

Balanced-State Electrolytes Overcome Crossover in Vanadium Redox Flow Batteries

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

Parts of this Peer Review File have been redacted as indicated to maintain the confidentiality of unpublished data.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript describes an electrolyte engineering strategy — “balanced-state electrolytes” (BSEs) — for mitigating vanadium crossover caused capacity fade in VRFBs. The benefits of applying BSEs are well validated, showing significant improvement over traditional symmetric electrolyte systems. However, several key areas still need clarification, strengthening, or additional experimental support, prohibiting the manuscript from meeting the standard for publishing on Nature Communication. Some comparison experiments are not rigorously conducted, and the scientific presentation could also be improved. Wherever the manuscript is going to be submitted, the following concerns should be resolved.

Major concerns:

1. Conceptual novelty and presentation

a, The idea of tuning both concentration and valence to manage crossover-induced capacity decay is interesting and well-motivated. However, regarding the scientific presentation, the authors are making simple things complicated. If starting with V3.5+ and assuming no side reaction, the only thing that crossover will lead to is the concentration imbalance of the positive side and the negative side. Keeping moving the electrolyte of the concentrated side into the diluted side to keep the amount of substance (total vanadium) identical for both sides will keep the cell balanced, until crossover of vanadium from both sides balancing each other. The eventual crossover-balanced electrolytes shall have the same concentration and volume as the BSE. By knowing the crossover constants of all vanadium ions under operation pressures would directly give the composition of BSE. BSE allows the amount of substance in the positive and negative side unchanged because the crossover cancels each other. Authors should explain the determination of the BSE composition in a more explicit and clear way.

Furthermore, from this perspective, the authors may consider building an automatic adjusting system, monitoring the volume and the concentration of each sides of the electrolyte and adding an automatic side-pumping system (with pumping rate balancing the osmosis pressure and sub-cell balancing the side reaction: DOI <https://doi.org/10.1039/D4EE02450H>) to realize the auto-optimized BSE. If such an automatic monitored system with near zero fading would be demonstrated, this manuscript can be accepted by Nature Communication.

b, The term “balanced-state electrolyte” lacks precise definition early in the manuscript, increasing the reading barrier to audiences.

c, Many experimental results are repetitive. Authors should consider moving some of the repetitive figures and supporting data into SI (e.g., Fig 4a(crossover is more time-dependent than cycling dependent), 4f-j, 5a-c).

d. Fig. 1e, 2s, S4, S6 are not helpful and confuse the readers. The authors should just write down the formula, the chemical reactions and balance them. The reviewer tried to count these colored balls and found them not even balanced regarding numbers. There is no point in using them if these figures are not accurate, can be simplified by words, only cause pain and are not aesthetically beautiful. The authors should simply use an example case and write the chemical composition to explain the problem of crossover and the authors’ solution.

e. The title is not accurate. The authors are dealing with the imbalance of crossover in vanadium redox flow battery, not

overcoming membrane limitations in flow batteries: membrane selectivity are not improved in this manuscript and this method is not useful for other flow batteries that uses different active species in the positive and genitive electrolyte.

2. Experimental design

- a, The exact procedure for determining the BSE composition is not clearly outlined in the main text. Authors should move essential elements of the BSE determination procedure into the main Methods section.
- b, The manuscript is about balancing the crossover of VRFB with various membranes, yet the permeation constants of all four Vanadium ions through each membranes are not quantified or measured in this manuscript. The manuscript also applied different flow rates on each side of the cell to control the osmosis pressure balance when using asymmetric BSEs. The pressure drop may also influence the permeation (crossover) of ions. The measurement of these conditioned constants can be scientifically and practically useful, since these constants should provide stronger rationale regarding the determination of BSE compositions.
- c. The testing parameters are not controlled, using comparison with two or more parameters changed (Figure 4a, 4c). The effect of cell configuration (electrode thickness, flow field, etc.) was not controlled across different membranes, especially for NC700 and N211 (see SI Section 3). Authors should consider justifying and quantifying how these differences in hardware design influence the results or standardize them across comparisons.

3. Modeling and theoretical analysis

- a, Authors should describe the performance of their cells using a mechanistic framework (e.g., based on Nernst–Planck, Poisson–Nernst, or coupled Fickian transport) equation, with permeation and migration constants measured as suggested, to demonstrate a straight-forward model that can guide designs of electrolytes. In this case, MD simulations are not as informatic for readers – the diffusion rates of ions are changed just because the concentration gradients/differences are changed.
- b, What is the chemical difference between TE and BSE rather than concentration? In that case, what is the physical explanation of TE and BSE having different “vanadium ions’ energies” in Nafion? This raises concern regarding the MD simulation results.
- c, If the authors insists on the MD simulations, the current MD simulations are oversimplified. The simulation is limited to ion diffusivity. The simulation should be coupled with membrane hydration and Donan potential shifts under real operating potential gradients with a longer simulation time.
- d, Fig. 3h is not informatic. What should readers learn from Fig 3h?
- e. Fig. 3i is not explained, and the abbreviation MSD showed without spelled out in the manuscript. What does MSD (nm²) mean?
- f. Fig. 3k may be too obvious: why would someone expect the hydration of V²⁺ changed if just changing a 1.7 M V²⁺ solution into a 2.0 M V²⁺ solution?

4. Electrochemical performance claims

- a, The authors mentioned side reactions at line 184, demonstrating adding V⁵⁺ to balance the cell SOC. Authors should specify the side reactions and their effects, noting that side reaction of carbon electrode aging is evitable by using inert electrodes. Side reactions of HER or ORR should be balanced by adding V⁴⁺ or introducing reactants (<https://doi.org/10.1039/D4EE02450H>, <https://doi.org/10.1016/j.jpowsour.2023.233770>)
- b, Fig 2h shows no apparent difference, contracting against the statement.
- c. Line 317: Fig. S16 does not show apparent difference between these two membranes, contracting against the statement.
- d. Line 373: no clear experimental evidence of modulating the interactions between vanadium ions and sulfonic acid groups, contracting against the statement. The authors only changed the concentration of the electrolytes.

Minor concerns:

5. Broader impact and scalability

The cost analysis (Fig. 5h) indicates the practical significance of the BSE approach. However, the assumptions behind the >40% cost reduction are not fully transparent. Author should include their detail TEA with a table listing assumptions (e.g., membrane price, electrolyte cost per kg, system lifetime) and perform a sensitivity analysis with fare comparison with previous/commercial rebalancing techniques.

6. Language and clarity

While the manuscript is generally readable, grammatical inconsistencies and stylistic issues detract from the clarity (e.g., line 209-210 sentence has no verb). Authors should also revise for clarity, especially in experimental procedures and descriptions of diffusion processes.

Reviewer #2

(Remarks to the Author)

In this work, the authors propose an electrolyte design based on balanced-state electrolytes, rather than membrane design, to mitigate the capacity decay of redox flow batteries. This approach addresses the trade-off between ion conductivity and the permeability of active materials in VRFBs. While the study presents an interesting strategy to enhance the cycling stability of flow batteries, certain sections require modification and further discussion. I would recommend publication in this journal after major revision.

1. In the Abstract, the authors state that "battery employing a 15 μm -thick Nafion membrane with balanced-state electrolytes achieves a 77.6% reduction in capacity decay rate (over 1,000 cycles) compared to a system using a 183 μm thick Nafion membrane with conventional electrolytes." It would be helpful to also provide the capacity fading rate per cycle or the capacity retention after 1,000 cycles. Additionally, please specify the total testing duration (in hours) for 1,000 cycles. Furthermore, for a more accurate evaluation of the electrolyte design effect on capacity decay, the comparison should be conducted using Nafion membranes of the same thickness.

2. In the Abstract, the authors state that "Crucially, the balanced state electrolyte approach removes membrane limitations in redox flow battery development and opens new avenues for advanced electrolyte design.". To claim that this approach can remove membrane limitations, it would be necessary to evaluate its performance with a wider variety of membrane types, rather than testing solely with a Nafion membrane.

3. In page 2, the authors state that "The cation exchange membrane (CEM) is a critical component in RFBs, ideally conducting proton while preventing the crossover of active species.". However, the choice of ion exchange membrane for an RFB depends on the type of active material used. Some active materials require an anion exchange membrane, while others can operate with a porous membrane without ion selectivity. For acidic electrolytes, proton conductivity is important, whereas in alkaline electrolytes, conductivity of other ions may be more relevant. Please clarify which specific type of RFB this study focuses on. Additionally, note that in many RFBs employing organic active materials such as quinones, capacity decay is generally not dominated by active material crossover.

4. In page 2, the authors state that "Despite these advances, challenges persist in the applicability of these membranes in inorganic/organic RFB systems, including low proton conductivity, scalability issues, escalated costs, and long-term stability concerns.". However, in most organic RFB systems, active material crossover is generally not a significant issue. This sentence should be revised accordingly.

5. In Figs. 1-3, please revise the discharge capacity units from Ah to volumetric discharge capacity (Ah/L), as volumetric capacity is a more relevant metric for evaluation.

6. In page 4, the authors state that "Fig. 1a shows that the discharge capacity of the VRFB with Nafion 212 first increases for a short period and then rapidly decays between about 10-200 cycles.". Please provide an explanation for the initial short-term increase in discharge capacity.

7. In page 6, the authors state that "The complex ion transport model in VRFBs, combined with the dynamic evolution of electrolytes over extended cycling, complicates this task.". Please explain more clearly on the meaning of "dynamic evolution" in this context, providing specific details.

8. In Fig. 3, could you also provide data on power density, voltage efficiency, or energy efficiency? In the Introduction, it is stated that this electrolyte design method can address the trade-off between ion conductivity and selectivity without compromising power density, which is a key advantage over membrane design. Therefore, this aspect should also be addressed and supported with relevant data in the study.

9. In Fig. 3, please also indicate the total testing time for 400 cycles.

10. In Fig. 4, the thickness of the Nafion membrane should be kept the same in order to isolate and accurately assess the effect of the electrolyte design on the stability of VRFBs with balanced-state electrolytes.

11. Overall, the experimental data presented focuses solely on VRFBs using a Nafion membrane. Although this system is described as a model, additional validation with other types of RFBs employing different active materials and membranes is necessary to substantiate the claim that this electrolyte design strategy is universally adaptable for RFBs without membrane limitations. Therefore, I recommend conducting further tests with at least two or three different combinations of active materials and membranes.

Reviewer #3

(Remarks to the Author)

This manuscript proposes balanced-state electrolytes (BSEs) that deliberately break symmetry in concentration and average valence between positive and negative tanks to counteract net crossover in vanadium redox flow batteries (VRFBs). By tuning concentration and valence, the authors claim to hold the net transmembrane flux near zero over a cycle, enabling thin Nafion membranes without sacrificing capacity retention. Representative results include: with BSEs, N212 (51 μm) outperforms N117 (183 μm) using traditional electrolytes, cutting the capacity-decay rate from 0.061% to 0.025% per cycle over 1,000 cycles and reaching CE = 97.79% at 50 mA cm⁻² (main Fig. 4a,d; p. 25–26).

The approach extends to N211 (25 μm) and NC700 (15 μm) with decay rates down to 0.015% per cycle, alongside a >41.7% CAPEX reduction projected for a 1 MW/4 MWh system (main abstract; Fig. 5e–h; pp. 15–16; SI Tab. S2).

Mechanistically, the authors quantify flux reversal/neutralization (net flux 4.59% vs 38.94% for BSEs vs TEs) using volume- and concentration-shift analysis (SI Eq. S13–S14; Fig. S15, p. 10–11).

The idea is practically appealing—use electrolyte design to escape the conductivity–selectivity trade-off of Nafion rather than inventing bespoke membranes.

Major comments

Generalizable, reproducible procedure for identifying the “balanced state.”

The present recipe infers BSEs from the first “horizontal region” (~107 h) in the discharge-capacity–time trace (main Fig. 2e–f), which is sensitive to current, SOC window, temperature, and cell hardware. Please formalize a predict–set–verify workflow: given membrane type, current density, SOC range, and temperature, output the target P/N concentrations and positive-tank average valence (with uncertainty). Publishing a minimal open script that couples Fig. 2b (net-flux map) with SI Sections 1 & 2 would make this widely reusable.

Disentangle temperature and water-migration effects.

The capacity ripples track day–night temperature changes (main Fig. 3b; SI Fig. S7), and hydraulic/viscous effects were probed via unequal flow (main Fig. 2h; SI Fig. S5), but the quantitative roles of water transport and acid strength remain unclear. Please (i) repeat a key N212/N211/NC700 comparison in a constant-temperature environment (e.g., 25 $\pm$ 0.1 °C), and (ii) co-track acid molarity/viscosity/volume on both sides with water content (e.g., titration or Karl Fischer). This will bound how much of the benefit arises from species flux versus water/osmotic effects.

Bridge the MD to measurable transport; release inputs.

The MD results suggest reduced V³⁺ diffusion and altered ion–sulfonate interactions under BSEs (main Fig. 3h–j; SI Fig. S11–S13). For reproducibility, please share topology/parameters and bench-mark simulated diffusivities against values inferred from self-discharge/EIS or literature for each ion/species. A brief sensitivity check (water content, ionic strength) would increase confidence in the mechanism.

Cost model sensitivity and operating envelope.

The >41.7% CAPEX reduction (main Fig. 5h) is compelling but scenario-dependent. Please add a tornado or scenario analysis varying membrane cost ($\pm$ 50%), energy efficiency (80–86%), lifetime (500–3,000 cycles), and pump power (viscosity-dependent) to test the robustness of the conclusion.

Adaptive maintenance of the balanced state.

Since electrode aging shifts SOC windows and kinetics (main Fig. 4e–h; SI Fig. S19/S24), demonstrate a closed-loop correction (periodic tiny additions of VO²⁺ or acid, or controlled dilution) that keeps the net flux near zero over long cycling, and report how often corrections are needed. This would strengthen the practicality claim.

Minor comments

a) Error bars and replicates. Many plots (e.g., Fig. 3c–f; Fig. 5a,b,e,f) lack uncertainty. Please report n and add error bars or shaded confidence bands.

b) UV–Vis quantification. Provide the calibration curves and fitting ranges for the A/B peaks used to back-calculate concentrations/valence (SI Fig. S17, S22).

c) Terminology and units. Standardize viscosity (mPa·s) and wording (replace “pulling acid” with “diluting with 3 M H₂SO₄” per SI Sec. 1.1).

d) Operating conditions. State EIS SOC and temperature for each spectrum; specify flow-field geometries per membrane in the main text (now mostly in SI §3).

e) Data and code. Provide raw cycling/OCV/self-discharge data and the script used to construct the net-flux map (main Fig. 2b) and cost model (Fig. 5h) as supplementary files.

Recommendation

Major revision. The concept is strong and well supported across membranes; addressing the above points—especially a portable method to determine/maintain the balanced state and clearer control of temperature/water transport—would make the paper suitable for Nature Communications

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have put considerable effort into the revision, and the manuscript has been improved substantially. The authors showed convincing evidence of the practicability of BSEs and extra benefit from concentrated positive side. The characterization of the V species in the membrane supported these benefits. Now the manuscript can be published on Nature Communication, with two things that the authors can consider.

1. Direct measurement of crossover

The authors successfully showed that SOC influences crossover, concentrations of V species affect diffusion coefficient. The authors also argued that measuring the crossover of V species is out of scope. The reviewer believes, however, measuring the crossover of these four species with a few different concentrations can not only strengthen the scientific clearance, but can also directly support many statements with a decoupled clean data. Since the authors claimed that diffusion is dominating the crossover (not electromigration), the measurement of such crossover becomes very easy: one H-cell containing one kind of V source in one side, with supporting electrolyte only (V-free) in the other, can give authors a convincing crossover flux, as a function of source concentration. Thus, the estimated diffusion coefficient can be calculated.

2. The accuracy of the title

Although the authors showed that the penalty from the crossover in Fe-V RFBs can be overcome using the same strategy, this strategy does not really solve the major problem caused by crossover in asymmetric RFBs such as Fe-Cr, Fe-V batteries. Ideally, these batteries should have Fe and Cr separated, since the existence of crossovered Fe into the other side introduces severe HER side reactions. Authors mixed Fe-V making an after-crossover electrolyte is a decent demonstration of BSEs, but such batteries may not be commercially favored (~50% of the V-Fe capacity wasted, co-existence Fe in V side). BSEs can still be useful for batteries using the same redox core in both sides, which is VRFB the authors focused on. The authors may consider adjusting the title into "Balanced-State Electrolytes Overcome Crossover in Vanadium Redox Flow Batteries", which is more accurate and straightforward.

Reviewer #2

(Remarks to the Author)

The authors have addressed my comments appropriately, and the manuscript has improved as a result. The remaining issues are minor and can be handled during the editorial process.

Reviewer #3

(Remarks to the Author)

Thank you for the thorough revision and detailed point-by-point response. The manuscript is significantly clearer and more convincing after revision.

The most important improvement is the explicit "balanced state/BSE determination" workflow now presented in the Methods and expanded in the SI. This makes the approach far more reproducible and portable across membranes and operating conditions. I also appreciate the addition of a physics-based transport model (COMSOL/Nernst-Planck) to place the performance trends and crossover mitigation into a mechanistic framework; this directly addresses my previous concern that the narrative relied too heavily on simplified interpretations of MD.

Finally, several presentation issues have been handled appropriately (e.g., removal of a non-informative panel, clearer discussion of side reactions and their impact on average valence, and new experimental evidence supporting ion-sulfonate interactions). I have no further major concerns.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors did a very good job of revising the manuscript, with all concerns resolved and statements supported.

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Dear Editors and Reviewers,

Thank you for your and reviewers' comments and affirmation to our manuscript entitled "Balanced-State Electrolytes Overcome Membrane Limitations in Redox Flow Batteries" (NCOMMS-25-45545-T), which are very valuable and helpful for improving this paper. We considered these comments seriously and revised the manuscript and supplementary information based on them. The point-to-point responses to the comments are listed as follows:

Comments from reviewers: in black

Author response: in blue

Revisions in manuscript, and SI: in red

The literature and figures mentioned in the responses are sorted in order of appearance in this letter starting with references labelled R, while literature and figures used in the revised manuscript are sorted in the order of the manuscript.

Reviewer #1

This manuscript describes an electrolyte engineering strategy — "balanced-state electrolytes" (BSEs) — for mitigating vanadium crossover caused capacity fade in VRFBs. The benefits of applying BSEs are well validated, showing significant improvement over traditional symmetric electrolyte systems. However, several key areas still need clarification, strengthening, or additional experimental support, prohibiting the manuscript from meeting the standard for publishing on Nature Communication. Some comparison experiments are not rigorously conducted, and the scientific presentation could also be improved. Wherever the manuscript is going to be submitted, the following concerns should be resolved.

Response:

We sincerely thank the reviewer for the valuable comments and for recognizing the merit of our work. We have elaborated the concept and scope of application of BSEs and have successfully validated their application in the vanadium-iron redox flow battery system. In addition,

we have moved the detailed procedures for BSEs to the main Method section, provided additional experimental evidence, incorporated additional modelling and theoretical analyses, specified working conditions for electrochemical tests, and polished the manuscript with the help of a native English speaker.

Point-by-point responses are provided below.

Major concerns:

1. Conceptual novelty and presentation

a, The idea of tuning both concentration and valence to manage crossover-induced capacity decay is interesting and well-motivated. However, regarding the scientific presentation, the authors are making simple things complicated.

a1) If starting with V3.5+ and assuming no side reaction, the only thing that crossover will lead to is the concentration imbalance of the positive side and the negative side.

Response:

We appreciate the reviewer for the valuable comments. Side reactions among vanadium ions induced by crossover are unavoidable during cycling, because V^{2+} and V^{3+} are reducing species whereas VO^{2+} and VO_2^+ are oxidizing species, as shown below. [R1]

Side reactions for the vanadium ion transport from the negative to the positive sides:



Side reactions for the vanadium ion transport from the positive to the negative sides:



Notably, one V^{2+} consumes two VO_2^+ species when it crosses the membrane from the negative to the positive side. Consequently, V^{2+} crossover causes not only concentration imbalance but also

valence imbalance (the amount of VO_2^+ less than that of V^{2+} on the negative side) between the positive and the negative electrolytes. Moreover, vanadium species diffuse through Nafion membranes at markedly different rates, in the order $\text{V}^{2+} > \text{VO}^{2+} > \text{VO}_2^+ > \text{V}^{3+}$. [R2]

V^{2+} exhibits the highest diffusion rate across Nafion membranes among vanadium ions, which drives a net flux of electrolyte from the negative to the positive side, rendering VO_2^+ depleted relative to V^{2+} . As a result, crossover leads to a surplus of V^{2+} on the negative side, whereas VO_2^+ becomes depleted in the positive side of VRFBs during cycling. As a result, crossover leads to both the concentration and valence imbalance between the positive and negative electrolytes. More details about the theoretical analysis of crossover and its experimental validation are provided in our previous study. [R3]

[R1] Li Y, Skyllas-Kazacos M, Bao J. A dynamic plug flow reactor model for a vanadium redox flow battery cell. *J. Power Sources*. 311: 57-67. (2016)

[R2] Sun C, Chen J, Zhang H, Han X, Luo Q. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. *J. Power Sources*. 195(3): 890-897 (2010)

[R3] Wang Z, et al. An electrolyte with elevated average valence for suppressing the capacity decay of vanadium redox flow batteries. *ACS Cent. Sci.* 9(1): 56-63 (2022)

a2) Keeping moving the electrolyte of the concentrated side into the diluted side to keep the amount of substance (total vanadium) identical for both sides will keep the cell balanced, until crossover of vanadium from both sides balancing each other. The eventual crossover-balanced electrolytes shall have the same concentration and volume as the BSE.

Response:

We thank the reviewer for this comment. In this work, the vanadium redox flow battery (VRFB) was assembled with a Nafion 212 membrane and initially filled with TEs (1.70 M $\text{V}^{3.5+}$, 40 mL) on both the positive and negative sides. The BSEs for the VRFB equipped with Nafion 212 operating at 200 mA cm^{-2} are 1.91 M $\text{V}^{3.55+}$ and 1.17 M $\text{V}^{3.50+}$ for the positive and negative electrolytes, respectively. To preserve the total vanadium mass balance, the electrolyte volumes

were adjusted to 35.60 mL for the positive side and 58.12 mL for the negative side under the BSE condition.

$$40 \times 1.70 / 1.91 = 35.60 \quad (\text{Eq. R5})$$

$$40 \times 1.70 / 1.17 = 58.12 \quad (\text{Eq. R6})$$

The combined volume of the positive (35.60 mL) and negative (58.12 mL) electrolytes in the VRFB employing BSEs totals 93.72 mL—higher than the 80 mL (40 + 40 mL) in the traditional-electrolyte VRFB (1.70 M $\text{V}^{3.50+}$). Therefore, even if the vanadium-ion amounts are maintained identically across the positive and negative sides of a VRFB through precise redistribution of electrolytes during cycling, the same concentration and volume cannot be achieved.

Furthermore, the BSE for a VRFB is defined by a crossover flux of vanadium ions from the negative to the positive side that is counterbalanced by an equivalent flux in the opposite direction. According to Fick's law (Eq. R7), the flux of vanadium ions across a membrane depends on their diffusion rate across the membrane and the concentration gradient between the two sides. Thus, both the electrolyte concentration and the state of charge (SOC) of a VRFB significantly influence the vanadium ion flux across the membrane, as depicted in Fig. 2b. This indicates that the balanced state represents a dynamic equilibrium during charge–discharge processes. The balanced state of a VRFB is therefore not a fixed state but varies with specific operating conditions. As demonstrated in this work, the BSEs (P 1.91 M $\text{V}^{3.55+}$; N 1.170 M $\text{V}^{3.50+}$) for a VRFB assembled with Nafion 212 membrane and operated at 200 mA cm^{-2} differs from that of a VRFB with an NC700 membrane (P 1.83 M $\text{V}^{3.54+}$; N 1.15 M $\text{V}^{3.50+}$).

$$J = -D \nabla C \quad (\text{Eq. R7})$$

where, J is the flux ($\text{mol m}^{-2} \text{ s}^{-1}$); D is the diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$) and ∇C is the concentration gradient.

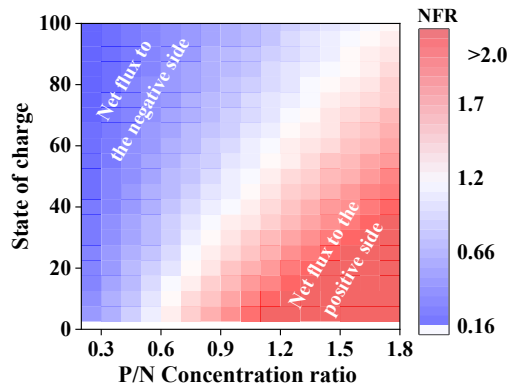


Fig. 2b Effect of electrolyte concentrations in the positive and negative sides on the net flux ratio at different SOC_s.

a3) By knowing the crossover constants of all vanadium ions under operation pressures would directly give the composition of BSE. BSE allows the amount of substance in the positive and negative side unchanged because the crossover cancels each other. Authors should explain the determination of the BSE composition in a more explicit and clear way.

Response:

We thank the reviewer for raising this point. We have clarified the description of the BSEs for a VRFB in the revised manuscript and added a section detailing how to determine the BSE composition in the revised supplementary information, as detailed below.

In practice, the direct measurement of the crossover quantities of all vanadium ions during charge–discharge cycling is extremely challenging, owing to side reactions and dynamic variations in electrolyte concentration, volume, and valence. Here, we treat VRFBs during cycling as dynamic diffusion systems and leverage their self-balancing capability to determine electrolyte concentration. Characterizing the electrolyte composition at the balanced state of a VRFB under specific operating conditions enables the design of corresponding BSEs. Consequently, our approach in this work does not require prior knowledge of the precise crossover constants of different Nafion membranes to determine the BSE compositions. This highlights the unique advantage of our proposed strategy: it provides a universal, experimentally driven framework for deriving balancing solutions for different membrane materials and operating scenarios, without the prerequisite of engaging in the characterization of intrinsic membrane parameters. Differences in cell configuration and operating conditions are inherently captured in the resulting balanced state, leading to distinct BSEs—as demonstrated by the differing BSE compositions for VRFBs

using N212 (P 1.91 M $V^{3.55+}$; N 1.170 M $V^{3.50+}$) versus N211 membranes (P 1.83 M $V^{3.54+}$; N 1.15 M $V^{3.50+}$).

In the revised Manuscript [Section BSE determination]

Determining the balanced state of a VRFB under specified operating conditions is essential for designing BSEs. Specifically, we define the balanced state under specific conditions as one where the capacity decay rate is less than 0.03% per cycle or 0.08% per hour. In addition, the test must last longer than 8 h and include more than 20 cycles, with the discharge capacity showing a monotonic decay versus time or cycle number over the investigated range. The electrolyte concentrations at the balanced state are used for designing BSEs. To ensure the accuracy of these measurements, we converted the electrolytes at the balanced state to $V^{3+}|VO^{2+}$ through full discharge followed by aerial oxidation. To compensate for the elevated average vanadium valence that occurs during cycling due to side reactions, the VO_2^+ content in the initial electrolyte was experimentally increased. The detailed procedure is described in the supplementary information.

In the revised Supplementary Information [Section BSE determination]

First, operate a VRFB under specified conditions and record the discharge capacity versus time curve. Second, calculate the capacity decay rates over 20 cycles in the quasi-steady region of the discharge capacity curve. Third, identify the region where the discharge capacity decay rate is below 0.03% per cycle. Fourth, stop cycling and fully discharge the battery at a constant voltage of 0.8 V until the current falls below 0.1 A. Fifth, stir the negative electrolyte using a magnetic stirrer and oxidize it in air for 4 hours to convert the surplus V^{2+} to V^{3+} . Sixth, dilute the negative and positive electrolytes 15-fold with deionized water and measure the V^{3+} and VO^{2+} concentrations using a UV-Visible Spectrophotometer.

a4) Furthermore, from this perspective, the authors may consider building an automatic adjusting system, monitoring the volume and the concentration of each sides of the electrolyte and adding an automatic side-pumping system (with pumping rate balancing the osmosis pressure and sub-cell balancing the side reaction: DOI <https://doi.org/10.1039/D4EE02450H>) to realize the auto-optimized BSE. If such an automatic monitored system with near zero fading would be demonstrated, this manuscript can be accepted by Nature Communication.

