insightful comment. Actually, we would like to clarify that our study goes beyond merely addressing iodide crossover.

Our primary focus is on the precisely selective sieving function of hydrated ions, which plays a critical role in alleviating water migration issues in Zn-based flow batteries (FBs). We would like to reorganize our description to emphasize the multifunctional effects of the ZMC-IMS membrane in our work. During the operation of FBs, substantial ion transfer occurs between posolytes and negolytes, with these ions typically transferring in the form of hydrated ions. Under conditions of high areal capacity and high energy density, the amount of transferred hydrated ions significantly increases, resulting in more severe water migration in terms of hydrated ions and accompanying side reactions (**Fig. R1a**). For Zn-based FBs, the Zn metal anode operates through deposition and dissolution processes, leading to more pronounced ion imbalance issues with more significant water migration. This phenomenon ultimately results in generally shorter lifespans for Zn-based FBs. Moreover, under high areal/volumetric capacity and high state of charge (SOC) conditions, extended charge and discharge processes in the Zn-I FB systems can also contribute to the crossover of iodine active species, lowering the Coulombic efficiency (CE) and hindering the long-term cycling of Zn-I FBs. Therefore, it is crucial to overcome both challenges under harsh testing conditions to ensure that Zn-I FBs can meet the requirements for long-life energy storage applications (**Fig. R1b**).

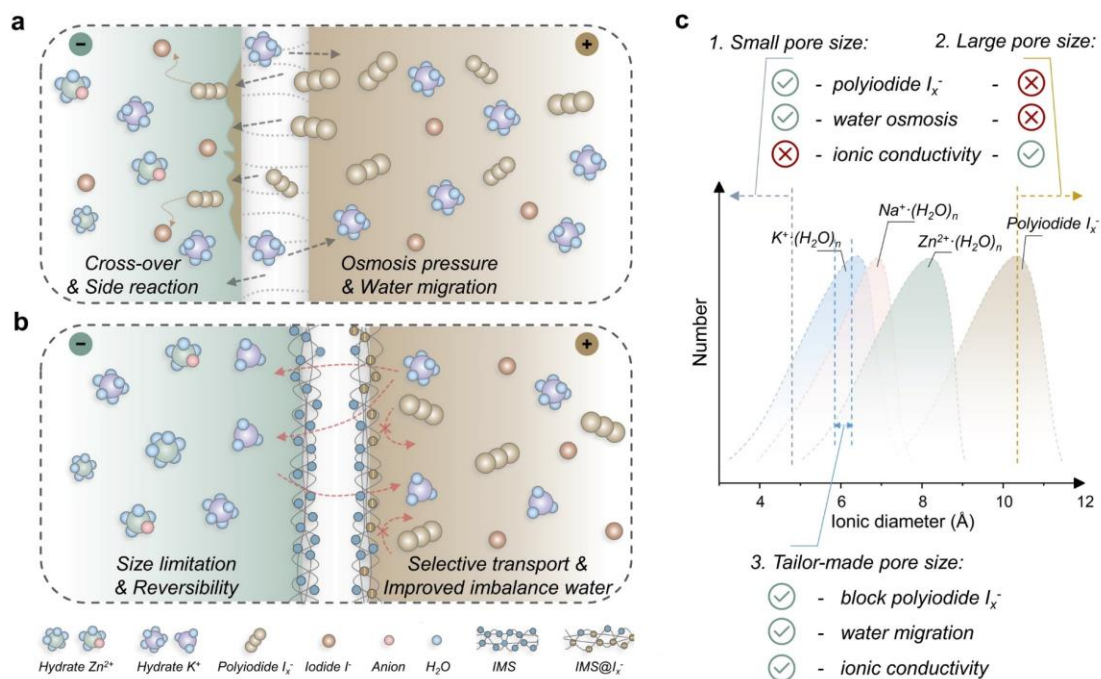


Fig. R1 (a) Crossover of polyiodide (I_x^-), side reaction, and severe water migration induced by pristine membranes lead to rapid cell failure of Zn-I FBs. (b) Alleviated crossover and water migration in Zn-I FBs using IMS-based membranes, where the volume of the posolyte and negolyte maintained a balance. (c) The properties and performances of membranes with different subnanometer pores towards hydrated ionic size.

For the existing literature mentioned in your comment (Nat Energy 6, 517–528, 2021), we would like to clarify that the working mechanisms are different from our work. The carbon-based membrane in this reference employs a surface charge enhancement strategy to mitigate the crossover issues of active materials through the charge Donnan effect. However, it is important to note that this approach used a high content of carbon and hydrophobic binders, leading to a significant reduction in ionic conductivity and energy efficiency. This carbon-based membrane does not address the critical issue of water migration induced by the out-of-balance of hydrated ions, especially for the Zn-based FB systems. Regarding our research, the membrane focuses on size-sieving effects to selectively allow permeation of specifically sized small-hydrated ions (a hydration number of 4 and a size of ~ 6 Å). Therefore, our results based on the size-sieving effect fundamentally differ from the surface charge enhancement effect in the mentioned reference.

Specifically, for our work, we develop a ZMC-IMS membrane to regulate the transport behaviors of hydrated ion clusters to enable their volumetric balance by precise size sieving effects of subnanometer pore sizes (**Fig R1c**). Meanwhile, it can block the polyiodide crossover via a localized high-concentration iodide-repelling layer of sub-nanochannel chemistries. This work reveals that the functional ZMC-IMS layer is capable of sieving hydrated ions of varying sizes. Meanwhile, the ZMC-IMS layer with pore size

ranging from 0.55 to 0.65 nm is revealed to selectively intercept large-hydrated ion clusters and effectively mitigate polyiodide shuttling, facilitating a highly reversible dis/charging process in Zn-I FBs. These functionalities are validated through experiments (adsorption tests, H-cell tests, small-angle X-ray scattering technology) and theoretical calculations and simulations (EPS, adsorption energy, and molecular dynamics simulations) (**Fig. 2 & 3** in our manuscripts).

As a result, the Zn-I FBs maintain stable rate performance due to high membrane ionic conductivity and efficient transport of small-hydrated ions, achieving energy efficiency of approximately 85% at 10 mA cm⁻² and around 46% at 50 mA cm⁻² (**Fig. R2a & 2b**). The ZMC-IMS membranes-based Zn-I FB systems operates stably for over 500 cycles (> 2050 h) with no significant CE decay at 50% SOC conditions, maintaining an average CE of 99.0% under high volumetric/areal capacities (53.2 Ah L⁻² posolyte, 66.4 mAh cm⁻²), as demonstrated in **Fig. R2c**. Furthermore, the low self-discharge performance shows no apparent CE decrement for ZMC-IMS membranes after different flowing periods (99.5% after 24 h; 98.5% after 168 h), while the CE for N117 membranes significantly decreased to 93.6% and 84.4% after static flowing for 24 h and 168 h, respectively (**Fig. R2d**). In our evaluation, we compared essential metrics (such as CE, volumetric/areal capacities, and operational lifetime against previously reported results for Zn-polyhalide FBs. The results demonstrate that the Zn-I FBs incorporating ZMC-IMS membranes outperform others significantly, showcasing enhanced areal/volumetric capacities along with a longer lifespan. Furthermore, our techno-economic analysis suggests that the ZMC-IMS membrane-enabled Zn-I FBs have the potential to achieve a competitive levelized cost of storage (LCOS) for long-life energy storage applications (**Fig. 5** in our manuscripts).

In summary, as discussed above, we believe this aspect of our work offers advancements in functional coatings to solve water migration and crossover issues, as it contributes to enhancing the overall performance and stability of the battery system. We are committed to providing a comprehensive exploration of these functions, which we hope to be recognized as a meaningful contribution to Nature Communications.

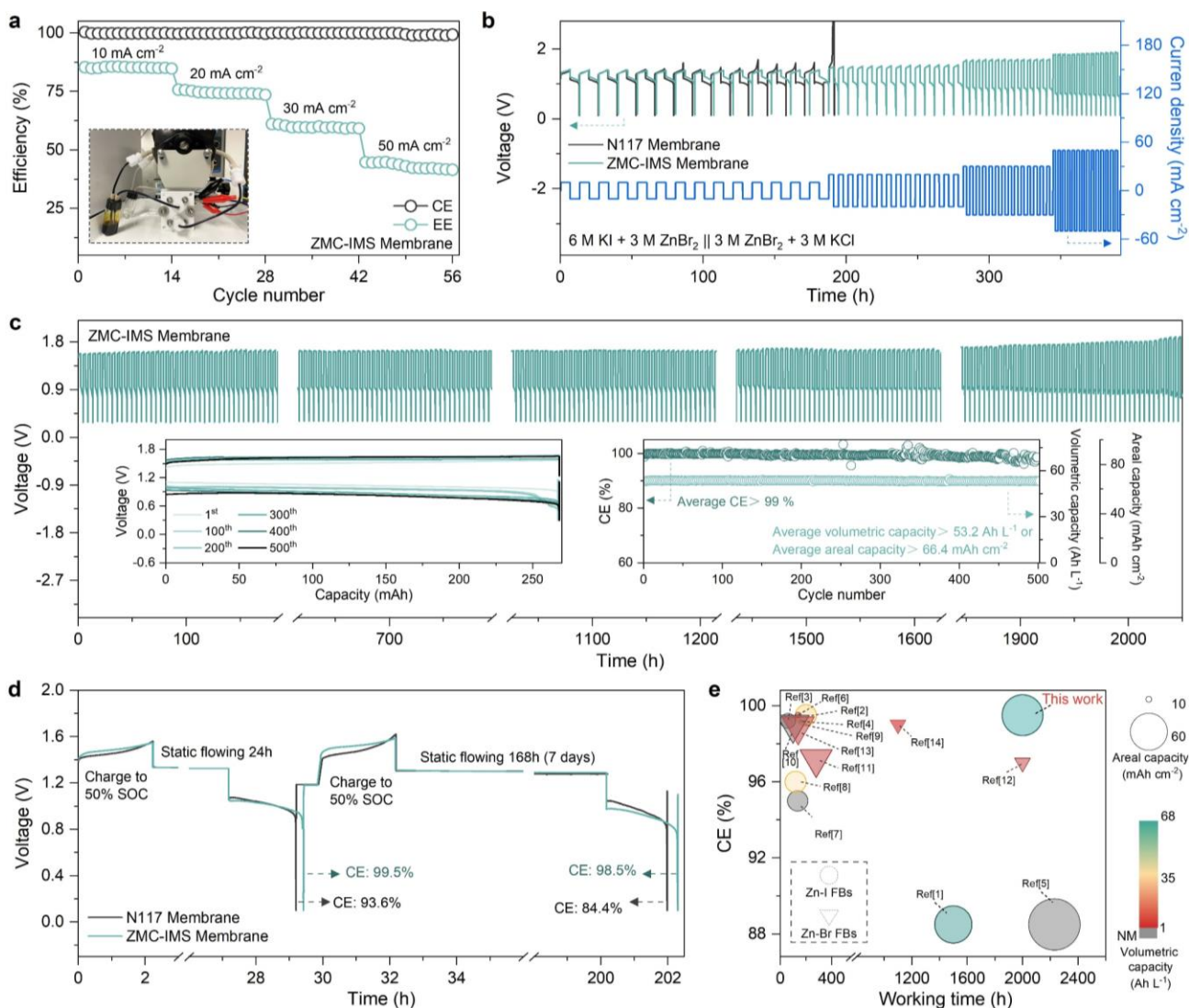


Fig. R2 (a) CE and EE of Zn-I FB cell (5 ml of 6 M KI + 3 M ZnBr₂ || ZMC-IMS membrane || 5 ml of 3 M ZnBr₂ + 3 M KCl, 4 cm² membrane area) under 10, 20, 30 and 50 mA cm⁻² at 50% SOC. The inset shows the prototype of Zn-I FBs flow-cell stack (5 ml of electrolytes, 4 cm² membrane area, for illustration). (b) Galvanostatic cycling of Zn-I FBs cell with ZMC-IMS and pristine N117 membranes. (c) Long cycling of high-energy Zn-I FB flow-cell (5 mL of 6 M KI + 3 M ZnBr₂ || ZMC-IMS membrane || 5 mL of 3 M ZnBr₂ + 3 M KCl, 4 cm² membrane area) at 30 mA cm⁻² with the designated discharge duration (energy to power ratio, E/P) of 2.23 h. The insets show the representative voltage profiles over cycling, CE, and volumetric/areal capacity during 500 cycles (2050 h). (d) Self-discharging performance of Zn-I FB flow-cell after charging to 50% SOC for static flowing 24 h and 168 h. (e) Comparison of Zn-based FBs in terms of CE, working time, and areal/volumetric capacity, where the symbol size and color scale show the corresponding areal capacity and volumetric capacity, respectively.

