

Reconciling Strong Coordination and Anion-Reinforced Solvation Structure Enables Nonflammable Electrolytes for Potassium-Ion Batteries

Corresponding Author: Professor Bingan Lu

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript presents a rational electrolyte design strategy based on side-chain engineering of phosphate solvents to simultaneously achieve non-flammability and enhanced electrochemical stability in potassium-ion batteries. By introducing side-chain engineering, the authors realize strong coordination while intentionally weakening bulk solvation strength, thereby inducing a weakly solvating environment. This synergistic modulation gives rise to an anion-rich solvation structure, which effectively stabilizes both anode and cathode interphases, providing a coherent molecular-to-electrochemical design framework. This manuscript is generally well written; however, the following points should be adequately addressed before publication.

1) The introduction of OOE as a co-solvent to mitigate the high viscosity of the TBXP-based electrolyte is reasonable and practically motivated. The electrochemical results demonstrate that the mixed electrolyte system performs effectively under the tested conditions. However, it remains unclear how TBXP behaves in the absence of OOE, and whether the solvation characteristics identified in the single-solvent analysis are preserved in the mixed electrolyte. Clarifying whether OOE primarily serves as a physical diluent or actively alters the solvation structure would help strengthen the connection between the molecular design principles and the practical electrolyte formulation.

2) The TEM results convincingly demonstrate the formation of a thin and uniform interphase in the TBXP-based electrolyte, which is consistent with the improved interfacial stability observed electrochemically. However, attributing this effect to the suppression of electron tunneling may be an overinterpretation, as electron tunneling behavior cannot be directly inferred from interphase thickness alone. Describing the observed effect in terms of chemical and electronic passivation that suppresses continuous electrolyte decomposition would provide a more rigorous and accurate interpretation of the TEM observations.

3) The manuscript describes the proposed electrolyte design as a general design strategy. However, the experimental validation is currently limited to potassium-ion batteries with specific electrode configurations. While the concept is promising, the use of "general" may be interpreted as extending beyond the demonstrated scope. Moderating this expression or explicitly defining the applicable system boundaries would help avoid potential overgeneralization and improve the accuracy of the claims.

Reviewer #2

(Remarks to the Author)

This work addresses the electrode compatibility issues of non-flammable electrolytes in PIBs through molecular design strategy. By introducing extended and functionalized side chains into the phosphate ester framework, a solvent molecule that combines strong coordination ability with weak solvation characteristics is obtained, thereby synergistically improving the cycling stability of both the anode and the cathode. The conclusions are well supported by substantial data. The molecular design concept offers valuable inspiration and reference value for other alkali-metal-ion batteries. I would like to recommend it for publication with the following issues being addressed.

1. Regarding the coordination numbers obtained from the molecular dynamics simulations for each electrolyte system, the manuscript should provide a clearer explanation of the calculation methodology, including details on the statistical approach

and determination criteria. Additionally, the multi-site coordination characteristics of the designed TBXP solvent molecule should be more explicitly articulated within the extracted structural analyses.

2. The TBXP-based electrolyte exhibits high compatibility with the graphite anode. To systematically evaluate its potassium storage kinetics, it is recommended to supplement the rate performance data of the graphite anode at different current densities in the manuscript.

3. If possible, please include the CV curves of the K||PB cells to clarify the potassium intercalation/de-intercalation potentials of the PB cathode. Additionally, some minor details require revision, such as specifying the scan rate used in the LSV tests.

4. The manuscript states that OOE was added to reduce the viscosity of the electrolyte, but supporting data are lacking and should be provided.

5. Compared to conventional ignition tests, measuring the solvent's self-extinguishing time and the total heat release during ignition provides a more quantitative and intuitive assessment of its flammability, thereby more accurately reflecting combustion behavior and safety risks under realistic conditions. It is better for the authors to refer to the following references for more details for safety tests and cite them (ACS Energy Lett. 2025, 10, 3143–3150; ACS Energy Lett., 2023, 8, 836–843)

Reviewer #3

(Remarks to the Author)

In this article, the authors proposed incorporating ether oxygen into non-flammable phosphate esters (herein, TMP) to construct multi-site chelation, aiming to enhance the stability of electrolytes for potassium-ion batteries. While the developed electrolyte exhibits certain advantages in electrochemical performance over previous reports, the proposed viewpoints remain unclear and unconvincing. I harbor concerns regarding several issues, particularly with respect to the innovation of the design concept. After careful evaluation, I regret to suggest that this manuscript does not meet the publication standards of the Nature communication in its current form. The following issues require careful reconsideration by the authors.

1. Line 125 claims that the divergent side-chain structure is unfavorable for the stability of the electrolyte system, yet no rationale is provided for this conclusion. Additionally, the schematic diagram in Figure 1 designates side-chains as side reaction sites without clarifying the cause. The authors should supplement verification or interpretative explanations for these assertions.

2. Line 200 describes TBXP as a strongly solvating solvent, a conclusion I can reasonably accept given its multidentate chelation property. However, Line 207 asserts that TBXP exhibits the weakest solvating capacity, creating an obvious contradiction. Regarding the ^{19}F NMR results: the observed downfield shift attributed to enhanced FSI^- anion coordination is actually a result of the fixed salt concentration (1 mol/L) used in your tests. Due to the large molar mass of TBXP, the actual salt-to-solvent molar ratio is higher, leading to more anions being passively coordinated with K^+ , which is analogous to the effect of high-concentration electrolytes. Similar contradictory statements appear elsewhere in the full manuscript and should be carefully reconsidered and revised.

3. In Line 239, you mention the average K-O distances. It would be advisable to present the average distances between K^+ and specific coordinating oxygen species in TBXP, such as $\text{P}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ moieties. Due to the obvious structural differences between these coordinating sites, directly comparing the coordination distances of all oxygen atoms may not be appropriate. The descriptions in lines 241–243 need to be reconsidered. Additionally, the statements in Lines 259–261 require re-evaluation.

4. In Figure 3a, KFSI-TMP exhibits the strongest reactivity. Calculated from the current and time, the side reaction capacity exceeds 1.2 mAh cm^{-2} , which is a considerably high value. However, in Figure 3b, KFSI-TMP still achieves an ICE of 78.1%, far superior to that of KFSI-TBP (50.3%). Additionally, why is the open-circuit voltage of the K||Cu cell with KFSI-TMP higher than 3 V in Figure 3a?

5. In Figure 3c, the cell with KFSI-TBP appears to exhibit a continuous capacity increase. What happens in the subsequent cycles that are not presented? And what is the underlying reason for this continuous capacity rise? Additionally, in Line 282, you mention that severe electrochemical polarization occurs in the K||graphite cell with KFSI-TBP electrolyte. Since KFSI-TBP shows comparable ionic conductivity to other electrolytes, what is the origin of this polarization?

6. The KFSI-TBP electrolyte enables the K||PB cell to cycle stably for over 500 cycles at 100 mA g^{-1} . However, in Supplementary Figure 31, obvious overcharge occurs in the cell after the rate capability test. How to understand this inconsistent phenomenon?

7. What do the "abusive conditions" specifically refer to in Figure 5i? Experimental testing methods and related details should be clearly included in the Methods section. Additionally, complete details about the tested batteries need to be provided, such as cycling conditions before the tests and the state of charge (SOC) during the test.

8. All cells tested have excessively low mass loading ($1\text{--}1.5 \text{ mg cm}^{-2}$). It is strongly recommended that full-cell performance tests under high mass loading conditions (cathode mass loading should exceed 20 mg cm^{-2}). In addition, details of the pouch cell, including electrode information (e.g., active material loading, electrode area, and thickness) and total capacity, are lacking and should be supplemented for evaluation.

9. Given that the core goal of this work is to design a non-flammable electrolyte for KIBs to enhance safety, supplementary safety tests (e.g., needle penetration test of pouch cells) are recommended to demonstrate the strategy's practicality.

Minor notes

Line 297, TBP should be TBXP.

In the title, "strong coordination and weak solvation" needs revision to avoid misunderstanding, as TBXP does not exhibit weak solvating ability.

Reviewer #4

(Remarks to the Author)

This manuscript reports the design of a nonflammable phosphate solvent (TBXP) that simultaneously enables multidentate coordination and molecular-size effects through side-chain engineering, leading to high-voltage stability, long cycle life, and enhanced safety in potassium-ion batteries. The concept of electrolyte molecular design is both novel and progressive.

However, the current manuscript lacks (1) direct evidence of the mechanism, (2) quantitative evaluation of safety tests, (3) quantification of the solvation structure, and (4) evaluation for practical use. Therefore, I recommend major revision before the manuscript can be considered for publication.