Response:

We thank the reviewer for raising this point. We have tried to validate the automatic balance system with a reflow setup, as shown in Fig. R1a-b. Initially, the positive and negative sides were filled with 1.7 M electrolyte volumes of 35.6 mL and 44.4 mL, respectively. The smaller positive volume was designed to compensate for the anticipated concentration increase due to vanadium crossover, thereby maintaining equal total vanadium content on both sides after equilibrium. As expected, gravity-driven flow through a connecting pipe occurred when the positive electrolyte volume increased due to crossover. The initial discharge capacity was low, which is attributed to a temporary shortage of positive electrolyte, but it increased with cycling (Fig. R1c). Early-cycle fluctuations are caused by non-equilibrium transport of ions and water across the Nafion membrane [R4]. The subsequent capacity increase is attributed to the rising positive electrolyte concentration caused by crossover, which enhances the vanadium content at the same volume. However, after reaching the values comparable to those of the VRFB employing BSE, the capacity decayed linearly. This linear decay might suggest that the final electrolyte characteristics in the reflow system differ from those in the BSEs, as further analysed in the response in a1 and a2.

To further demonstrate the effectiveness and applicability of our proposed BSEs method, we have extended it to iron-vanadium flow batteries (IVFBs), which suffer from severe crossover issues. As shown in Fig. R2, the accumulated discharge capacity improved 56.36% from 388.37 to 607.25 Ah over 400 cycles when conventional electrolytes were replaced with the BSEs, demonstrating good effectiveness and applicability. Details on the BSEs for IVFBs have been added to the revised manuscript and supplementary information, as detailed below.

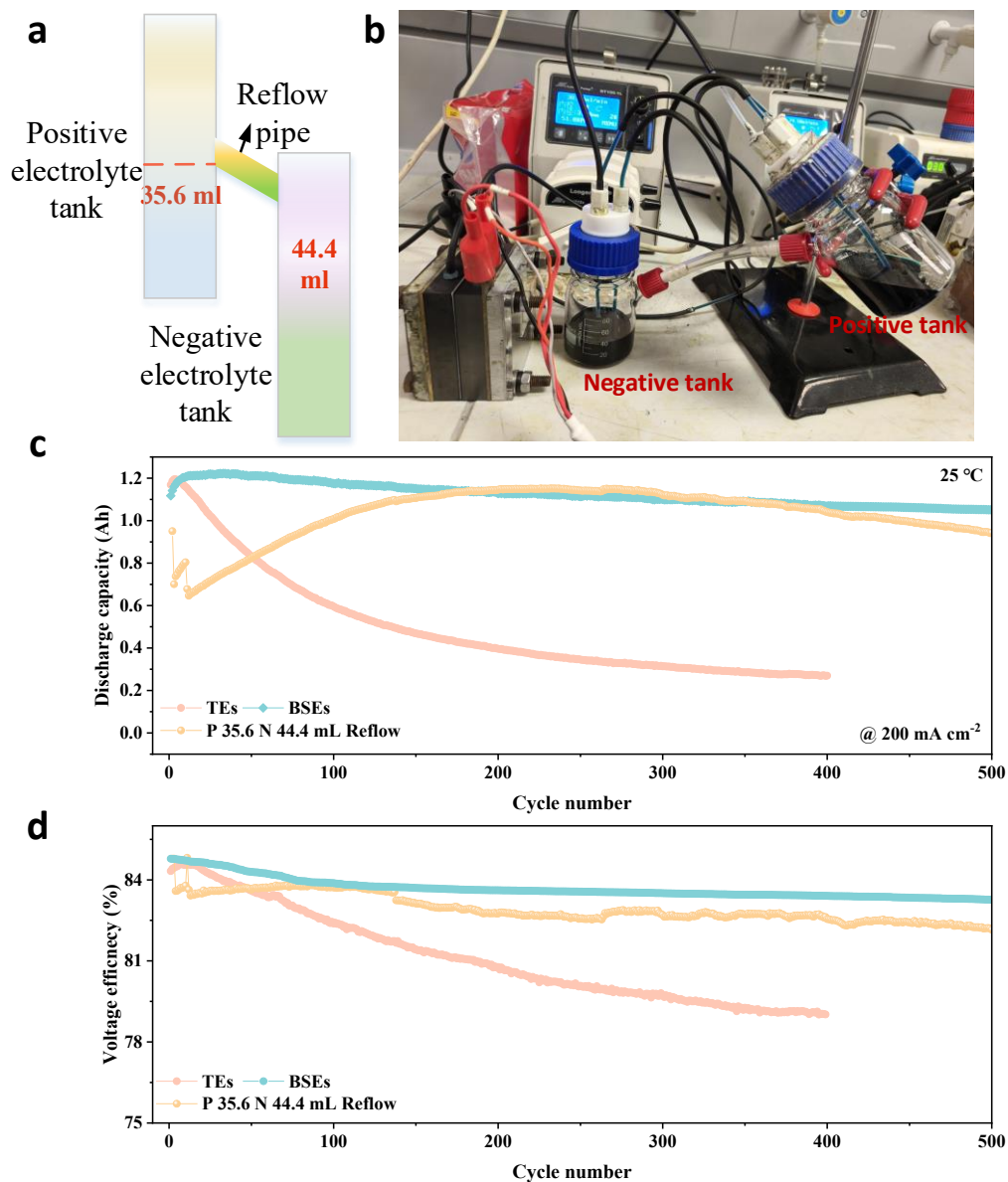


Fig. R1 Reflow setup for automatically balancing electrolytes between the positive and negative sides of VRFBs during cycling. **a**, Schematic of the reflow setup. **b**, Optical image of the reflow system for VRFBs. **c-d**, Discharge capacity and voltage efficiency of VRFBs with TEs, BSEs, and reflow system.

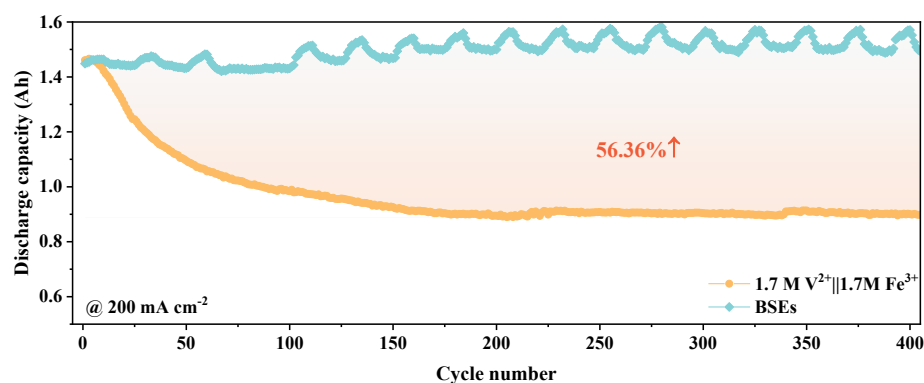


Fig. R2 Comparison of iron-vanadium flow batteries using conventional electrolytes (P 1.7 M V^{2+} ; N 1.7 M Fe^{3+}) versus balanced state electrolytes (BSEs, P 1.072 M V^{2+} + 0.876 M Fe^{2+} ; N 1.324 M Fe^{3+} + 0.914 M VO^{2+}).

In the revised Manuscript [Fig. 5]

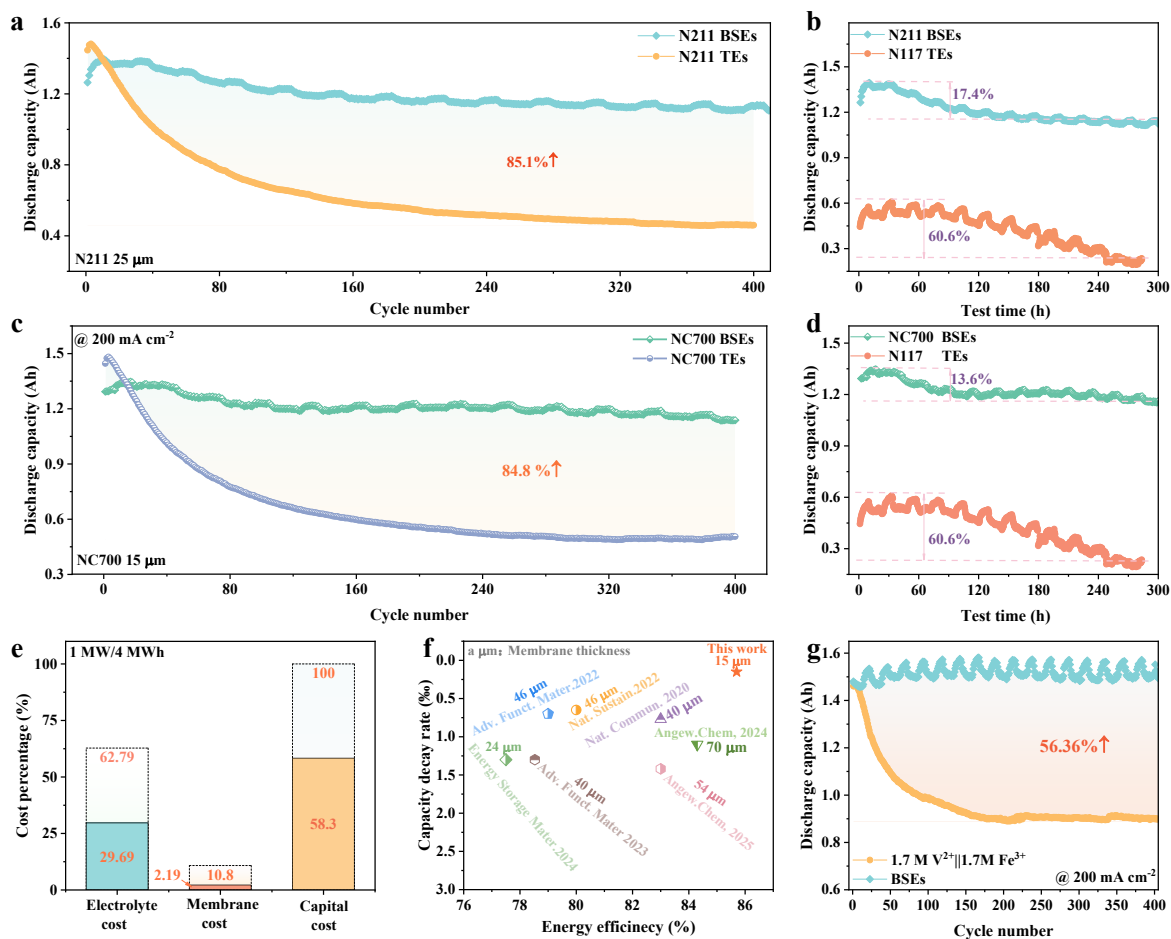


Fig. 5 Suppression of crossover with BSEs in RFBs. Effects of BSEs on improving **a**, discharge capacity of the VRFB with N211. **b**, Discharge capacity comparison between the VRFBs with N211 and N117. **c**, Effects of BSEs on improving the capacity retention rate of the VRFB with NC700. **d**, Capacity retention

rates comparison between the VRFB with NC700/BSEs and that of N117/TEs. **e**, Capital cost analysis in a 1 MW/4 MWh system between an advanced commercial case and using BSEs strategy. **f**, Comparison of VRFBs with advanced designed membranes reported in the last five years. **g**, Effects of BSEs (P 1.072 M V^{2+} + 0.876 M Fe^{2+} ; N 1.324 M Fe^{3+} + 0.914 M VO^{2+}) on improving the capacity retention rate of the IVFB with N212.

In the revised Manuscript [Line 373, Page 15]

To further demonstrate the effectiveness and applicability of our proposed BSEs method, we have extended it to iron-vanadium flow batteries (IVFBs), which suffer from severe crossover issues. The accumulated discharge capacity improved 56.36% from 388.37 to 607.25 Ah over 400 cycles when conventional electrolytes (P 1.70 M V^{2+} ; N 1.70 M Fe^{3+}) were replaced with the BSEs (P 1.072 M V^{2+} + 0.876 M Fe^{2+} ; N 1.324 M Fe^{3+} + 0.914 M VO^{2+}), indicating successful suppression of the crossover, as shown in Fig. 5g.

In the revised Manuscript [Section Materials]

Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$ CAS Number: 7782-63-0) and Iron (III) chloride hexahydrate $FeCl_3 \cdot 6H_2O$ (CAS Number: 7447-40-7) were purchased from Sigma-Aldrich.

In the revised Manuscript [Section Battery tests]

A VRFB cell equipped with Nafion 212 was adapted for IVFBs testing by replacing vanadium electrolytes with iron-vanadium electrolytes.

In the revised Manuscript [Section Electrolytes preparation]

1.70 M Fe^{3+} /3.00 M H_2SO_4 electrolyte was prepared by dissolving $FeCl_3 \cdot 6H_2O$ in 3.00 M H_2SO_4 solution.

In the revised Manuscript [Section Characterization techniques]

Ion concentrations in the positive and negative electrolytes of IVRFs were measured using an Inductively Coupled Plasma –Optical Emission Spectrometer (Avio-200, PerkinElmer) following 7500-fold dilution with deionized water.

In the revised Manuscript [Section Battery tests]

All the battery tests were conducted under N₂ protection using Arbin 179539 (Arbin instruments, USA) for data recording. The cut-off voltage range was 0.90-1.60 V for all VRFB experiments and 0.60-1.60 V for IVFB experiments.

In the revised Supplementary Information [Section 1.2 Electrolyte preparation for IVFBs]

The BSEs for IVFBs were prepared as follows. For the positive side, 11.62 g VOSO₄·5H₂O was added to 40 mL of 1.70 M Fe³⁺/3.00 M H₂SO₄ solution and then diluted with 11.36 mL of 3.00 M H₂SO₄, serving as the positive electrolyte. For the negative side, 11.45 g FeSO₄·7H₂O was added to 40 mL of 1.70 M V²⁺/3.00 M H₂SO₄ solution and then diluted with 23.43 mL of 3.00 M H₂SO₄, serving as the negative electrolyte.

In the revised Supplementary Information [Section 1.4.2 BSEs for IVFBs]

The definition and identification method for the balanced state in IVFBs are the same as those for VRFBs. Here, we selected the state of an IVFB after 160 cycles as its balanced state and measured ion concentration using an Inductively Coupled Plasma –Optical Emission Spectrometer (Avio-200, Perkin Elmer) following 7500-fold dilution with deionized water. The results show that vanadium ion concentrations are 0.914 M and 1.072 M in the positive and negative electrolytes, respectively, and iron ion concentrations are 1.324 M and 0.876 M, respectively.

In the revised Supplementary Information [Section 4 IVFB test]

First, a VRFB assembled with Nafion 212 was fully charged using 40 mL of V^{3.5+}/3.00 M H₂SO₄ as both the positive and negative electrolytes, yielding 40 mL of V²⁺/3.00 M H₂SO₄ on the negative side. Then, the positive electrolytes (VO₂⁺) were pumped into tank and the positive-side chamber was washed with deionized water and purged with N₂ for 1 min. Finally, the positive electrolyte was replaced with 1.70 M Fe³⁺/3.00 M H₂SO₄ electrolytes. In IVFB testing with the BSEs, the same flow battery cell was employed.

In the revised Supplementary Information [Fig. S38]

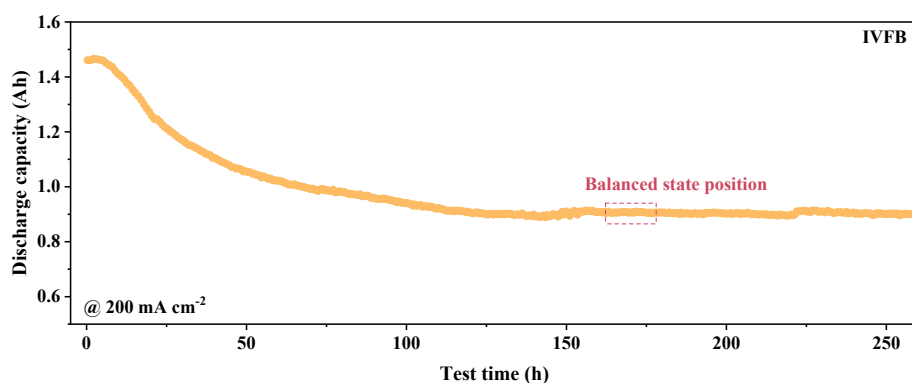


Fig. S38 Discharge capacity versus time for an IVFB using TEs (P 1.70 M $\text{Fe}^{3.0+}$; N 1.70 M $\text{V}^{2.0+}$).

[R4] Mu D, Zhao Y, Yu L, et al. Asymmetric vanadium flow batteries: long lifespan via an anolyte overhang strategy. *Phys. Chem. Chem. Phys.* 19(43): 29195-29203 (2017).

b, The term "balanced-state electrolyte" lacks precise definition early in the manuscript, increasing the reading barrier to audiences.

Response:

We appreciate the reviewer for the valuable comments. We have clarified the definition of the balanced state of electrolytes (BSE) for VRFBs in the revised manuscript upon its first introduction, with details provided below.

In the revised Manuscript [Line 79, Page 3]

Ideally, the balanced-state electrolyte in a VRFB is defined by a crossover flux of vanadium ions from the negative to the positive side that is counterbalanced by an equivalent flux in the opposite direction.

c, Many experimental results are repetitive. Authors should consider moving some of the repetitive figures and supporting data into SI (e.g., Fig 4a (crossover is more time-dependent than cycling dependent), 4f-j, 5a-c).

Response:

Thanks for your important suggestion. The repeated experimental data have been moved to the SI in the revised manuscript, as shown below.

In the revised Manuscript [Figs. 4 and 5]

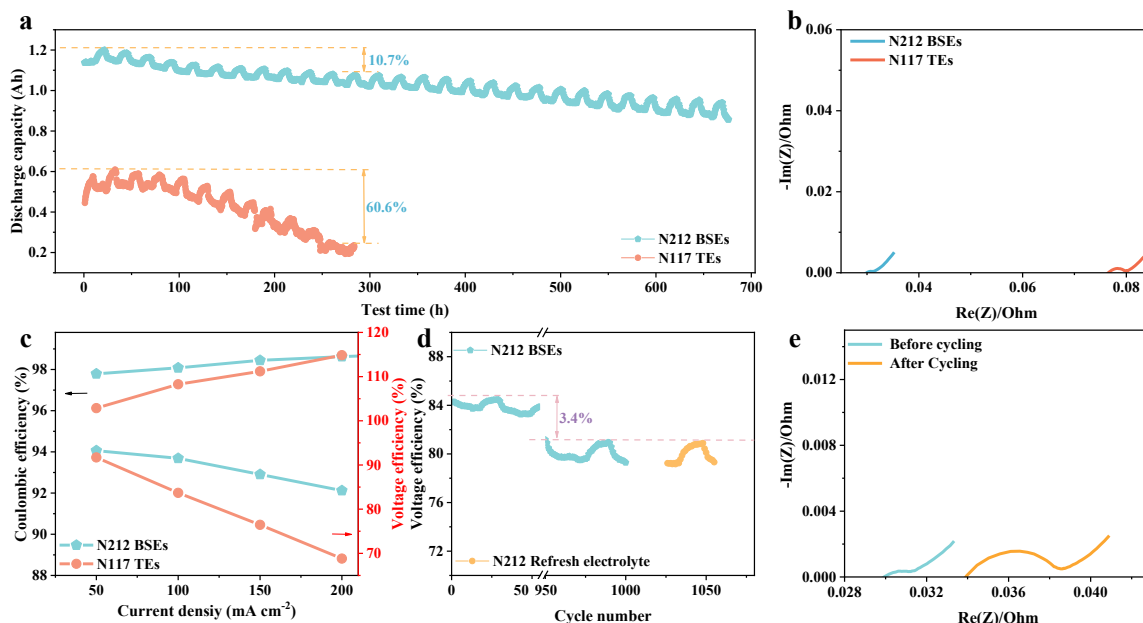


Fig. 4 Stability of VRFBs with balanced-state electrolytes. Comparison of VRFBs with BSEs (P 1.91 M $\text{V}^{3.55+}$; N 1.17 M $\text{V}^{3.50+}$) combining with N212 (51 μm) and TEs (P 1.70 M $\text{V}^{3.50+}$; N 1.70 M $\text{V}^{3.50+}$) combining with N117 (183 μm) in **a**, discharge capacity vs. test time, **b**, EIS spectrum, **c**, coulombic/voltage efficiency. **d**, Voltage efficiency and **e**, EIS spectrum of the VRFB with BSEs before and after cycling.

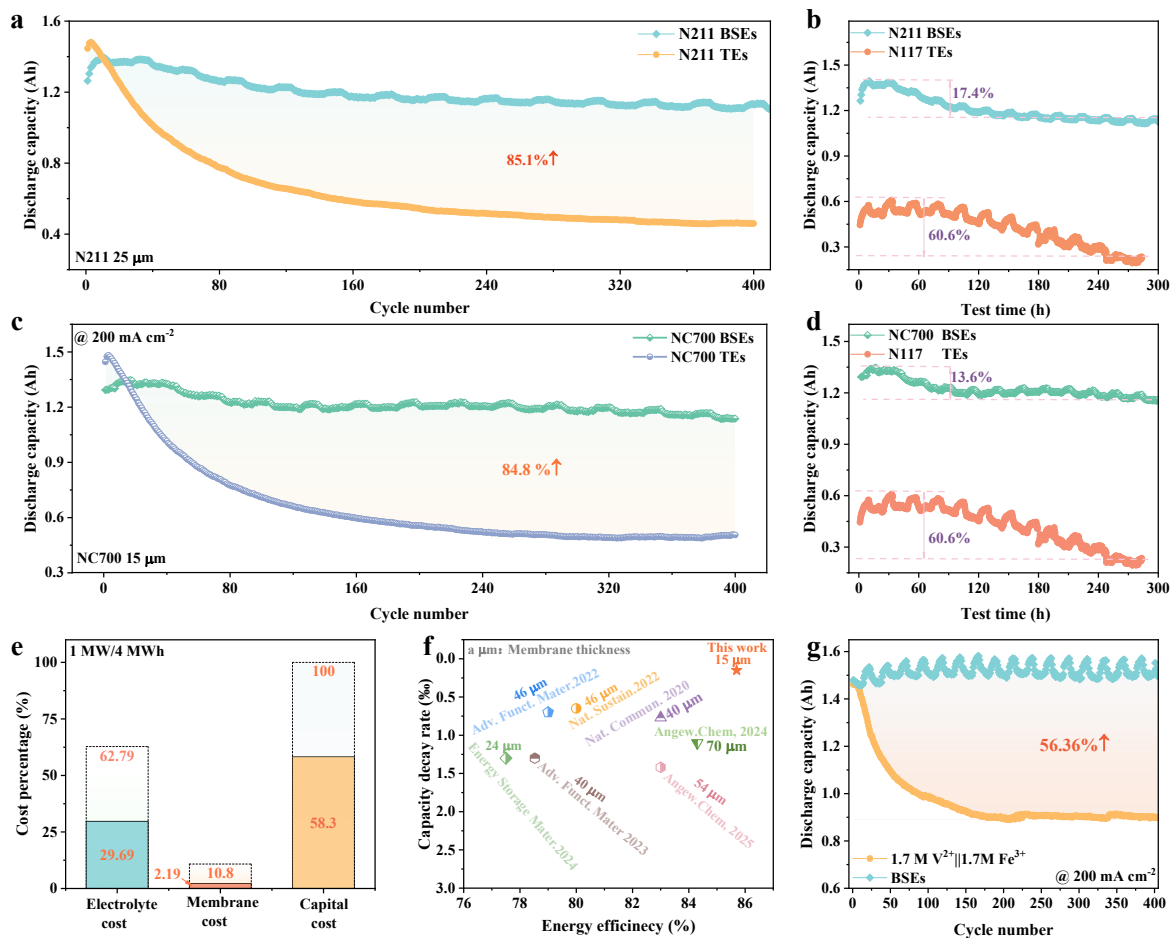


Fig. 5 Suppression of crossover with BSEs in RFBs. Effects of BSEs on improving **a**, discharge capacity of the VRFB with N211. **b**, Discharge capacity comparison between the VRFBs with N211 and N117. **c**, Effects of BSEs on improving the capacity retention rate of the VRFB with NC700. **d**, Capacity retention rates comparison between the VRFB with NC700/BSEs and that of N117/TEs. **e**, Capital cost analysis in a 1 MW/4 MWh system between an advanced commercial case and using BSEs strategy. **f**, Comparison of VRFBs with advanced designed membranes reported in the last five years. **g**, Effects of BSEs (1.072 M V^{2+} + 0.876 M Fe^{2+} ; 1.324 M Fe^{3+} + 0.914 M VO^{2+}) on improving the capacity retention rate of the IVFB with N212.

In the revised Supplementary Information, we have added Fig. S19, S20, S22, S29, S30, and S34, with details provided below.

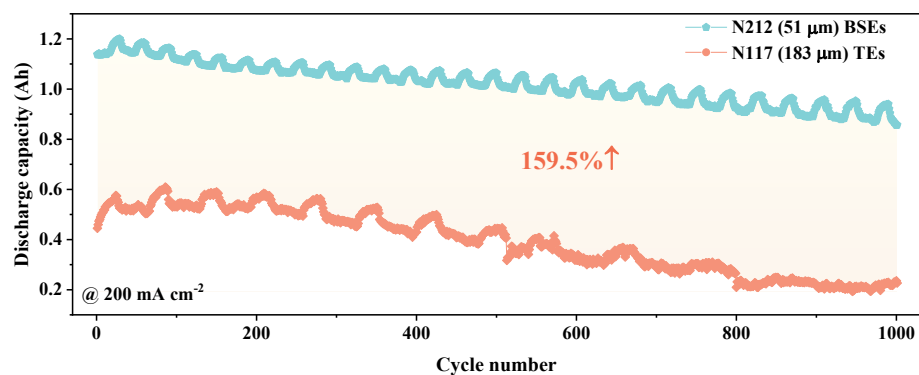


Fig. S19 Cycling performance of VRFBs comparing BSEs (P 1.91 M $\text{V}^{3.55+}$; N 1.17 M $\text{V}^{3.50+}$) combining with N212 (51 μm) to TEs (P 1.70 M $\text{V}^{3.50+}$; N 1.70 M $\text{V}^{3.50+}$) with N117 (183 μm).

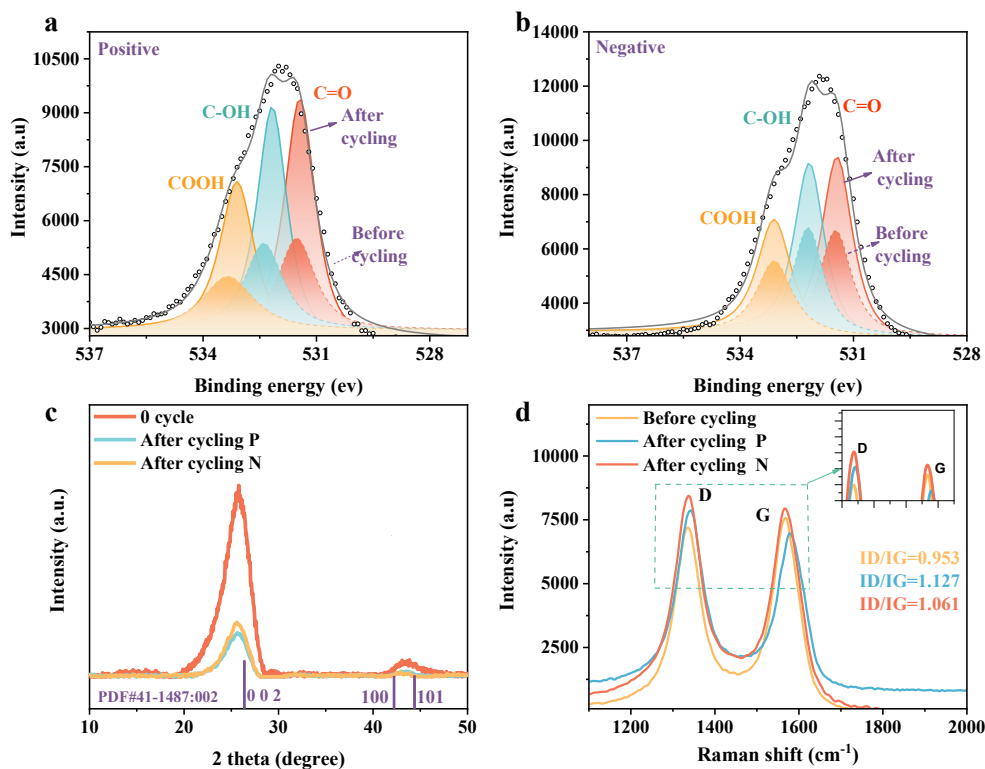


Fig. S20 Electrode degradation in VRFBs with BSEs after cycling. **a-b**, XPS spectra of the electrode on the positive and negative sides before and after cycling. **c**, XRD and **d**, Raman spectra of electrodes before and after cycling.