Comment 1: Ion Permeability Calculation: The ion permeability is assessed using an H-type cell with the feed reservoir containing 2 M KI₃, and the permeate side filled with deionized water. It is unclear how the authors address the osmotic pressure that could affect the results. Please provide clarification on this aspect.

Response: Thank you for your valuable and helpful comment. We sincerely apologize for not providing a sufficient description of ion permeability in our manuscript, and we have reorganized the content in the following sections for better understanding.

Firstly, it should be recognized that using an H-type cell with a feed reservoir containing 2 M KI₃ and a permeated side filled with deionized water will lead to a higher osmotic pressure. It was intended to assess the permeability of the membrane to active materials I₃⁻ and hydrated ions under such harsh conditions with higher osmotic pressure. Following your suggestion, to mitigate the influence of osmotic pressure, we have employed another H-type cell with a feed reservoir containing a lower concentration of KI₃ (0.1 M) and a permeate side filled with supporting salts (0.1 M KCl) to re-evaluate the permeability of all membranes (**Fig. R3a**). Notably, this testing approach is also widely utilized in other permeability assessments (such as Nat. Mater., 2020, 19, 195–202; Nat Commun, 2022, 13, 3184), which use equal concentrations of cations on the two sides to exclude the influence of cations. As shown in **Fig. R3**, the permeability of I₃⁻ through the N117 membrane exhibits a high value of $9.481 \times 10^{-6} \text{ cm}^2 \text{ h}^{-1}$, indicating poor blocking efficiency against polyiodides. When introducing ionic-molecular sieve (IMS)-based layers with different pore sizes, it is obviously observed that the MOF-5-IMS membrane ($1.0513 \times 10^{-6} \text{ cm}^2 \text{ h}^{-1}$) with large pore size ($\sim 12 \text{ \AA}$) shows only a slight improvement in blocking effectiveness for polyiodides, while both the ZMC-IMS ($1.7585 \times 10^{-7} \text{ cm}^2 \text{ h}^{-1}$) and ZIF-8-IMS ($6.9762 \times 10^{-8} \text{ cm}^2 \text{ h}^{-1}$) membranes demonstrate superior blocking performance (**Fig. R4-R6**). This suggests that regulating the ion channel size can effectively suppress crossover (**Fig. R7**). Therefore, the permeation results obtained from the low osmotic pressure H-cell align with the trends observed in the previous measurements (**Fig. 2e** in our manuscripts). This confirms that the ZMC-IMS membrane can precisely control the transport of hydrated ions to overcome both the challenges of polyiodide crossover and water migration. Benefiting from these advantages, as shown in **Fig. R2**, we can obtain that the Zn-I FBs with ZMC-IMS-based membranes demonstrated stable cycling under harsh operation conditions, i.e., at a high areal/volumetric capacity of $66.4 \text{ mAh cm}^{-2}/53.2 \text{ Ah L}^{-1}_{\text{posolyte}}$ over 2000 h (500 cycles, cumulative capacity of 132.8 Ah) and 50% SOC. The developed Zn-I FBs with ZMC-IMS membranes delivered a low self-discharge rate, retaining a high Coulombic efficiency of 98.5% after static flowing for 3 days at 50% SOC.

In summary, we apologize for the unclear discussion of this point in our original manuscript, and we have cautiously revised the discussions about the H-cell. Meanwhile, following your comment, we have provided the permeation rates of polyiodides by H-cell with equal concentrations of cations on the two sides under low osmotic pressure. Please see the highlighted section on **Page 8** in the revised manuscripts and the corresponding **Supplementary Figs. 14-18 (Pages S19-S23)**.

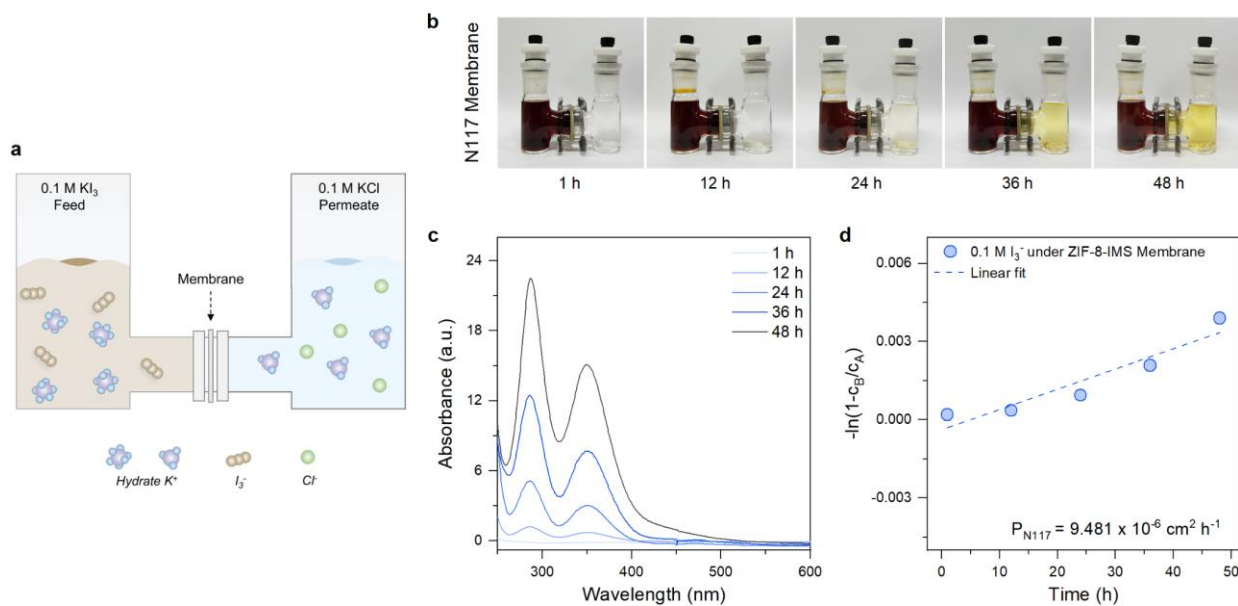


Fig. R3 (a) Two-compartment H-cell testing configuration of 0.1 M M KI_x feed side and 0.1 M KCl permeate side. (b) Photographs of the 0.1 M KI_x permeate solutions under the N117 membrane. (c) UV-vis of the KI_x permeate side. (c) $-\ln(1-C_B/C_A)$ vs. permeation time for determining permeability of 0.1 M KI_x under the N117 membrane. The fits in the $-\ln(1-C_B/C_A)$ vs. t (time) plots in (d) were obtained by linear fitting.

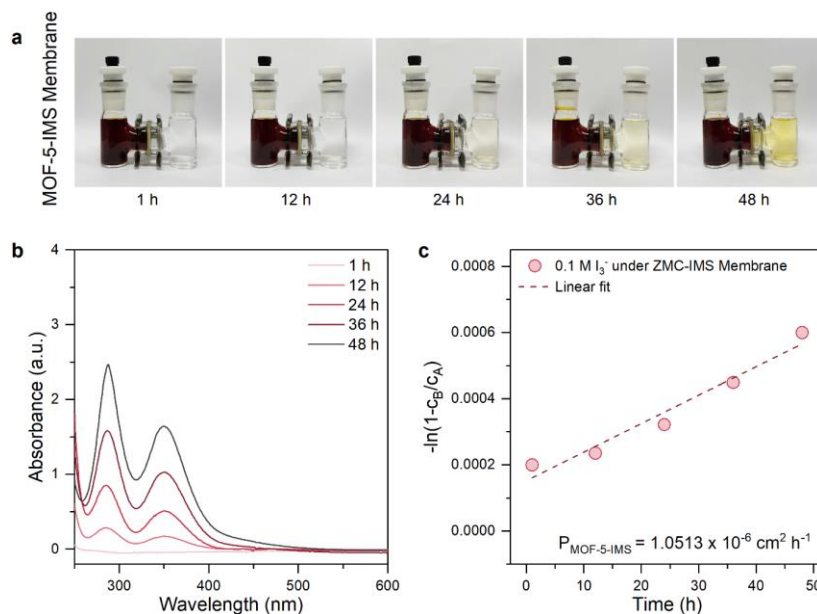


Fig. R4 (a) Photographs of the 0.1 M KI_x permeate solutions under the MOF-5-IMS membrane. (b) UV-vis of the KI_x permeate side. (c) $-\ln(1-C_B/C_A)$ vs. permeation time for determining permeability of 0.1 M KI_x under the MOF-5-IMS membrane. The fits in the $-\ln(1-C_B/C_A)$ vs. t (time) plots in (c) were obtained by linear fitting.

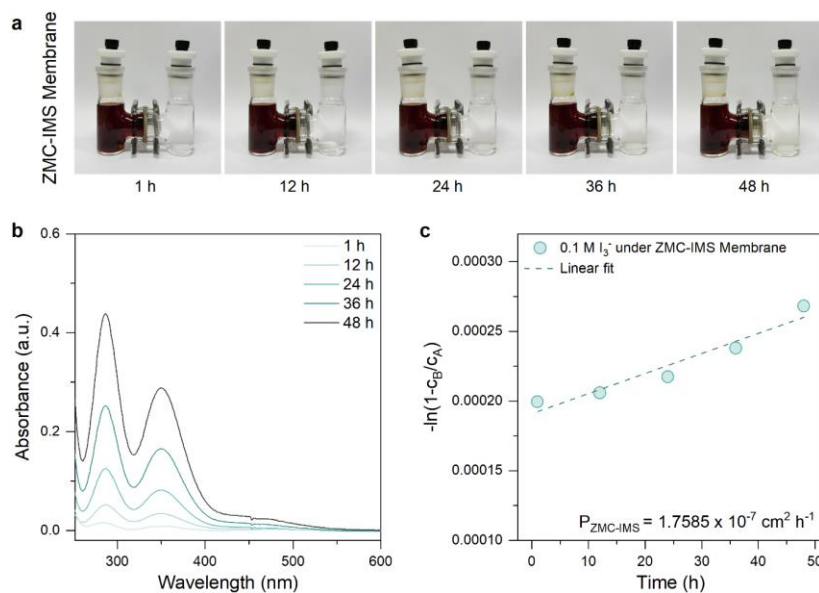


Fig. R5 (a) Photographs of the 0.1 M KI_x permeate solutions under the ZMC-IMS membrane. (b) UV-vis of the KI_x permeate side. (c) $-\ln(1-C_B/C_A)$ vs. permeation time for determining permeability of 0.1 M KI_x under the ZMC-IMS membrane. The fits in the $-\ln(1-C_B/C_A)$ vs. t (time) plots in (c) were obtained by linear fitting.