(1) Direct evidence of the mechanism

While the manuscript claims that ether oxygen atoms in side-chains coordinate with K^+ , the direct experimental evidence is lacking. Highly recommended techniques would include, for example, IR/Raman or ^{17}O -NMR measurements focusing on the TBXP molecule itself, which would show coordination-induced vibrational shifts or electronic shielding corresponding to the ether oxygen atoms in side-chains. Alternatively, it is also preferable to add experimental data using triheptyl phosphate that does not contain -O- groups in side-chains as a comparative example.

(2) Quantitative evaluation of safety tests

Battery safety (thermal tests, overcharge tests, and nail penetration tests, etc.) is strongly linked to the thermal stability of the electrodes. For safety measures, it is more important to improve the heat resistance of the electrode interface than to make it flame retardant. It is strongly recommended to carry out the above safety tests on pouch cells or to perform DSC measurements on the electrodes (cathode and anode) using electrolytes with TMP, TBP, and TBXP.

(3) Quantification of the solvation structure

A central argument of the manuscript is that reduced free solvent content promotes anion-derived, inorganic-rich SEI/CEI formation. Therefore, quantification of the free solvent ratio and solvent-ion species (SSIP/CIP/AGG) is required. For example, peak separation analysis of Raman measurements, detailed shift analysis of NMR results, and chemical potential measurements using a ferrocene reference electrode conducted by Prof. Yamada et al. Furthermore, in the evaluation of KFSI-TMP, KFSI-TBP, and KFSI-TBXP, the molecular weights of the solvents differ significantly, so the discussion should be based on fixed stoichiometry (molar ratio) rather than molar concentration; otherwise it would be unfair.

(4) Evaluation for practical use

Considering the practical use of batteries, the ionic conductivity of the KFSI-TBXP electrolyte at 25°C (1.75 mS cm^{-1}) is extremely low. The ionic conductivity of current electrolytes must be at least 7 mS cm^{-1} at 25°C, even for prismatic and pouch-type cells. It is necessary to evaluate low-temperature performance (e.g., -20 to 0 deg.C) or rate performance when the amount of electrode loading is increased.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have thoroughly addressed the reviewer comments and provided clear, well-reasoned revisions that substantially strengthen the manuscript. The additional experiments and clarifications regarding the electrolyte formulation, solvation structure, and interfacial interpretation have improved both the mechanistic clarity and the scientific rigor of the work. The revised manuscript now presents a coherent and convincing case for the proposed molecular design strategy for nonflammable electrolytes in potassium-ion batteries. In its current form, the manuscript is suitable for publication in this journal.

Reviewer #2

(Remarks to the Author)

The authors have addressed my comments. I don't have further questions.

Reviewer #3

(Remarks to the Author)

Following substantial revisions, the authors have evidently devoted considerable effort to enhancing the manuscript across multiple aspects.

Most of my concerns have been adequately addressed. The only remaining issue is that the side chain in TBXP shows the lowest BDE value, corresponding to the worst stability. Is this inconsistent with the main claim of the manuscript?

Reviewer #4

(Remarks to the Author)

This manuscript presents an interesting and well-designed electrolyte concept based on combining multidentate

coordination and molecular-size effects. The revised version has been significantly improved, and I appreciate the authors' efforts in addressing the previous comments. In particular, the added mechanistic evidence, comparative experiments, and quantitative safety evaluations substantially strengthen the manuscript.

I have one remaining concern regarding the practical applicability of the electrolyte. The ionic conductivity ($\sim 1.75 \text{ mS cm}^{-1}$ at 25°C) is relatively low compared to typical practical systems, which may impose limitations under realistic conditions. Although higher mass loading data are now provided, the areal capacity and cycle life remain somewhat limited, suggesting non-negligible transport constraints.

In addition, low-temperature performance has not been evaluated, which is relevant given the expected decrease in conductivity at reduced temperatures. The manuscript also uses terms such as "practical" (e.g., in the Abstract) or implies applicability to realistic battery systems; however, given the relatively low ionic conductivity, the scope of such applicability should be more clearly defined.

I recommend the authors briefly clarify these points and specify the applicable operating conditions to avoid overgeneralization.

Overall, I believe this can be addressed within a minor revision.

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Point-by-point Response to the Reviewers' Comments

Nature Communications manuscript NCOMMS-25-97130

Title: Reconciling Strong Coordination and Anion-Reinforced Solvation Structure

Enables Nonflammable Electrolytes for Potassium-Ion Batteries

Dear Referees:

Thank you very much for your precious time and effort in reviewing our manuscript (Manuscript number: **NCOMMS-25-97130**) and for providing insightful and constructive comments. We have carefully read and thoroughly considered all your suggestions, and have revised the manuscript accordingly to the best of our ability. These comments are highly valuable and have significantly improved the quality and clarity of our work. We have addressed each comment point-by-point in the following response, and all revised content in the manuscript is highlighted in yellow. We sincerely appreciate your valuable contribution to refining this work and hope that you will approve the revised manuscript for publication in “*Nature Communications*”.

Instructions.

Blue: comments from Reviewers;

Black: our response to reviewer's comments;

Highlighted text in yellow: revisions made in the revised manuscript.

Reviewer #1:

This manuscript presents a rational electrolyte design strategy based on side-chain engineering of phosphate solvents to simultaneously achieve non-flammability and enhanced electrochemical stability in potassium-ion batteries. By introducing side-chain engineering, the authors realize strong coordination while intentionally weakening bulk solvation strength, thereby inducing a weakly solvating environment. This synergistic modulation gives rise to an anion-rich solvation structure, which effectively stabilizes both anode and cathode interphases, providing a coherent molecular-to-electrochemical design framework. This manuscript is generally well written; however, the following points should be adequately addressed before publication.

Response:

We greatly appreciate the time and effort you dedicated to reviewing our manuscript. Your insightful and thought-provoking comments are invaluable in helping us refine and strengthen our manuscript, and in providing important direction for our ongoing research. In response to your suggestions, we have carefully revised the manuscript accordingly. Our point-by-point responses are provided below. We hope that the revised manuscript meets your expectations.

1) The introduction of OOE as a co-solvent to mitigate the high viscosity of the TBXP-based electrolyte is reasonable and practically motivated. The electrochemical results demonstrate that the mixed electrolyte system performs effectively under the tested conditions. However, it remains unclear how TBXP behaves in the absence of OOE, and whether the solvation characteristics identified in the single-solvent analysis are preserved in the mixed electrolyte. Clarifying whether OOE primarily serves as a physical diluent or actively alters the solvation structure would help strengthen the connection between the molecular design principles and the practical electrolyte formulation.

Response:

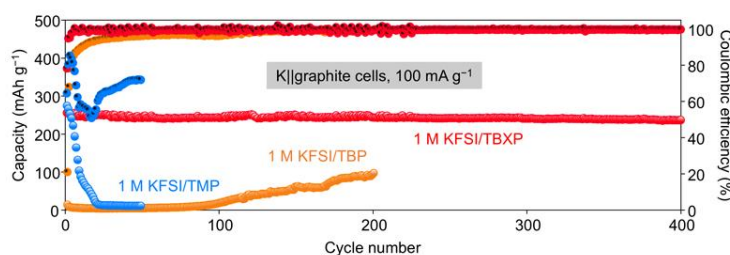
We thank the reviewer for the insightful suggestion to clarify the role of OOE

co-solvent further. In response, we have conducted additional experiments to address this point.

First, we evaluated the electrochemical performance of K||graphite and K||PB cells using the single-solvent electrolyte without OOE (**Supplementary Figs. 11 and 12**). Among the three single-solvent systems (TMP, TBP, and TBXP), the TBXP-based electrolyte exhibited the best electrochemical performance in both cell configurations, confirming the intrinsic advantage of the TBXP molecular design.

Second, we performed Raman spectroscopy to investigate the solvation structures of the single-solvent electrolytes and their OOE-containing counterparts (**Fig. 2e and Supplementary Fig. 19**). The spectral analysis reveals that introducing 30 vol% OOE leads to subtle shifts in the coordination environment. Notably, the core solvation structure established by TBXP is largely preserved, accompanied by a modest increase in anion-involved coordination, leading to a slight increase in aggregate (AGG) formation.