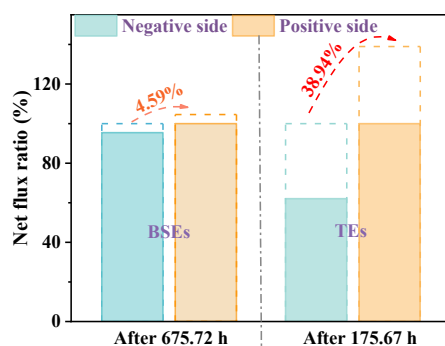


Fig. S22 Electrolyte net flux between the positive and negative sides in VRFBs with BSEs (P 1.91 M $V^{3.55+}$; N 1.17 M $V^{3.50+}$) and TEs (P 1.70 M $V^{3.50+}$; N 1.70 M $V^{3.50+}$) combining with N212 before and after cycling.

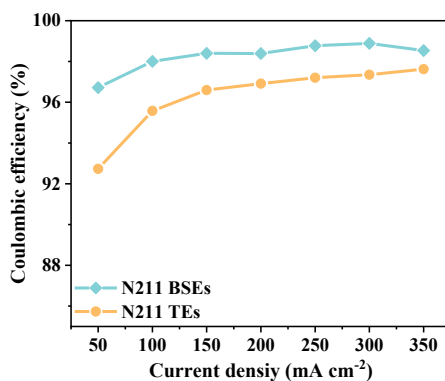


Fig. S26 Effects of BSEs on improving the coulombic efficiency of the VRFB with N211.

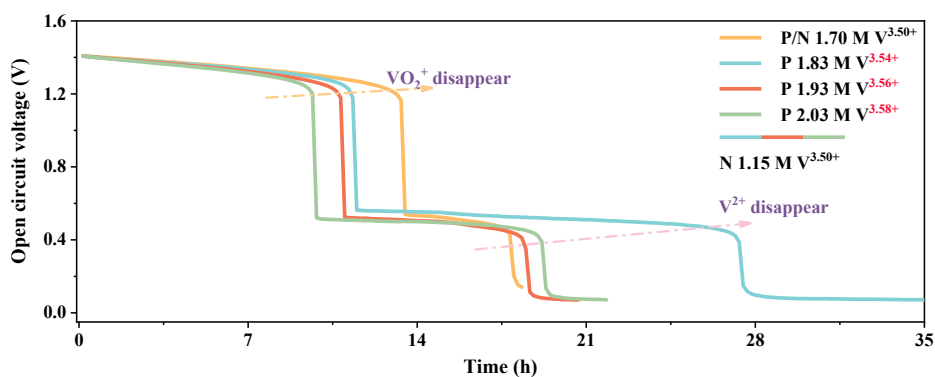


Fig. S27 Self-discharge curves of VRFBs with the N211 membrane and different electrolytes.

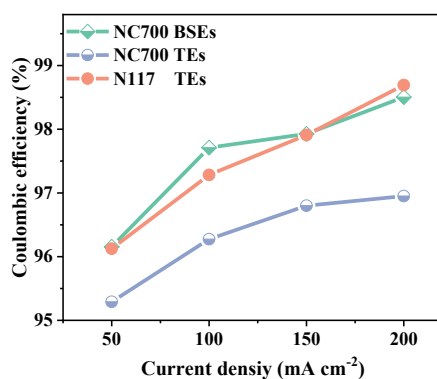


Fig. S33 Effects of BSEs on improving the coulombic efficiency of the VRFB with an NC700.

d. Fig. 1e, 2s, S4, S6 are not helpful and confuse the readers. The authors should just write down the formula, the chemical reactions and balance them. The reviewer tried to count these colored balls and found them not even balanced regarding numbers. There is no point in using them if these figures are not accurate, can be simplified by words, only cause pain and are not aesthetically beautiful. The authors should simply use an example case and write the chemical composition to explain the problem of crossover and the authors' solution.

Response:

We sincerely apologize for the unsatisfactory experience. The relevant content has been removed, and the corresponding descriptions have been simplified in both the revised manuscript and the supplementary information, as detailed below.

In the revised Manuscript [Fig. 1]

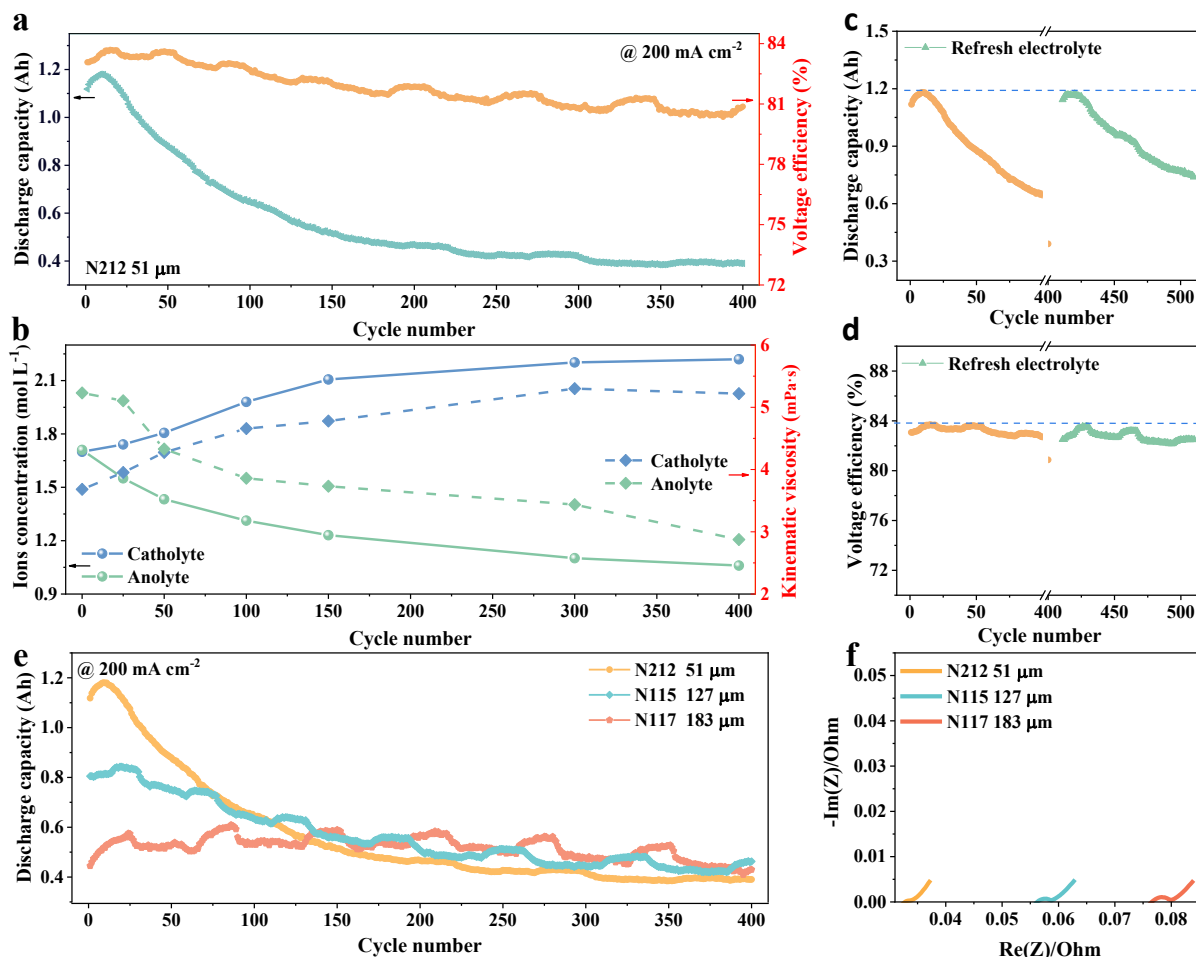


Fig. 1 Battery performances and electrolyte properties vary with cycling. **a**, Discharge capacity/voltage efficiency and **b**, electrolytes' concentration/viscosity change with cycling of the VRFB equipped with Nafion 212 and traditional electrolytes at 200 mA cm^{-2} . **c**, Discharge capacity and **d**, voltage efficiency of VRFB after refreshing electrolytes. **e**, Comparison of discharge capacity decay and **f**, electrochemical impedance spectroscopy (EIS) in VRFBs with Nafion 212/115/117 (Named as N212/N115/N117).

In the revised Manuscript [Line 115, Page 4]

Specifically, it results in a deficiency of VO_2^+ on the positive side (supplementary information, section 3)...

In the revised Manuscript [Fig. 2]

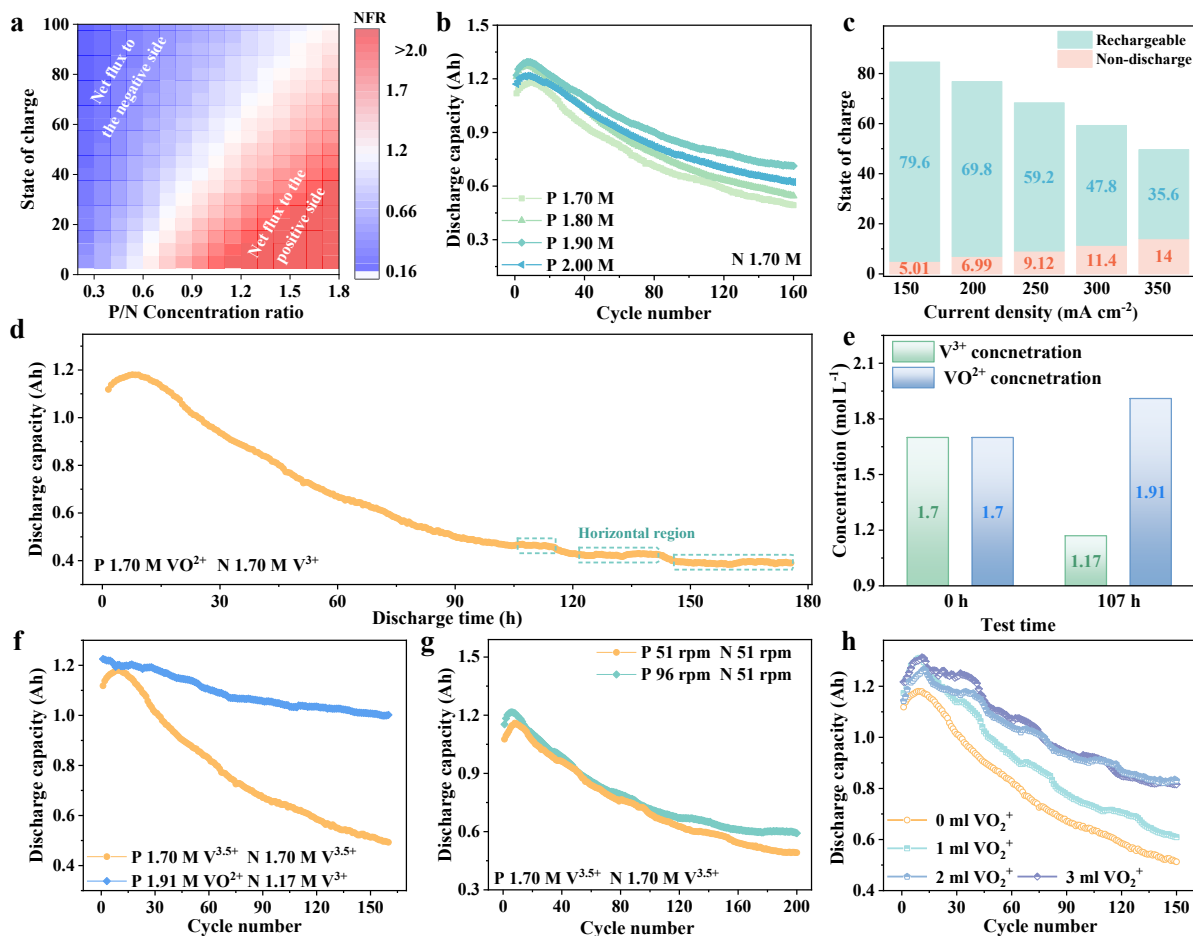


Fig. 2 Suppressing capacity decay of VRFBs via the adjustment of vanadium ion transport across the membrane. **a**, Electrolyte concentrations on the positive and negative sides affect the net flux ratio under different SOC (the diffusion rates were based on Sun's²³ study (Table S1), NFR is the net flux ratio between the positive and negative sides). **b**, Effects of increasing the concentration of VO_2^+ electrolyte on capacity decay. **c**, Range of SOC in the discharge process under different current densities. **d**, Discharge capacity varies with test time. **e**, Concentration of electrolytes on the positive and negative sides after 107.56 h (200 cycles). **f**, Performance of VRFB with the electrolyte concentrations at balanced state (P 1.91 and N 1.17 M). **g**, Hydro pressure effects on suppressing capacity decay of VRFBs. **h**, Additional VO_2^+ effects on suppressing capacity decay of VRFBs (Letters P and N represent positive and negative electrolyte respectively).

In the revised Manuscript [Line 145, Page 6]

Specifically, reducing the negative electrolyte concentration while increasing that of the positive concentration mitigates vanadium ion crossover from negative to positive and promotes its reverse

transport. Consequently, these opposing fluxes counter each other, resulting in minimal net crossover and stable cell balance.

In the revised Supplementary Information [Section 3.1]

In VRFBs, the vanadium ions transported from one side to the other side induce side reactions, that cause an imbalance in electrolyte valence on the positive and negative sides, as illustrated below. [S1]

Reactions associated with vanadium ion transport from the negative side to the positive side:



Reactions associated with vanadium ion transport from the positive side to the negative side:



As shown in Eq. (S5) - (S10), the crossover of V^{3+} and VO^{2+} consumes equivalent amounts VO_2^+ and V^{2+} , respectively. While the crossover of V^{2+} and VO_2^+ ultimately consumes twice as much as VO_2^+ and V^{2+} , respectively. Combine with the diffusion rates of vanadium ions across the Nafion series membranes ($\text{V}^{2+} > \text{VO}^{2+} > \text{VO}_2^+ > \text{V}^{3+}$).[S2]; this results in a net flux of V^{2+} transport from the negative to the positive side during cycling, accompanied by twice the expected consumption of VO_2^+ . Consequently, crossover leads to the accumulation of surplus V^{2+} on the negative side, whereas a deficiency of VO_2^+ arises on the positive side.

In the revised Supplementary Information, we have added Figs. S1 and S7.

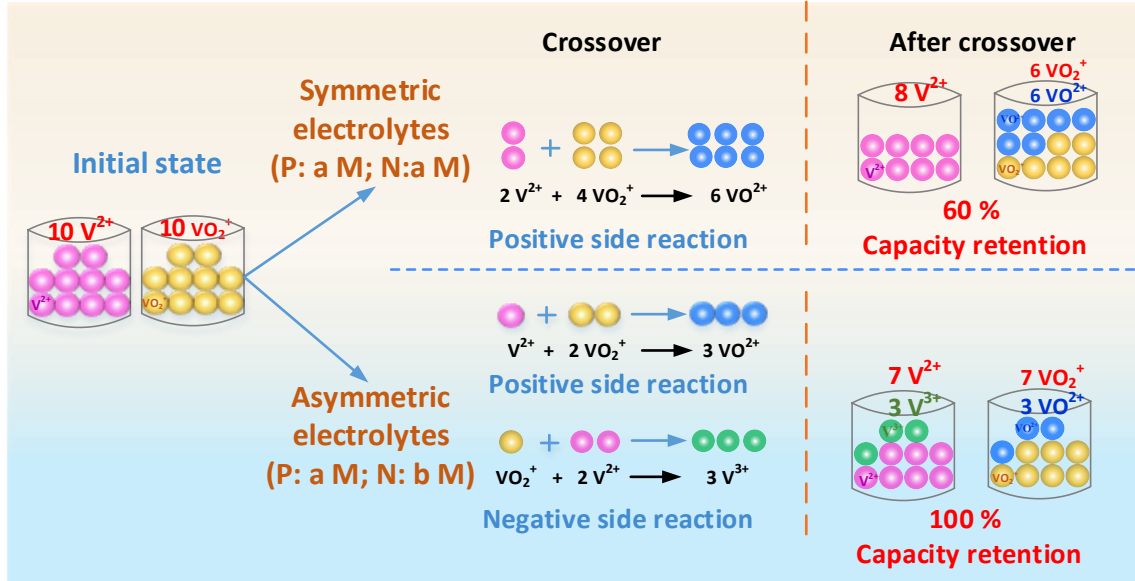


Fig. S1 Schematic illustration of the enhanced discharge capacity in a VRFB employing an asymmetric electrolyte (Note: P and N denote the positive and negative electrolytes, respectively).

As depicted in Fig. S1, the initial state assumes 10 V^{2+} and 10 VO_2^+ on the negative and positive sides, respectively. In a VRFB operated with symmetric electrolytes, crossover leads to the transport of two V^{2+} ions from the negative to the positive side, accompanied by the consumption of 4 VO_2^+ ions. This imbalance in vanadium-ion content and valence across the two sides consequently reduces the capacity to 60%. By contrast, in the VRFB working with asymmetric electrolytes the amount of V^{2+} transport from the negative to the positive side is counterbalanced by an equivalent flux of VO_2^+ in the opposite direction. Therefore, the contents and valence of vanadium ions on the positive and negative sides remain balanced, preserving 100% capacity despite crossover.

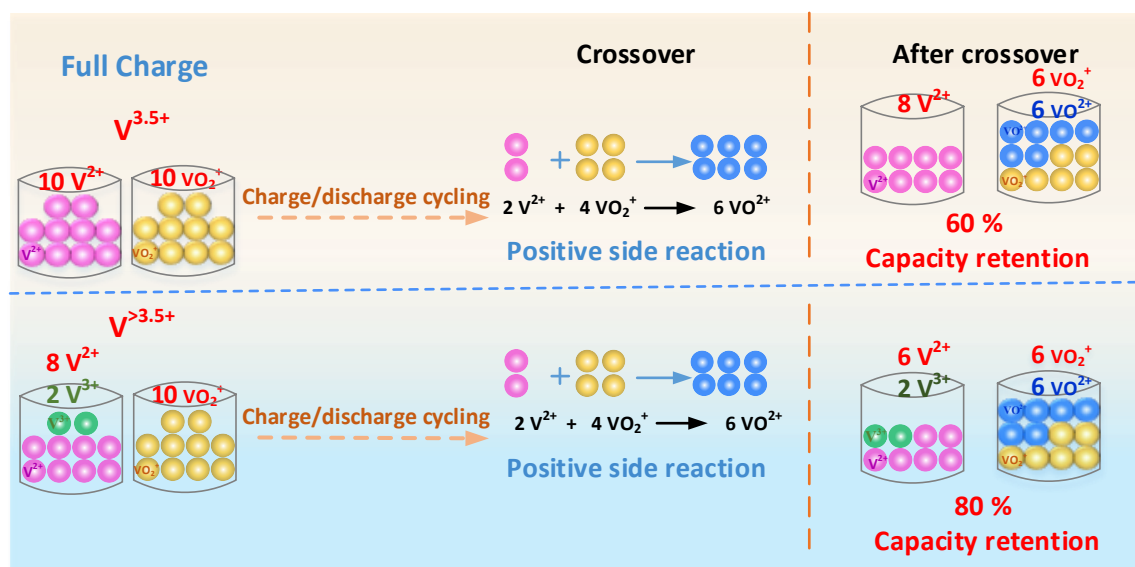


Fig. S7 Schematic of surplus VO_2^+ for suppressing capacity decay.

Fig. S7 demonstrates that increasing the average vanadium valence of electrolyte improves the balance between the positive and negative electrolytes under equivalent crossover conditions, thereby substantially reducing the capacity decay rate.

[S1] Li Y, Skyllas-Kazacos M, Bao J. A dynamic plug flow reactor model for a vanadium redox flow battery cell. *J. Power Sources*. 311: 57-67. (2016)

[S2] Sun C, Chen J, Zhang H, Han X, Luo Q. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. *J. Power Sources*. 195(3): 890-897 (2010)

e. The title is not accurate. The authors are dealing with the imbalance of crossover in vanadium redox flow battery, not overcoming membrane limitations in flow batteries: membrane selectivity are not improved in this manuscript and this method is not useful for other flow batteries that uses different active species in the positive and genitive electrolyte.

Response:

We thank the reviewer for this insightful comment. We have revised the title from “Balanced-State Electrolytes Overcome Membrane Limitations in Redox Flow Batteries” to “Balanced-State Electrolytes Overcome Crossover in Redox Flow Batteries” Furthermore, we have successfully

applied the BSE strategy to iron-vanadium flow batteries with promising results, as detailed in our responses to points a4) and c.

2. Experimental design

a, The exact procedure for determining the BSE composition is not clearly outlined in the main text. Authors should move essential elements of the BSE determination procedure into the main Methods section.

Response:

We thank the reviewer for this valuable suggestion. We have moved the determination procedure of BSE into the main Method section in the revised manuscript, as shown below.

In the revised Manuscript [Section BSE determination]

Determining the balanced state of a VRFB under specified operating conditions is essential for designing BSEs. Specifically, we define the balanced state under specific conditions as one where the capacity decay rate is less than 0.03% per cycle or 0.08% per hour. In addition, the test must last longer than 8 h and include more than 20 cycles, with the discharge capacity showing a monotonic decay versus time or cycle number over the investigated range. The electrolyte concentrations at the balanced state are used for designing BSEs. To ensure the accuracy of these measurements, we converted the electrolytes at the balanced state to $V^{3+}|VO^{2+}$ through full discharge followed by aerial oxidation. To compensate for the elevated average vanadium valence of electrolytes that occurs during cycling due to side reactions, the VO_2^+ content in the initial electrolyte was experimentally increased. The detailed procedure is described in the supplementary information.

b, The manuscript is about balancing the crossover of VRFB with various membranes, yet the permeation constants of all four Vanadium ions through each membrane are not quantified or measured in this manuscript. The manuscript also applied different flow rates on each side of the cell to control the osmosis pressure balance when using asymmetric BSEs. The pressure drop may also influence the permeation (crossover) of ions. The measurement of these conditioned constants

can be scientifically and practically useful, since these constants should provide stronger rationale regarding the determination of BSE compositions.

Response:

We thank the reviewer for these insightful and constructive comments. We fully appreciate the concern regarding the quantification of individual vanadium ion permeation coefficients, which is indeed an important aspect of membrane studies. The core objective of our work, however, was to propose and validate a balancing strategy that does not rely on the prior acquisition of these intrinsic membrane parameters.

To directly address the reviewer's concern regarding pressure effects, we have quantified the effects of pressure drop on vanadium ion transport across the Nafion membrane in the revised supplementary information. The quantified results clearly demonstrate that the pressure drop within the operational range has an insignificant effect on vanadium ion permeation rates, further supporting the previous report [R5] that diffusion is the dominant transport mechanism. Detailed information is provided below. In VRFBs, vanadium ion transport across the membrane is predominantly governed by diffusion, with net migratory and convective fluxes being negligible [R5]. Therefore, the diffusion rates of vanadium ions across the Nafion membrane, as reported in [R2] and summarized in Tab. S1, were used to evaluate the influence of electrolyte concentration on the net flux ratio between the positive and negative sides (Fig. 2a).

Furthermore, the methodological cornerstone of this study is the exploitation of the self-balancing capability of VRFBs. We operated a VRFB equipped with a Nafion membrane under specific operating conditions until it reached a balanced state. By characterizing the electrolytes in VRFBs operating at this balanced state, we determined the concentrations required for the BSEs. Thus, this approach yields distinct BSE compositions for VRFBs under varying operating conditions, independent of direct knowledge of vanadium-ion permeation across different Nafion membranes. As demonstrated here, the BSEs for a VRFB assembled with N212 are (P 1.91 M $V^{3.55+}$; N 1.170 M $V^{3.50+}$), whereas those for a VRFB using N211 are (P 1.83 M $V^{3.54+}$; N 1.15 M $V^{3.50+}$).

Consequently, our approach in this work does not require prior knowledge of the precise permeation constants of different Nafion membranes to determine the BSE compositions. This highlights the unique advantage of our proposed strategy: it provides a universal, experimentally driven framework for deriving balancing solutions for different membrane materials and operating

scenarios, without the prerequisite of engaging in the characterization of intrinsic membrane parameters.

We believe this conceptual innovation offers a fresh perspective for membrane research and electrolyte engineering in VRFBs. We thank the reviewer again for prompting us to articulate this more clearly.

Tab. S1 The diffusion rate of vanadium ions across Nafion membranes. [S1]

Vanadium ions	V^{2+}	V^{3+}	VO^{2+}	VO_2^+
Diffusion coefficient/ $\text{cm}^2 \text{s}^{-1}$	8.767×10^{-7}	3.222×10^{-7}	6.825×10^{-7}	5.897×10^{-7}

In the revised Supplementary Information [Fig. S6].

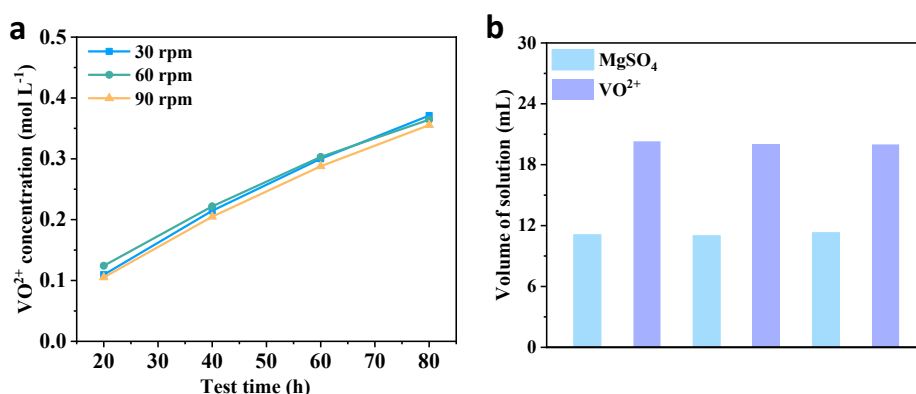


Fig. S6 Pressure drop effects on vanadium ions crossover across the membrane. a, Concentration of VO^{2+} varies with time at different symmetric flow rates. **b,** Volume of $MgSO_4$ and VO^{2+} solution after 80 hours (Note: The reported volume of $MgSO_4$ solution excludes the volume removed for sampling).

In Fig. S6 tests, a flow battery cell assembled with N212 membrane was employed. Two pieces of electrodes with a size of $20.00 \times 20.00 \text{ mm}^2$ were used as the electrodes. 20.00 mL of 1.70 M $MgSO_4$ and 1.70 M $VOSO_4$ solution were pumped into the two sides of the cell using a peristaltic pump, Longer BT100. Hydraulic pressure differences were generated and studied by changing the pump speed from 30 to 90 rpm.

As shown in Fig. S6, neither the VO^{2+} concentration in the $MgSO_4$ solutions nor the solution volumes changed significantly over the tested flow rates, indicating that the effect of pressure drop differences on vanadium ion crossover is negligible.

- [R5] Pilonetto L F, Staciaki F, Nobrega E, et al. Mitigating the capacity loss by crossover transport in vanadium redox flow battery: A chemometric efficient strategy proposed using finite element method simulation. *Chem. Eng. J.* 474: 145336 (2023).
- [R2] Sun C, Chen J, Zhang H, Han X, Luo Q. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. *J. Power Sources.* 195(3): 890-897 (2010)

c. The testing parameters are not controlled, using comparison with two or more parameters changed (Figure 4a, 4c). The effect of cell configuration (electrode thickness, flow field, etc.) was not controlled across different membranes, especially for NC700 and N211 (see SI Section 3). Authors should consider justifying and quantifying how these differences in hardware design influence the results or standardize them across comparisons.

Response:

Thanks for your valuable comment. We have moved Fig. 4a into the supplementary information in the revised manuscript, as detailed in our response to question (c) on conceptual novelty and presentation.

To compare the electrolyte utilization during long-term cycling, discharge capacity versus cycle number is appropriate. This is because VRFBs with different membranes and electrolytes deliver identical cumulative discharge capacities when operated for the same duration at the same current density. In contrast, discharge capacity versus time is more suitable for analysing capacity decay rates according to Fick's law. Therefore, to comprehensively demonstrate the improvement in electrolyte utilization and the reduction in capacity decay afforded by BSEs in VRFBs, both representations—against cycle number and against time—are necessary.