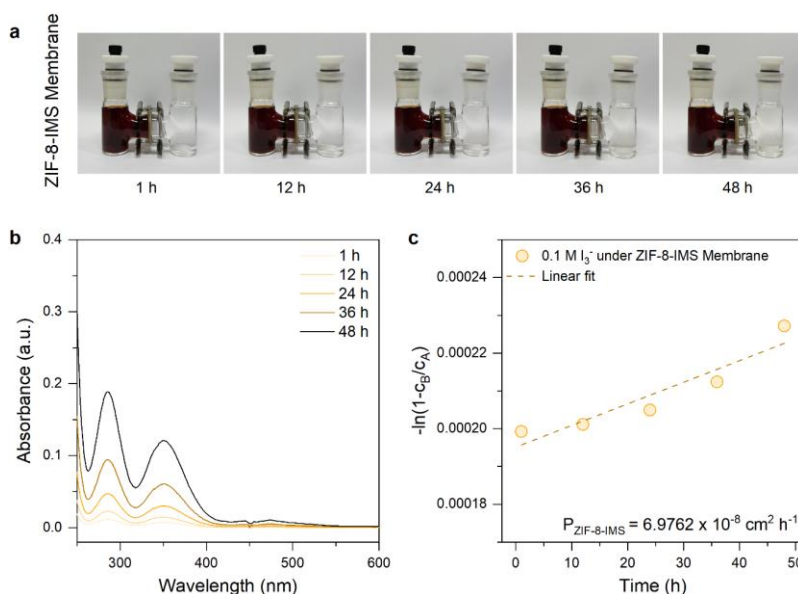


Fig. R6 (a) Photographs of the 0.1 M KI_x permeate solutions under the ZIF-8-IMS membrane. (b) UV-vis of the KI_x permeate side. (c) $-\ln(1-C_B/C_A)$ vs. permeation time for determining permeability of 0.1 M KI_x under the ZIF-8-IMS membrane. The fits in the $-\ln(1-C_B/C_A)$ vs. t (time) plots in (c) were obtained by linear fitting.

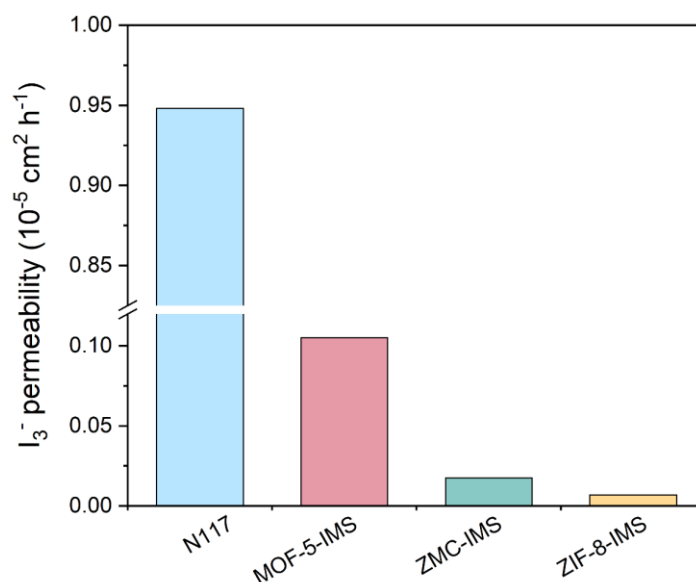


Fig. R7 The I_3^- permeability of N117, MOF-5-IMS, ZMC-IMS, and ZIF-8-IMS membranes.

Comment 2: Diffusion Through Zn-MOF: The authors claim that ion diffusion occurs through the pores of the Zn-MOF. However, in a solvent casting method using PVDF as a binder, a non-porous structure is often generated. This may hinder the diffusion of iodide ions, although diffusion of other cations, such as Zn^{2+} , could still occur. Please comment on this potential issue and provide supporting documentation.

Response: Thanks for your constructive comments. We appreciate your insights and would like to clarify that the small amount of PVDF utilization serves primarily as a binder in the coating layer in our study, which functions as a binder to attach the IMS onto the supporting membrane. We are sorry for not clarifying the amount of PVDF utilized, which may result in the formation of non-porous membranes and impede ion transport. Specifically, we reanalyze the diffusion of ions within the membrane in the following sections.

As shown in **Fig. R1** from “**Comment 1**”, the low permeability of polyiodides indicates that regulating the size of the ion transport channel can effectively hinder the diffusion of active materials. Additionally, according to the results of ionic transport number in **Fig. R8**, the cation transference number of hydrated potassium ions in the ZMC-IMS membrane decreases only slightly compared to the larger pore MOF-5-IMS membrane and the pristine N117 membrane. In contrast, the smaller pore ZIF-8-IMS membrane shows a significant reduction in transference number, indicating its tendency to intercept hydrated K^+ . Thus, those results indicate that the ZMC-IMS membrane can selectively retain larger hydrated ions while maintaining a high flux for smaller hydrated ions through precise size sieving. Notably, the large-pore MOF-5-IMS membrane exhibits ion conductivity similar to that of the pristine N117 membrane. These results follow the tendency of the size-sieving effect of ion-selective transport

based on the same mass ratio of PVDF utilized, and it indicates that the amount of PVDF binder here has little impact on ion conductivity.

To further validate the size-sieving effect of the IMS layer, we tested the intrinsic ionic conductivity of different ions (K^+ , Na^+ , Zn^{2+}) within the membrane. As shown in **Fig. R9 & R10**, the ionic conductivity of all membranes decreases with increasing size of the hydrated cations ($K^+ \cdot (H_2O)_6$ with $\sim 6.62 \text{ \AA} < Na^+ \cdot (H_2O)_3$ ($\sim 7.16 \text{ \AA}$) $< Zn^{2+} \cdot (H_2O)_6$ $\sim 8.60 \text{ \AA}$), which is consistent with the transport number results. Similarly, the ionic conductivity of hydrated K^+ in the ZMC-IMS membrane declines only slightly compared to the larger pore MOF-5-IMS membrane and the pristine N117 membrane, while the smaller pore ZIF-8-IMS membrane shows a significant reduction in K^+ ion conductivity. In other words, based on the precise design of ion channel size, the ZMC-IMS membrane can selectively block larger hydrated ions while maintaining high diffusion rates for smaller hydrated ions.

On the other hand, benefiting from its excellent electrochemical stability and chemical inertness, the strategy of employing PVDF as a binder in the coating functional layer has been widely adopted, such as ion separation membranes (Science, 2021, 372, 296–299; Nat. Mater., 2021, 20, 1551–1558; Nat Commun, 2022, 13, 3315), gas separation membranes (Nat Commun, 2016, 7, 11315; J. Membr. Sci., 2015, 495, 384–391), fuel cell separators (Nat Commun, 2020, 11, 1191; J. Power Sources, 2015, 288, 121–127), battery separators (Nat Commun, 2022, 13, 6788; Nat Commun, 2022, 13, 172), and electrode materials (Nat Commun, 2017, 8, 2277; Nat Energy, 2023, 8, 129–137). Furthermore, in the field of MOF, PVDF is also a commonly used binder (Nat Rev Mater, 2016, 1, 16078). Its ability to effectively bond MOF particles ensures structural integrity while facilitating efficient reactions (Chem. Sci., 2018, 9, 8842–8849). Therefore, by using PVDF as a binder, active materials can be effectively bonded without hindering their active sites or pore sizes. This ensures that charge carriers can still transport within the membrane structure.

In summary, as discussed above, PVDF as a binder can effectively facilitate the preparation of ZMC-IMS-based membranes without compromising the functionality of ZMC-IMS. We sincerely apologize for not clarifying and emphasizing the quantity and role of PVDF in the article, which may have led to reader misunderstandings. We have revised the description of the details of PVDF usage in the method, as highlighted in yellow in our revised manuscript (**Page 7**) and **Supplementary Fig. 4 & 5 (Page S10 & S11)**.

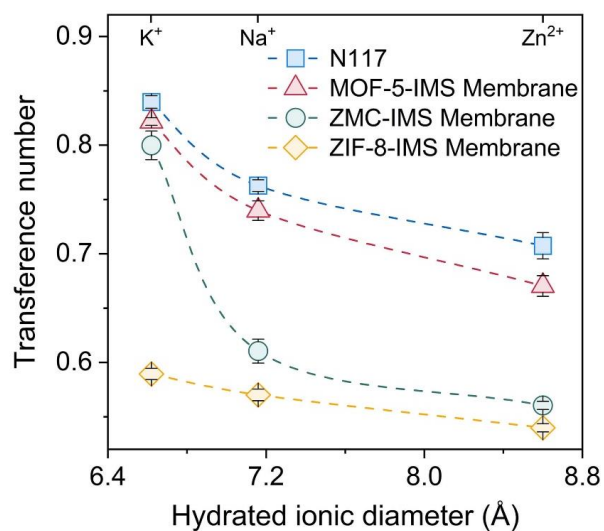


Fig. R8 Cation (K^+ , Na^+ and Zn^{2+}) mobilities calculated using I/V profiles by N117, MOF-5-IMS, ZMC-IMS and ZIF-8-IMS membranes.