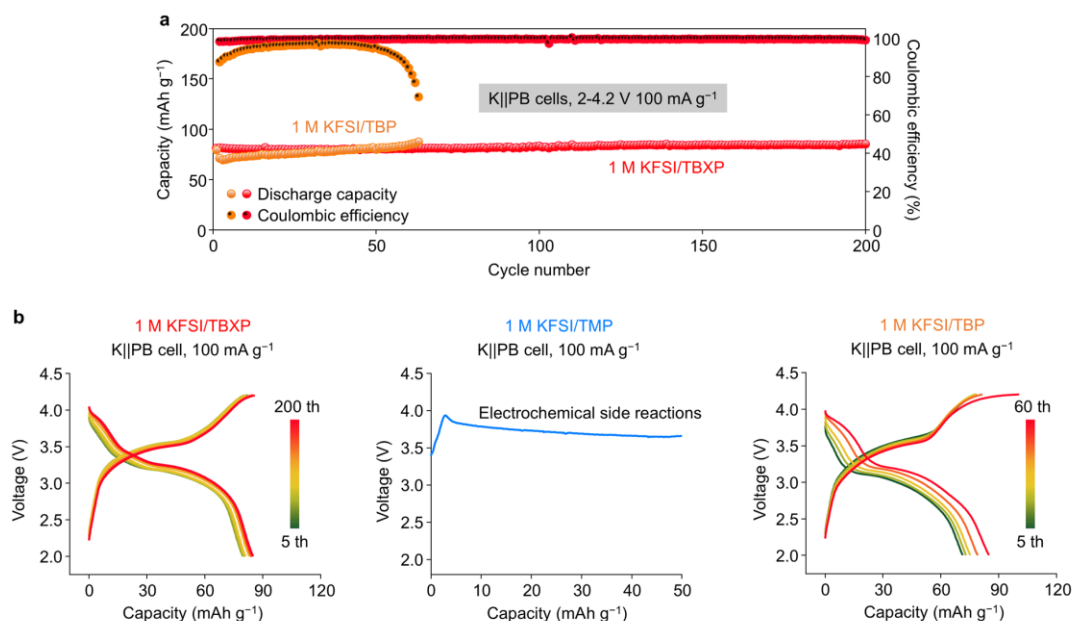
Based on these findings, we believe that OOE primarily serves as a physical diluent to reduce viscosity, while exerting a secondary, limited influence on the solvation structure. This dual role helps optimize the electrolyte formulation without compromising the key solvation structure imparted by the TBXP solvent. These clarifications strengthen the connection between our molecular design strategy and the practical electrolyte formulation.



Supplementary Fig. 11. Cycling performance of K||graphite cell in the three electrolytes at 100 mA g⁻¹.

To evaluate the cycling performance of K||graphite cells using 1 M KFSI in single-solvent electrolytes, the cells were tested under the same conditions. The results show that the 1 M KFSI/TMP electrolyte exhibits poor reversibility, retaining

a low specific capacity of only 18.8 mAh g⁻¹ after 20 cycles with a CE below 80%. In the 1 M KFSI/TBP electrolyte, severe polarization results in capacity limitations and a sluggish activation process. In contrast, the 1 M KFSI/TBXP electrolyte demonstrates significantly improved cycling stability, delivering a reversible capacity of 236.6 mAh g⁻¹ after 400 cycles with a capacity retention of 90.7%.



Supplementary Fig. 12. (a) Cycling performance and (b) corresponding charge-discharge profiles of K||PB cells in the three electrolytes.

To evaluate the cycling performance of K||PB cells using 1 M KFSI in single-solvent electrolytes, the cells were tested at a cut-off voltage of 4.2 V at 100 mA g⁻¹. The results demonstrate that the 1 M KFSI/TBXP electrolyte enables excellent cycling stability, with negligible capacity decay after 200 cycles and an average CE exceeding 99%. In contrast, the 1 M KFSI/TMP electrolyte exhibits severe side reactions at high voltage, preventing complete initial charging. For the 1 M KFSI/TBP electrolyte, the CE drops to 84.4% after 60 cycles, indicating progressive oxidative decomposition under high-voltage conditions.

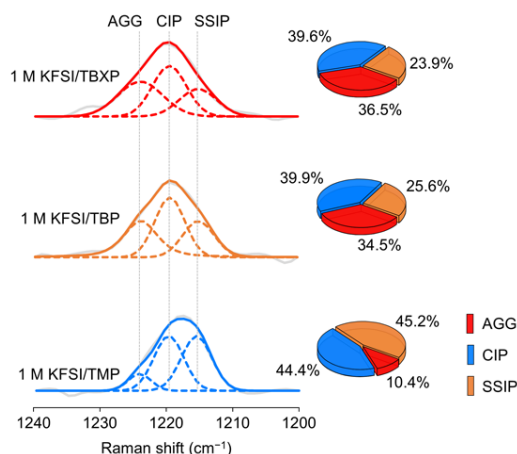
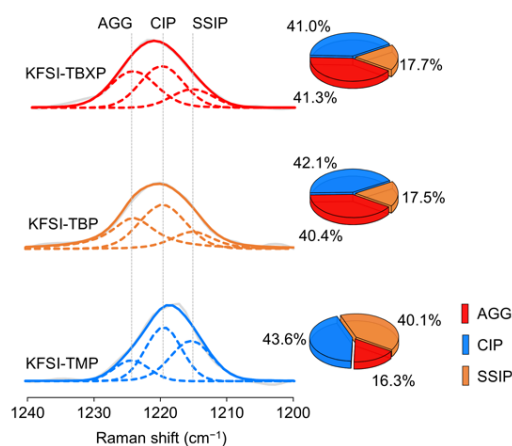


Fig. 2e. Raman spectra in the 1200-1240 cm^{-1} region corresponding to the S=O stretching mode of FSI^- for single-solvent electrolytes (1 M KFSI in TMP, TBP, and TBXP).



Supplementary Fig. 19. Raman spectra in the 1200-1240 cm^{-1} region corresponding to the S=O stretching mode of FSI^- for mixed electrolytes containing 30 vol% OOE (denoted as KFSI-TMP, KFSI-TBP, and KFSI-TBXP).

Raman spectroscopy was further employed to examine the solvation structures of the electrolytes containing 30 vol% OOE co-solvent. The results show that the introduction of OOE co-solvent leads to a slight increase in the proportion of AGGs across all three electrolyte systems, indicating a modest promotion of FSI^- participation in the K^+ solvation sheath. Specifically, the AGG fraction increases from 36.5% to 41.3% for the TBXP-based electrolyte, from 34.5% to 40.4% for the TBP-based system, and from 10.4% to 16.3% for the TMP-based electrolyte. Notably, even after the introduction of OOE co-solvent, the TBXP-based electrolyte maintains

the highest AGG proportion among the three electrolyte systems. This demonstrates that the TBXP solvent intrinsically facilitates the incorporation of FSI⁻ anions into the inner solvation sheath of K⁺ more effectively than TBP and TMP under comparable electrolyte formulations. This characteristic promotes the formation of an anion-derived inorganic-rich interphase.

Revisions:

Results and Discussion Section:

“Fig. 2e shows the Raman spectra and peak positions of FSI⁻ anions, indicating K⁺-FSI⁻ ion-pairing behavior.^{38, 39} Fitting analysis of the Raman peaks in this range showed that the TBXP-based electrolyte has a higher fraction of ion aggregates (AGGs, an anion coordinating to two or more K⁺) at 36.5%, compared to 10.4% for the TMP-based electrolyte. Further electrochemical tests demonstrate that the TBXP-based electrolyte enables enhanced cycling stability for both the graphite anode and the Prussian blue (PB) cathode (Supplementary Figs. 11 and 12).”

“Furthermore, Raman analysis revealed that the solvation structure evolution trend remained largely unchanged after the introduction of the OOE co-solvent, whereas the AGG ratio increased only slightly (Supplementary Fig. 19).”

2) The TEM results convincingly demonstrate the formation of a thin and uniform interphase in the TBXP-based electrolyte, which is consistent with the improved interfacial stability observed electrochemically. However, attributing this effect to the suppression of electron tunneling may be an overinterpretation, as electron tunneling behavior cannot be directly inferred from interphase thickness alone. Describing the observed effect in terms of chemical and electronic passivation that suppresses continuous electrolyte decomposition would provide a more rigorous and accurate interpretation of the TEM observations.

Response:

Thank you to the reviewer for the valuable suggestions regarding our interpretation of the interfacial layer. To avoid any potential misunderstandings, we have removed the

discussion of electron tunneling suppression from the revised manuscript. We now clearly describe the interphase as providing chemical and electronic passivation, thereby effectively suppresses continuous electrolyte decomposition. This interpretation aligns more closely with the functional understanding of the interphase and is fully consistent with your suggestion. We believe this revision enhances the rigor and clarity of our discussion.