Given the significantly different mechanical properties of Nafion membranes, corresponding electrode adjustments were made. To isolate hardware-related effects, we compared their cycling performances (Fig. R3). All configurations exhibited stable long-term performance. VRFBs assembled with GF-2.5 and GF-1.75 showed nearly identical performance in discharge capacity, coulombic efficiency, and voltage efficiency. The VRFB with carbon cloth (CC) exhibited a similar discharge capacity trend to those with GF-2.5 and GF-1.75 for the first 100 cycles, and a higher capacity thereafter (Fig. R3a). This is attributed to CC's superior mass transfer ability, resulting

from its smaller electrode thickness (0.7 mm vs. 2.5 mm and 1.75 mm), which enhances performance as concentration polarization from crossover becomes more significant. This advantage is also reflected in its higher voltage efficiency after 100 cycles (Fig. R3b).

Furthermore, as noted in our response to comment b in the Experimental section, BSE concentrations were determined by characterizing electrolytes from VRFBs operating at a balanced state. Differences in cell configuration and operating conditions are inherently captured in the resulting balanced state, leading to distinct BSEs—as demonstrated by the differing BSE compositions for VRFBs using N212 (P 1.91 M $V^{3.55+}$; N 1.17 M $V^{3.50+}$) versus N211 membranes (P 1.83 M $V^{3.54+}$; N 1.15 M $V^{3.50+}$). Thus, the effectiveness and applicability of the BSE method remain unaffected by hardware variations, demonstrating its universality. This highlights the unique advantage of our proposed strategy: it provides a universal, experimentally driven framework for deriving balancing solutions for different hardware materials and operating scenarios.

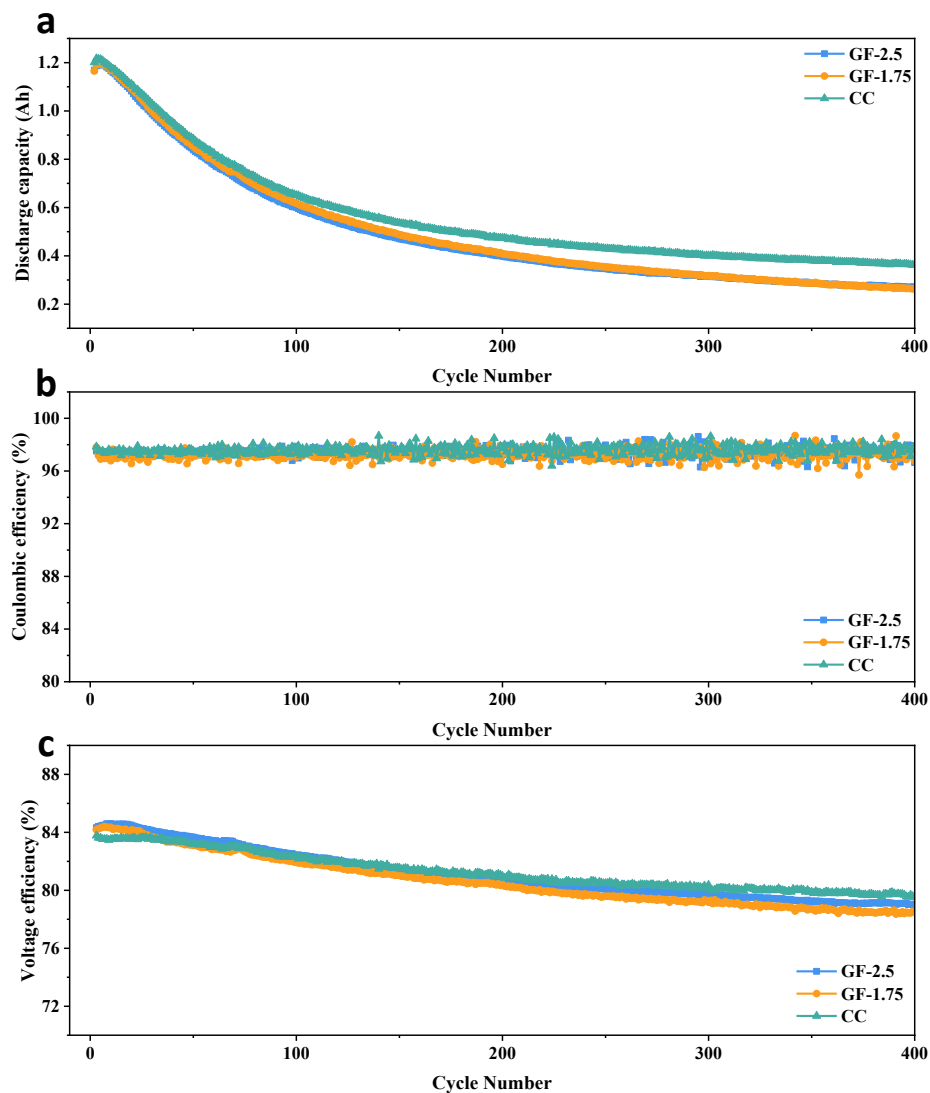


Fig. R3 Battery performance of VRFBs with different electrodes and hardware. a-c discharge capacity (a), coulombic efficiency (b), and voltage efficiency (c) of VRFBs using different electrodes and graphite plates. (Note: GF-2.5 and GF-1.75 denote graphite felt electrodes of 2.5 and 1.75mm thickness, respectively; CC denotes a carbon cloth electrode of 0.7 mm thickness.)

VRFBs assembled with GF-2.5 and GF-1.75 electrodes used graphite plates with serpentine flow fields, whereas the VRFB assembled with the CC electrode used graphite plates with interdigitated flow fields. All VRFB tests employed Nafion 212 as the separator and 40 mL of 1.70 M $V^{3.5+}$ as electrolytes on the positive and negative sides.

3. Modeling and theoretical analysis

a, Authors should describe the performance of their cells using a mechanistic framework (e.g., based on Nernst–Planck, Poisson–Nernst, or coupled Fickian transport) equation, with permeation and migration constants measured as suggested, to demonstrate a straight-forward model that can guide designs of electrolytes. In this case, MD simulations are not as informative for readers – the diffusion rates of ions are changed just because the concentration gradients/differences are changed.

Response:

Thank you for your valuable suggestion. In this work, MD simulations were employed to partially elucidate the effects of BSEs on vanadium ion transport across the membrane at the molecular scale. We agree with your idea about using Nernst–Planck based mechanistic framework to describe battery performances and have incorporated a 2D simulation model (Fig. R4a) generated using Comsol-Multiphysics® software, as shown below.

Fig. R4b illustrates that the theoretical capacity of a VRFB with TEs decreases significantly over time owing to crossover. This stems from the substantially disparate diffusion rates of vanadium ions across Nafion membranes ($V^{2+} > VO^{2+} > VO_2^+ > V^{3+}$), which results in the net flux of electrolyte transport from the negative to the positive sides, producing a steadily increasing concentration disparities between the two sides (Fig. R4c). During cycling, V^{2+} and VO_2^+ are consumed on the negative and positive sides, respectively, due to side reactions (Eqs. R1-R4). Consequently, the contents of V^{2+} and VO_2^+ diminish substantially over time, while those of V^{3+} and VO^{2+} increase, leading to a widening disparity between them over time (Fig. R4d). Hence, enhancing vanadium ion transport from the positive to the negative side while reducing the reverse flux can mitigate crossover-induced capacity loss. As demonstrated in a VRFB using BSEs, crossover is effectively counteracted by elevating the positive-side electrolyte concentration and lowering that on the negative side, reflected in its stable theoretical capacity over time (Fig. R4e). The electrolyte concentrations on both sides likewise remain at stable values over time within the BSE-equipped VRFB (Fig. R4f). In contrast to the progressively widening disparities in V^{2+}/VO_2^+ and VO^{2+}/V^{3+} contents over time in the VRFB with TEs (Fig. R4d), the contents in the VRFB with BSEs were stably maintained at a high matching value (Fig. R4g).

The initially lower theoretical capacity of the BSE-based VRFB compared with the TE-based system arises from the elevated average vanadium valence ($V^{3.55+}$), which results in a reduction of capacity. Nevertheless, long-term testing reveals that raising the average vanadium valence from 3.50 to 3.55 enhances VRFB stability, as evidenced in Fig. R5. These results align closely with the experimental data. We have added the simulation results in the revised supplementary information.

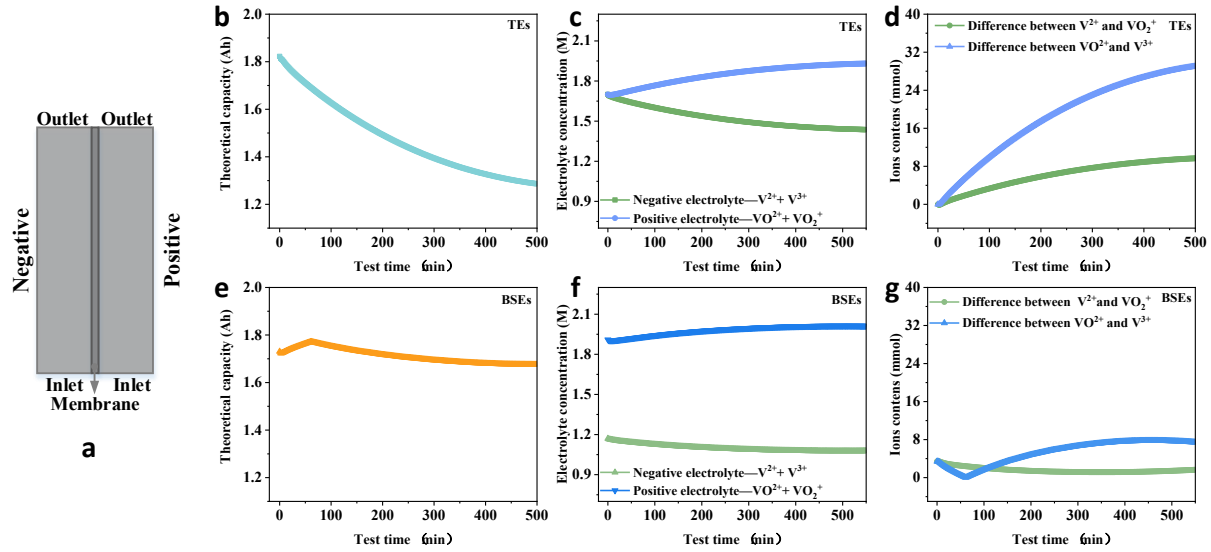


Fig. R4 Simulated cell performance using the TEs (P 1.70 M $V^{3.50+}$; N 1.70 M $V^{3.50+}$) and BSEs (P 1.91 M $V^{3.55+}$; N 1.170 M $V^{3.50+}$). **a**, 2D model built with Comsol software. **b-d**, Theoretical capacity, electrolyte concentration on the positive and negative sides, and difference between V^{2+} and VO_2^+ , as well as V^{3+} and VO^{2+} in the VRFB with TEs at different times. **e-f**, Theoretical capacity, electrolyte concentration on the positive and negative sides, and difference (absolute value) between V^{2+} and VO_2^+ as well as V^{3+} and VO^{2+} in the VRFB with BSEs at different times. [R3]

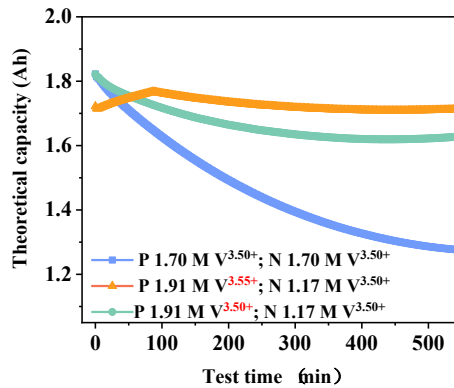


Fig. R5 Effect of elevating the average vanadium valence on capacity decay.

All simulations in Figs. R4 and R5 were performed at 50 states of charge (SOC). A comparative analysis of VRFB performance using TEs and BSEs across different SOC ranges is presented in Fig. R6. Experimental results indicate that the SOC for a VRFB equipped with an N212 and operated at 200 mA cm^{-2} ranges from about 10 to 80 (Fig. 2c). Accordingly, we compared the theoretical capacity of VRFBs using BSEs after 250 and 500 min to that employing TEs over this SOC range, as depicted in Fig. R6a-b. The data reveal that BSEs deliver superior performance to TEs over most of the SOC range, particularly at high SOC values. At SOC values of 10 and 20, the crossover from the positive to the negative side dominates vanadium ion flux across the membrane, consequently resulting in lower performance than that observed with TEs. Throughout the entire charge–discharge process, the net crossover in VRFBs with BSEs was minimized between the positive and negative sides, which enabled a stable discharge capacity over time.

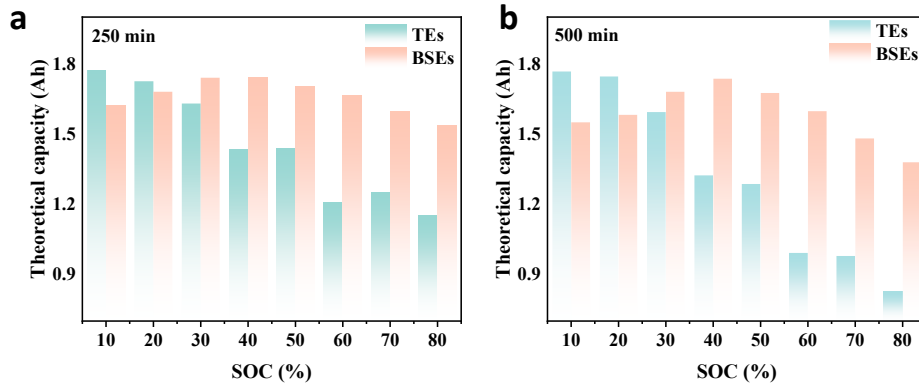


Fig. R6 Performance comparison of VRFBs using TEs and BSEs at different SOC values. Battery performance after **a**, 250 and **b**, 500 min.

In VRFBs, vanadium ion transport across membrane is predominantly governed by diffusion, with net migratory fluxes being negligible [R1]. Accordingly, electric field and electrochemical reactions were excluded from the simulation, which focused on evaluating theoretical capacity retention governed by vanadium ions crossover and side reactions—an approach widely adopted in VRFB modeling studies [R6–8]. The transport of vanadium ions through the electrodes and membrane is described using the Nernst–Planck equation (Eq. R8). The side reactions induced by vanadium ions crossover are summarized in Eqs. R1–R4. The simulation was studied using the Transport of Diluted Species in Porous Media and Chemistry modules in Comsol-Multiphysics® software.

$$\vec{N}_i = -D_i \nabla C_i - z_i \frac{F}{RT} D_i C_i \nabla \phi_i + \vec{v} C_i \quad (\text{Eq. R8})$$

where $\vec{N}_i$, D_i , C_i , and ϕ_i are the flux, diffusion coefficient, bulk concentration, and ionic potential of vanadium ions ($i= 2, 3, 4, 5$, represents V^{2+} , V^{3+} , VO^{2+} , and VO_2^+), respectively, within the electrode and membrane; F , R , T , and v are the Faraday's constant, the universal gas constant, temperature, and electrolyte velocity. Here, the velocity of ions transport in electrode and membrane was set to 0.00439 m/s and 0, respectively.

Side reactions for the vanadium ions transport from the negative to the positive sides:



Side reactions for the vanadium ions transport from the positive to the negative sides:



As shown in Eqs. (R1) - (R4), the crossover of V^{3+} and VO^{2+} consumes equivalent amounts VO_2^+ and V^{2+} , respectively. While the crossover of V^{2+} and VO_2^+ ultimately consumes twice as much as VO_2^+ and V^{2+} , respectively. Consequently, because vanadium species exhibit markedly different diffusion coefficients through Nafion membranes ($V^{2+} > VO^{2+} > VO_2^+ > V^{3+}$), crossover results in net transport of V^{2+} from the negative to the positive sides. This leads to the accumulation of surplus V^{2+} on the negative side, whereas a deficiency of VO_2^+ arises on the positive side. As a result, crossover leads to both concentration and valence imbalances between the positive and negative electrolytes.

The Electrolyte concentration (M) at different SOC's is listed below.

Tab. R1 Electrolyte concentration (M) at different SOC's.

SOC	P/N 40 mL 1.7 M $V^{3.50+}$ Commercial electrolyte		P 35.6 mL 1.91 M $V^{3.55+}$, N 58.1 mL 1.17 M $V^{3.50+}$ BSEs		P 35.6 mL 1.91 M $V^{3.50+}$, N 58.1 mL 1.17 M $V^{3.50+}$ BSEs	
	V^{2+}/V^{3+}	VO^{2+}/VO_2^+	V^{2+}/V^{3+}	VO^{2+}/VO_2^+	V^{2+}/V^{3+}	VO^{2+}/VO_2^+
10	0.170/1.530	1.530/0.170	0.117/1.053	1.624/0.286	0.117/1.053	1.719/0.191
20	0.340/1.360	1.360/0.340	0.234/0.936	1.432/0.478	0.234/0.936	1.528/0.382
30	0.510/1.190	1.190/0.510	0.351/0.819	1.241/0.669	0.351/1.349	1.337/0.573
40	0.680/1.020	1.020/0.680	0.468/0.702	1.050/0.860	0.468/0.702	1.146/0.764
50	0.850/0.850	0.850/0.850	0.585/0.585	0.859/1.051	0.585/0.585	0.955/0.955
60	1.020/0.680	0.680/1.020	0.702/0.468	0.668/1.242	0.702/0.468	0.764/1.146
70	1.190/0.510	0.510/1.190	0.819/0.351	0.477/1.433	0.819/0.351	0.573/1.337
80	1.360/0.340	0.340/1.360	0.936/0.234	0.286/1.624	0.936/0.234	0.382/1.528

Here, the SOC in the VRFB using BSEs is defined as being equivalent to that in a VRFB using TEs at the same charge capacity. The diffusion rate of vanadium ions in electrolytes and across the Nafion membrane is adopted from reported works [R2, R8].

[R2] Sun C, Chen J, Zhang H, Han X, Luo Q. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. *J. Power Sources*. 195(3): 890-897 (2010)

[R3] Wang Z, et al. An electrolyte with elevated average valence for suppressing the capacity decay of vanadium redox flow batteries. *ACS Cent. Sci.* 9(1): 56-63 (2022)

[R5] Pilonetto L F, Staciaki F, Nobrega E, et al. Mitigating the capacity loss by crossover transport in vanadium redox flow battery: A chemometric efficient strategy proposed using finite element method simulation. *Chem. Eng. J.* 474: 145336 (2023).

[R6] Chou Y S, Yen S C, Arpornwichanop A, et al. Mathematical model to study vanadium ion crossover in an all-vanadium redox flow battery. *ACS Sustainable Chem. Eng.* 9(15): 5377-5387 (2021).

- [R7] Oreiro S N, Bontien A, Sloth J, et al. Crossover analysis in a commercial 6 kW/43kAh vanadium redox flow battery utilizing anion exchange membrane. *Chem. Eng. J.* 490: 151947 (2024).
- [R8] You D, Zhang H, Sun C, et al. Simulation of the self-discharge process in vanadium redox flow battery. *J. Power Sources*, 196(3): 1578-1585 (2011).

b, What is the chemical difference between TE and BSE rather than concentration? In that case, what is the physical explanation of TE and BSE having different “vanadium ions’ energies” in Nafion? This raises concern regarding the MD simulation results.

Response:

We appreciate the reviewer for the valuable comments. Besides the concentration difference, the average vanadium valence differs between TE ($V^{3.5+}$) and BSE ($V^{3.55+}$). Changing the vanadium ion concentration influences the affinity of vanadium ions for water, as reported by Li et al. [R9]. Additionally, V-O-V and V-O-S interactions (between SO_4^{2-} , HSO_4^- , and VO_2^+) are strengthened as the electrolyte concentration increasing [R10]. To probe the changes in solvation and coordination, we performed ^{51}V NMR and V K-space (k^3 -weighted) extended X-ray absorption fine structure (EXAFS) of VO_2^+ at different concentrations. (Fig. R7). Both the upfield shift of the ^{51}V resonance and the slight shift of the V-O peak to larger R values with decreasing VO_2^+ concentration indicate a modified coordination environment. These data support the view that increasing the positive electrolyte concentration and the average vanadium valence in BSEs alters the interaction strength of vanadium ions with the sulfonate groups of Nafion. In the MD simulations, these experimentally motivated compositional differences between TEs and BSEs are explicitly implemented in the simulation boxes. The different "vanadium ions’ energies" obtained in Nafion therefore arise naturally from the altered local environment, that is, from changes in ion-water and ion-sulfonate interactions induced by the BSE formulation.

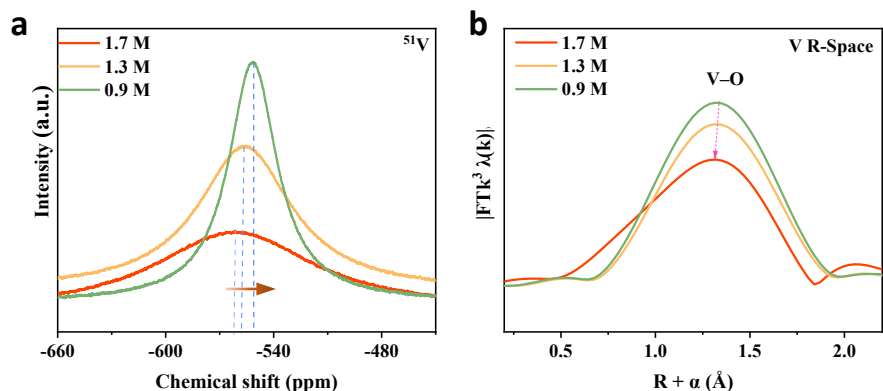


Fig. R7 Variations of VO_2^+ in hydrated solvent structures at different concentrations. a-b Nuclear magnetic resonance of ^{51}V and k^3 -weighted X-ray absorption fine structure for VO_2^+ electrolyte at concentrations of 1.7/1.3/0.9 M.

[R9] Mu, C., Li, T., Zhan, C., Fu, Q., Zhang, Y., Zhang, L., & Li, X. "Harnessing Solvation Chemistry of Pentavalent Vanadium for Wide-temperature Range Vanadium Flow Batteries. *Angew. Chem. Int. Edit.*: e202508456 (2025).

[R10] Kausar, N., Howe, R., & Skyllas-Kazacos, M. Raman spectroscopy studies of concentrated vanadium redox battery positive electrolytes. *J. Appl. Electrochem.*, 31(12), 1327-1332 (2001).

c, If the authors insists on the MD simulations, the current MD simulations are oversimplified. The simulation is limited to ion diffusivity. The simulation should be coupled with membrane hydration and Donnan potential shifts under real operating potential gradients with a longer simulation time.
Response:

Thank you for this insightful suggestion regarding the coupling of membrane hydration and Donnan potential shifts. We agree that incorporating these phenomena would provide a more comprehensive view. However, simulating ion transport under real operating potential gradients over macroscopic timescales (hours to days, as relevant for diffusion in VRFBs) presents a fundamental challenge for molecular dynamics (MD). The computational cost of simulating beyond microsecond timescales with explicit chemistry and external fields is currently prohibitive. In this work, MD simulations were not employed as a quantitative predictive tool but rather served to provide qualitative support for the proposed mechanism. Therefore, our MD simulations were focused on revealing a key intrinsic property—the inherent diffusion energy

barrier of vanadium ions across various Nafion membranes. MD simulations are uniquely suited to resolve the transient interactions between ions and the polymer matrix, thereby revealing the effects of BSEs on vanadium ion transport across the membrane at the molecular scale. We agree that a continuum-based model (e.g., based on the Nernst-Planck framework) is the more appropriate and feasible tool. We have added a 2D simulation model (Fig. R4a) using Comsol-Multiphysics® software, as detailed in the response to question 3a.

Fig. R4b illustrates that the theoretical capacity of a VRFB with TEs decreases significantly over time owing to crossover. This stems from the substantially disparate diffusion rates of vanadium ions across Nafion membranes ($V^{2+} > VO^{2+} > VO_2^+ > V^{3+}$), which results in the net flux of electrolyte transport from the negative to the positive sides, producing a steadily increasing concentration disparities between the two sides (Fig. R4c). Specifically, the contents of V^{2+} and VO_2^+ diminish substantially over time, while those of V^{3+} and VO^{2+} increase, leading to a widening disparity between them over time due to crossover and side reactions (Fig. R4d). Hence, enhancing vanadium ion transport from the positive to the negative side while reducing the reverse flux can mitigate crossover-induced capacity loss. In a VRFB using BSEs, crossover is effectively counteracted by elevating the positive-side electrolyte concentration and lowering that on the negative side, reflected in its stable theoretical capacity over time (Fig. R4e). The electrolyte concentrations on both sides likewise remain at stable values over time within the BSE-equipped VRFB (Fig. R4f). In contrast to the progressively widening disparities in V^{2+}/VO_2^+ and VO^{2+}/V^{3+} contents over time in the VRFB with TEs (Fig. R4d), the contents in the VRFB with BSEs were stably maintained at a high matching value (Fig. R4g).

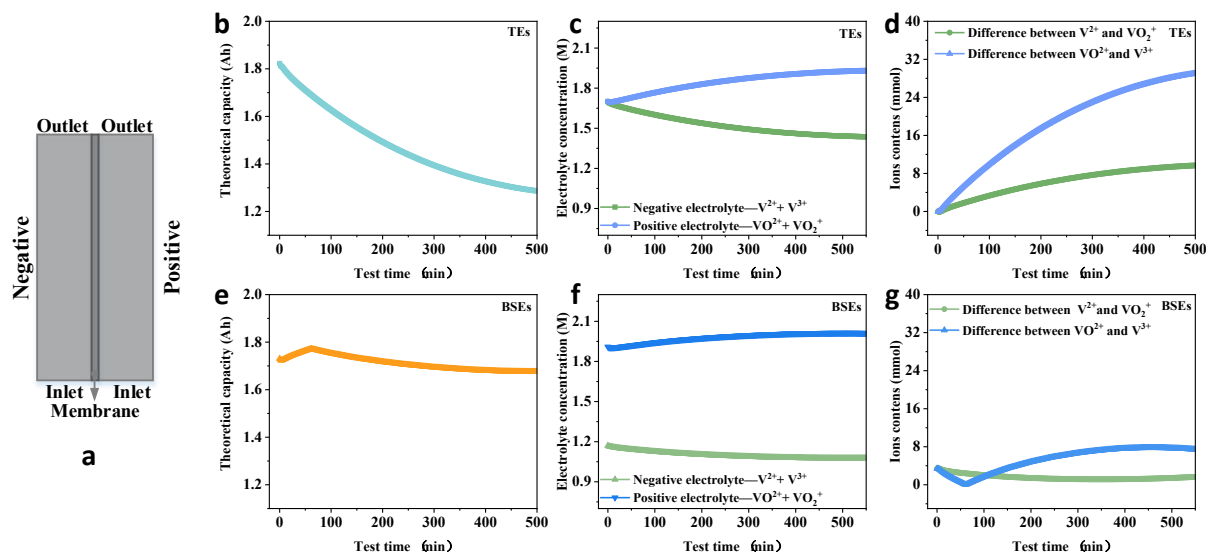


Fig. R4 Simulated cell performance using the TEs (P 1.70 M $V^{3.50+}$; N 1.70 M $V^{3.50+}$) and BSEs (P 1.91 M $V^{3.55+}$; N 1.170 M $V^{3.50+}$). **a**, 2D model built with Comsol software. **b-d**, Theoretical capacity, electrolyte concentration on the positive and negative sides, and difference between V^{2+} and VO_2^{+} , as well as V^{3+} and VO^{2+} in the VRFB with TEs at different times. **e-f**, Theoretical capacity, electrolyte concentration on the positive and negative sides, and difference (absolute value) between V^{2+} and VO_2^{+} as well as V^{3+} and VO^{2+} in the VRFB with BSEs at different times.

The initially lower theoretical capacity of the BSE-based VRFB compared with the TE-based system arises from the elevated average vanadium valence ($V^{3.55+}$), which results in a reduction of capacity. Nevertheless, long-term testing reveals that raising the average vanadium valence from 3.50 to 3.55 enhances VRFB stability, as evidenced in Fig. R5. These results align closely with the experimental data. We have added the simulation results in the revised supplementary information.

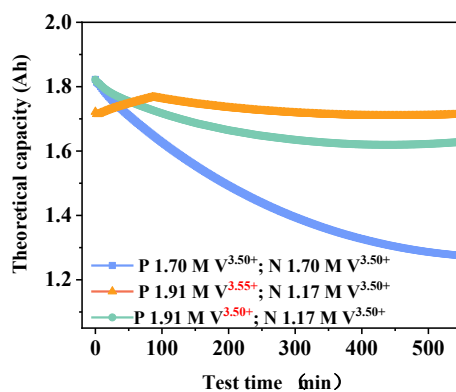


Fig. R5 Effect of elevating the average vanadium valence on capacity decay.

d, Fig. 3h is not informative. What should readers learn from Fig 3h?