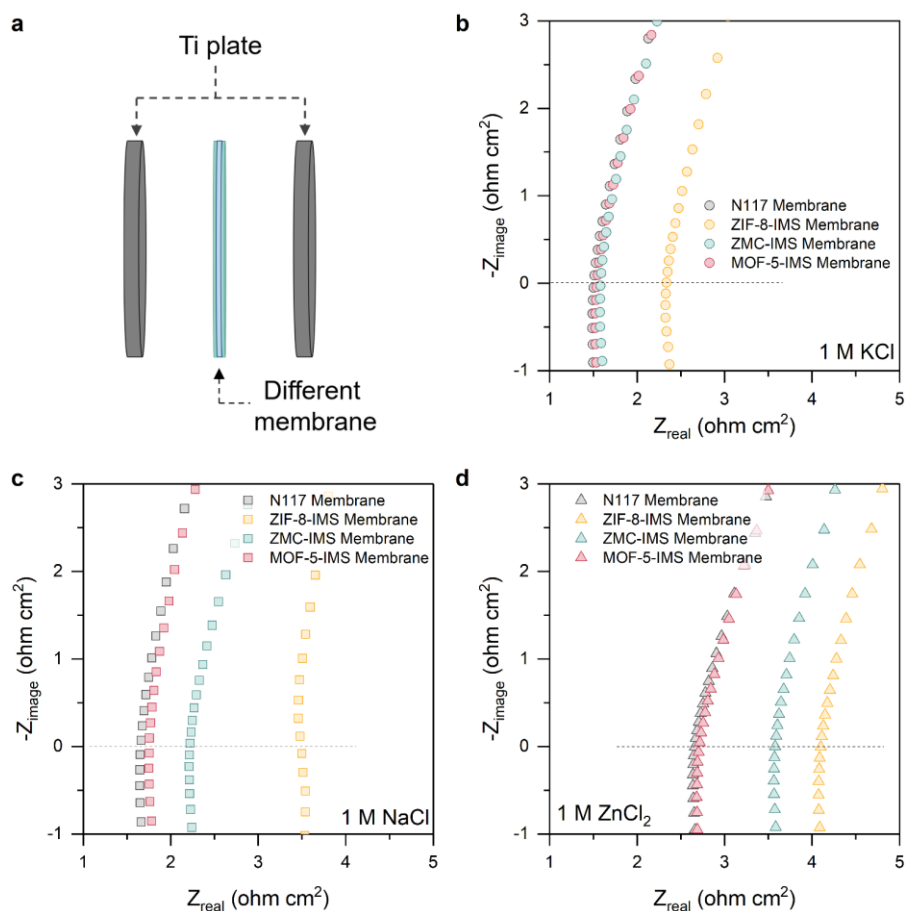


Fig. R9 (a) Schematic diagram for membrane resistance measurement. (b), (c) & (d) Nyquist plots of different membranes in 1 M KCl, 1 M NaCl, and 1 M $ZnCl_2$.

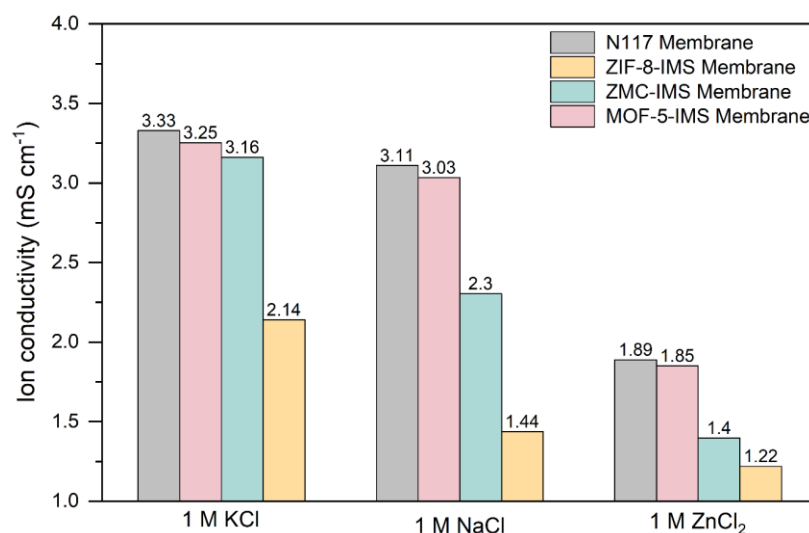


Fig. R10 Ion conductivity of different membranes in 1 M KCl, 1 M NaCl, and 1 M ZnCl₂.

Comment 3: Transport Number Calculation: Please verify the formula used for calculating the transport number of bivalent ions by the membrane potential method. Ensure that it is correct and clearly described.

Response: Thanks for your insightful observation and comments. We are sorry for our oversight and mistake. Following your comment, we have reorganized the ionic transport number calculation, as shown in the following:

The cation (t^-) and anion (t^+) transference numbers can be calculated by testing the reversal potential (Nature, 2023, 617, 299–305; Science, 2017, 357, 792–796; Science, 1971, 174, 4006). When solutions of different concentrations are added to the two chambers, a concentration gradient exists across the membrane (**Fig. R11**). The voltage measured when the applied voltage is zero is referred to as the reversal potential or diffusion potential. This potential arises from the differing migration rates of cations and anions, allowing for calculating their transference numbers. Specifically, the results of t^+ are calculated by Goldman–Hodgkins–Katz equation that originated from the Nernst equation as follows (Nature, 2023, 617, 299–305; Science, 2017, 357, 792–796; ACS Energy Lett. 2020, 5, 3, 742–748; Microfluid Nanofluid, 2010, 9, 1215–1224; J. Membr. Sci., 2021, 62, 119246):

$$V_{\text{rev}} = (2t_{\text{K}^+, \text{Na}^+ \text{ or } \text{Zn}^{2+}} - 1) \frac{RT}{nF} \ln \frac{a_{\text{cis}}c_{\text{cis}}}{a_{\text{trans}}c_{\text{trans}}}$$

$$t_+ + t_- = 1$$

Where V_{rev} is the measured reversal potential; R is the gas constant; T is the temperature of the solution; n is the charge number; F is the Faraday constant; a_{cis} and a_{trans} is the activity of the ionic species (refer

from CRC Handbook of Chemistry and Physics); c_{cis} and c_{trans} is the concentration of ionic species. All cation transference numbers of different membranes are shown in **Fig. R11b & R12**.

Specifically analyzing the selective ionic transport modes in IMS-coated membranes (ZIF-8-IMS, ZMC-IMS, and MOF-5-IMS) and the pristine N117 membrane were investigated using concentration-driven dialysis diffusion tests (**Fig. R11 & R12**). As shown in **Fig. R8**, all membranes displayed a consistent trend: the cation transference number decreased with increasing cation size. Ions exist in hydrated forms within the electrolyte, with effective diameters of $K^+ \cdot (H_2O)_6$ (~6.62 Å), $Na^+ \cdot (H_2O)_3$ (~7.16 Å), and $Zn^{2+} \cdot (H_2O)_6$ (~8.60 Å). The MOF-5-IMS membranes exhibited similar ionic selectivity to pristine N117 membranes due to their larger pore size of ~12 Å. In contrast, ZIF-8-IMS membranes show the lowest metal cation transference number, attributed to the interception of hydrated $K^+ \cdot (H_2O)_6$ by the small subnanometer pore size (<3 Å). The ZMC-IMS membranes demonstrated selective interception, leading to a slightly reduced transference number for hydrated K^+ and a significantly suppressed capability for hydrated Na^+/Zn^{2+} . Notably, the radius of hydrated ion differs with the quantity of water in the solvation shell layer, in which the hydration degree of $K^+ \cdot (H_2O)_n$ ($n = 1-8$) follows a normal distribution (the optimal coordination number: 6, the corresponding diameter: 6.62 Å) (J. Am. Chem. Soc., 2010 132, 1873-1877; Proc. Nat. Acad. Sci., 2007, 104, 9260-9265; Chem. Rev., 1993, 93, 1157-1204). Smaller hydrated $K^+ \cdot (H_2O)_{ns}$ ($ns = 1-4$) can pass through the ZMC-IMS layer, maintaining high ionic conductivity of the hydrated $K^+ \cdot (H_2O)_{ns}$ ($ns = 1-4$). Thus, by analyzing the variation in the ion transport number, this study indirectly confirms that the ZMC-IMS membrane with tailor-made pores can effectively impede the transport of larger hydrated K^+ ions through a size-sieving mechanism while simultaneously maintaining the high flux transport of smaller hydrated ions. Meanwhile, the ion transport numbers of divalent Zn^{2+} in ZIF-8-IMS, ZMC-IMS, and MOF-5-IMS membranes are recalculated to be 0.701, 0.58, and 0.56, respectively. This indicates that the selective interception of divalent ions is more pronounced due to its larger size.

Thanks for your delicate observation on keeping our data consistent. We are sorry for our mistake in calculation, and we have corrected all relevant calculations, accordingly, as highlighted in yellow in our revised manuscript (**Fig. 2d, Page 6**) and **method (Page S4)**.

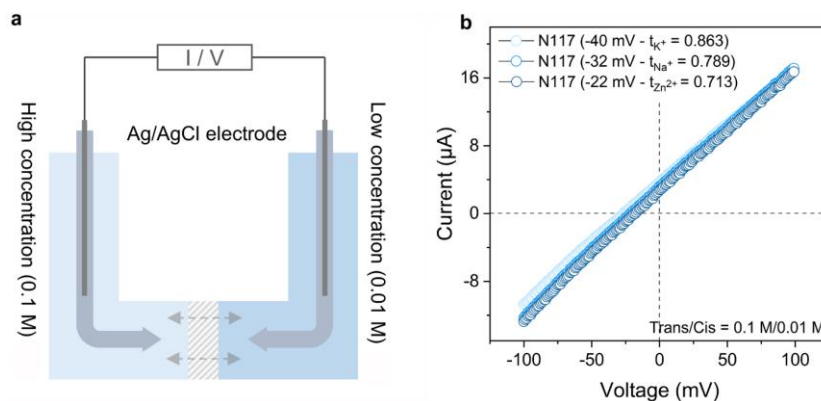


Fig. R11 (a) Schematic illustration of V-I testing device; (b) the cation transference numbers of K^+ , Na^+ , Zn^{2+} . The transference numbers calculated from V-I profiles for 0.1 M/0.01 M concentration gradients in the two reservoirs connected by an N117 membrane.

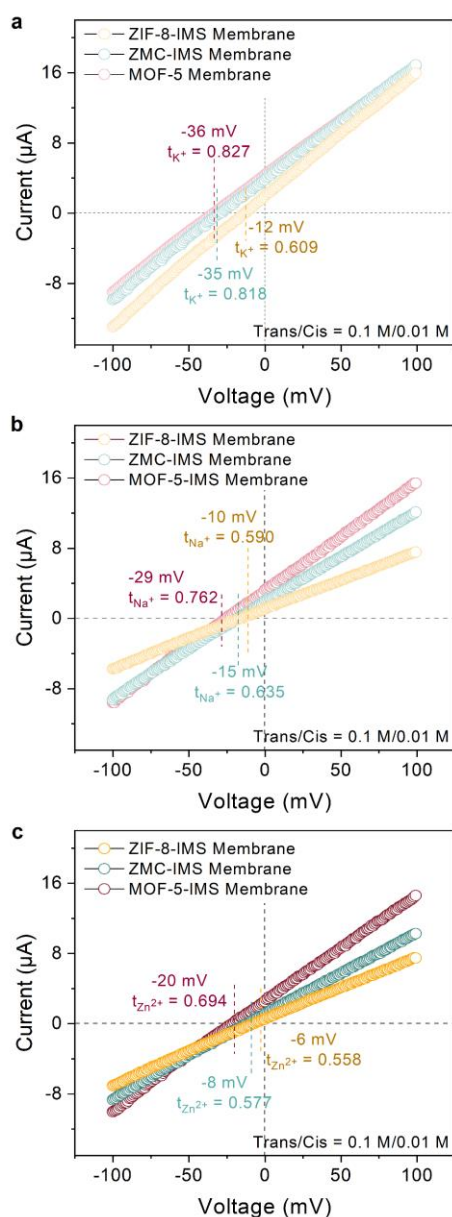


Fig. R12 The cation transference numbers of (a) K^+ , (b) Na^+ , (c) Zn^{2+} under ZIF-8-IMS membranes, ZMC-IMS membranes and MOF-5-IMS membranes. The transference numbers calculated from V-I profiles for 0.1 M/0.01 M concentration gradients in the two reservoirs.