Revisions:

Results and Discussion Section:

“Under transmission electron microscopy (TEM), a thin and uniform SEI of around 5 nm was observed on the graphite anode in the KFSI-TBXP electrolyte (Fig. 3e), indicating that the interphases provide effective chemical and electronic passivation to suppress continuous electrolyte decomposition.”

3) The manuscript describes the proposed electrolyte design as a general design strategy. However, the experimental validation is currently limited to potassium-ion batteries with specific electrode configurations. While the concept is promising, the use of “general” may be interpreted as extending beyond the demonstrated scope. Moderating this expression or explicitly defining the applicable system boundaries would help avoid potential overgeneralization and improve the accuracy of the claims.

Response:

We thank the reviewer for the valuable suggestion regarding the precision of our wording. We acknowledge that describing the proposed electrolyte design strategy as a “general design strategy” in the original manuscript was indeed not sufficiently accurate, especially given that this work primarily focuses on potassium-ion batteries with specific electrode configurations. To avoid overgeneralization, we have revised the manuscript to define the scope of this strategy clearly. This modification improves the scientific rigor of our discussion.

Revisions:

Abstract section:

“This work demonstrates a practical and efficient molecular design strategy for advanced electrolyte engineering in PIBs.”

Once again, we sincerely thank the reviewer for their insightful feedback and constructive suggestions, which have significantly strengthened the clarity and academic depth of our analysis and elevated the overall quality of the manuscript. We greatly appreciate the reviewer’s time and expertise devoted to this work, and sincerely hope that the revised version meets with their approval.

Reviewer #2:

This work addresses the electrode compatibility issues of non-flammable electrolytes in PIBs through molecular design strategy. By introducing extended and functionalized side chains into the phosphate ester framework, a solvent molecule that combines strong coordination ability with weak solvation characteristics is obtained, thereby synergistically improving the cycling stability of both the anode and the cathode. The conclusions are well supported by substantial data. The molecular design concept offers valuable inspiration and reference value for other alkali-metal-ion batteries. I would like to recommend it for publication with the following issues being addressed.

Response:

We sincerely thank the reviewer for their positive evaluation and recommendation for publication. We are pleased that the reviewer recognizes the value of our molecular design strategy in addressing electrode compatibility issues. The reviewer's insightful comments and suggestions are greatly appreciated, as they help us further improve the clarity and rigor of our manuscript. In response to the issues raised, we have carefully revised the manuscript accordingly. Point-by-point responses to all comments are provided below. We hope that the revised version now meets the expectations for publication.

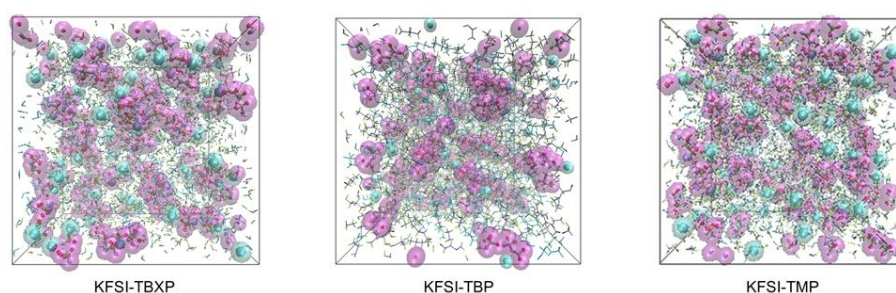
1. Regarding the coordination numbers obtained from the molecular dynamics simulations for each electrolyte system, the manuscript should provide a clearer explanation of the calculation methodology, including details on the statistical approach and determination criteria. Additionally, the multi-site coordination characteristics of the designed TBXP solvent molecule should be more explicitly articulated within the extracted structural analyses.

Response:

We thank the reviewer for the valuable suggestions regarding the quantitative and qualitative analysis of the molecular dynamics (MD) simulations. To clarify the calculation methodology, we have now provided additional details in the revised

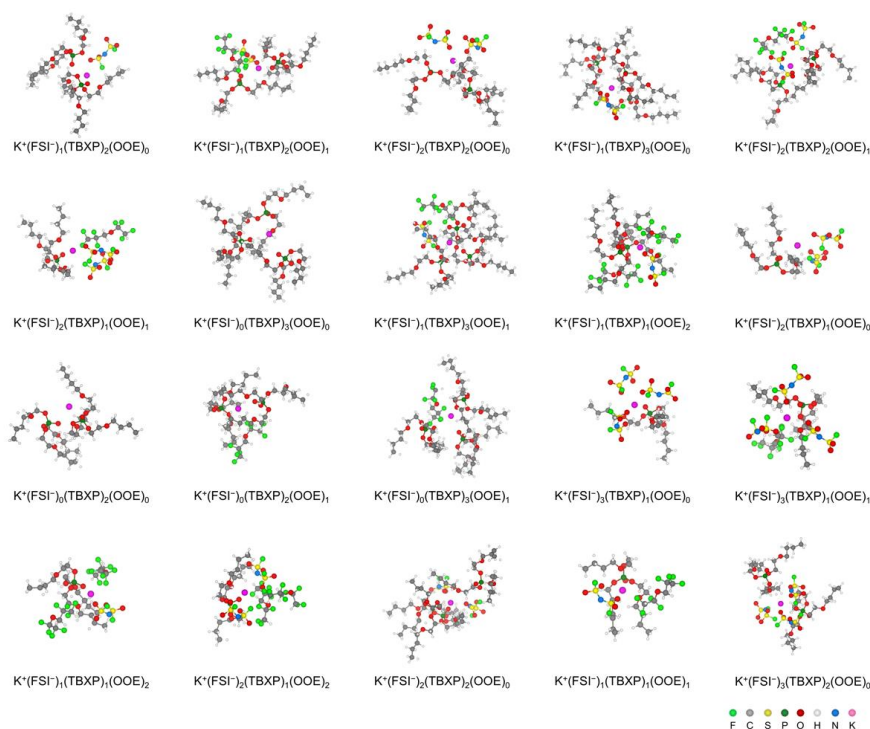
manuscript. Specifically, the radial distribution functions (RDFs) for each electrolyte system were obtained using LAMMPS, and the coordination numbers were determined by integrating the RDF up to the first minimum after the primary peak. These details have been included in the Methods section.

Furthermore, to more clearly and accurately illustrate the coordination distances between K^+ and various solvent molecules, we extracted the top 20 most probable solvation structures from MD simulations of the three-electrolytes, which together account for approximately 90% of the total solvation configurations (**Supplementary Figs. 20-23**). To better articulate the multi-site coordination characteristics of the designed TBXP solvent molecule, we have now highlighted the contributions from different coordination sites using distinct colors in the corresponding structural representations (**Fig. 2f and Supplementary Fig. 24**). These revisions help to more explicitly convey the coordination behavior and molecular design features discussed in the manuscript.

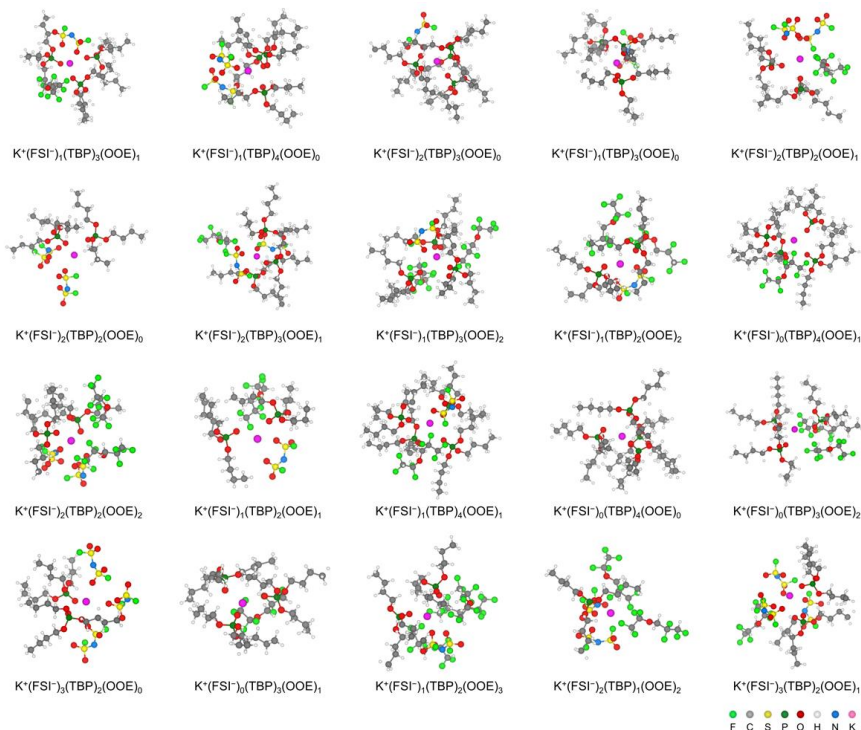


Supplementary Fig. 20. Snapshots of the MD simulated cells for different electrolytes.