Response:

We thank the reviewer for raising this point. We have deleted Fig. 3h in the revised manuscript.

e. Fig. 3i is not explained, and the abbreviation MSD showed without spelled out in the manuscript. What does MSD (nm²) mean?

Response:

We apologize for this oversight. MSD refers to the Mean Squared Displacement. The full definition has been added to the revised manuscript, as indicated below.

In the revised Manuscript [Page 10, Fig. 3i]

i, Mean Squared Displacement (MSD) of ...

f. Fig. 3k may be too obvious: why would someone expect the hydration of V²⁺ changed if just changing a 1.7 M V²⁺ solution into a 2.0 M V²⁺ solution?

Response:

We thank the reviewer for this comment. According to the study by Kausar et al. [R10], various copolymeric vanadium species form when the electrolyte concentration exceeds 2.0 M, which strengthens the V–O–V and V–O–S interactions (involving SO₄²⁻, HSO₄⁻, and VO₂⁺). In this work, we reduced the V²⁺ concentration from 1.70 M to 1.17 M and adjusted the concentrations of other vanadium ions during the preparation of the BSEs. These modifications may attenuate variations in the hydrated structure of V²⁺.

[R10] Kausar, N., Howe, R., & Skyllas-Kazacos, M. Raman spectroscopy studies of concentrated vanadium redox battery positive electrolytes. *J. Appl. Electrochem.*, 31(12), 1327-1332 (2001).

4. Electrochemical performance claims

a, The authors mentioned side reactions at line 184, demonstrating adding V^{5+} to balance the cell SOC. Authors should specify the side reactions and their effects, noting that side reaction of carbon electrode aging is evitable by using inert electrodes. Side reactions of HER or ORR should be balanced by adding V^{4+} or introducing reactants

(<https://doi.org/10.1039/D4EE02450H>, <https://doi.org/10.1016/j.jpowsour.2023.233770>)

Response:

We thank the reviewer for raising this point. Side reactions in VRFBs comprise the aerial oxidation of V^{2+} (Eq. S11) and the hydrogen evolution reaction (HER) (Eq. S12). The oxidation of V^{2+} induced by air increases the contents of V^{3+} , thereby improving the concentration of VO_2^+ on the positive side during charging. The HER generates more VO_2^+ on the positive side than the amount of V^{2+} on the negative side during the charge process. These two side reactions elevate the average vanadium valence in the electrolytes during cycling. We have specified these side reactions in the revised manuscript and supplementary information.



Electrode ageing can be avoided by using inert electrodes; however, to ensure batteries have a good performance, a trade-off between side reactions and electrode activity has been implemented. In this work, although the cells were operated under N_2 protection during battery tests, air ingress remains unavoidable during electrolyte and cell preparation, as well as in flow pipes. Additionally, we set the cut-off voltage to 1.6-0.9 V [R11] during VRFB tests, which is lower than 1.7 V adopted in the second mentioned reference to limit side reactions of HER and ORR. Nevertheless, HER may still exist during long-term cycling coupled with air-induced V^{2+} oxidation, thereby elevating the average vanadium valence of electrolytes. In the first mentioned reference, the authors demonstrated that VO_2^+ electrolyte can be reduced to lower valence electrolyte working as catholyte count to formic acid anolytes in their LFARFCs. In this work, we aimed to identify the balanced state of electrolytes to prepare BSEs. Therefore, we added VO_2^+ to the positive

electrolytes to match the balanced state, which features an elevated average vanadium valence of electrolytes induced by HER and aerial oxidation.

[R11] Wei X, Nie Z, Luo Q, et al. Nanoporous polytetrafluoroethylene/silica composite separator as a high-performance all-vanadium redox flow battery membrane[J]. Advanced Energy Materials, 2013, 3(9): 1215-1220.

In the revised Manuscript [Line 190, Page 7]

Besides concentration variations, the average vanadium valence of the electrolyte is also elevated during cycling due to side reactions (hydrogen evolution reaction and air-induced V^{2+} oxidation, Eq. S15, Eq. S16) on the negative side...

In the revised Supplementary Information [Section 3.2]



V^{2+} is highly sensitive to oxygen and is readily oxidized to V^{3+} by air. The oxidation of V^{2+} with air increases V^{3+} content, thereby improving the concentration of VO_2^+ on the positive side during charging.



The HER generates more VO_2^+ on the positive side than the amount of V^{2+} on the negative side during the charge process. The air-induced V^{2+} oxidation and HER elevate the average vanadium valence of electrolytes during cycling.

b, Fig 2h shows no apparent difference, contracting against the statement.

Response:

We thank the reviewer for raising this point. Yes, there is no apparent difference between the two flow rates in Fig. 2h. In the manuscript, we described that the pressure drop difference between the positive and negative sides is increased due to the viscosity variation after adjusting the

electrolyte concentrations for the balanced state. However, this asymmetric pressure drop has a minimal effect in suppressing capacity decay, as evidenced by the experimental results (Fig. 2h). To make the description clearer, we changed the phraseology in the revised manuscript, as shown below.

In the revised Manuscript [Line 179, Page 7]

Although adjusting electrolyte concentrations to achieve the balanced state increases the pressure drop difference between the positive and negative sides owing to viscosity changes (Fig. S5a), this exerts only a negligible effect on mitigating capacity decay, as evidenced by the lack of discernible differences in Fig. 2g.

c. Line 317: Fig. S16 does not show apparent difference between these two membranes, contracting against the statement.

Response:

We thank the reviewer for raising this point. The discharge capacity curves versus cycle number for VRFBs using N212 and N211 do not have an apparent difference after 50 cycles, by which point the electrolytes are close to the balanced state. The discharge capacity of the VRFB with N211 is higher than that with N212 at the initial stage, but decreases rapidly to similar values to those with N212 after around 50 cycles, as shown in Fig. S16. To enhance clarity, we have added clarifying phrases in the revised manuscript, as shown below.

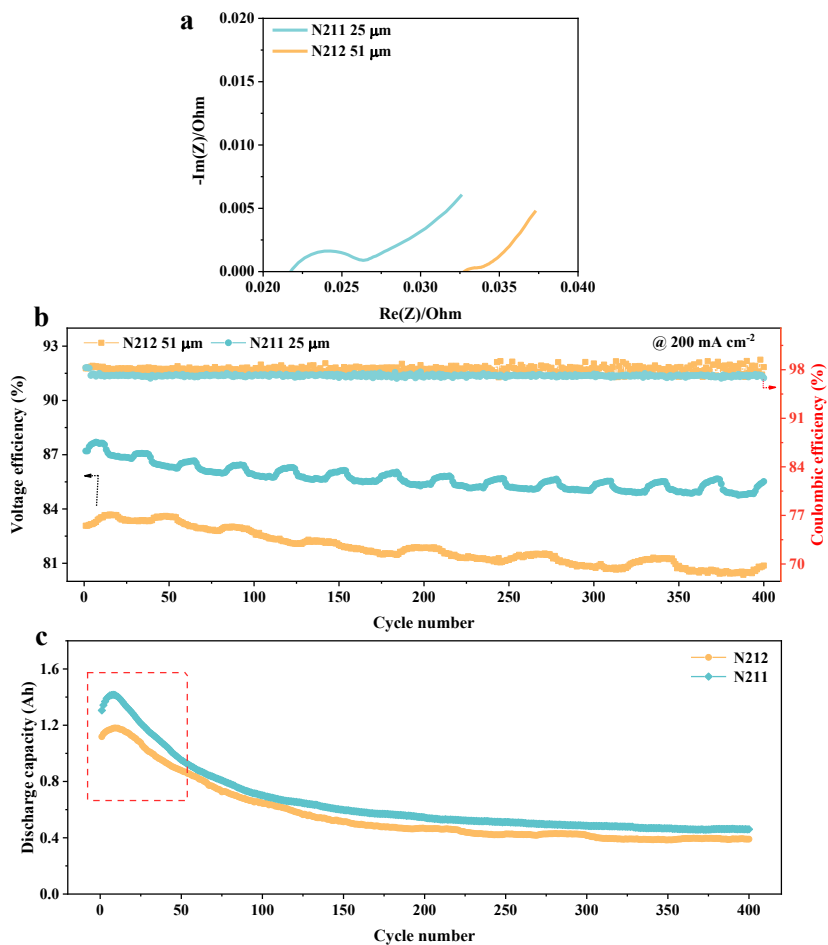


Fig. S16 Performance comparison of VRFBs employing N212 and N211 membranes with traditional electrolytes. a, The EIS spectrum b, voltage/coulombic efficiency, and c, discharge capacity of VRFBs using N212 and N211 membranes over cycling.

In the revised Manuscript [Line 310, Page 13]

Decreasing the Nafion membrane thickness from 51 μm (N212) to 25 μm (N211) greatly reduces membrane resistance and improves voltage efficiency. However, it leads to more severe capacity decay than N212 in the first 50 cycles (Fig. S23).

d. Line 373: no clear experimental evidence of modulating the interactions between vanadium ions and sulfonic acid groups, contracting against the statement. The authors only changed the concentration of the electrolytes.

Response:

We thank the reviewer for this insightful comment. We have added Raman and XPS spectra in the revised supplementary information to validate the interactions between vanadium ions and sulfonic acid groups (Fig. S17). Results show that the Raman peak position of sulfonic acid groups shifts upon immersion of the Nafion membrane in vanadium electrolytes, demonstrating the interactions between vanadium ions and sulfonic acid groups [R12]. It is more evident in the XPS results (Fig. S17b), where both the position and intensity of the O 1s peak attributable to the sulfonic acid groups (534.89 eV) markedly shift to lower values after introducing vanadium ions into Nafion membranes [R13, R14]. These results are consistent with prior reports of such interactions between vanadium ions and the sulfonic acid groups in Nafion membranes by Cho [R15] and Vijayakumar [R16]. Furthermore, increasing the vanadium ion concentration strengthens the interaction between vanadium ions and the sulfonic acid sites of Nafion, thereby reducing vanadium ion permeability. [R16]

In the revised Supplementary Information [Fig. S17]

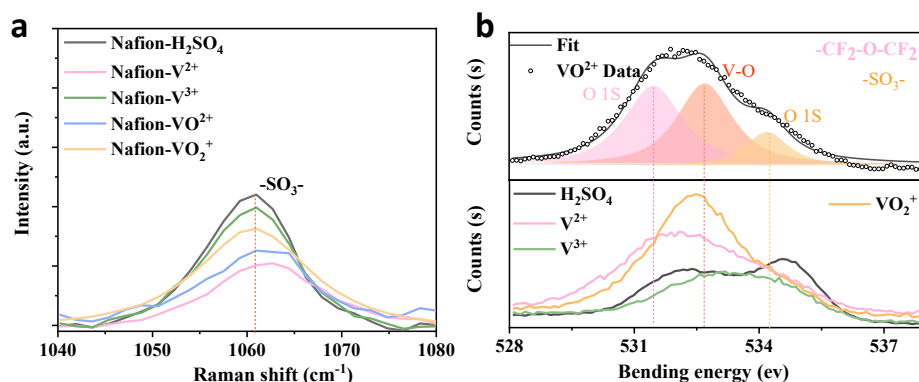


Fig. S17 Interactions between vanadium ion and sulfonic acid groups. **a**, Raman and **b**, XPS spectra of Nafion 212 immersed in different solutions.

In these tests, Nafion 212 was immersed separately for 5 days in 3.0 M H₂SO₄, 1.7 M V²⁺, V³⁺, VO²⁺, and VO₂⁺. As depicted in Fig. S17a, the Raman peak position of sulfonic acid groups shifts upon immersion of the Nafion membrane in vanadium electrolytes, demonstrating the interactions between vanadium ions and sulfonic acid groups [S5]. It is more evident in the XPS results (Fig. S17b), where both the position and intensity of the O 1s peak attributable to the sulfonic acid

groups (534.89 eV) markedly shift to lower values after introducing vanadium ions into Nafion membranes [S6, S7].

- [R12] Choi, J. S., Tsui, J. H., Xu, F., Lee, S. H., Sung, S. K., Lee, H. J., & Kim, D. H. Fabrication of micro-and nanopatterned Nafion thin films with tenable mechanical and electrical properties using thermal evaporation-induced capillary force lithography. *Adv. Mater. Interfaces*, 8(7), 2002005, (2021).
- [R13] Nguyen, H. T. T., Jung, D., Park, C. Y., & Kang, D. J. (2015). Synthesis of single-crystalline sodium vanadate nanowires based on chemical solution deposition method. *Mater. Chem. Phys.* 165, 19-24.
- [R14] Ma Andersen S. The importance of ion selectivity of perfluorinated sulfonic acid membrane for the performance of proton exchange membrane fuel cells. *J. Fuel Cell Sci. Tech.* 12(6): 061010, (2015).
- [R15] Cho H S, Ohashi M, Van Zee J W. Absorption behaviour of vanadium in Nafion®. *J. Power Sources*. 267: 547-552 (2014).
- [R16] Vijayakumar M, Govind N, Li B, et al. Aqua-vanadyl ion interaction with Nafion® membranes. *Front. Energy Res.* 3: 10, (2015).

Minor concerns:

5. Broader impact and scalability

The cost analysis (Fig. 5h) indicates the practical significance of the BSE approach. However, the assumptions behind the >40% cost reduction are not fully transparent. Author should include their detail TEA with a table listing assumptions (e.g., membrane price, electrolyte cost per kg, system lifetime) and perform a sensitivity analysis with fare comparison with previous/commercial rebalancing techniques.

Response:

We thank the reviewer for this suggestion. A detailed calculation process and a cost table have been included in the supplementary information, as provided below.

Our cost analysis focused solely on the membrane and electrolyte components. As shown in Fig. 3, VRFBs employing BSEs demonstrate superior energy efficiency compared to those using

traditional electrolytes (TEs). This higher efficiency translates into an advantage in power-density-related costs. Furthermore, the average viscosity of the BSEs is 3.958 mPa·s, lower than the 4.456 mPa·s of the TEs, suggesting a reduction in pump power loss. However, no direct correlation exists between capital costs and power density or pump power. We therefore consider only the membrane and electrolyte costs as a proportion of the overall system costs (based on a 1 MW/4 MWh system) when calculating the capital cost reduction upon adoption of BSEs. The details of this calculation are provided below.

In the revised Supplementary Information [Section 7]

Tab. S2 Electrolyte utilization in VRFBs with different systems.

VRFB system	Accumulated discharge capacity over 400 cycles (Ah)	Discharge capacity over 400 cycles (Ah cycle ⁻¹ mol ⁻¹)
Current advanced system	225.10281	4.137919301
System with BSEs	486.2741	8.938862132

The discharge capacity of electrolytes per cycle per mol ($D_{CP}/\text{Ah mol}^{-1}$) is calculated as follows:

$$D_{CP} = \frac{D_{AC}}{C_{NO}} \times \frac{1000}{V_E \cdot E_C} \quad (\text{Eq. S24})$$

where D_{AC} , C_{NO} , V_E , and E_C represent the accumulated discharge capacity (Ah), the cycle number, the electrolyte volume (mL), and the electrolyte concentration (M), respectively.

The capital cost reduction for a VRFB system using BSEs and NC700 can be calculated as below:

$$C_{Cr} = (C_{R-M} + C_{R-E}) - (C_{R-M} \times M_{CR} + C_{R-E} \times E_{CR}) \quad (\text{Eq. S25})$$

where, C_{Cr} is the capital cost reduction ratio; C_{R-M} and C_{R-E} are the cost ratio of membrane (10.08%) and electrolyte (62.79%), respectively, over the capital cost of a current advanced 1 MW/4 MWh VRFB system; [32] M_{CR} and E_{CR} are the corresponding cost ratios of the membrane and electrolyte in the BSEs and NC700 based system [33] relative to a currently advanced VRFB system.

$$M_{CR} = \frac{472.281}{2329.825} \quad (\text{Eq. S26})$$

$$E_{CR} = \frac{4.137919}{8.938862} \quad (\text{Eq. S27})$$

Hence, the capital cost reduction for a VRFB system with BSEs compared to the current advanced VRFB system can be obtained:

$$C_{Cr} = (10.08 + 62.79) - \left(10.08 \times \frac{472.281}{2329.825} + 62.79 \times \frac{4.137919}{8.938862} \right) = 41.76 \quad (\text{Eq. S28})$$

The specific costs of electrolyte and membrane in different VRFB systems are listed in Tab. S3.

Tab. S3 Membrane and electrolyte costs as a proportion of the capital cost in a 1 MW/4 MWh VRFB system. [S8, S9]

	Membrane type	Membrane cost/ m ² (\$)	Membrane to capital cost ratio	Discharge capacity over 400 cycles (Ah cycle ⁻¹ mol ⁻¹)	Electrolyte to capital cost ratio
Current advanced system	N212	2329.825	10.80%	4.14	62.79%
System with BSEs	NC700	472.281	2.19%	8.94	29.08%

[S8] Chen H, Zhang X, Wu S, et al. A comparative study of iron-vanadium and all-vanadium flow battery for large scale energy storage. *Chem. Eng. J.* 429: 132403 (2022).

[S9] [https://www.fuelcellstore.com/pfsa-d50u-proton-exchange-membrane-87010020?search=Nafion 212](https://www.fuelcellstore.com/pfsa-d50u-proton-exchange-membrane-87010020?search=Nafion+212)

6. Language and clarity

While the manuscript is generally readable, grammatical inconsistencies and stylistic issues detract from the clarity (e.g., line 209-210 sentence has no verb). Authors should also revise for clarity, especially in experimental procedures and descriptions of diffusion processes.

Response:

We are grateful for these corrections. We have revised the manuscript to address the grammatical

inconsistencies and stylistic issues, and to improve clarity throughout. The manuscript has been refined by a native English speaker.

Reviewer #2 (Remarks to the Author):

In this work, the authors propose an electrolyte design based on balanced-state electrolytes, rather than membrane design, to mitigate the capacity decay of redox flow batteries. This approach addresses the trade-off between ion conductivity and the permeability of active materials in VRFBs. While the study presents an interesting strategy to enhance the cycling stability of flow batteries, certain sections require modification and further discussion. I would recommend publication in this journal after major revision.

Response:

We are grateful to the reviewer for their encouraging assessment. We have provided a point-by-point response to each of their detailed comments below.

1. In the Abstract, the authors state that “battery employing a 15 μm -thick Nafion membrane with balanced-state electrolytes achieves a 75.4% reduction in capacity decay rate (over 1,000 cycles) compared to a system using a 183 μm thick Nafion membrane with conventional electrolytes.” It would be helpful to also provide the capacity fading rate per cycle or the capacity retention after 1,000 cycles. Additionally, please specify the total testing duration (in hours) for 1,000 cycles. Furthermore, for a more accurate evaluation of the electrolyte design effect on capacity decay, the comparison should be conducted using Nafion membranes of the same thickness.

Response:

Thanks for your valuable suggestions. We have added the fading rate per cycle in the revised manuscript as shown below. The test duration of the VRFB employing a 15 μm -thick Nafion membrane with balanced-state electrolytes is 695.65 h over 1,000 cycles, whereas that of the

VRFB using a 183 μm -thick Nafion membrane with traditional electrolytes is 283.54 h. We have compared the BSEs effects on the capacity decay of VRFB with Nafion 212 in Fig. 3a. It shows that the capacity decay rate of a VRFB with the BSEs reduced by 86.3% from 0.182% to 0.025% per cycle, over 400 cycles. To enhance clarity, we have emphasized that the tests were conducted in VRFBs using Nafion 212, as detailed below. The comparison between a battery employing a 15 μm -thick Nafion membrane with balanced-state electrolytes and a system using a 183 μm -thick Nafion membrane with conventional electrolytes aims to highlight the advantages of BSEs.

In the revised Manuscript [Line 25, Page 1, Section abstract]

a battery employing a 15 μm -thick Nafion membrane with balanced-state electrolytes achieves a 75.4% reduction in capacity decay rate— from 0.061% to 0.015% per cycle over 1,000 cycles— compared to a system using a 183 μm -thick Nafion membrane with traditional electrolytes.

In the revised Manuscript [Fig. 3a]

A VRFB employing an N212 membrane with the BSEs (P 1.91 M $\text{V}^{3.55+}$; N 1.170 M $\text{V}^{3.50+}$) exhibit an 86.3% reduction in capacity decay rate—from 0.182% to 0.025% per cycle—and a 71.0% increase in accumulated discharge capacity (from 256.97 to 439.35 Ah) over 400 cycles, compared to that using traditional electrolytes (P 1.70 M $\text{V}^{3.50+}$; N 1.70 M $\text{V}^{3.50+}$) (Fig. 3a).

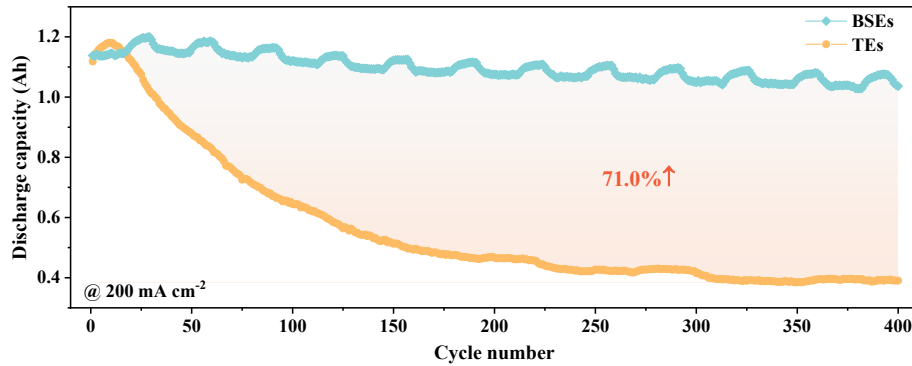


Fig. 3a, Effects of BSEs (P 1.91 M $\text{V}^{3.55+}$; N 1.17 M $\text{V}^{3.50+}$) on suppressing capacity decay of VRFBs using N212.

2. In the Abstract, the authors state that “Crucially, the balanced state electrolyte approach removes membrane limitations in redox flow battery development and opens new avenues for advanced electrolyte design.”. To claim that this approach can remove membrane limitations, it would be necessary to evaluate its performance with a wider variety of membrane types, rather than testing solely with a Nafion membrane.

Response:

Thanks for your suggestions. The BSEs are defined by a crossover flux of vanadium ions from the negative to the positive side that is counterbalanced by an equivalent flux in the opposite direction. The methodological cornerstone of this study is the exploitation of the self-balancing capability of VRFBs. We operated a VRFB equipped with a Nafion membrane under specific operating conditions until it reached a balanced state. By characterizing the electrolytes in VRFBs operating at this balanced state, we determined the concentrations required for the BSEs. We evaluated two other widely studied membranes—polybenzimidazole (PBI) and sulfonated poly(ether ether ketone) (SPEEK)—both of which exhibited a linear decay in discharge capacity with cycling and failed to reach a balanced state [R17, R18] (Figs. R8 and R9), suggesting that they are not viable. To be more rigorous, we have corrected “the balanced-state electrolyte approach removes membrane limitations” to “significantly reduces membrane limitations” in the revised manuscript, as shown below.

[Figure Redacted]

[Figure Redacted]

In the revised Manuscript [Line 28, Page 1 and Section conclusion]

Crucially, the balanced-state electrolyte approach significantly reduces membrane limitations in redox flow battery...

Furthermore, this work significantly reduces membrane limitations in redox flow battery development...

3. In page 2, the authors state that “The cation exchange membrane (CEM) is a critical component in RFBs, ideally conducting proton while preventing the crossover of active species.”. However, the choice of ion exchange membrane for an RFB depends on the type of active material used. Some active materials require an anion exchange membrane, while others can operate with a porous membrane without ion selectivity. For acidic electrolytes, proton conductivity is important, whereas in alkaline electrolytes, conductivity of other ions may be more relevant. Please clarify

which specific type of RFB this study focuses on. Additionally, note that in many RFBs employing organic active materials such as quinones, capacity decay is generally not dominated by active material crossover.

Response:

Thanks for your valuable suggestions. In this work, our focus is specifically on aqueous flow batteries employing acidic electrolytes. We have clarified this scope in the revised manuscript, as indicated below.

In the revised Manuscript [Line 37, Page 2]

The cation exchange membrane (CEM) is a critical component in aqueous RFBs operating in acidic electrolytes.

4. In page 2, the authors state that “Despite these advances, challenges persist in the applicability of these membranes in inorganic/organic RFB systems, including low proton conductivity, scalability issues, escalated costs, and long-term stability concerns.”. However, in most organic RFB systems, active material crossover is generally not a significant issue. This sentence should be revised accordingly.

Response:

Thanks for your corrections. We have we have revised the manuscript and clarified the types of RFBs to aqueous RFBs employing acidic electrolytes, as detailed below.

In the revised Manuscript [Line 44and 46, Page 2]

Despite these advances, challenges persist in the applicability of these membranes in aqueous RFBs with acidic electrolytes ...

Consequently, almost all the commercially available membranes for such RFBs are Nafion-based membranes...

5. In Figs. 1-3, please revise the discharge capacity units from Ah to volumetric discharge capacity (Ah/L), as volumetric capacity is a more relevant metric for evaluation.

Response:

Thanks for your suggestion. In VRFBs, electrolyte volumes change during cycling, making the unit Ah/L problematic for assessing long-term performance. Furthermore, in this work, we mitigated capacity decay by formulating BSEs. This approach required different electrolyte volumes for BSEs and TEs to maintain identical total vanadium contents. Consequently, converting discharge capacity from Ah to Ah/L would yield different initial values, obscuring a direct comparison of cycling performance between the two systems.

6. In page 4, the authors state that “Fig. 1a shows that the discharge capacity of the VRFB with Nafion 212 first increases for a short period and then rapidly decays between about 10-200 cycles.”. Please provide an explanation for the initial short-term increase in discharge capacity.

Response:

We thank the reviewer for this insightful comment. The initial increase in discharge capacity arises from non-equilibrium transport of ions and water across the Nafion membrane. [R4] As shown in Fig. R10a, voltage efficiency remains unchanged during this increase, indicating that it does not stem from variations in activity. At this stage, the limiting factor for capacity is the active material in the positive electrolyte. [R4] Crossover drives vanadium-ion transport from the negative to the positive side (Figs. 1b and S21) and increases VO^{2+} contents on the positive side through side reactions (Eq. S5 & S7). This interpretation is supported by the experiment in Fig. R10b: adding 10 mL of VO^{2+} electrolyte to the positive side markedly improved the discharge capacity and eliminated the initial rising trend.

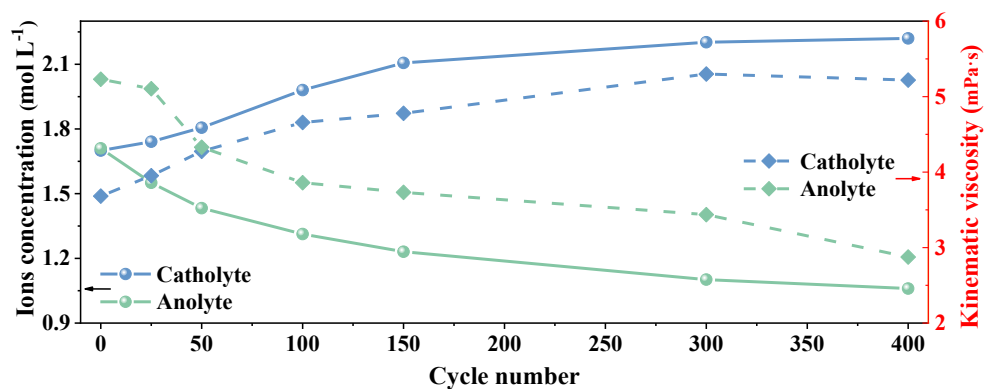


Fig. 1b Electrolyte concentration/viscosity change with cycling of the VRFB equipped with Nafion 212 and traditional electrolytes at 200 mA cm⁻².