Responses to Reviewer's Comments

Reviewer #3:

The manuscript presents the development of the Zn-MOF-CJ3 tailoring ionic-molecular sieve (ZMC-IMS) membrane, representing a significant advancement in Zn-I flow batteries. The authors successfully address challenges related to ion transport and polyiodide crossover through precisely tuned subnanometer pore sizes, enhancing the selectivity for large-hydrated ion clusters and facilitating a reversible charge/discharge process. The systematic investigation of membrane properties supports the effectiveness of the ZMC-IMS design, demonstrating cycling stability under high-capacity conditions. The low self-discharge rate and high Coulombic efficiency further underscore its suitability for long-life energy storage. Additionally, the techno-economic analysis highlights the competitive cost-effectiveness of this system. Overall, the manuscript meets high standards with enough advancement in innovation and performance for publication in Nature Communications. The reviewer has raised some comments regarding this study, which could improve the quality of the manuscript. After a careful and complete review.

General Response: Thanks for your professional evaluation of our work. We appreciate your positive assessments. We have provided more explanations and experiment results to address your comments.

Comment 1: The presence of CNTs in the ZMC-IMS membrane should be clearly explained. This will help to highlight the contributions of the ZMC component and its overall effectiveness.

Response: Thanks for your constructive comments. We incorporate CNTs as a membrane-forming agent in our ZMC-IMS slurry to enhance membrane formation. The addition of CNTs improves the uniformity and adhesion of the membrane, ensuring a more consistent and stable structure (Chem. Rev. 2010, 110, 10, 5790). Additionally, CNTs contribute to the electrical conductivity of the membrane to enhance charge transport, which can facilitate the reversible redox cycling of the iodide-based active materials, ensuring efficient and stable electrochemical reactions (Nat Commun., 2017 8, 14628; Nat Commun,

2021, 12, 4519). Furthermore, incorporating CNTs can improve the mechanical properties of the membrane, providing greater resilience and stability during operation (Nature Nanotech, 2010, 5, 853). Therefore, as shown in **Fig. R1 & R2**, the incorporation of CNTs in this work can enhance the mechanical behavior of the ZMC-IMS layer, resulting in good film-forming capabilities.

According to your suggestion, we have provided them in Supporting Information as **Supplementary Fig. 45 (Page S50)**.

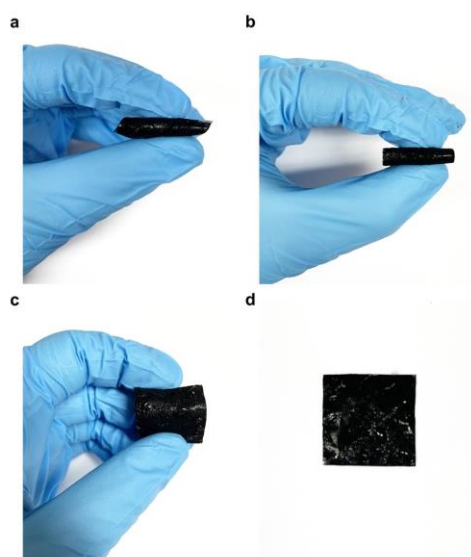


Fig. R1 (a - d) Photographs of ZMC-IMS membranes after 100 times of bending, and no coating fragments were found peeling off due to frequent bending from the photographs.

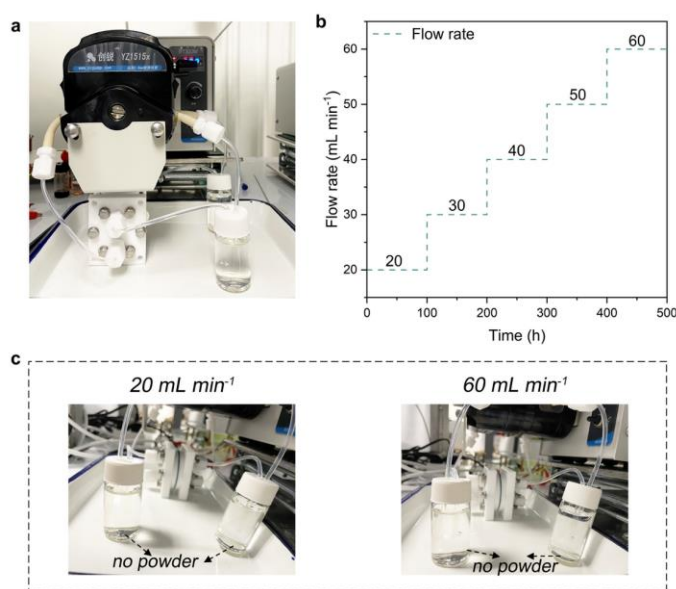


Fig. R2 (a) Photographs of the water flushing experiment on ZMC-IMS membranes. (b & c) digital images of residual in the water tank after 500 hours of water flushing under different flow rates.

Comment 2: The coating method employed for the ZMC-IMS is a crucial aspect that may influence the rate performance of the battery. It is essential that this point is clarified in the manuscript to ensure a comprehensive understanding of the research.

Response: We appreciate your helpful and valuable suggestions. For our work, we have minimized polarization caused by long transport paths by carefully controlling the loading and thickness of the coating. Additionally, precise retention of hydrated ions by the ZMC-IMS membrane can allow smaller hydrated ions to rapidly transport through the membrane channels, thereby avoiding energy losses associated with dehydration and rehydration that can occur in ultra-small pore sizes (Sci. Adv., 2024, 10, eadn0944). As shown in **Fig. R3**, the GCD curves of Zn-I FBs with the ZMC-IMS membrane exhibit a slight increase compared to those with the N117 membrane. Despite this minor effect, under high SOC and high areal capacity testing conditions, the ZMC-IMS membrane enables highly stable and reversible cycling of the Zn-I FBs at current densities ranging from 10 to 50 mA cm⁻² (**Fig. 4a,b** in the manuscript). Therefore, we believe that the introduction of the coating layer has a minimal impact on polarization at high rates, primarily serving to enhance the cycle life of the flow battery. We are sorry for not providing those discussions in our original manuscript. According to your suggestion, we have provided them on Supporting Information in **Supplementary Fig. 40 (Page S50)**.

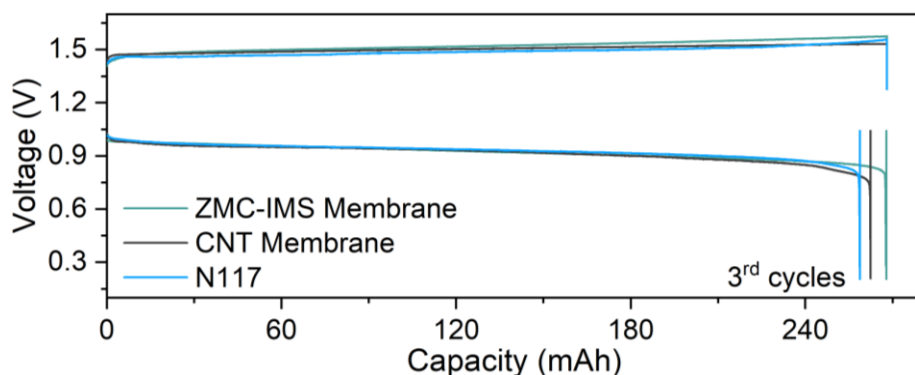


Fig. R3 Comparison of voltage profiles of Zn-I FBs with N117, CNT, and ZMC-IMS membranes (5 ml of 6 M KI + 3 M ZnBr₂ || 5 ml of 3 M ZnBr₂ + 3 M KCl, 4 cm² membrane area, 50% SOC) under 30 mA cm⁻².

Comment 3: Some of the Figures, particularly Fig. 5 (Techno-economic cost analysis), could benefit from more explicit labeling and a clearer distinction between the E-Cost, O&M, and Investment results. This would help readers follow the discussion more easily.

Response: Thanks for the constructive comments from the reviewer. We believe this is an illusion caused by the inappropriate choice of the vertical axis in **Fig. 4b** (in the original manuscript). As shown in **Supplementary Table 1** in the supporting information, the operational and maintenance (O&M) unit

costs of energy and power are the same as 12 USD/kW-year and 1 USD/MWh across different FB systems, including AQ FBs, Zn-Fe FBs, Zn-Br FBs, and Zn-I FBs. Since the vanadium redox FB systems is the most mature and commercialized, it serves as a key reference point for LCOS analysis. This similarity in O&M unit costs arises from common factors such as system complexity, maintenance requirements, and the necessity for regular monitoring and servicing, which do not significantly differ between various FBs types. Therefore, different FB systems exhibit similar O&M unit costs.

Finally, calculated by monetizing the energy storage systems (www.EnergyStorage.ninja, accessed: 18th September 2020), we obtained the total O&M costs for different Zn-based FB systems (Zn-Br, Zn-Fe, Zn-I FBs) under the simulation conditions of an 8-hour duration, 180 annual cycles, and an electricity cost of 20 USD MWh⁻¹. As shown in **Fig. R4**, the total O&M costs were 19.03, 11.26, and 12.99 USD MWh⁻¹, respectively. The Zn-Fe FBs has the lowest O&M cost due to its relatively inexpensive electrolyte design. However, the Zn-I FBs designed in this work offers a longer lifespan, contributing to a comparably low O&M cost as well. In contrast, the Zn-Br FBs has the highest O&M cost, primarily due to the expensive electrode and electrolyte prices, coupled with its lower cycling lifespan.

We apologize for not clearly presenting this point in our original manuscript. In response to your comment, we have carefully added a magnified version of the figure to enhance readability and understanding for the readers. Please see the highlighted section on **Page 16** in the revised manuscripts and the corresponding **Supplementary Fig. 50 (Pages S60)**.

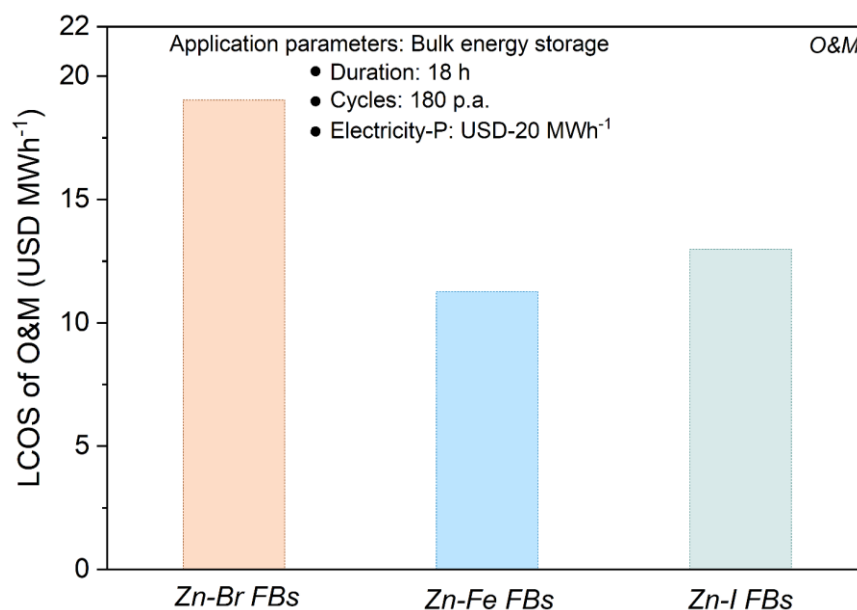


Fig. R4 Breakdown of the LCOS of O&M cost with a discharge duration of 18 h for Zn-Br FBs, Zn-Fe FBs, and Zn-I FBs.