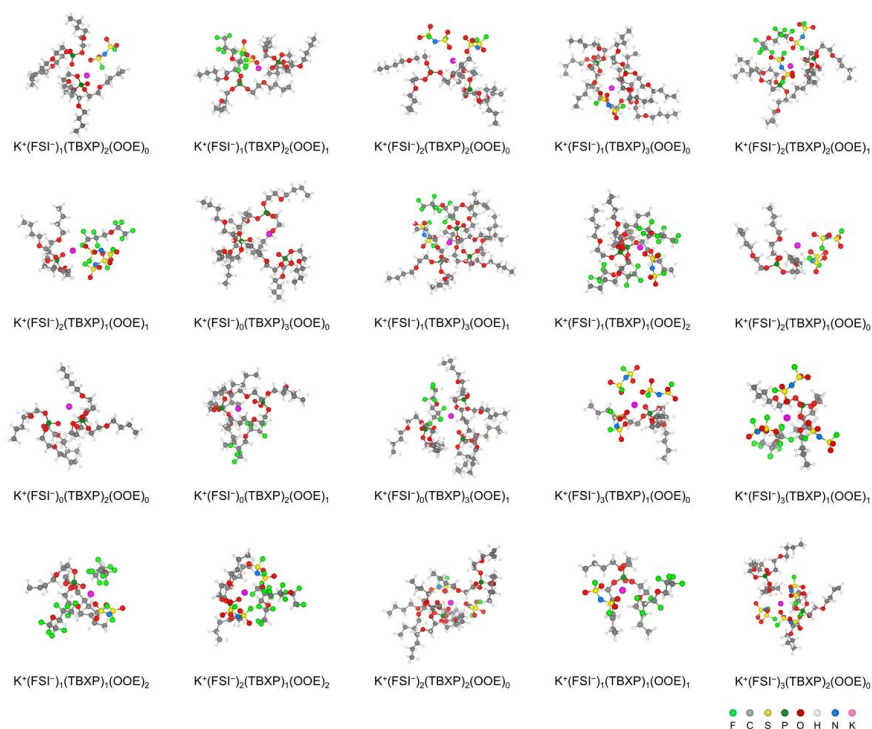
Classical MD simulations simulated the structures of the three electrolytes. The K^+ and FSI $^-$ are depicted as ball-and-stick models, while solvent molecules are represented as wireframe models. As expected, these coordinated structures are uniformly dispersed in each electrolyte.



Supplementary Fig. 21. Representative K^+ solvation structures derived from MD simulations in the KFSI-TBXP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).



Supplementary Fig. 22. Representative K^+ solvation structures derived from MD simulations in the KFSI-TBP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).



Supplementary Fig. 23. Representative K^+ solvation structures derived from MD simulations in the KFSI-TMP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).

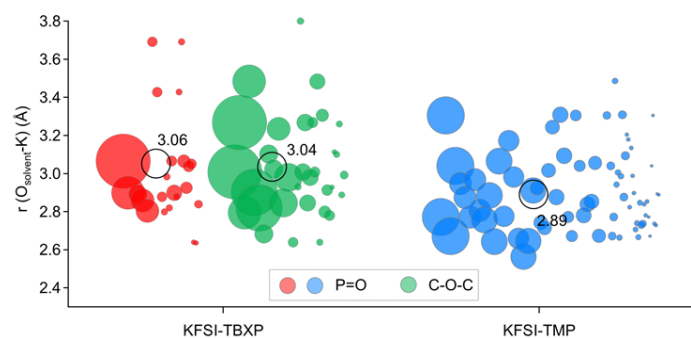
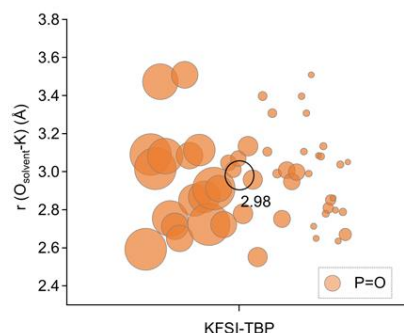


Fig. 2f. Coordination distances between K^+ and $O_{solvent}$ in KFSI-TBXP and KFSI-TMP electrolytes obtained from MD simulations. Shaded circular areas indicate the proportion.



Supplementary Fig. 24. Coordination distances between K^+ and $O_{solvent}$ in KFSI-TBP electrolyte by MD simulations. Shaded circular areas indicate the proportion.

Revisions:

Results and Discussion Section:

“Molecular dynamics (MD) simulations were employed to examine the solvation structure characteristics of the three electrolytes (Supplementary Fig. 20). For each electrolyte, twenty representative coordination configurations were sampled to systematically compare the variations in their solvation structures (Supplementary Figs. 21-23). We first determined the distribution of distances between K^+ and the primary coordinating oxygen atoms (the $O_{solvent}$, $P=O$ and $C-O-C$ sites are denoted as $OP=O$ and $OC-O-C$, respectively), and calculated a weighted average across all data. The results reveal that the average $K^+-OP=O$ distance in KFSI-TBXP electrolyte is $3.06 \text{ \AA}$, which is greater than those in KFSI-TMP ($2.89 \text{ \AA}$) and KFSI-TBP ($2.98 \text{ \AA}$) electrolytes (Fig. 2f and Supplementary Fig. 24). Additionally, the average $K^+-OC-O-C$ distance in the KFSI-TBXP electrolyte is $3.04 \text{ \AA}$. The observed coordination involving both the $P=O$ and $C-O-C$ groups demonstrates the multi-site chelation characteristic of the TBXP solvent, and the longer $K^+-O_{solvent}$ distance may favor FSI⁻ anions into the K^+ solvation sheath.”

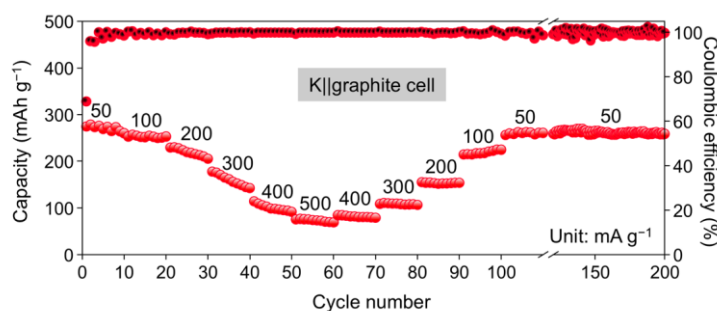
Methods section:

“The radial distribution functions were obtained using LAMMPS, with the coordination numbers of the cation solvation shells calculated by integrating to the first minimum following the first radial distribution function peak.”

2. The TBXP-based electrolyte exhibits high compatibility with the graphite anode. To systematically evaluate its potassium storage kinetics, it is recommended to supplement the rate performance data of the graphite anode at different current densities in the manuscript.

Response:

We thank the reviewer for the constructive suggestion. Rate performance is an effective approach to evaluate the potassium storage kinetics of electrode materials. Following the reviewer's suggestion, we have supplemented the rate performance of the graphite anode in the KFSI-TBXP electrolyte at various current densities in the revised manuscript (**Supplementary Fig. 33**). The results demonstrate that the graphite anode exhibits good rate capability in the KFSI-TBXP electrolyte, delivering a reversible capacity of 74.0 mAh g^{-1} at 500 mA g^{-1} . Moreover, after the current density returns to 50 mA g^{-1} , the electrode retains excellent capacity recovery and cycling stability. These results provide a more systematic assessment of the K^+ storage kinetics and further support the superior electrochemical performance of the KFSI-TBXP electrolyte.



Supplementary Fig. 33. Rate performance of graphite electrode in the KFSI-TBXP electrolyte.