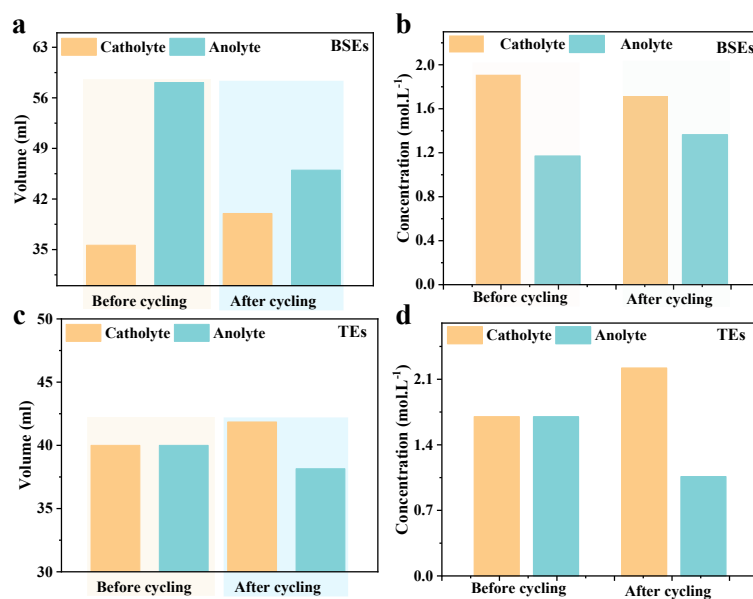


Fig. S21 Changes in electrolytes before and after cycling. (a-b) Volume and concentration changes in VRFBs with BSEs (P 1.91 M V^{3.55+}; N 1.17 M V^{3.50+}) (c-d) Volume and concentration changes in VRFBs with TEs (P 1.70 M V^{3.50+}; N 1.70 M V^{3.50+}).

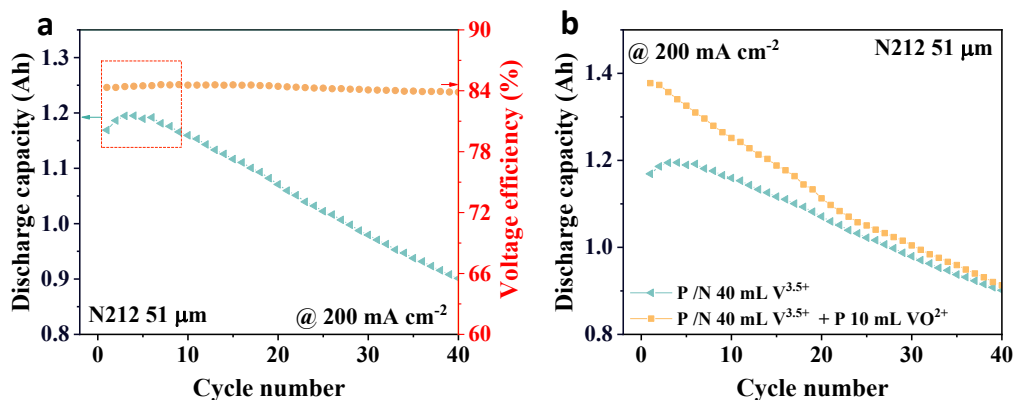


Fig. R10 Initial rise in the discharge capacity of VRFBs. a, Cycling performance showing discharge capacity and voltage efficiency. **b,** Influence of VO²⁺ concentration in the positive electrolyte on the discharge capacity (All tests were conducted at 25 °C).



[R4] Mu D, Zhao Y, Yu L, et al. Asymmetric vanadium flow batteries: long lifespan via an anolyte overhang strategy. *Phys. Chem. Chem. Phys.* 19(43): 29195-29203 (2017).

7. In page 6, the authors state that “The complex ion transport model in VRFBs, combined with the dynamic evolution of electrolytes over extended cycling, complicates this task.”. Please explain more clearly on the meaning of “dynamic evolution” in this context, providing specific details.

Response:

We thank the reviewer for this comment. The concentration and volume of positive and negative electrolytes vary with cycling caused by crossover, as illustrated in Figs. 1a-b and Fig. S21. Furthermore, side reactions (detailed below) triggered by crossover result in an imbalance both in the concentration and vanadium valence of electrolytes between the positive and negative sides, which influences the SOC of electrolytes during the charge and discharge process. This SOC variation, which significantly affects the vanadium ion flux across the membrane (Fig. 2b), along with concentration-driven water transfer, governs the dynamic behaviour. Moreover, changes in electrolyte concentration affect water transport between the positive and negative sides. Vanadium ions drag different amounts of water during crossover ($\text{V}^{2+} \cdot 6\text{H}_2\text{O}$, $\text{V}^{3+} \cdot 6\text{H}_2\text{O}$, $\text{VO}^{2+} \cdot 5\text{H}_2\text{O}$,

$\text{VO}_2^+ \cdot 4\text{H}_2\text{O}$) [R4], compelling $\text{H}^+ \cdot 2\text{H}_2\text{O}$ transport in the opposite direction to maintain the electroneutrality. [R2] The complex interplay during ion transport results in the characteristic multi-stage dynamics of discharge capacity observed during cycling (Fig. 1a), consistent with prior reports [R19].

Side reactions for the vanadium ions transport from the negative to the positive sides:



Side reactions for the vanadium ions transport from the positive to the negative sides:

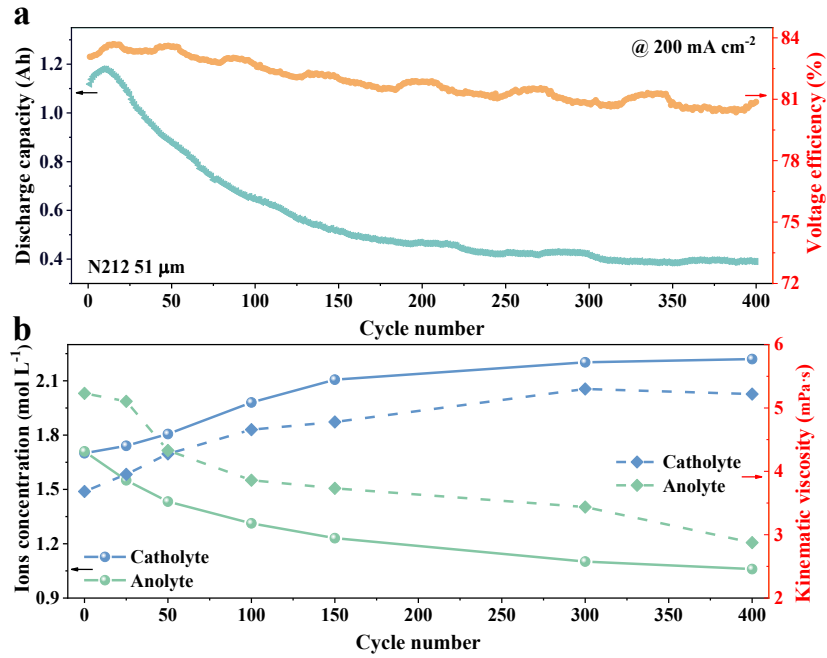


Fig. 1 Battery performances and electrolyte properties vary with cycling. a, Discharge capacity/voltage efficiency and **b,** electrolytes' concentration/viscosity change with cycling of the VRFB equipped with Nafion 212 and traditional electrolytes at 200 mA cm⁻².

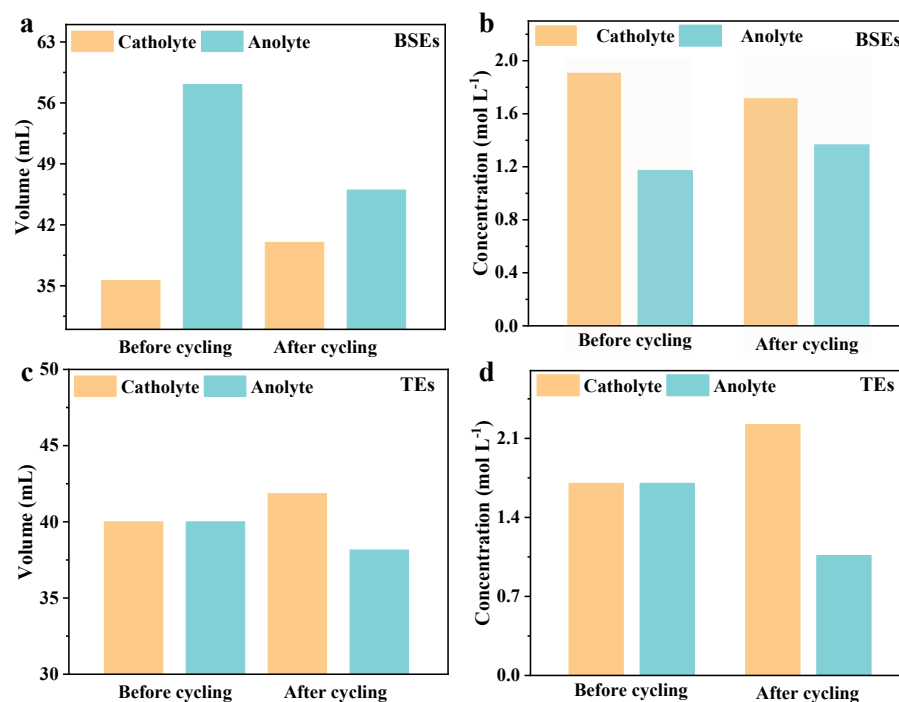


Fig. S21 Changes in electrolytes before and after cycling. (a-b) Volume and concentration changes in VRFBs with BSEs (P 1.91 M V^{3.55+}; N 1.17 M V^{3.50+}) **(c-d)** Volume and concentration changes in VRFBs with TEs (P 1.70 M V^{3.50+}; N 1.70 M V^{3.50+}).

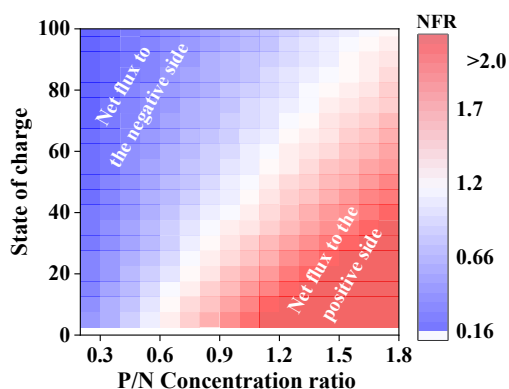


Fig. 2b Electrolyte concentrations on the positive and negative sides affect the net flux ratio under different SOC.

- [R2] Sun C, Chen J, Zhang H, et al. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. *J. Power Sources*. 195(3): 890-897, (2010).
- [R4] Mu D, Zhao Y, Yu L, et al. Asymmetric vanadium flow batteries: long lifespan via an anolyte overhang strategy. *Phys. Chem. Chem. Phys.* 19(43): 29195-29203 (2017).

[R19] Lei Y, Zhang B W, Bai B F, et al. A transient electrochemical model incorporating the Donnan effect for all-vanadium redox flow batteries. *J. Power Sources*. 299: 202-211, (2015).

8. In Fig. 3, could you also provide data on power density, voltage efficiency, or energy efficiency? In the Introduction, it is stated that this electrolyte design method can address the trade-off between ion conductivity and selectivity without compromising power density, which is a key advantage over membrane design. Therefore, this aspect should also be addressed and supported with relevant data in the study.

Response:

Thanks for your valuable suggestion. We have included a comparison of the power density in VRFBs using BSEs and TEs in the revised manuscript. Fig. 3h shows that the power density of VRFB is improved by adopting BSEs compared to that employing TEs due to the enhanced VE (Fig. S9). To clarify the influence of BSEs on VRFB power density, we have added relevant discussion in the revised text, as detailed below.

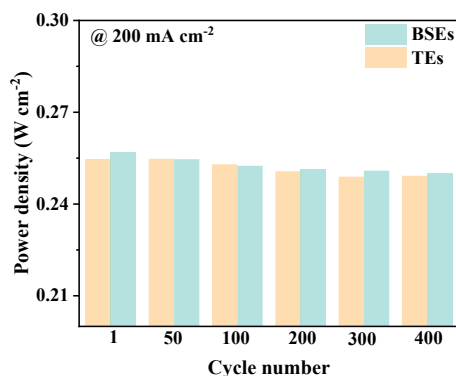


Fig. 3h Power density of VRFBs with BSEs and TEs at different cycles (calculated with medium voltage).

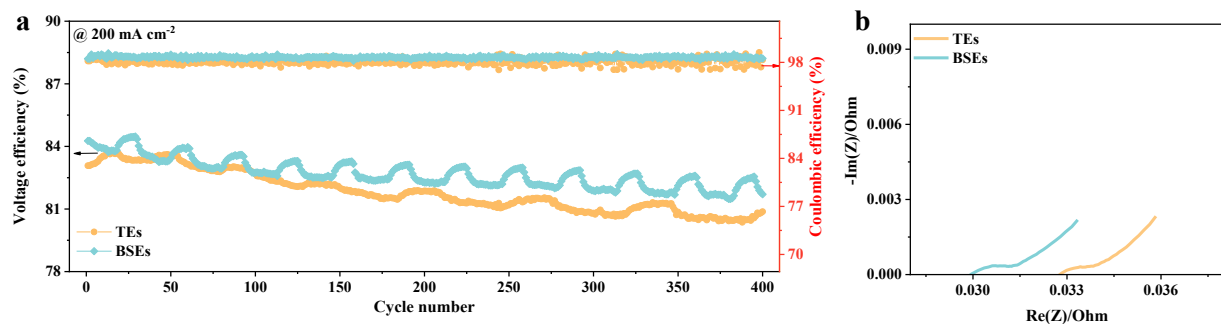


Fig. S9 Performance comparison of VRFBs with balanced-state electrolytes (BSEs) and traditional electrolytes (TEs). Comparison of **a**, the voltage/coulombic efficiency and **b**, electrochemical impedance spectroscopy (EIS) spectrum.

In the revised Manuscript [Fig. 3h]

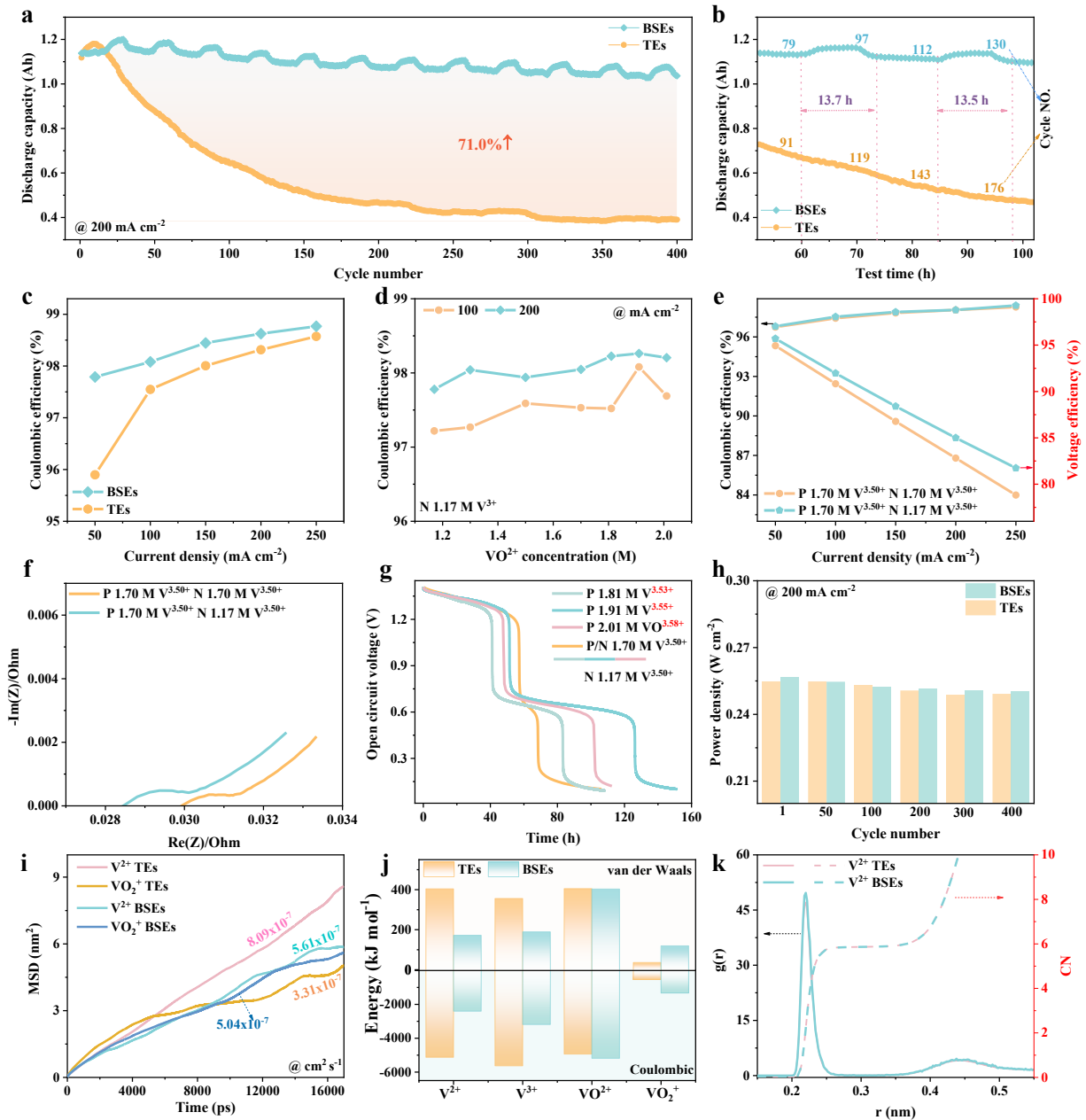


Fig. 3 Mechanism of suppressing crossover using balanced-state electrolytes. a, Effects of BSEs (P 1.91 M V^{3.55+}; N 1.17 M V^{3.50+}) on suppressing capacity decay of VRFBs using N212. **b**, Fluctuation of discharge capacity over time due to temperature variation. **c**, Effects of BSEs on coulombic efficiency. **d**, Coulombic efficiency vs. VO²⁺ concentration. **e**, Coulombic/voltage efficiency and **f**, VRFB resistance, after decreasing the concentration of negative electrolyte from 1.7 to 1.17 M. **g**, Self-discharge curves of a VRFB with different electrolyte concentrations. **h**, Comparison of VRFB power density using BSEs and TEs. **i**, Mean Squared Displacement (MSD) of V²⁺ and VO₂⁺ ions. **j**, van der Waals, and coulombic energy between

vanadium ions and sulfonic acid groups. **k**, Radial distribution function/coordination numbers of V^{2+} in Nafion membrane with the BSEs and TEs (P 1.70 M $V^{3.50+}$; N 1.70 M $V^{3.50+}$).

In the revised Manuscript [Line234, Page 9]

Furthermore, the power density of the VRFB does not decrease using BSEs; rather, it improves markedly compared with that of the system using TE (Fig. 3h) due to the enhanced VE (Fig. S9).

9. In Fig. 3, please also indicate the total testing time for 400 cycles.

Response:

We thank the reviewer for this comment. The VRFB employing BSEs exhibited a total testing duration of 289.49 hours over 400 cycles, which is significantly longer than the 175.67 hours recorded for the system with TEs. This comparative data has been added to the revised supplementary information.

In the revised Supplementary Information [Line 243, Page 12]

The VRFB employing BSEs operated for 289.49 hours over 400 cycles, which is significantly longer than the 175.67 hours achieved by the VRFB with TEs.

10. In Fig. 4, the thickness of the Nafion membrane should be kept the same in order to isolate and accurately assess the effect of the electrolyte design on the stability of VRFBs with balanced-state electrolytes.

Response:

We thank the reviewer for this suggestion. We have directly compared the effect of BSEs on capacity decay in VRFBs equipped with the same thickness of Nafion membrane (Nafion 212) in Fig. 3a. The data show that the use of BSEs reduces the capacity decay rate by 86.3%, from 0.182% per cycle to 0.025% per cycle over 400 cycles. To further highlight the practical benefit of this approach, we also compare a system employing BSEs with a thin (15 μm) Nafion membrane against one using traditional electrolytes with a thick (183 μm) membrane in Fig. 4a-d. This comparison underscores the significant advantage of BSEs in enabling high performance with thinner, lower-resistance membranes. To enhance clarity, we have emphasized that the tests were conducted in VRFBs using Nafion 212, as detailed below.

In the revised Manuscript [Fig. 3a]

A VRFB employing an N212 membrane with the BSEs (P 1.91 M $V^{3.55+}$; N 1.170 M $V^{3.50+}$) exhibit an 86.3% reduction in capacity decay rate—from 0.182% to 0.025% per cycle—and a 71.0% increase in accumulated discharge capacity (from 256.97 to 439.35 Ah) over 400 cycles, compared to that using traditional electrolytes (P 1.70 M $V^{3.50+}$; N 1.70 M $V^{3.50+}$) (Fig. 3a).

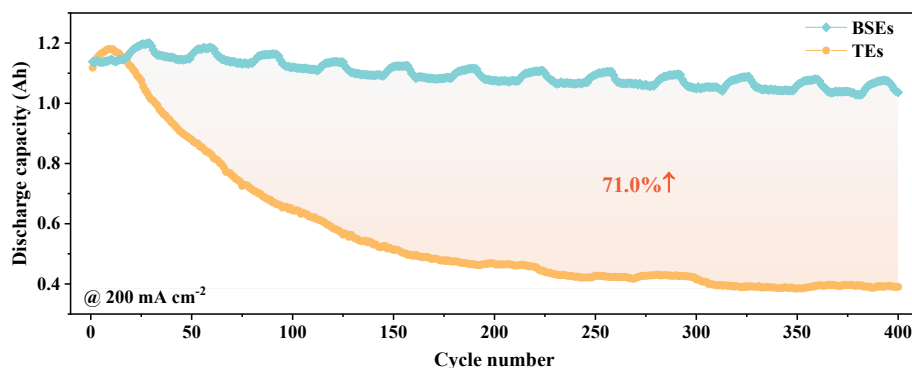


Fig. 3a Effects of BSEs (P 1.91 M $V^{3.55+}$; N 1.17 M $V^{3.50+}$) on suppressing capacity decay of VRFBs using N212.

11. Overall, the experimental data presented focuses solely on VRFBs using a Nafion membrane. Although this system is described as a model, additional validation with other types of RFBs employing different active materials and membranes is necessary to substantiate the claim that this electrolyte design strategy is universally adaptable for RFBs without membrane limitations. Therefore, I recommend conducting further tests with at least two or three different combinations of active materials and membranes.

Response:

Thanks for your valuable suggestions. We have applied this method to iron–vanadium flow batteries (IVFBs), which suffer from severe crossover issues. The accumulated discharge capacity improved 56.36% from 388.37 to 607.25 Ah over 400 cycles when conventional electrolytes were replaced with the BSEs, demonstrating good effectiveness and applicability, as shown in Fig. R2. Details regarding the IVFBs and the corresponding BSEs have been added to the revised manuscript and supplementary information, with details provided below.

Here, we treat VRFBs during cycling as dynamic diffusion systems and leverage their self-balancing capability to determine electrolyte concentration. The methodological cornerstone of this study is the exploitation of the self-balancing capability of VRFBs. We operated a VRFB equipped with a Nafion membrane under specific operating conditions until it reached a balanced state. By characterizing the electrolytes in VRFBs operating at this balanced state, we determined the concentrations required for the BSEs. As described in response to question 2, we have evaluated the effects of BSEs on two other widely studied membranes—polybenzimidazole (PBI) and sulfonated poly (ether ether ketone) (SPEEK). However, both PBI and SPEEK exhibit a linear decay in discharge capacity with cycling [R17, R18] (Figs. R7, R8), which does not conform to the definition of the balanced state.

To be more rigorous, we have corrected “the balanced-state electrolyte approach removes membrane limitations” to “significantly reduces membrane limitations” in the revised manuscript, as shown below.

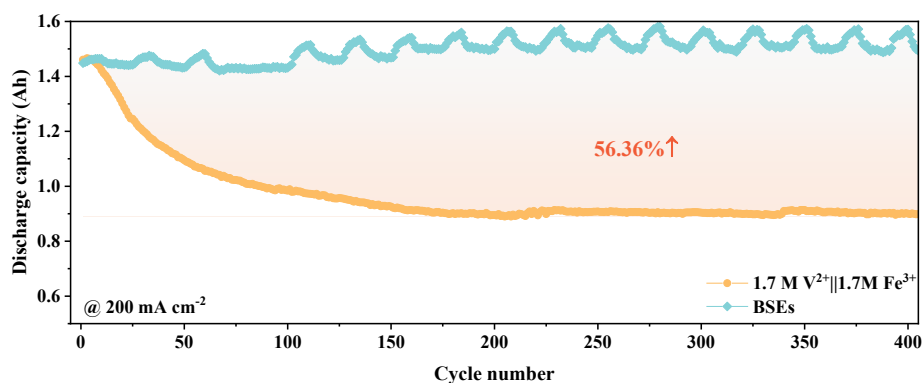


Fig. R2 Comparison of iron-vanadium flow batteries using conventional electrolytes (P 1.7 M V^{2+} ; N 1.7 M Fe^{3+}) versus balanced state electrolytes (BSEs, P 1.072 M V^{2+} + 0.876 M Fe^{2+} ; N 1.324 M Fe^{3+} + 0.914 M VO^{2+}).

[R17] Wang Z, Ren J, Sun J, et al. The anion conductivity of acid-doped polybenzimidazole membrane and utilization in mitigating the capacity decay of vanadium redox flow battery stacks. *Chem. Eng. J.*, 474: 145621, (2023).

[R18] Ding M, Ling X, Yuan D, et al. SPEEK membrane of ultrahigh stability enhanced by functionalized carbon nanotubes for vanadium redox flow battery. *Front. Chem.* 6: 286, (2018).

In the revised Manuscript [Fig. 5]

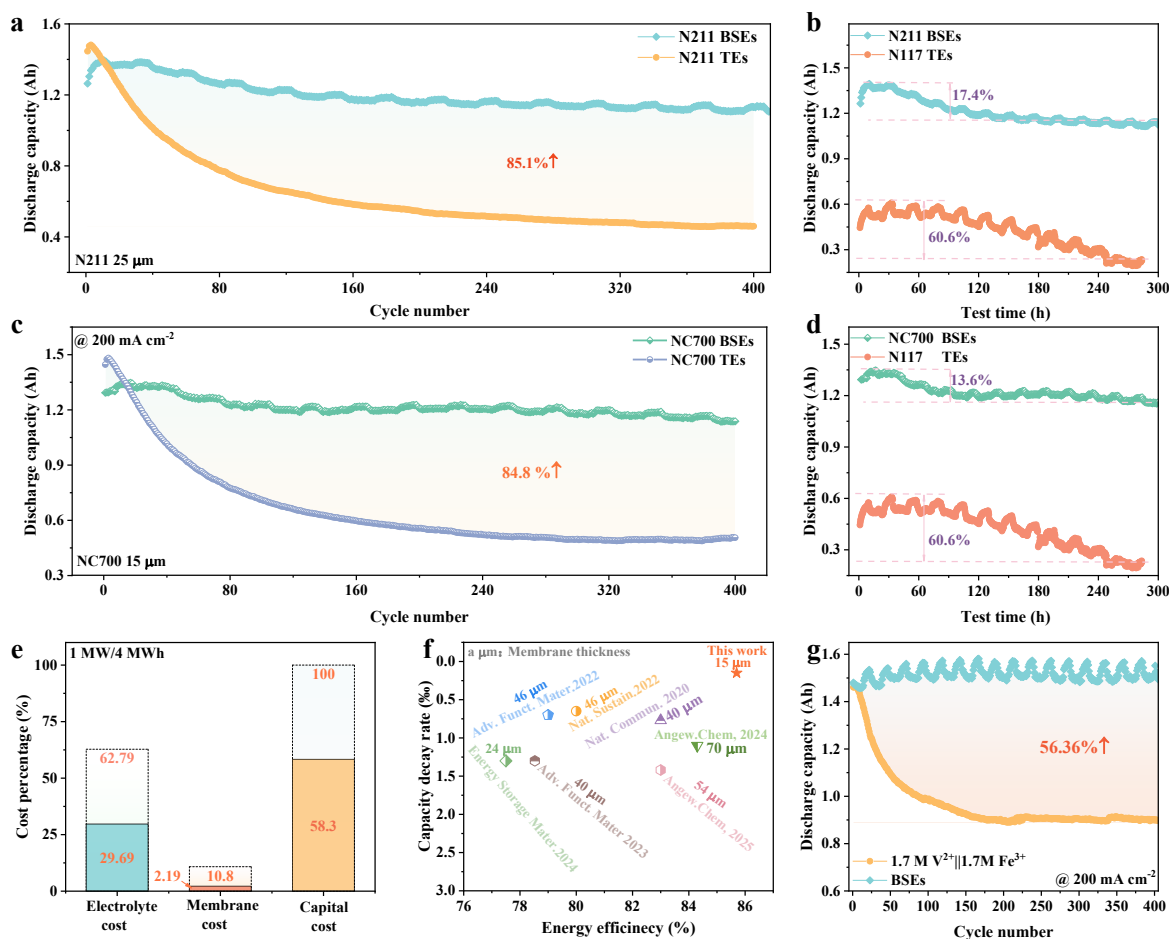


Fig. 5 Suppression of crossover with BSEs in RFBs. Effects of BSEs on improving **a**, discharge capacity of the VRFB with N211. **b**, Discharge capacity comparison between the VRFBs with N211 and N117. **c**, Effects of BSEs on improving the capacity retention rate of the VRFB with NC700. **d**, Capacity retention rates comparison between the VRFB with NC700/BSEs and that of N117/TEs. **e**, Capital cost analysis in a 1 MW/4 MWh system between an advanced commercial case and using BSEs strategy. **f**, Comparison of VRFBs with advanced designed membranes reported in the last five years. **g**, Effects of BSEs (P 1.072 M V^{2+} + 0.876 M Fe^{2+} ; N 1.324 M Fe^{3+} + 0.914 M VO^{2+}) on improving the capacity retention rate of the IVFB with N212.