Comment 4: In progress, Zn-based flow batteries also face issues with Zn metal anodes, such as uneven deposition and dendrite formation. Could the authors clarify how the issues are addressed in this work?

Response: Thanks for your constructive comments. Following your suggestions, we applied Zn-based activation energy to evaluate the reversibility of Zn metal anodes. We discussed the results as follows.

Zn-based side reactions during battery cycling are crucial factors affecting battery stability. As shown in **Fig. R5a**, SEM images of N117 membranes on the negolyte side during discharge exhibit an irregular and mossy morphology with a rugged surface. This change can be attributed to the formation of dead dendrites or the by-products $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and ZnO , as verified by XRD results (**Fig. R6a**). In contrast, a cleaner surface of the ZMC-IMS membranes was observed after the same cycling (**Fig. R5b & R6b**). These results suggest that ZMC-IMS membranes can enhance the cycling reversibility of Zn plating/stripping on the negolyte side through their nano-channel chemistries. Notably, MOF materials can effectively adjust ion solvation structure at the reaction interface, facilitating Zn deposition (Adv. Mater. 2021, 33, 2102415). As shown in **Fig. R7 & R8**, the ZMC-IMS membrane demonstrates lower Zn desolvation energy, indicating a more favorable and uniform Zn deposition at the interface between the carbon felt and the membrane, thereby suppressing Zn dendrite formation and side reactions.

As demonstrated in the above analysis, the ZMC-IMS layer can optimize the Zn plating/stripping process for improving the cycling reversibility of Zn plating/stripping on the negolyte side. We are sorry for not providing these results in our original manuscript. According to your suggestion, we have provided them on **Page 14** in the revised manuscript and **Supplementary Figs. 41-44 (Page S46-S49)**.

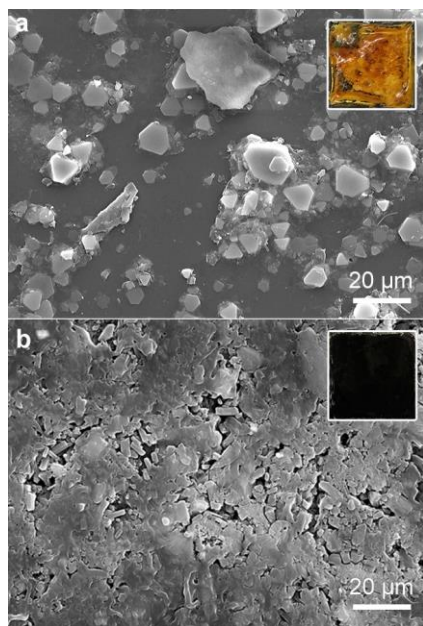


Fig. R5 SEM images of (a) N117 membrane and (b) ZMC-IMS membrane on the anode side in the discharging state after cycles. (The inset: photographs of N117 and ZMC-IMS membranes after cycles)

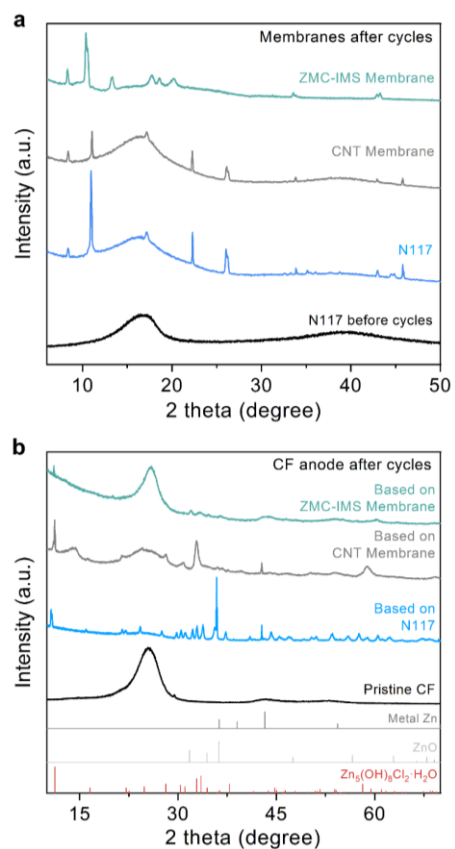


Fig. R6 (a) XRD pattern of N117, CNT, and ZMC-IMS membranes on the anode side in the discharging state after cycles. (b) XRD pattern of CF anode using N117, CNT, and ZMC-IMS membranes in the discharging state after cycles, wherein PDF card of $Zn_5(OH)_8Cl_2 \cdot H_2O$ and ZnO by-products are #07-0155 and #36-1451.

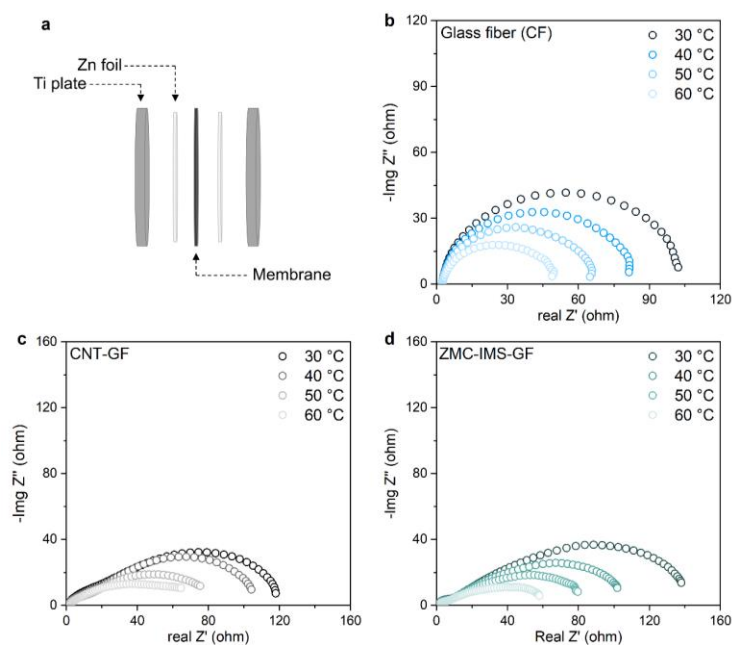


Fig. R7 (a) Schematic illustration of Zn symmetric cells for testing Nyquist plots. Nyquist plots of Zn symmetric cells with (b) glass fiber, (c) CNT-GF, and (d) ZMC-IMS-GF membrane in different temperatures.

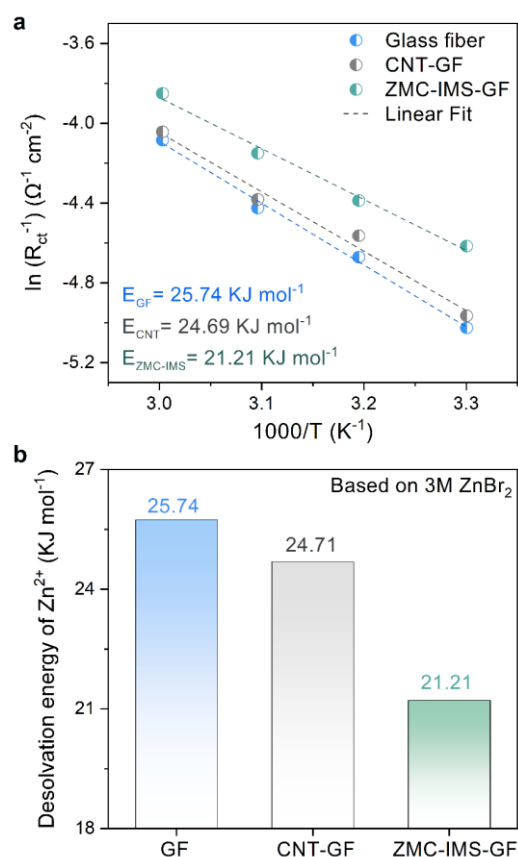


Fig. R8 (a) The Arrhenius plot and (b) calculated desolvation energy based on the charge-transfer resistances with glass fiber, CNT-GF, and ZMC-IMS-GF membrane.

Comment 5: There are a few grammatical errors and instances of awkward phrasing that could be improved. Additionally, some language in the manuscript may come across as hyperbolic. Consider more precise and measured wording.

Response: Thanks for your constructive suggestions. Based on your kind suggestions, we have carefully corrected the grammatical errors and unsuitable phrasing throughout our whole manuscript. Moreover, we also have carefully corrected our manuscript to strip the opinion statements in the description of the results and, simultaneously, to avoid using hyperbolic words. All revisions are highlighted in yellow in our revised manuscript.

Summary response: Thanks for your instructive comments. These comments are all valuable and helpful for revising and improving our manuscript, as well as the important guiding significance to our

research. We have studied the comments carefully and made corrections, and we hope to meet with your approval. Revised portions are highlighted in yellow in the revised manuscript.

Sincerely,

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Responses to Reviewer's Comments

Reviewer #2:

The manuscript had been thoroughly revised, it is suitable for its publication in the current form.

Response: Thank you for your professional and insightful comment.

Responses to Reviewer's Comments

Reviewer #4:

The authors present a study showing how using a Nafion membrane modified with CNT-MOF layers can improve the performance of a Zn-I flow battery. While the authors have presented rigorous work characterizing and testing this concept, the idea of modifying a current commercial membrane with a size excluding layer is not new (<https://doi.org/10.1002/ange.201510849> as one of many examples). I acknowledge that MOFs are getting a lot of attention in recent years as researchers expand their uses past the traditional catalyst field, but, in terms of a “Nature worthy” revelation, they are simply just another material used to modify a membrane in this work. Another big issue that prevents me from accepting publication of this work in this journal is the fact that the authors use Nafion 117 as the support. Ever since Nafion was invented, a major focus of the flow battery and fuel cell fields has been to find cheaper, less environmentally challenging replacements for Nafion. Without demonstrating a replacement for Nafion, I do not feel this work is impactful enough to be published in this journal.

The authors have put a lot of time and effort into the characterization, analysis and presentation of this work. I think it is worthy of publication in another journal within the field. However, there are still some major issues that should be addressed:

Response: We respectfully disagree with the comments that "*the idea of modifying a current commercial membrane with a size-excluding layer is not new*" and the critique of "*Nafion 117 as the support*". In fact, neither of these points represents the main focus of our work.

Our core novelty resides in establishing a design paradigm that systematically correlates MOF pore size control and chemistry with ion hydration dynamics rather than merely applying a size-exclusion layer. The use of Nafion 117 is a benchmark substrate to validate this universal principle, which is intentionally substrate-agnostic. We have reorganized our response below in the hopes of addressing your concerns.

Our primary focus is on the precisely selective sieving function of hydrated ions, which is critical in alleviating water migration issues in Zn-based flow batteries (FBs). Please note that all previous reports focus on the ions-shuttling of active species and water migration was not solved in the previous reports.