The rate capability of K||graphite cells in the KFSI-TBXP electrolyte was evaluated at current densities ranging from 50 to 500 mA g^{-1} , with reversible capacities of 260.1, 216.7, 151.7, 109.5, 81.7, and 74.0 mAh g^{-1} , respectively. Upon returning the current density to 50 mA g^{-1} , the cell recovered a reversible capacity of 256.2 mAh g^{-1} and exhibited no capacity decay over 100 cycles at this current density, demonstrating excellent rate recovery and cycling stability.

Revisions:

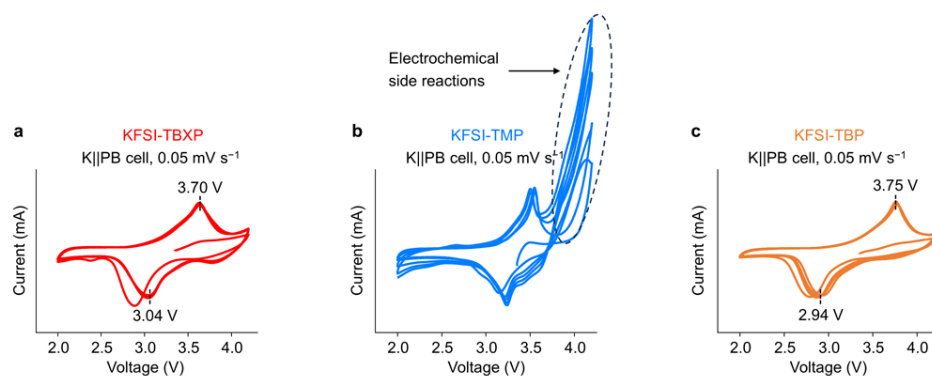
Results and Discussion Section:

“Furthermore, the K||graphite cell exhibits good rate performance in the KFSI-TBXP electrolyte (Supplementary Fig. 33).”

3. If possible, please include the CV curves of the K||PB cells to clarify the potassium intercalation/de-intercalation potentials of the PB cathode. Additionally, some minor details require revision, such as specifying the scan rate used in the LSV tests.

Response:

We thank the reviewer for the valuable comments. In the revised manuscript, we have included the initial five CV cycles of the K||PB cells in different electrolytes (Supplementary Fig. 45). In the KFSI-TMP electrolyte, a pronounced irreversible oxidation peak is observed at high voltage, which can be attributed to electrolyte decomposition under oxidative conditions. Compared with the KFSI-TBP electrolyte, the KFSI-TBXP electrolyte exhibits a lower polarization overpotential, with K^+ de-intercalation and intercalation potentials of 3.70 V and 3.04 V, respectively. Furthermore, the highly overlapped CV profiles observed in the KFSI-TBXP electrolyte indicate excellent electrochemical reversibility and cycling stability. Additionally, relevant experimental parameters, including the scan rate used in the LSV measurements, have been specified in the Methods section. We believe these revisions address the reviewer's comments appropriately.



Supplementary Fig. 45. CV profiles of K||PB cells in (a) KFSI-TBXP, (b) KFSI-TMP, and (c) KFSI-TBP electrolytes at 0.05 mV s^{-1} .

In the KFSI-TBXP electrolyte, the poor overlap of the initial CV profile is primarily attributed to electrode activation and the formation of the CEI layer. The subsequent cycles (2nd to 5th) exhibit a high degree of overlap, indicating excellent cycling stability of the K||PB cell in the KFSI-TBXP electrolyte (Supplementary Fig. 45a). In contrast, the KFSI-TMP electrolyte, due to its poor oxidative stability, displays a distinct oxidation peak associated with electrochemical side reactions at high voltage (Supplementary Fig. 45b). Meanwhile, the KFSI-TBP electrolyte shows relatively poorer CV profile overlap, suggesting inferior cycling stability compared to the KFSI-TBXP electrolyte (Supplementary Fig. 45c). Furthermore, analysis of the K^+ intercalation/de-intercalation potentials reveals a lower overpotential in the KFSI-TBXP electrolyte, with K^+ de-intercalation and intercalation potentials of 3.70 V and 3.04 V, respectively.

Revisions:

Results and Discussion Section:

“Similarly, the K||PB cell with the KFSI-TBP electrolyte experienced a sharp decline in CE after 600 cycles. Furthermore, the CV profiles of the K||PB cells in different electrolytes corroborate the performance advantages of the KFSI-TBXP electrolyte (Supplementary Fig. 45). These observed deteriorations in CE are likely attributed to side reactions, such as the corrosion of Al foil or the oxidative decomposition of the electrolytes.”

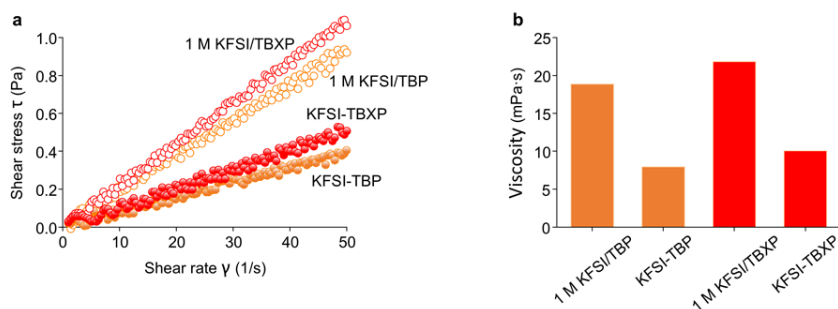
Methods section:

“The Linear sweep voltammetry (LSV), Cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were measured on a CHI660e electrochemical system. Specifically, LSV measurements were conducted on K||Al cells over a voltage window of 2.5-5.0 V at a scan rate of 1 mV s⁻¹, while CV measurements were performed on K||Cu cells over a range of 0.01-2.5 V at 0.1 mV s⁻¹ and on K||PB cells over a range of 2.0-4.2 V at 0.05 mV s⁻¹.”

4. The manuscript states that OOE was added to reduce the viscosity of the electrolyte, but supporting data are lacking and should be provided.

Response:

We sincerely thank the reviewer for this important comment. To support the statement regarding viscosity reduction, we have now included the viscosity data of the electrolytes with and without the OOE co-solvent in the revised manuscript (**Supplementary Fig. 17**). As described, the introduction of OOE co-solvent effectively reduces the viscosity of the electrolyte, and the experimental results are consistent with this claim. The corresponding data have been added to the main text to substantiate this point. We believe this revision adequately addresses the reviewer's concern.



Supplementary Fig. 17. Viscosities of TBP- and TBXP-based electrolytes with and without OOE as co-solvent.

Due to the increased solvent viscosity from the long side-chain structure, the viscosities of 1 M KFSI/TBP and 1 M KFSI/TBXP electrolytes are 18.9 and 21.8 mPa·s, respectively. Upon introducing 30 vol% OOE as a co-solvent, the viscosities of the KFSI-TBP and KFSI-TBXP electrolytes decrease to 7.9 and 10.1 mPa·s, respectively, demonstrating that OOE co-solvent effectively reduces electrolyte viscosity.

Revisions:

Results and Discussion Section:

“To address the high-viscosity of macromolecular phosphate solvents, we introduced 30 vol% of a low-viscosity fluorinated ether (1,1,2,2,5,5,6,6-octafluoro-3-oxahexane,

OOE) as a co-solvent to optimize the electrolyte system (Supplementary Fig. 9). The introduction of OOE co-solvent effectively mitigates the high-viscosity issue (Supplementary Fig. 17).”

5. Compared to conventional ignition tests, measuring the solvent's self-extinguishing time and the total heat release during ignition provides a more quantitative and intuitive assessment of its flammability, thereby more accurately reflecting combustion behavior and safety risks under realistic conditions. It is better for the authors to refer to the following references for more details for safety tests and cite them (ACS Energy Lett. 2025, 10, 3143–3150; ACS Energy Lett., 2023, 8, 836–843).

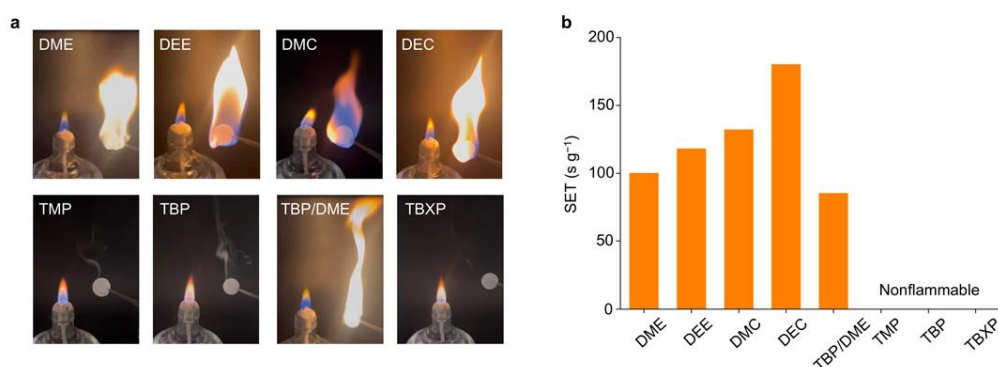
Response:

We sincerely appreciate the reviewer for the valuable and constructive comments on the quantitative evaluation of electrolyte flammability. We fully agree that the self-extinguishing time and total heat release during combustion provide a more quantitative and intuitive characterization of flammability, which can more reliably reflect the actual combustion behavior and safety risks under practical conditions.