In the revised Manuscript [Fig. 5g]

To further demonstrate the effectiveness and applicability of our proposed BSEs method, we have extended it to iron-vanadium flow batteries (IVFBs), which suffer from severe crossover issues. The accumulated discharge capacity improved 56.36% from 388.37 to 607.25 Ah over 400 cycles

when conventional electrolytes (P 1.70 M V^{2+} ; N 1.70 M Fe^{3+}) were replaced with the BSEs (P 1.072 M V^{2+} +0.876 M Fe^{2+} ; N 1.324 M Fe^{3+} +0.914 M VO^{2+}), indicating successful suppression of the crossover, as shown in Fig. 5g.

In the revised Manuscript [Section Materials]

Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$ CAS Number: 7782-63-0) and Iron (III) chloride hexahydrate $FeCl_3 \cdot 6H_2O$ (CAS Number: 7447-40-7) were purchased from Sigma-Aldrich.

In the revised Manuscript [Section Battery tests]

A VRFB cell equipped with Nafion 212 was adapted for IVFBs testing by replacing vanadium electrolytes with iron-vanadium electrolytes.

In the revised Manuscript [Section Electrolytes preparation]

The 1.70 M V^{2+} /3.00 M H_2SO_4 , 1.70 M V^{3+} /3.00 M H_2SO_4 and 1.70 M VO^{2+} /3.00 M H_2SO_4 were obtained by charging the commercial (1.70 M $V^{3.50+}$ /3.00 M H_2SO_4) electrolytes. 1.70 M Fe^{3+} /3.00 M H_2SO_4 electrolyte was prepared by dissolving $FeCl_3 \cdot 6H_2O$ in 3.00 M H_2SO_4 solution.

In the revised Manuscript [Section Characterization techniques]

Ion concentrations in the positive and negative electrolytes of IVRFs were measured using an Inductively Coupled Plasma –Optical Emission Spectrometer (Avio-200, PerkinElmer) following a 7500-fold dilution with deionized water.

In the revised Manuscript [Section Battery tests]

All the battery tests were conducted under N_2 protection using Arbin 179539 (Arbin Instruments, USA) for data recording. The cut-off voltage range was 0.90-1.60 V for all VRFB experiments and 0.60-1.60 V for IVFB experiments.

In the revised Supplementary Information [Section 1.2 Electrolyte preparation for IVFBs]

The BSEs for IVFBs were prepared as follows. For the positive side, 11.62 g $VOSO_4 \cdot 5H_2O$ was added to 40 mL of 1.70 M Fe^{3+} /3.00 M H_2SO_4 solution and then diluted with 11.36 mL of 3.00 M H_2SO_4 , serving as the positive electrolyte. For the negative side, 11.45 g $FeSO_4 \cdot 7H_2O$ was added

to 40 mL of 1.70 M V^{2+} /3.00 M H_2SO_4 solution and then diluted with 23.43 mL of 3.00 M H_2SO_4 , serving as the negative electrolyte.

In the revised Supplementary Information [Section 4 IVFB test]

First, a VRFB assembled with Nafion 212 was fully charged using 40 mL of $V^{3.5+}$ /3.00 M H_2SO_4 as both the positive and negative electrolytes, yielding 40 mL of V^{2+} /3.00 M H_2SO_4 on the negative side. Then, the positive electrolytes (VO_2^+) were pumped into the tank and the positive-side chamber was washed with deionized water and purged with N_2 for 1 min. Finally, the positive electrolyte was replaced with 1.70 M Fe^{3+} /3.00 M H_2SO_4 electrolytes. In IVFB testing with the BSEs, the same flow battery cell was employed.

In the revised Supplementary Information [Section 1.4.2 BSEs for IVFBs]

The definition and identification method for the balanced state in IVFBs are the same as those for VRFBs. Here, we selected the state of an IVFB after 160 cycles as its balanced state and measured ion concentration using an Inductively Coupled Plasma –Optical Emission Spectrometer (Avio-200, Perkin Elmer) following 7500-fold dilution with deionized water. The results show that vanadium ion concentrations are 0.914 M and 1.072 M in the positive and negative electrolytes, respectively, and iron ion concentrations are 1.324 M and 0.876 M, respectively.

In the revised Supplementary Information [Fig. S38]

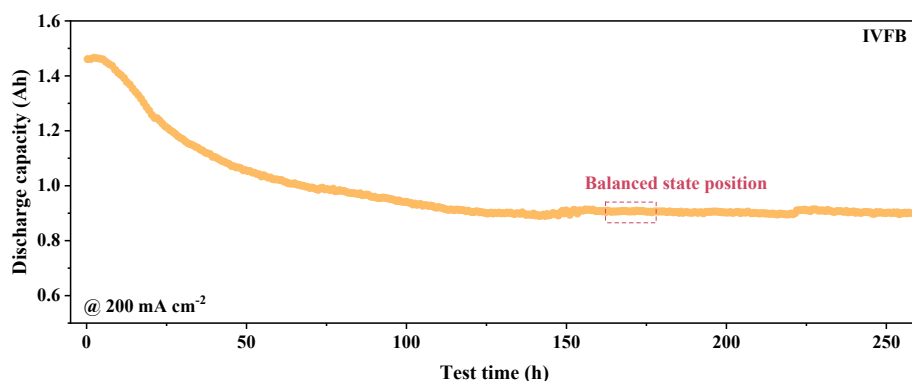


Fig. S38 Discharge capacity versus time for an IVFB using TEs (P 1.70 M $Fe^{3.0+}$; N 1.70 M $V^{2.0+}$).

Reviewer #3 (Remarks to the Author):

This manuscript proposes balanced-state electrolytes (BSEs) that deliberately break symmetry in concentration and average valence between positive and negative tanks to counteract net crossover in vanadium redox flow batteries (VRFBs). By tuning concentration and valence, the authors claim to hold the net transmembrane flux near zero over a cycle, enabling thin Nafion membranes without sacrificing capacity retention. Representative results include: with BSEs, N212 (51 μm) outperforms N117 (183 μm) using traditional electrolytes, cutting the capacity-decay rate from 0.061% to 0.025% per cycle over 1,000 cycles and reaching $\text{CE} = 97.79\%$ at 50 mA cm^{-2} (main Fig. 4a, d; p. 25–26). The approach extends to N211 (25 μm) and NC700 (15 μm) with decay rates down to 0.015% per cycle, alongside a $>41.7\%$ CAPEX reduction projected for a 1 MW/4 MWh system (main abstract; Fig. 5e–h; pp. 15–16; SI Tab. S2). Mechanistically, the authors quantify flux reversal/neutralization (net flux 4.59% vs 38.94% for BSEs vs TEs) using volume- and concentration-shift analysis (SI Eq. S13–S14; Fig. S15, p. 10–11).

The idea is practically appealing—use electrolyte design to escape the conductivity–selectivity trade-off of Nafion rather than inventing bespoke membranes.

Response: We appreciate the reviewer for taking the time to provide valuable comments and suggestions that have helped improve the quality and clarity of our manuscript. We have thoroughly addressed all comments, and the revisions have significantly strengthened the paper.

Major comments

1. Generalizable, reproducible procedure for identifying the “balanced state.” The present recipe infers BSEs from the first “horizontal region” ($\sim 107 \text{ h}$) in the discharge-capacity–time trace (main Fig. 2e–f), which is sensitive to current, SOC window, temperature, and cell hardware. Please formalize a predict–set–verify workflow: given membrane type, current density, SOC range, and temperature, output the target P/N concentrations and

positive-tank average valence (with uncertainty). Publishing a minimal open script that couples Fig. 2b (net-flux map) with SI Sections 1 & 2 would make this widely reusable.

Response:

Thanks for your suggestions. In Fig. 2e, a VRFB was assembled in a zero-gap structure using graphite plates with serpentine flow fields. Two pieces of graphite felts (2.5 mm thickness, Liaoning Jingu Carbon Material Co., Ltd.) with the size of $40.00 \times 40.00 \text{ mm}^2$ were used as the electrodes separated with a piece of Nafion 212. 40.00 mL of 1.70 M $\text{V}^{3.50+}$ / 3.00 M H_2SO_4 electrolytes (supplied by Sichuan Xingming Energy Material Co., Ltd) were stored in the positive and negative reservoirs and circulated via a Longer BT100 peristaltic pump (Longer Precision Pump Co., Ltd., UK). The VRFB was tested in a laboratory where the temperature fluctuated between 25 and 30 °C over diurnal cycles. The charge and discharge cycling was conducted using Arbin 179539 (Arbin instruments, USA) at 200 mA cm^{-2} with N_2 protection, with cut-off voltages of 0.90-1.60 V. The SOC of this VRFB ranges from 6.99% to 76.79 % at the initial stage, as shown in Fig. 2c.

Furthermore, in this work, we leveraged the self-balancing capability of VRFBs equipped with a Nafion membrane to identify the balanced state under specific operating conditions. By characterizing the electrolytes in VRFBs operating at this balanced state, we determined the concentrations required for the BSEs. Differences in membrane type, current density, SOC range, and temperature are inherently captured in the resulting balanced state, leading to distinct BSEs—as demonstrated by the differing BSE compositions for VRFBs using N212 (P 1.91 M $\text{V}^{3.55+}$; N 1.170 M $\text{V}^{3.50+}$) versus N211 membranes (P 1.83 M $\text{V}^{3.54+}$; N 1.15 M $\text{V}^{3.50+}$). Thus, the effectiveness and applicability of the BSE method remain unaffected by hardware variations, demonstrating its universality. This highlights the unique advantage of our proposed strategy: it provides a universal, experimentally driven framework for deriving balancing solutions for different hardware materials and operating scenarios. We believe this conceptual innovation offers a fresh perspective for membrane research and electrolyte engineering in VRFBs. We thank the reviewer again for prompting us to articulate this more clearly.

We clarified the description of the BSEs for a VRFB in the revised manuscript and added a section detailing how to determine the BSE composition in the revised supplementary information, as detailed below.

The workflow for balanced state characterization and the script of Fig. 2b have been added in the revised manuscript and supplementary information, as shown below.

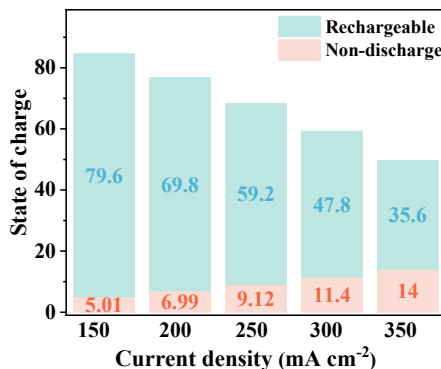


Fig. 2d Range of SOC in the discharge process under different current densities.

In the revised Manuscript [Section BSE determination]

Determining the balanced state of a VRFB under specified operating conditions is essential for designing BSEs. Specifically, we define the balanced state under specific conditions as one where the capacity decay rate is less than 0.03% per cycle or 0.08% per hour. In addition, the test must last longer than 8 h and include more than 20 cycles, with the discharge capacity showing a monotonic decay versus time or cycle number over the investigated range. The electrolyte concentrations at the balanced state are used for designing BSEs. To ensure the accuracy of these measurements, we converted the electrolytes at the balanced state to $V^{3+}|VO^{2+}$ through full discharge followed by aerial oxidation. To compensate for the elevated average vanadium valence that occurs during cycling due to side reactions, the VO_2^+ content in the initial electrolyte was experimentally increased. The detailed procedure is described in the supplementary information.

In the revised Supplementary Information [Section BSE determination]

First, operate a VRFB under specified conditions and record the discharge capacity versus time curve. Second, calculate the capacity decay rates over 20 cycles in the quasi-steady region of the discharge capacity curve. Third, identify the region where the discharge capacity decay rate is

below 0.03% per cycle. Fourth, stop cycling and fully discharge the battery at a constant voltage of 0.8 V until the current falls below 0.1 A. Fifth, stir the negative electrolyte using a magnetic stirrer and oxidize it in air for 4 hours to convert the surplus V^{2+} to V^{3+} . Sixth, dilute the negative and positive electrolytes 15-fold with deionized water and measure the V^{3+} and VO^{2+} concentrations using a UV-Visible Spectrophotometer.

In the revised Supplementary Information [At the end of this document]

The script of Fig. 2b can be found in the following link.

<https://figshare.com/s/fdae8069727545502da4>

2. Disentangle temperature and water-migration effects.

The capacity ripples track day–night temperature changes (main Fig. 3b; SI Fig. S7), and hydraulic/viscous effects were probed via unequal flow (main Fig. 2h; SI Fig. S5), but the quantitative roles of water transport and acid strength remain unclear. Please (i) repeat a key N212/N211/NC700 comparison in a constant-temperature environment (e.g., 25 ± 0.1 °C), and (ii) co-track acid molarity/viscosity/volume on both sides with water content (e.g., titration or Karl Fischer). This will bound how much of the benefit arises from species flux versus water/osmotic effects.

Response:

Thanks for your suggestion. We retested the effect of BSEs in a VRFB assembled with N212 at a controlled temperature of 25 °C, as shown in Fig. R11. The results demonstrate that replacing TEs with BSEs enhances the accumulated discharge capacity by 106.0%.

We also comparatively studied the acidity, viscosity, and volume of electrolyte in VRFBs using TEs and BSEs before and after cycling, as depicted in Fig. R12. Results show that the pH values exhibit no substantial change after cycling for VRFBs both employing TEs and BSEs (Fig. R12a). However, in TEs-based VRFBs, the viscosity of the positive electrolyte increases markedly, whereas that of the negative electrolyte decreases substantially after cycling (Fig. R12b), owing to concentration variations (Fig. 1b). In contrast, the viscosity decreases in the positive electrolyte but increases in the negative electrolyte, highlighting the ability of BSEs to counteract crossover. Furthermore, the electrolyte volume in TE-based VRFBs expands slightly on the positive side and

contracts on the negative side after cycling, whereas these volume changes are more pronounced when BSEs are employed (Fig. R12c), underscoring the enhanced role of water transfer in the latter configuration.

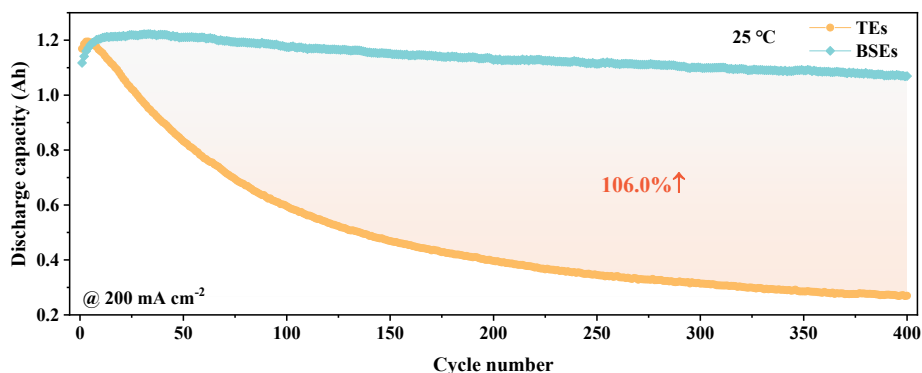


Fig. R11 Effects of BSEs (P 1.91 M $V^{3.55+}$; N 1.17 M $V^{3.50+}$) on suppressing capacity decay of VRFBs at 25 °C.

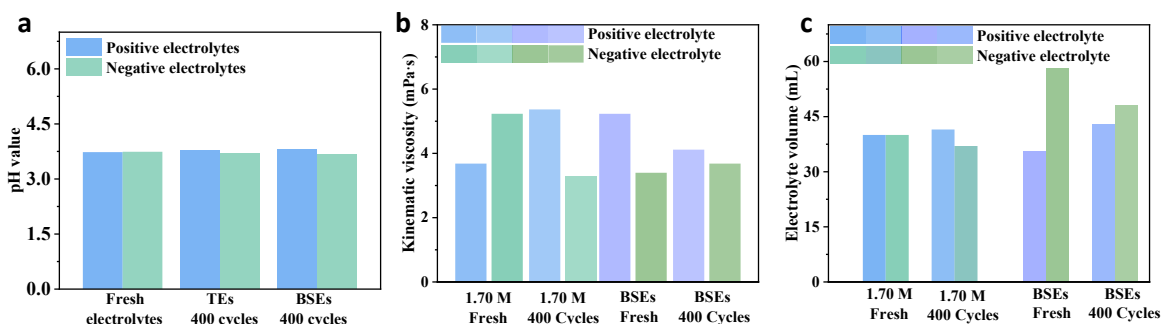


Fig. R12 Variation of electrolyte composition after cycling. **a**, pH value **b**, kinematic viscosity, and **c**, volume of electrolytes in VRFBs using TEs and BSEs before and after cycling operating at 25 °C.

In the electrolyte pH tests, samples (1 mL) were diluted 60-fold with deionized water, and the pH was measured using a pH pen (AZ8693; ERMANDA, China).

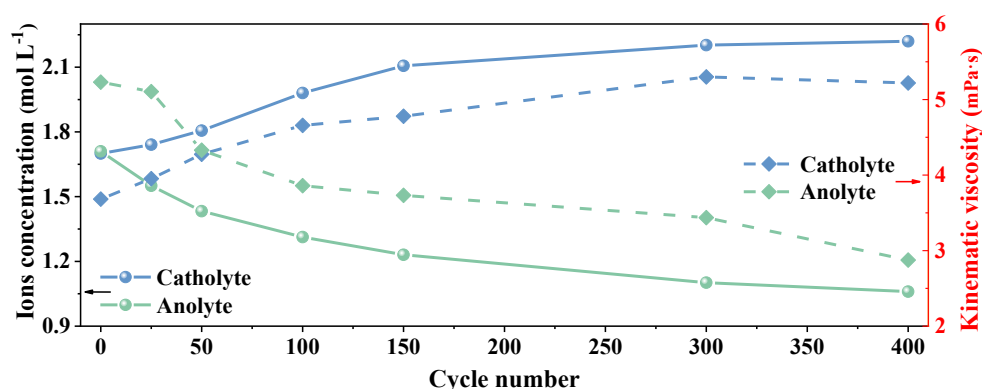


Fig. 1b, Electrolyte concentration/viscosity change with cycling of the VRFB equipped with Nafion 212 and traditional electrolytes at 200 mA cm⁻².

3. Bridge the MD to measurable transport; release inputs.

The MD results suggest reduced V^{3+} diffusion and altered ion–sulfonate interactions under BSEs (main Fig. 3h–j; SI Fig. S11–S13). For reproducibility, please share topology/parameters and bench-mark simulated diffusivities against values inferred from self-discharge/EIS or literature for each ion/species. A brief sensitivity check (water content, ionic strength) would increase confidence in the mechanism.

Response:

We thank the reviewer for this comment. The topology/parameters of H_3O^+ , V^{2+} , V^{3+} , VO^{2+} , and VO_2^+ are listed in Table R2–R6. The topology/parameters for Nafion structure are available via the following link, owing to the large number of parameters:

<https://figshare.com/s/fdae8069727545502da4>

We have now benchmarked our MD simulations against experimental data and performed the requested sensitivity analyses as follows:

The simulated diffusivities (Fig. R13) are compared with the experimental results (Tab. S1) reported by Professor Zhang [R2]. The simulated trends and orders of magnitude align well with these independent experimental measurements, validating our model's predictive capability for relative ion transport rates.

To assess the sensitivity of the simulations, models incorporating varying water contents were constructed. The compositions of the different species in the simulation boxes are detailed in Tables R7–R9. The results (Fig. R14) reveal that the diffusivity of V^{2+} increases substantially with rising water content in both TEs and BSEs systems, consistent with previous reports [R20]— the water content of Nafion membranes exerts a profound influence on ion transport across the membrane. The diffusivities of V^{2+} in BSEs-based system with different water contents are all lower than those in the TEs-based system.

Tab. R2 Topology/parameters of H_3O^+ in MD simulation.

Atoms	O	H1	H2	H3
Position x (nm)	-0.268	-0.307	-0.158	-0.311
Position y (nm)	0.141	0.207	0.136	0.040
Position z (nm)	-0.002	0.079	0.004	0.009
Mass	15.999405	1.007941	1.007941	1.007941
Charge	-0.4001	0.4667	0.4667	0.4667
Bond length O-H (nm)	—	0.0960	0.0960	0.0960
Bond Stretching O-H (kJ/mol/nm ²) / $\times 10^5$	—	2.31154	2.31154	2.31154
O-H Angle (degree)	—	104.500	104.500	104.500
O-H Angle Bending (kJ/mol/rad ²) / $\times 10^2$	—	4.182	4.182	4.182
sigma (nm) / $\times 10^{-1}$	3.118146	2.571134	2.571134	2.571134
epsilon (kJ/mol) / $\times 10^{-1}$	2.510400	1.840960	1.840960	1.840960

Tab. R3 Topology/parameters of V²⁺ in MD simulation.

Atoms	V ²⁺
Position x (nm)	0.100
Position y (nm)	-0.007
Position z (nm)	0.007
Charge	2.0000
Mass	50.941465
sigma (nm) / $\times 10^{-1}$	2.800986
epsilon (kJ/mol) / $\times 10^{-1}$	6.694400

Tab. R4 Topology/parameters of V³⁺ in MD simulation.

Atoms	V ³⁺
Position x (nm)	0.093
Position y (nm)	-0.004
Position z (nm)	0.005
Charge	3.000
Mass	50.941465
sigma (nm) / $\times 10^{-1}$	2.800986
epsilon (kJ/mol) / $\times 10^{-1}$	6.694400

Tab. R5 Topology/parameters of VO²⁺ in MD simulation.

Atoms	V	O
Position x (nm)	-0.328	-0.227
Position y (nm)	0.078	0.098
Position z (nm)	0.000	0.165
Mass	50.941465	15.999405
Charge	2.400800	-0.400800
Bond length O-V (nm)	0.1770	
Bond Stretching O-V (kJ/mol/nm ²) / $\times 10^5$	3.095449	
sigma (nm) / $\times 10^{-1}$	2.800986	3.118146
epsilon (kJ/mol) $\times 10^{-2}$	6.694400	25.10400

Tab. R6 Topology/parameters of VO₂⁺ in MD simulation.

Atoms	V	O1	O2
Position x (nm)	-0.283	-0.374	-0.193
Position y (nm)	0.018	0.185	-0.150
Position z (nm)	0.062	0.019	0.104
Mass	50.941465	15.999405	15.999405
Charge	1.4008	-0.200400	-0.2004
Bond length O-V (nm)	—	0.1960	0.1960
Bond Stretching O-V (kJ/mol/nm ²) /×10 ⁵	—	2.286179	2.286179
Angle (degree) O-V	—	180.00	180.00
Angle Bending O-V (kJ/mol/rad ²) /×10 ²	—	2.4776	2.4776
sigma (nm) /×10 ⁻¹	2.800986	3.118146	3.118146
epsilon (kJ/mol) ×10 ⁻²	6.694400	25.10400	25.10400

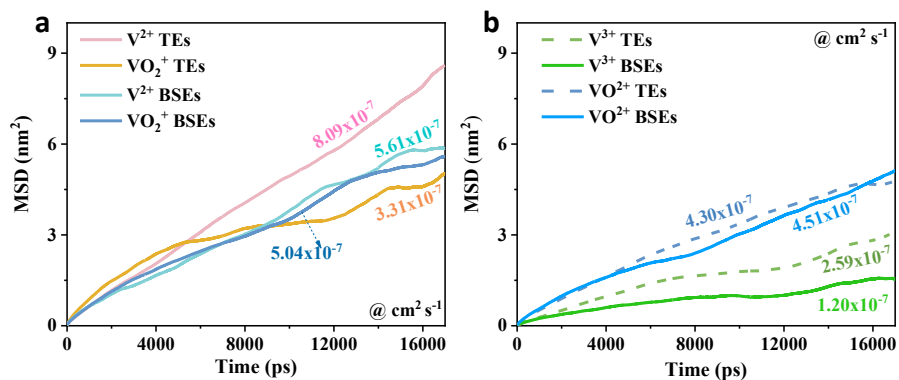


Fig. R13 Simulated diffusivities of vanadium ions across Nafion membrane. a-b, Mean Squared Displacement (MSD) of V²⁺ /VO₂⁺ and V³⁺ / VO²⁺ across membrane.

Tab. S1 The diffusion rate of vanadium ions across Nafion membranes. [S1]

Vanadium ions	V ²⁺	V ³⁺	VO ²⁺	VO ₂ ⁺
Diffusion coefficient/ cm ² s ⁻¹	8.767 × 10 ⁻⁷	3.222 × 10 ⁻⁷	6.825 × 10 ⁻⁷	5.897 × 10 ⁻⁷

Tab. R7 Number of molecules added in different simulation systems.

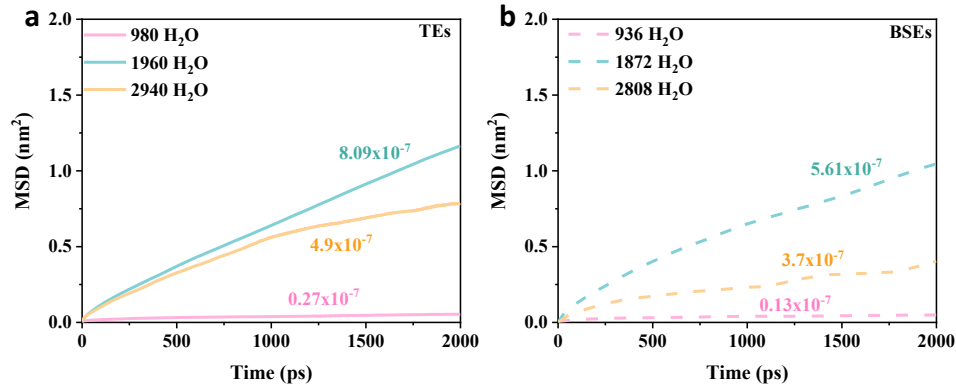
	Nafion ($2\times(-\text{SO}_3^-)$)	V^{2+}	V^{3+}	VO^{2+}	VO_2^+	H_3O^+	H_2O
TEs	100	20	7	14	12	99	980
BSEs	100	14	5	17	15	108	936

Tab. R8 Number of molecules added in different simulation systems.

	Nafion ($2\times(-\text{SO}_3^-)$)	V^{2+}	V^{3+}	VO^{2+}	VO_2^+	H_3O^+	H_2O
TEs	100	20	7	14	12	99	2940
BSEs	100	14	5	17	15	108	2808

Tab. R9 Number of molecules added in different simulation systems.

	Nafion ($2\times(-\text{SO}_3^-)$)	V^{2+}	V^{3+}	VO^{2+}	VO_2^+	H_3O^+	H_2O
TEs	100	20	7	14	12	99	2940
BSEs	100	14	5	17	15	108	2808

**Fig. R14 Water content effects on V^{2+} diffusion rate across Nafion membrane. a-b,** Mean Squared Displacement (MSD) of V^{2+} at traditional electrolytes (TEs) and balanced state electrolytes (BSEs).

- [R2] Sun C, Chen J, Zhang H, Han X, Luo Q. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. *J. Power Sources*. 195(3): 890-897 (2010)
- [R20] Mauritz, K. A., & Moore, R. B. State of understanding of Nafion. *Chem. Rev.* 104(10), 4535-4586, (2004).

4. Cost model sensitivity and operating envelope.

The >41.7% CAPEX reduction (main Fig. 5h) is compelling but scenario-dependent. Please add a tornado or scenario analysis varying membrane cost ($\pm 50\%$), energy efficiency (80–86%), lifetime (500–3,000 cycles), and pump power (viscosity-dependent) to test the robustness of the conclusion.

Response:

We thank the reviewer for this suggestion. A detailed calculation process and a cost table have been included in the supplementary information, as provided below.