We would like to reorganize our description to emphasize the multifunctional effects of the ZMC-IMS membrane in our work. During the operation of FBs, substantial ion transfer occurs between posolytes and negolytes, with these ions typically transferring in the form of hydrated ions. Under conditions of high areal capacity and high energy density, the amount of transferred hydrated ions significantly increases, resulting in more severe water migration in terms of hydrated ions and accompanying side reactions (**Fig. R1a**). Especially, for Zn-based FBs, the Zn metal anode operates through deposition and dissolution processes with inevitable ion concentration variations, leading to more pronounced ion imbalance issues with more significant water migration. This phenomenon ultimately results in generally shorter lifespans for Zn-based FBs. Moreover, under high areal/volumetric capacity and high state of charge (SOC) conditions, extended charge and discharge processes in the Zn-I FB systems can also contribute to the crossover of iodine active species, lowering the Coulombic efficiency (CE) and hindering the long-term cycling of Zn-I FBs. Therefore, it is crucial to overcome both challenges under harsh testing conditions to ensure that Zn-I FBs can meet the requirements for long-life energy storage applications (**Fig. R1b**).

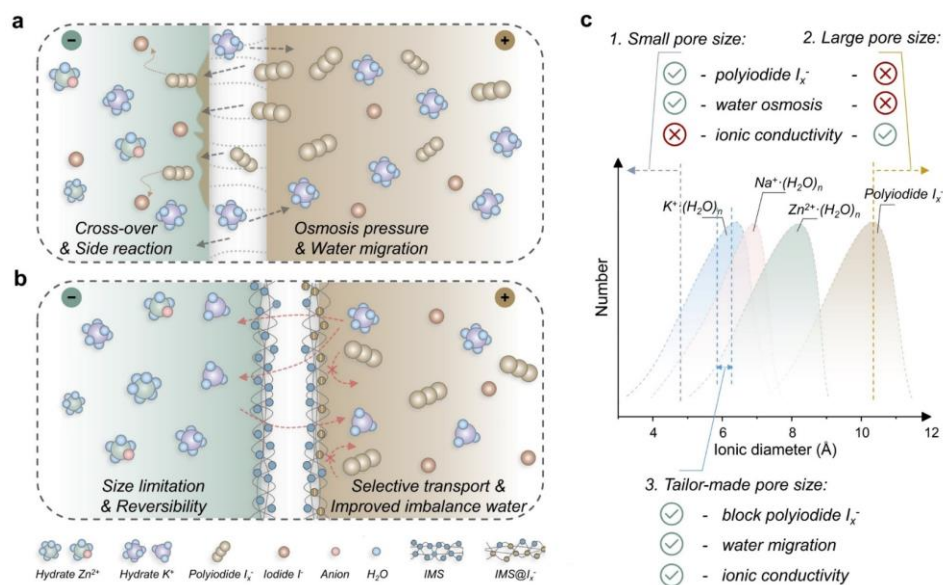


Fig. R1 (a) Crossover of polyiodide (I_x^-), side reaction, and severe water migration induced by pristine membranes lead to rapid cell failure of Zn-I FBs. (b) Alleviated crossover and water migration in Zn-I FBs using IMS-based membranes, where the volume of the posolyte and negolyte maintained a balance.

(c) The properties and performances of membranes with different subnanometer pores towards hydrated ionic size.

While the cited work (DOI:10.1002/ange.201510849) from Reviewer 4 and similar studies primarily emphasize size-exclusion mechanisms for redox-active species, most of them overlook the critical challenge of water management, which is the focus of our design. More specifically, the novelty of MOF-based coatings lies not merely in material substitution but in uncovering the importance of water molecule migration and establishing a design principle. By correlating the MOF pore size with the hydration shell diameter, we demonstrate that sub-nanometer confinement combined with ligand interactions (absorbing I_3^- to construct localized high-negative-charged rejection) simultaneously suppresses polyiodide crossover and water migration. This synergy by the ZMC-IMS layer enables long cycling stability (over 2000 h with a high CE of >99%). Our framework extends beyond Zn-I FBs, offering generalizable guidelines and membrane design principles by tailoring porous materials to ion-specific redox systems.

On the other hand, the pursuit of next-generation membranes and the optimization of incumbent materials like Nafion represent complementary rather than mutually exclusive research pathways. As evidenced by recent studies (*Nat Energy*, 2021, 6, 517–528 and *Nat Sustain*, 2022, 5, 1080–1091), Nafion remains a paradigmatic material for benchmarking due to its unmatched chemical robustness with stability in acidic/redox environments and industrial dominance deployed in the majority of commercial FBs, enabling direct performance comparison with prior studies. Therefore, our study leverages Nafion to demonstrate a novel pore size control method in which the enhanced Zn-I FBs performance is superior to other Nafion-based Zn-I FBs. These improvements highlight the potential of methods to optimize commercial membranes for practical Zn-I FBs applications and can offer guidelines for future-developing low-cost membranes.

In summary, as discussed above, we believe this aspect of our work offers advancements in functional coatings to solve water migration and crossover issues, as it enhances the overall performance and stability of the battery system. We are committed to providing a comprehensive exploration of these functions, which we hope to be recognized as a meaningful contribution to *Nature Communications*.

Comment 1: *Page 7 – the authors need to mention in the main text that this is a layer being placed on Nafion 117. This is important because the fact that it still uses Nafion 117 means it will still be expensive and use environmentally challenging materials.*

Response: Thank you for your comment. In fact, on **Page 8**, we have already mentioned that the ZMC layer was coated on both sides of the Nafion membrane. Additionally, detailed preparation instructions are provided in the experimental section. Based on your comment, we have added a description on **Page 7** stating that the IMS layer is coated on the Nafion membrane.

Comment 2: *Page 8, line 173 – the comment that “there are few differences” between the CNT-Nafion and pristine Nafion membranes is misleading. According to the authors’ own data there is an order of magnitude difference between the permeability with (3E-6) and without (2E-5) the CNT.*

Response: Thanks for your comment. CNTs possess a certain adsorption capacity, yet they primarily facilitate film formation in this work. Based on your suggestion, we have revised the relevant description on **Page 8, line 173**, to avoid causing any misunderstanding among readers.

Comment 3: *The claims about the MOFs absorbing I₃⁻ and preventing I₃⁻ crossover due to a high concentration are unsupported. The absorption experiment was only done in a KI solution. Please repeat in the actual flow battery electrolyte, where both Br⁻ and Cl⁻ are competing anions that could also uptake into the MOF. Or better yet, run the characterization after cycling.*

Response: Thanks for your comments. Firstly, in the I₃⁻ permeability experiment shown in **Fig. 2e in the revised manuscripts**, it can be observed that the ZMC membrane exhibits a strong blocking effect on I₃⁻, and meanwhile, those results can also be confirmed by the zeta potential measurements (**Fig. 2g in the revised manuscripts**). Additionally, the developed Zn-I FBs demonstrated higher coulombic efficiency during cycling and self-discharging performance than pristine membrane-based FBs (**Fig. 4 in the revised manuscripts**), strongly indicating that the ZMC-IMS layer can effectively block I₃⁻ to relieve the crossover issues. Therefore, we believe studying the competitive adsorption effects of Br⁻ and Cl⁻ is unnecessary for this work, and the active materials I₃⁻ should be the focus.

Comment 4: *SI Figure 2 – wrong caption.*

Response: We are sorry for our oversight and mistake. According to your suggestion, we have revised them in Supporting Information as **Supplementary Fig. 2 (Page S9)**.

Comment 5: *SI Figures 14 and 15 – wrong membrane label in Figure c.*

Response: Thanks for your comments. We are sorry for our oversight and mistake. According to your suggestion, we have revised them in Supporting Information as **Supplementary Fig. 14 and 15 (Page S19 and 20)**.

Comment 6: *The authors are clearly overselling their work. This type of salesmanship should be kept out of research publications. For instance, the term “high-energy” flow battery is used throughout the publication even though any flow battery can be high-energy by simply adding more electrolyte. If they mean “high energy density” that is also misleading because, although they have high concentrations of electrolytes, they operate at low current densities, with a 50% OCV of 1.35 V, and a DoD of 50%. Those are hardly “high energy dense” conditions.*

Response: It should be divided between aqueous batteries and non-aqueous batteries. Highly safe aqueous FBs are better suited for large-scale energy storage applications and, therefore, should not be compared to conventional Li-ion batteries. In contrast to currently commercial vanadium redox (VR) FBs with an energy density constrained to 20 Wh L⁻¹, our work demonstrated an enhanced energy density of 71.82 Wh L⁻¹ (53.2 Ah L⁻¹). This value not only surpasses that of VR-based systems but also outperforms other aqueous flow battery technologies, including alkaline Zn-Fe FBs with ~ 12 Wh L⁻¹ (*iScience*, 2018, 3, 40-49; *Nat Commun*, 2023, 14, 1149) and organic redox FBs with 4~11 Wh L⁻¹ (*Nat Commun*, 2025, 16, 47; *J. Am. Chem. Soc.* 2025, 147, 6, 5071–5079). Therefore, we believe that the developed Zn-I FBs can be considered as high energy density instead of the type of salesmanship.

To avoid misunderstandings among readers, we have revised "high energy density" to "achievable energy density is high" throughout the revised manuscript.

Comment 7: *Same comment as above, but with the term “harsh conditions” Their most harsh conditions are a 20 mA/cm² operation for 50% DoD for 3 hours. Those are not harsh.*

Response: It should be clarified that current densities of 20–50 mA cm⁻² are reasonable for conventional FBs using Nafion membrane. This current limitation is primarily due to the membrane with low ion conductivity and high ohmic resistance. Despite operating in soft conditions, reported cycle lifetimes of Zn-I FBs remain disappointingly short. Despite these soft conditions, reported cycle lifetimes of Zn-I FBs remain disappointingly short. Meanwhile, high SOC (>50%) risks I₂ solid precipitation in I-based posolyte, severely degrading performance, which means 50% SOC represents a practical upper limit for Zn-I FB systems in the normal electrolyte. However, many studies use excess electrolyte volumes at low SOC (<20%) to neglect water migration issues of Zn-I FBs (for example, (1) 6 Ah L⁻¹ with <97% CE under only 8.39% SOC for 0.3 hours in *Nat Commun*, 2024, 15, 6234; (2) 27.6 Ah L⁻¹ with <99% CE

under only 1.28% SOC for 2.76 hours in *J. Mater. Chem. A*, 2024, 12, 24468), which sacrifices capacity utilization and increases costs. In stark contrast, to the best of our knowledge, our work achieves the highest I-based SOC condition with 2000 h of stable cycling at 30 mA cm⁻² and >99% high CE and 53.2 Ah L⁻¹ high volumetric energy density, demonstrating resilience under conditions that are indeed “harsh” for Zn-I FBs chemistry.

Comment 8: *In the same vein as the previous two comments, Page 11, Line 256 – the authors refer to the hydrated potassium clusters as small and large even though one is 2.7 nm and the other 3.5 nm. Just be quantitative and give the numbers.*

Response: We would like to clarify that the SAXs technique was used to investigate the size of water clusters at the microscopic level within the membrane rather than to quantify the number of water molecules (*Nat. Mater.*, 2008, 7, 75–83; *Nat Energy*, 2021, 6, 517–528). For our work, our results indicate that the pristine N117 membrane exhibits larger water clusters, whereas the ZMC-IMS layer shows smaller water clusters. This observation indirectly suggests that only smaller hydrated ions can pass through the ZMC-IMS layer. Therefore, the results of SAXs in our work were to demonstrate selective interception of membranes for hydrated ions indirectly.