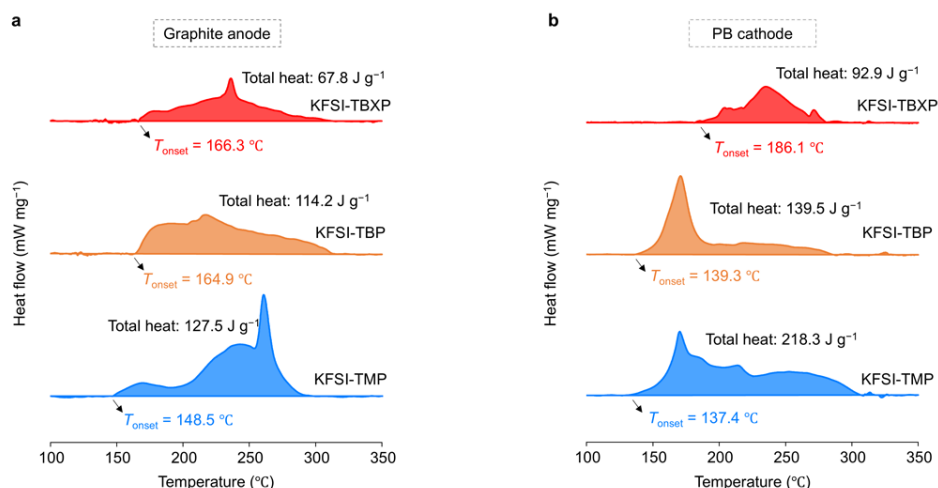
In response, we have supplemented the self-extinguishing time measurements for all investigated electrolytes. The results show that the phosphate-based solvents (TMP, TBP, and TBXP) exhibit a self-extinguishing time of 0 s, unambiguously verifying their non-flammable nature (**Supplementary Fig. 15**). We apologize for not being able to conduct the total heat release measurements due to current instrumental limitations. Nevertheless, we have fully recognized the critical significance of developing non-flammable electrolytes for advanced potassium-ion batteries, as emphasized in the representative literature (*Nat. Energy* 2025, 10, 1493-1502; *Adv. Mater.* 2024, 36, 2307220). Furthermore, we have carefully read and cited the two recommended references (*ACS Energy Lett.* 2025, 10, 3143-3150; *ACS Energy Lett.* 2023, 8, 836-843) and integrated the corresponding discussions to further illustrate the intrinsic safety advantages of phosphate-based electrolytes. As reported in the literature, phosphate esters can generate phosphorus-centered radicals (PO•) at high temperatures, which effectively scavenge the highly reactive H• and OH• radicals that

dominate the combustion chain reaction, thereby suppressing heat release and flame propagation. Such excellent flame-retardant properties originate from the intrinsic molecular structure of the phosphate group.

To further meet the requirement for quantitative safety analysis, we have additionally conducted differential scanning calorimetry (DSC) measurements to evaluate the thermal stability of the anode and cathode in contact with the electrolytes (**Supplementary Fig. 60**). The DSC results provide additional insights into the thermal behavior and safety characteristics of the TBXP-based electrolyte system. These supplementary experimental results and in-depth discussions have been incorporated into the revised manuscript, with proper citations to the suggested references. We believe these additions significantly strengthen the safety evaluation of our proposed electrolyte system. We sincerely thank the reviewer again for these insightful and helpful comments.



Supplementary Fig. 15. (a) Flammability analysis and (b) self-extinguishing time (SET) of various solvents.



Supplementary Fig. 60. DSC profiles of (a) potassiated graphite anodes (0.01 V) and (b) fully charge-state PB cathodes (4.2 V) mixed with relevant electrolyte.

The thermal compatibility of the graphite anode and PB cathode in different electrolytes was evaluated using differential scanning calorimetry (DSC). For the potassiated graphite anode, the mixture with KFSI-TBXP electrolyte exhibited an exothermic reaction onset temperature (T_{onset}) of 166.3 °C and a total heat release of 67.8 J g⁻¹. In comparison, the anode mixed with KFSI-TBP electrolyte showed a T_{onset} = 164.9 °C with a total heat release of 114.2 J g⁻¹, while the KFSI-TMP electrolyte showed the lowest T_{onset} (148.5 °C) and the highest total heat release (127.5 J g⁻¹). Notably, although the T_{onset} of KFSI-TBXP and KFSI-TBP were similar, KFSI-TBXP significantly suppressed the total heat release, demonstrating superior thermal stability. For the charge-state PB cathode (4.2 V), the mixture with KFSI-TBXP electrolyte delivered a T_{onset} = 186.1 °C and a total heat release of 92.9 J g⁻¹, markedly outperforming the KFSI-TBP (139.3 °C, 139.5 J g⁻¹) and KFSI-TMP (137.4 °C, 218.3 J g⁻¹) counterparts. These results indicate that the KFSI-TBXP electrolyte effectively suppresses exothermic reactions between the electrodes and electrolyte, thereby enhancing battery safety under thermal runaway conditions.

Revisions:

Results and Discussion Section:

“The solvent species in electrolytes are a critical determinant of the battery safety

risk.^{40, 41} To evaluate the safety of solvents, we conducted flammability tests. As shown in Supplementary Fig. 15, phosphate-based solvents exhibit a self-extinguishing time (SET) of 0 s g⁻¹, indicating complete non-flammability under open flame conditions, in stark contrast to conventional carbonate- and ether-based solvents. The excellent flame-retardant properties of phosphate-based solvents arise from the generation of PO• radicals under high temperature. These radicals can efficiently scavenge highly reactive H• and OH• radicals that drive the combustion chain reaction, thereby significantly reducing heat release and suppressing flame propagation, thereby lowering the thermal runaway risk of batteries.^{42, 43} Notably, given the presence of ether oxygen groups in the side-chain of the TBXP solvent molecule, we also prepared a physically blended mixture of dimethyl ether (DME) and TBP (1:1 by volume) for flammability comparison. The results demonstrate that physical blending fails to preserve the non-flammability inherent to phosphate solvents (SET = 85 s g⁻¹).”

“Furthermore, differential scanning calorimetry (DSC) was employed to assess the thermal abuse tolerance of both the potassiated graphite-electrolyte and charged PB cathode-electrolyte mixtures. Compared to the KFSI-TBP and KFSI-TMP electrolytes, the KFSI-TBXP electrolyte exhibited a higher exothermic onset temperature and lower total heat release, indicating superior capability in mitigating thermal runaway (Supplementary Fig. 60).”

Methods Section:

“Differential scanning calorimetry (DSC) measurements were performed on a thermal analyzer (China-DZ-DSC300C). Potassiated graphite anodes were retrieved from cells discharged to 0.01 V at 20 mA g⁻¹ in the corresponding electrolytes, while charged PB cathodes were obtained from cells charged to 4.2 V at 100 mA g⁻¹. Both electrodes were carefully rinsed with dimethyl carbonate (DMC) three times to remove residual electrolyte. After overnight drying, the electrode powders were mixed with the selected electrolyte solutions and sealed in 100 μL high-pressure gold DSC capsules. The DSC profiles were recorded from 30 to 400 °C at a heating rate of 10 °C min⁻¹.”

References Section:

- [40] Yang C, et al. Ultrafast thermo-responsive electrolyte for enhanced safety in lithium metal batteries. *Nat. Energy* **10**, 1493-1502 (2025).
- [41] Yang C, et al. Engineering A Boron-Rich Interphase with Nonflammable Electrolyte toward Stable Li||NCM811 Cells Under Elevated Temperature. *Adv. Mater.* **36**, 2307220 (2023).
- [42] Yang A, et al. Benchmarking the Safety Performance of Organic Electrolytes for Rechargeable Lithium Batteries: A Thermochemical Perspective. *ACS Energy Lett.* **8**, 836-843 (2023).
- [43] Zhou X, Yang C, Hu W, Han J, You Y. Assessment of Thermal Safety for Organic Electrolytes: from Material to Cell Level. *ACS Energy Lett.* **10**, 3143-3150 (2025).