Our cost analysis focused solely on the membrane and electrolyte components. As shown in Fig. 3, VRFBs employing BSEs demonstrate superior energy efficiency compared to those using traditional electrolytes (TEs). This higher efficiency translates into an advantage in power-density-related costs. Furthermore, the average viscosity of the BSEs is 3.958 mPa·s, lower than the 4.456 mPa·s of the TEs, suggesting a reduction in pump power loss. However, no direct correlation exists between capital costs and power density or pump power. We therefore consider only the membrane and electrolyte costs as a proportion of the overall system costs (based on a 1 MW/4 MWh system) when calculating the capital cost reduction upon adoption of BSEs. The details of this calculation are provided below.

In the revised Supplementary Information [Section 7]

Tab. S2 Electrolyte utilization in VRFBs with different systems.

VRFB system	Accumulated discharge capacity over 400 cycles (Ah)	Discharge capacity over 400 cycles (Ah cycle ⁻¹ mol ⁻¹)
Current advanced system	225.10281	4.137919301
System with BSEs	486.2741	8.938862132

The discharge capacity of electrolytes per cycle per mol ($D_{CP}/\text{Ah mol}^{-1}$) is calculated as follows:

$$D_{CP} = \frac{D_{AC}}{C_{NO}} \times \frac{1000}{V_E \cdot E_C} \quad (\text{Eq. S24})$$

where D_{AC} , C_{NO} , V_E , and E_C represent the accumulated discharge capacity (Ah), the cycle number, the electrolyte volume (mL), and the electrolyte concentration (M), respectively.

The capital cost reduction for a VRFB system using BSEs and NC700 can be calculated as below:

$$C_{Cr} = (C_{R-M} + C_{R-E}) - (C_{R-M} \times M_{CR} + C_{R-E} \times E_{CR}) \quad (\text{Eq. S25})$$

where, C_{Cr} is the capital cost reduction ratio; C_{R-M} and C_{R-E} are the cost ratios of membrane (10.08%) and electrolyte (62.79%), respectively, over the capital cost of a current advanced 1 MW/4 MWh VRFB system; [32] M_{CR} and E_{CR} are the corresponding cost ratios of the membrane and electrolyte in the BSEs and NC700 based system [33] relative to a currently advanced VRFB system.

$$M_{CR} = \frac{472.281}{2329.825} \quad (\text{Eq. S26})$$

$$E_{CR} = \frac{4.137919}{8.938862} \quad (\text{Eq. S27})$$

Hence, the capital cost reduction for a VRFB system with BSEs compared to the current advanced VRFB system can be obtained:

$$C_{Cr} = (10.08 + 62.79) - \left(10.08 \times \frac{472.281}{2329.825} + 62.79 \times \frac{4.137919}{8.938862} \right) = 41.76 \quad (\text{Eq. S28})$$

The specific costs of electrolyte and membrane in different VRFB systems are listed in Tab.

S3.Tab. S3 Membrane and electrolyte costs as a proportion of the capital cost in 1 MW/4 MWh VRFBs systems. [S8, S9]

	Membrane type	Membrane cost/ m ² (\$)	Membrane to capital cost ratio	Discharge capacity over 400 cycles (Ah cycle ⁻¹ mol ⁻¹)	Electrolyte to capital cost ratio
Current advanced system	N212	2329.825	10.80%	4.14	62.79%
System with BSEs	NC700	472.281	2.19%	8.94	29.08%

[S8] Chen H, Zhang X, Wu S, et al. A comparative study of iron-vanadium and all-vanadium flow battery for large scale energy storage. *Chem. Eng. J.* 429: 132403 (2022).

[S9] [https://www.fuelcellstore.com/pfsa-d50u-proton-exchange-membrane-87010020?search=Nafion 212](https://www.fuelcellstore.com/pfsa-d50u-proton-exchange-membrane-87010020?search=Nafion+212)

5. Adaptive maintenance of the balanced state.

Since electrode aging shifts SOC windows and kinetics (main Fig. 4e–h; SI Fig. S19/S24), demonstrate a closed-loop correction (periodic tiny additions of VO^{2+} or acid, or controlled dilution) that keeps the net flux near zero over long cycling, and report how often corrections are needed. This would strengthen the practicality claim.

Response:

Thanks for your valuable suggestion. All VRFB tests reported here were conducted over 400 or 1000 cycles without any corrective interventions during cycling. The observed capacity decay thus encompasses the natural, gradual aging process of the electrodes, which is an intrinsic component of the long-term performance in these systems. We have clarified this point in the revised manuscript.

In the revised Manuscript [Section, Battery tests]

All VRFB and IVFB tests were conducted over 400 or 1000 cycles without any interventions during cycling.

Minor comments

a) Error bars and replicates. Many plots (e.g., Fig. 3c–f; Fig. 5a, b, e, f) lack uncertainty. Please report n and add error bars or shaded confidence bands.

Response:

We thank the reviewer for raising this point. The efficiency data for VRFBs under different working conditions, presented in Figs. 3c–e and 5b, f are based on triplicate measurements (Fig. R15 and R16). Note: The recording interval for all tests in this experiment was set to 1 s to mitigate substantial fluctuations in the calculated efficiency arising from the data.

These repeated experiments show that the voltage efficiency exhibits considerably less fluctuation than the coulombic efficiency (Fig. R15c).

In Fig. 3f, the EIS spectrum of VRFBs with different electrolytes was measured once, but the quality of contact between the battery tabs and electrochemical fixtures was repeatedly verified during tests. In Fig. 3f, the reduction in battery resistance stems from the dilution of the negative electrolyte with 3.0 M H_2SO_4 .

In the long-term cycling (Fig. 5a and e), the effects of BSEs in suppressing capacity decay were repeatedly verified across different membranes (N212, N211, and NC700), underscoring their excellent repeatability and applicability.

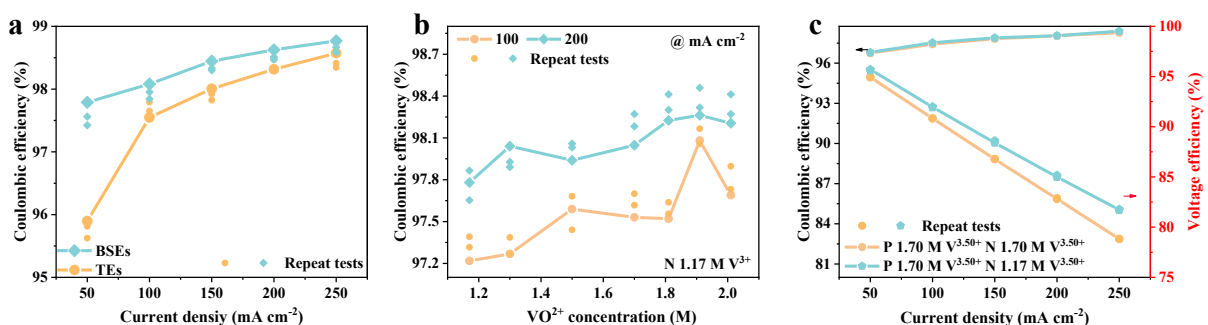


Fig. R15 Replicate measurements of coulombic and voltage efficiency in VRFBs with different electrolytes. a, Comparison of coulombic efficiency in VRFBs with TE and BSEs. **b,** Positive electrolyte concentration effects on the coulombic efficiency of VRFBs. **c,** Negative electrolyte concentration effects on the coulombic/voltage efficiency of VRFBs.

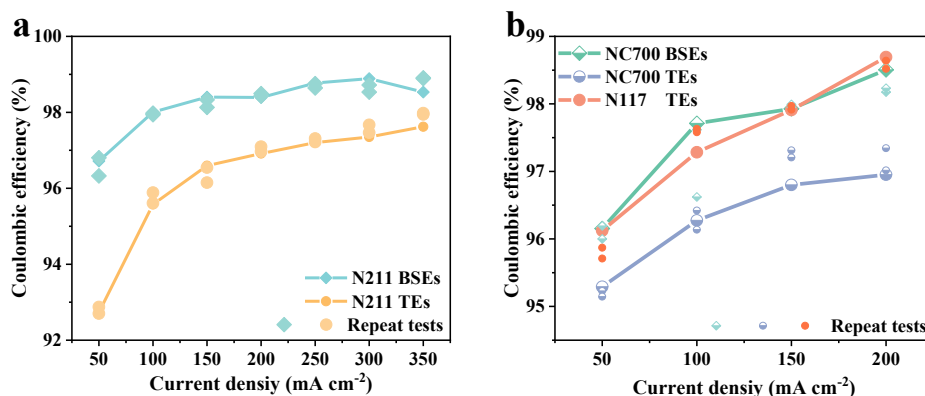


Fig. R16 Repeat tests of coulombic/voltage efficiency in VRFBs. a-b, Effects of BSEs on coulombic efficiency of the VRFB with N211 and NC700.

b) UV–Vis quantification. Provide the calibration curves and fitting ranges for the A/B peaks

used to back-calculate concentrations/valence (SI Fig. S17, S22).

Response:

Thanks for your suggestion. The UV-Vis calibration curves have been added to the supplementary information. The corresponding concentration ranges for V^{3+} and VO^{2+} are 0.296–1.954 mol L⁻¹ and 0.452–2.322 mol L⁻¹, respectively, which encompass all concentrations investigated in this study.

In the revised Supplementary Information [Fig. S25].

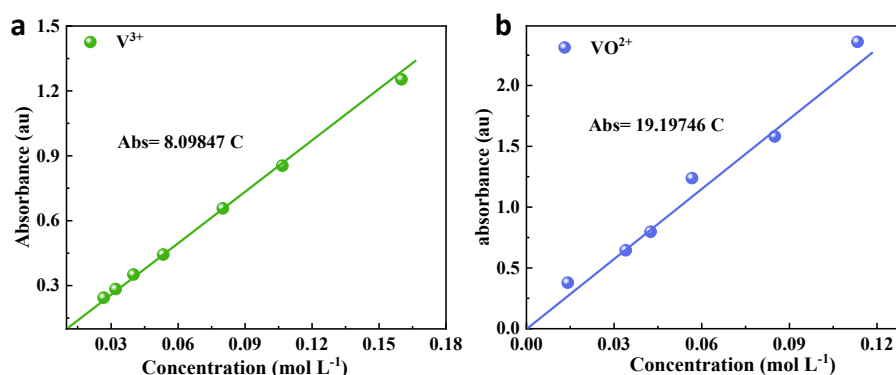


Fig. S25 UV–Vis calibration curves. a–b Calibration curves for V^{3+} and VO^{2+} after 15-fold dilution with deionized water.

c) Terminology and units. Standardize viscosity (mPa·s) and wording (replace “pulling acid” with “diluting with 3 M H₂SO₄” per SI Sec. 1.1).

Response:

Thanks for your corrections. We have corrected the unit of viscosity to mPa·s in both the main text and the supplementary information. The term "pulling acid" has been replaced throughout the manuscript and supplementary information documents. The specific revisions are detailed below.

In the revised Manuscript [Fig. 1b and Fig. S5a]

The viscosity unit has been revised from cP to mPa·s.

In the revised Supplementary Information [Page 1, Section 1.1].

By solving Eq. S1, we prepared the 1.17 M V^{3+} and $V^{3.5+}$ electrolytes through separate dilution of 40 mL of 1.70 M electrolytes with 18.12 mL of 3 M H_2SO_4 each. Similarly, the 1.15 M $V^{3.5+}$ electrolyte was obtained by diluting 40 mL of 1.70 M $V^{3.5+}$ with 19.13 mL of 3 M H_2SO_4 .

d) Operating conditions. State EIS SOC and temperature for each spectrum; specify flow-field geometries per membrane in the main text (now mostly in SI §3).

Response:

Thanks for your suggestions. We have added the operating conditions and the specific flow-field geometry of the graphite plates used with each membrane in the revised manuscript. The detailed revisions are provided below.

In the revised Manuscript [Section, Characterization]

All the tests were conducted at room temperature.

In the revised Manuscript [Section, Battery tests]

Specifically, batteries with Nafion 212, 115, and 117 membranes employed 2.50 mm-thick graphite felt electrodes and graphite bipolar plates with serpentine flow fields (SFFs). The battery with a Nafion 211 membrane incorporated 1.75-mm-thick graphite felt electrodes and bipolar plates with serpentine flow fields SFFs. The battery with an NC700 was assembled with 0.70 mm-thick carbon clothes electrodes and bipolar plates with interdigitated flow fields.

e) Data and code. Provide raw cycling/OCV/self-discharge data and the script used to construct the net-flux map (main Fig. 2b) and cost model (Fig. 5h) as supplementary files.

Response:

Thanks for your suggestions. We have included data used in the main text, the script of Fig. 2b, and cost model of Fig. 5h in the revised supplementary information, as shown below.

In the revised Supplementary Information [Section 8].

All data for the figures in the main text and the script for Fig. 2b are available via the following link.

<https://figshare.com/s/fdae8069727545502da4>

Dear Editors and Reviewers,

We sincerely thank you for the valuable comments and positive feedback on our revised manuscript entitled “Balanced-State Electrolytes Overcome Crossover in Redox Flow Batteries” (NCOMMS-25-45545A). These comments and feedback are highly valuable and have greatly helped us improve the paper. We considered these comments seriously and revised the manuscript and supplementary information based on them. The point-to-point responses to the comments are listed as follows:

Comments from reviewers: in black

Author response: in blue

Revisions in manuscript, and SI: in red

Reviewer #1

The authors have put considerable effort into the revision, and the manuscript has been improved substantially. The authors showed convincing evidence of the practicability of BSEs and extra benefit from concentrated positive side. The characterization of the V species in the membrane supported these benefits. Now the manuscript can be published on Nature Communication, with two things that the authors can consider.

1. Direct measurement of crossover

The authors successfully showed that SOC influences crossover, concentrations of V species affect diffusion coefficient. The authors also argued that measuring the crossover of V species is out of scope. The reviewer believes, however, measuring the crossover of these four species with a few different concentrations can not only strengthen the scientific clearance, but can also directly support many statements with a decoupled clean data. Since the authors claimed that diffusion is dominating the crossover (not electromigration), the measurement of such crossover becomes very easy: one H-cell containing one kind of V source in one side, with supporting electrolyte only (V-free) in the other, can give authors a convincing crossover flux, as a function of source concentration. Thus, the estimated diffusion coefficient can be calculated.

Response:

We sincerely thank the reviewer for these valuable comments. To address this concern, we have performed vanadium ion diffusion tests using a flow battery cell assembled with a Nafion 212 membrane and two electrodes under conditions that closely approximate actual vanadium redox flow battery (VRFB) operating conditions. The diffusion test for V^{2+} was conducted under N_2 protection to avoid the influence of air-induced V^{2+} oxidation (Eq. R1). As shown in Fig. R1a, the flux of V^{2+} exhibits the highest value followed by those of VO^{2+} , VO_2^+ , and V^{3+} , which is consistent with a previous report. [R1] Moreover, Fig. R1b-e demonstrates that decreasing the electrolyte concentration profoundly reduces vanadium ion flux across the Nafion membrane, whereas increasing the concentration markedly enhances the flux. These results confirm that the transport of vanadium ions across the Nafion membrane can be approximated by Fick's law. [R2]

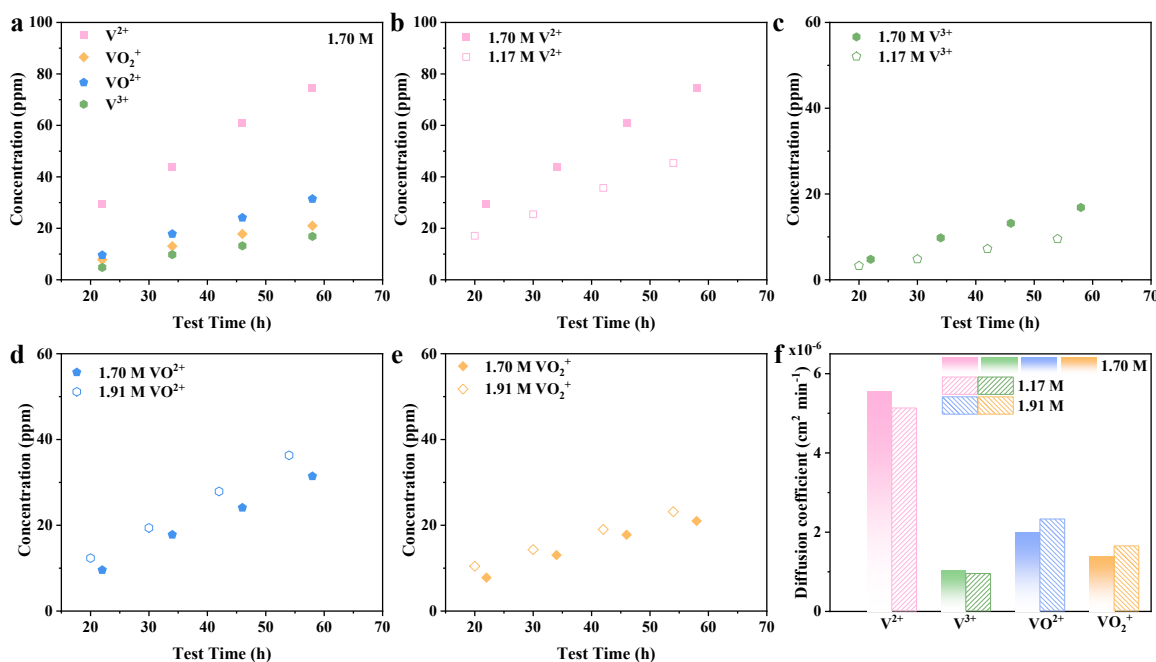


Fig. R1 Vanadium ion diffusion tests across an N212 membrane. **a**, Diffusion fluxes of various vanadium ions in 1.70 M electrolyte. **b-c**, Effect of reducing electrolyte concentration from 1.70 to 1.17 M on the diffusion fluxes of V^{2+} and V^{3+} . **d-e**, Effect of increasing electrolyte concentration from 1.70 to 1.91 M on the diffusion fluxes of VO^{2+} and VO_2^+ . **f** Variation of vanadium ion diffusion coefficients with electrolyte concentration.

The diffusion coefficients of vanadium ions across a Nafion 212 membrane were calculated using the following equation: [R1]

$$\ln\left(\frac{C_A}{C_A - C_B}\right) = D \frac{A}{V_B L} t \quad (\text{Eq. R2})$$

where D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), A is the effective membrane area (m^2), L is the membrane thickness (m), C_A is the vanadium ion concentration on the enrichment side (mol L^{-1}), C_B is the vanadium ion concentration on the deficiency side (mol L^{-1}), and t is the test time (s). In this calculation, the volume of deficiency side (V_B) and C_A were assumed constant.

The resulting values (Fig. R1f) exhibit good agreement with independent measurements reported previously. [R1] These results further demonstrate that modulating the concentration of vanadium ions alters their diffusion rate across the Nafion membrane. We have added these experiments to the revised manuscript and the supplementary information.

In these experiments, a flow battery cell equipped with a Nafion 212 membrane and two electrodes with a size of $40.00 \times 40.00 \text{ mm}^2$ was employed. For each test, 20 mL of vanadium electrolyte was circulated on one side of the cell, while an equimolar MgSO_4 solution in 3 M H_2SO_4 served as the counter electrolyte on the opposite side. Both solutions were pumped at a flow rate corresponding to 51 rpm using a Longer BT100-2J peristaltic pump.

The paired electrolyte compositions were as follows:

- 1) Standard concentration (1.70 M): 1.70M V^{2+} , V^{3+} , VO^{2+} , or VO_2^+ in 3 M H_2SO_4 versus 1.70 M MgSO_4 in 3 M H_2SO_4 .
- 2) Reduced concentration (1.17 M): 1.17 M V^{2+} or V^{3+} in 3 M H_2SO_4 versus 1.17 M MgSO_4 in 3 M H_2SO_4 .
- 3) Increased concentration (1.91 M): 1.91 M VO^{2+} or VO_2^+ in 3 M H_2SO_4 versus 1.91 M MgSO_4 in 3 M H_2SO_4 .

Vanadium ion concentrations were determined using an Inductively Coupled Plasma–Optical Emission Spectrometer (Avio-200, PerkinElmer). Samples (0.2 ml) were withdrawn and diluted 7500-fold (for vanadium electrolytes) or 750-fold (for counter solutions) with deionized water prior to analysis.

[R1] Sun C, Chen J, Zhang H, Han X, Luo Q. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. *J. Power Sources*. 195(3): 890-897 (2010)

[R2] Sukkar T, Skyllas-Kazacos M. Membrane stability studies for vanadium redox cell applications. *J. Appl. Electrochem*. 34: 137-145 (2004)

In the revised manuscript [Line 250, Page 11]

The effects of varying electrolyte concentration on the crossover flux and diffusion coefficients of vanadium ions across the Nafion membrane were confirmed by diffusion experiments (Fig. S16).

In the revised supplementary information [Line 293, Page 15]

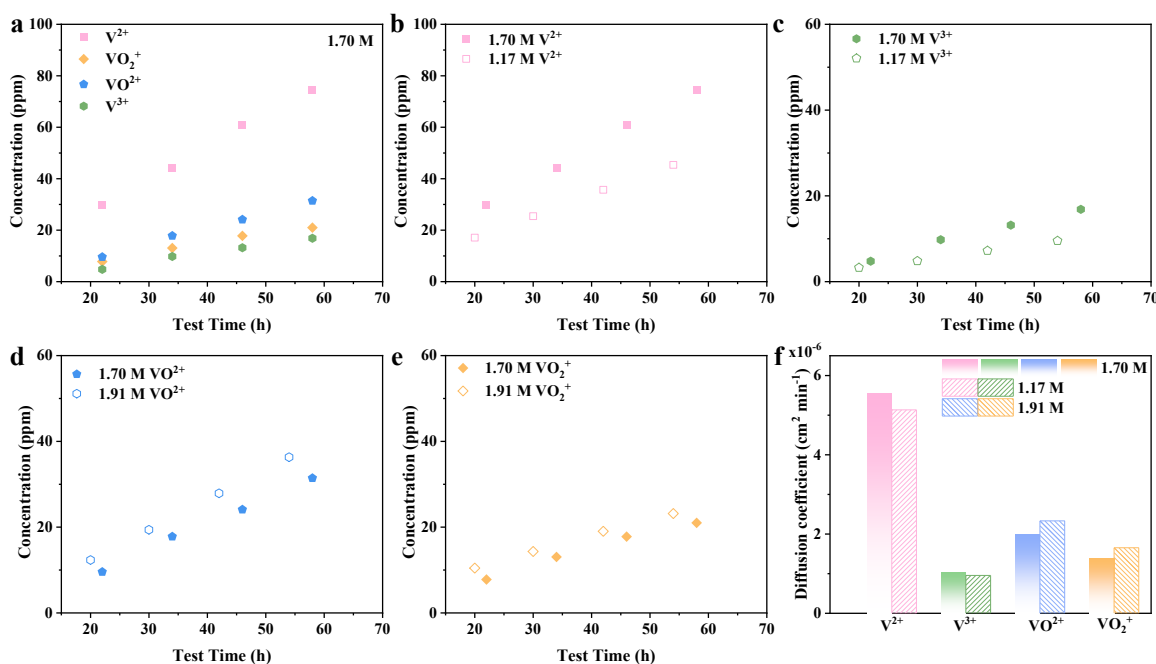


Fig. S16 Vanadium ion diffusion tests across an N212 membrane. **a**, Diffusion fluxes of various vanadium ions in 1.70 M electrolyte. **b-c**, Effect of reducing electrolyte concentration from 1.70 to 1.17 M on the diffusion fluxes of V^{2+} and V^{3+} . **d-e**, Effect of increasing electrolyte concentration from 1.70 to 1.91 M on the diffusion fluxes of VO^{2+} and VO_2^+ . **f** Variation of vanadium ion diffusion coefficients with electrolyte concentration.

As shown in Fig. S16a, the flux of V^{2+} exhibits the highest value followed by those of VO^{2+} , VO_2^+ , and V^{3+} , which is consistent with a previous report.^{S2} Moreover, Fig. S16b-e demonstrates that

decreasing the electrolyte concentration profoundly reduces vanadium ion flux across the Nafion membrane, whereas increasing the concentration markedly enhances the flux. These results confirm that the transport of vanadium ions across the Nafion membrane can be approximated by Fick's law.^{S7}

The diffusion coefficients of vanadium ions across a Nafion 212 membrane were calculated using the following equation:^{S2}

$$\ln\left(\frac{C_A}{C_A - C_B}\right) = D \frac{A}{V_B L} t \quad (\text{Eq. S22})$$

where D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), A is the effective membrane area (m^2), L is the membrane thickness (m), C_A is the vanadium ion concentration on the enrichment side (mol L^{-1}), C_B is the vanadium ion concentration on the deficiency side (mol L^{-1}), and t is the test time (s). In this calculation, the volume of deficiency side (V_B) and C_A were assumed constant.

The resulting values (Fig. S16f) exhibit good agreement with independent measurements reported previously.^{S2} These results further demonstrate that modulating the concentration of vanadium ions alters their diffusion rate across the Nafion membrane.

In these experiments, a flow battery cell equipped with a Nafion 212 membrane and two electrodes with a size of $40.00 \times 40.00 \text{ mm}^2$ was employed. The diffusion test for V^{2+} was conducted under N_2 protection to avoid the influence of air-induced V^{2+} oxidation. For each test, 20 mL of vanadium electrolyte was circulated on one side of the cell, while an equimolar MgSO_4 solution in 3 M H_2SO_4 served as the counter electrolyte on the opposite side. Both solutions were pumped at a flow rate corresponding to 51 rpm using a Longer BT100-2J peristaltic pump.

The paired electrolyte compositions were as follows:

- 1) Standard concentration (1.70 M): 1.70M V^{2+} , V^{3+} , VO^{2+} , or VO_2^+ in 3 M H_2SO_4 versus 1.70 M MgSO_4 in 3 M H_2SO_4 .
- 2) Reduced concentration (1.17 M): 1.17 M V^{2+} or V^{3+} in 3 M H_2SO_4 versus 1.17 M MgSO_4 in 3 M H_2SO_4 .
- 3) Increased concentration (1.91 M): 1.91 M VO^{2+} or VO_2^+ in 3 M H_2SO_4 versus 1.91 M MgSO_4 in 3 M H_2SO_4 .

Vanadium ion concentrations were determined using an Inductively Coupled Plasma–Optical Emission Spectrometer (Avio-200, PerkinElmer). Samples (0.2 ml) were withdrawn and diluted

7500-fold (for vanadium electrolytes) or 750-fold (for counter solutions) with deionized water prior to analysis.

2. The accuracy of the title

Although the authors showed that the penalty from the crossover in Fe-V RFBs can be overcome using the same strategy, this strategy does not really solve the major problem caused by crossover in asymmetric RFBs such as Fe-Cr, Fe-V batteries. Ideally, these batteries should have Fe and Cr separated, since the existence of crossovered Fe into the other side introduces severe HER side reactions. Authors mixed Fe-V making an after-crossover electrolyte is a decent demonstration of BSEs, but such batteries may not be commercially favored (~50% of the V-Fe capacity wasted, co-existence Fe in V side). BSEs can still be useful for batteries using the same redox core in both sides, which is VRFB the authors focused on. The authors may consider adjusting the title into "Balanced-State Electrolytes Overcome Crossover in Vanadium Redox Flow Batteries", which is more accurate and straightforward.

Response:

We sincerely thank the reviewer for the valuable comments. We have changed the title to "Balanced-State Electrolytes Overcome Crossover in Vanadium Redox Flow Batteries" in the revised manuscript and supplementary information.

In the revised manuscript [Title]

Balanced-State Electrolytes Overcome Crossover in **Vanadium** Redox Flow Batteries

In the revised supplementary information [Title]

Balanced-State Electrolytes Overcome Crossover in **Vanadium** Redox Flow Batteries

Reviewer #2

The authors have addressed my comments appropriately, and the manuscript has improved as a result. The remaining issues are minor and can be handled during the editorial process.

Response:

We are grateful to the reviewer for their recognizing the merit of our work.

Reviewer #3

Thank you for the thorough revision and detailed point-by-point response. The manuscript is significantly clearer and more convincing after revision.

The most important improvement is the explicit “balanced state/BSE determination” workflow now presented in the Methods and expanded in the SI. This makes the approach far more reproducible and portable across membranes and operating conditions. I also appreciate the addition of a physics-based transport model (COMSOL/Nernst–Planck) to place the performance trends and crossover mitigation into a mechanistic framework; this directly addresses my previous concern that the narrative relied too heavily on simplified interpretations of MD.

Finally, several presentation issues have been handled appropriately (e.g., removal of a non-informative panel, clearer discussion of side reactions and their impact on average valence, and new experimental evidence supporting ion–sulfonate interactions). I have no further major concerns.

Response:

We really appreciate the reviewer’s positive comments on our work.