Comment 9: *Page 12, line 269 – authors claim more hydrophobic properties even though contact angles were quite similar (88.2 vs. 92.6 degrees). These are very similar values and could even be the same depending on the repeatability of the experiment.*

Response: Thanks for your comments. We believe that the observed contact angle values are reasonable and repeatable. Our results demonstrated the anti-swelling effect of the ZMC-IMS membrane through the increase in contact angle (from 88.2° to 92.6°), which supported the selective sieving of hydrated ions. Notably, a significantly larger increase in contact angle would indicate excessive hydrophobicity, which could substantially increase membrane resistance and reduce ionic conductivity, ultimately compromising the performance of the FBs.

Comment 10: *Page 8, line 184 – the language makes it seem like you used XRD to determine thickness as opposed to just confirming the material is there. Please fix.*

Response: Thanks for your comments. According to your suggestion, we have revised them on **Page 8**.

Comment 11: *Figure 3 analysis – 4.5 V/nm is a very high electric field. Please justify that selection.*

Response: Thanks for your comments. We believe that the selected electric field (4.5 V/nm) is reasonable, allowing us to obtain statistically significant ion flux results within a relatively short simulation time (~ns). This approach is commonly used in molecular dynamics simulations for ion separation studies (*Sci. Adv.* 2018;4: eaaq0066). Additionally, we have already provided an explanation in the Methods section to clarify this choice (**Page S7**).

Comment 12: *For all electrochemical data, please make clear what is meant by 20% and 50% SOC in the text and figures. Does that mean cycling from 0-20% and 0-50%?*

Response: Thanks for your constructive comments. Active redox materials in the discharged state are dissolved in the electrolyte, serving as the initial condition for the FBs. Subsequently, during charging, the concentration of the active materials changes, achieving different SOC based on the charging process. Therefore, all experiments in this manuscript charged from 0 to 20% or 50% SOC.

Comment 13: *The electrolyte in the FB experiments is highly concentrated. What are the saturation limit and viscosity with respect to temperature? These are important to know whether we can expect crash-out and/or excessive pumping issues in this system.*

Response: Thanks for your suggestions. At room temperature, the theoretical solubility of potassium iodide is 8.4 M (*CRC Handbook of Chemistry and physics*), thus not reaching saturation limits. All our battery tests are conducted at room temperature, where the electrolyte maintains low viscosity and high ionic conductivity, as evidenced by the normal Zn-I charge-discharge curves (**Fig. 4 in the revised manuscripts**). Therefore, Crash-out and/or excessive pumping issues will be tested in future studies.

Comment 14: *Page 14, line 304 – 10-50 mA/cm² is not a wide range. V/V can be run up to 200 mA/cm². Please be more quantitative with less excess adjectives that make it feel like this work is being oversold.*

Response: Thanks for your comments. According to your suggestion, we deleted the word “wide” and revised it on **Page 14**.

Comment 15: *Page 14, line 325 – The EIS data is showing the opposite of the authors claims that the MOF membrane has better interfacial resistance. I understand the Arrhenius constant is lower for the MOF membrane, but the EIS data is showing that the MOF containing membrane has the highest charge transfer resistance at all temperatures. In addition, the presence of ZnO and ZnOH (SI Fig. 42) in the pristine membrane shows that the worse performance in the pristine membrane is likely due to a pH rise*

that causes the formation of passivating species, not because the MOF membrane has improved “Zn plating/stripping processes” as the authors claim.

Response: Thank you for your comments. We believe the ZMC-IMS-integrated membrane ZMC-IMS exhibited higher charge transfer resistance in the EIS data than the pristine membrane is reasonable. This is consistent with its more hydrophobic surface and reduced ion mobility within the ZMC-IMS structure. However, the focus of the temperature-dependent EIS analysis was not to directly compare absolute interfacial resistance but to evaluate the desolvation energy barrier for Zn deposition. The lower Arrhenius activation energy for ZMC-IMS reflects its role in stabilizing Zn^{2+} ions transport pathways, thereby facilitating a more uniform plating/stripping process. Regarding the pristine membrane, we acknowledge that pH shifts (evidenced by ZnO species in **Supplementary Fig. S42**) likely drive passivation and degradation. However, these pH changes are themselves a consequence of poor interfacial stability in the pristine membrane, which accelerates side reactions (e.g., dendrites, gas evolution). Thus, the EIS data and degradation mechanisms collectively highlight how ZMC-IMS could mitigate these cascading failures by improving interfacial kinetics.

Comment 16: *Figure 4e – comparison only works if batteries are cycled at the same current density for the same amount of time. CE losses due to migration/drag are current dependent. CE loss due to diffusion is time dependent. I suggest limiting the comparison to as close to the same conditions as possible and including the current and time values in the SI table. Also, including Zn-Br is confusing. Your membrane works by excluding I_3^- and some water crossover. I_3^- is not present in Zn-Br. On a similar vein, it may also be useful to pick comparison cases with similar electrolyte compositions, assuming demonstrating the membrane effectiveness is the main goal. These should also be listed in the SI table.*

Response: Thank you for your comments. The strict uniformity in testing conditions (e.g., current density, cycling time) is ideal for direct comparisons and actually, our intention is also to conduct comparisons under the same set of parameters. In our analysis, the current densities and capacities of the compared systems are detailed in **Supplementary Table 1**. However, as noted by the reviewer, standardized testing protocols for flow batteries remain limited in non-commercial research settings, making identical conditions challenging to achieve across studies.

Regarding the inclusion of Zn-Br, we grouped Zn-I and Zn-Br as Zn-halogen FB systems due to their mentioned similar neutral/weakly acidic Zn anode chemistry and common challenges (e.g., water migration, crossover). While I_3^- is absent in Zn-Br, water-related migration, and active redox-related crossover remain a critical degradation factor in all Zn-halogen systems, and our goal was to broadly

highlight membrane effectiveness in addressing this issue. To improve clarity, we will explicitly list electrolyte compositions and testing parameters in the revised **Supplementary Table 1 (Page S54)** and refine the discussion to emphasize comparisons with similar electrolyte systems.

Comment 17: *Page 15, line 349 – please be quantitative about the water change and provide the numbers.*

Response: Thank you for your comment. We would like to clarify that measuring the electrolyte volume during the reaction process inevitably leads to some loss when transferring it to a precise measuring device, which could negatively impact battery cycling and lifespan. Additionally, estimating volume based on the rising liquid level introduces significant measurement errors. Therefore, we opted to document the electrolyte level through periodic digital photography, providing a direct visual representation of water migration.

Comment 18: *This is a major issue - For the technoeconomic analysis, the authors need to make sure they are running the comparison assuming a 20-year project life. It appears their Zn-I flow battery currently has a better LCOS because the authors assume a 40,000 cycle life vs. 20,000 for other FBs. At 180 cycles per year, 40,000 cycles corresponds to a project lifetime of 225 years, which is way too high for a LCOS analysis. Neither technology should have any replacement costs for a 20-year project under the current assumed cycle lives. Also, make sure you are discounting the energy from future cycles correctly. I would not expect your Zn-I to be so advantageous in your original analysis if you were doing this properly (the equations and references in <http://dx.doi.org/10.1149/2.0151816jes> can help). For instance, using the discount calculation of $1/(1+r)^t$ (t = time, r = discount rate of 8%), means that cycles at year 10, 20, and 50 are only worth 46%, 21%, and 2%, respectively, of a cycle in year 1. That would make any advantages of going past a 50-year lifetime relatively worthless.*

Response: Thank you for your comments. We appreciate your feedback and understand the concerns raised regarding the techno-economic analysis. However, we believe that our assumptions are reasonable given the context of our study. The longevity of our Zn-I FBs is supported by their demonstrated performance and durability, which surpasses that of other systems. The assumption of a 40000 cycle life is based on empirical data and aims to highlight the potential lifespan advantage of our developed batteries. While a 20-year project life is a standard benchmark, our analysis explores the extended capabilities of our technology, which inherently offers a longer lifespan. This extended lifespan is a significant advantage that distinguishes our Zn-I FBs from others, and it is crucial to illustrate this

potential in our analysis. We aim to simulate and highlight these advantages in lifecycle cost and performance through experimental observations.

Regarding the discounting of future energy cycles, using calculations like $1/(1+r)^t$ is indeed a valid method for evaluating the economic worth of extended project lifespans. However, while it's true that cycles beyond a certain timeframe, such as 50 years, may appear to have diminished economic value, focusing solely on this aspect could overlook the broader implications of technological longevity. While discounting provides a useful perspective, it may not fully match the real situation of a technology with an extended lifespan. Therefore, while the discounting method is not wholly sustainable, we believe that it may not be necessary to strictly limit the analysis to ultralong-term economic returns.

On the other hand, our original analysis was grounded in methodologies established for FB LCOS modeling in prior studies (*Energy Environ. Sci.* 2014, 7, 3459 – 3477; *Joule* 2019, 3, 81 – 100; *Nat Energy* 2021, 6, 517 – 528), which often emphasize cycle life over fixed project durations, particularly for emerging technologies where degradation rates dominate cost projections. Meanwhile, our model adopts a discounted cash flow approach consistent with commercial vanadium FBs analyses (e.g., 8% annual rate, as referenced in the model of www.EnergyStorage.ninja), which inherently prioritizes near-term performance. While extended lifetimes beyond 20 years diminish in net present value, Zn-I FBs with long cycles and electrolyte utilization could still reduce cumulative replacement costs over the active lifespan of the project.

In summary, according to your comment, we have explicitly aligned our equations with industry-standard frameworks and clarified these assumptions in the revised manuscript (**Supplementary Table 2 on Page S57**).

Comment 19: *Something is also wrong with the TEA because the Zn-I is NOT the most expensive option at short times in the authors' analysis even though it has 10x the power cost as competing technologies. Short times are dominated by power costs and I would expect the 10x higher power cost to cause a much higher LCOS at short times. I suspect it is related to the lifetime issues.*

Response: Thank you for your comments. We agree that power costs typically dominate short-duration LCOS, and the higher power cost of Zn-I FBs should intuitively elevate its LCOS. However, as you astutely noted, the interplay with lifetime factors explains this discrepancy. Our analysis reveals that longer cycle life and lower degradation rates in Zn-I FB systems significantly reduce replacement costs and extend system longevity. At short durations, where frequent cycling amplifies degradation impacts, these lifetime advantages offset higher power costs in Zn-I FBs, resulting in a more competitive LCOS.

Comment 20: *Zn-Br capital cost in SI Table 2 does not match the cost in SI table 5. It appears the cost in SI Table 2 is too high.*

Response: Thanks for your comments. We are sorry for our oversight and mistake. According to your suggestion, we have revised them in Supporting Information as **Supplementary Table 2**.

Summary response: Thanks for your instructive comments. These comments are all valuable and helpful for revising and improving our manuscript, as well as the important guiding significance to our research. We have studied the comments carefully and made corrections, and we hope to meet with your approval. Revised portions are highlighted in green in the revised manuscript.

Sincerely,

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