Once again, we sincerely thank the reviewer for their insightful feedback and constructive suggestions, which have significantly strengthened the clarity and academic depth of our analysis and elevated the overall quality of the manuscript. We greatly appreciate the reviewer's time and expertise devoted to this work, and sincerely hope that the revised version meets with their approval.

Reviewer #3:

In this article, the authors proposed incorporating ether oxygen into non-flammable phosphate esters (herein, TMP) to construct multi-site chelation, aiming to enhance the stability of electrolytes for potassium-ion batteries. While the developed electrolyte exhibits certain advantages in electrochemical performance over previous reports, the proposed viewpoints remain unclear and unconvincing. I harbor concerns regarding several issues, particularly with respect to the innovation of the design concept. After careful evaluation, I regret to suggest that this manuscript does not meet the publication standards of the Nature communication in its current form. The following issues require careful reconsideration by the authors.

Response:

We are deeply grateful for your rigorous and prudent evaluation of our manuscript. The core innovation of our work lies in the TBXP solvent, which integrates multidentate coordination chelation and bulky molecular-size effects to achieve both strong cation coordination and an anion-reinforced solvation structure, breaking the inherent dilemma of traditional solvent design: strongly solvating solvents hinder anion into the solvation sheath and limit SEI stability, while weakly solvating solvents suffer from severe oxidative decomposition of free solvents, and no previous research has realized the coexistence of strong coordination and anion-reinforced solvation in a single solvent system. We have devoted extensive efforts to revising the manuscript to meet the high publication standards of *Nature Communications*, and our point-by-point responses are provided below. We sincerely hope you will approve our revised manuscript. Thank you again for your invaluable, constructive comments.

1. Line 125 claims that the divergent side-chain structure is unfavorable for the stability of the electrolyte system, yet no rationale is provided for this conclusion. Additionally, the schematic diagram in Figure 1 designates side-chains as side reaction sites without clarifying the cause. The authors should supplement verification or interpretative explanations for these assertions.

Response:

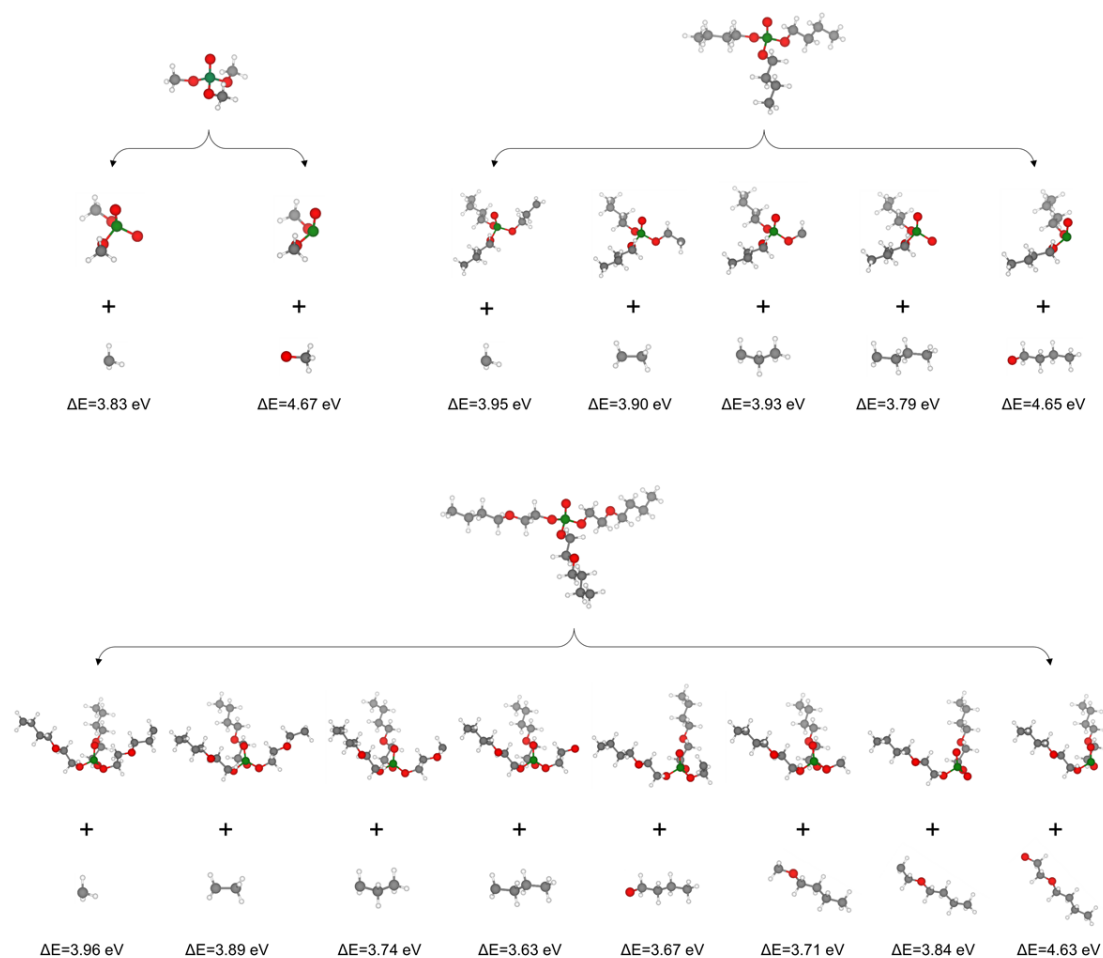
We sincerely appreciate the reviewer for raising this insightful and critical point. We fully recognize the importance of this concern, and it has guided us to conduct targeted supplementary research and rigorous revision to enhance the scientific rationality and mechanistic completeness of this work. To thoroughly address the issues raised, we have conducted additional theoretical calculations to provide solid support for the relevant conclusions and have comprehensively revised the corresponding sections of the manuscript to supplement detailed mechanistic interpretations.

First, bond dissociation energies (BDEs) are an effective parameter for determining the structural stability and reactive sites of solvent molecules (*Energy Environ. Sci.* **2025**, *18*, 1032810337; *ACS Nano* **2022**, *16*, 9883-9893). To clarify the inherent reason why side-chains are defined as parasitic side reaction sites, we calculated the stepwise BDEs of three solvent molecules (TMP, TBP, and TBXP) (**Supplementary Fig. 6**). The calculated results demonstrate that the main-chain skeletons of these three solvent molecules possess consistently high bond dissociation energies, with values of 4.67 eV, 4.65 eV, and 4.63 eV, respectively, which confirms the excellent structural stability of their main-chain backbones. In sharp contrast, the side-chain moieties of these molecules are identified as the thermodynamically unstable sites, with the minimum BDE values of 3.83 eV for TMP, 3.79 eV for TBP, and 3.63 eV for TBXP. This distinct difference in BDE between the main-chain and side-chains directly confirms that, compared to the main-chains, the side-chains are significantly more prone to bond cleavage and decomposition, thereby providing a definitive theoretical basis for identifying the side-chains as the parasitic reaction sites.

To further rationalize the conclusion that divergent side-chain structures compromise stability, we performed an in-depth LUMO analysis of K^+ -solvent coordination clusters to elucidate the intrinsic stability mechanism (**Fig. R1**). In electrolyte systems, the unavoidable coordination between solvents and ions directly determines the reductive decomposition behavior. For TBP solvent, which contains only a single main-chain P=O coordination site, the long alkyl side chains impose substantial steric hindrance (*J. Am. Chem. Soc.* **2021**, *143*, 18703-18713), forcing the K^+ -TBP complex

into a divergent side-chain configuration. This complex exhibits an extremely low LUMO energy of -4.73 eV, indicating a high propensity for reductive decomposition. For the TBXP solvent, which possesses multisite coordination sites on both the main-chain and side-chains, we analyzed multiple representative coordination modes. When only the main-chain coordinates with K^+ while the side chains remain divergent (**Configuration II**), the complex shows a low LUMO level (-4.44 eV) and poor stability. In sharp contrast, when the side chains participate in K^+ coordination (**Configurations I, III, and IV**), this is accompanied by a significant upshift in the LUMO energy (-3.42 eV, -3.51 eV, and -3.44 eV, respectively) that effectively suppresses reductive decomposition. This direct comparison confirms that divergent side-chain arrangements are the core origin of instability, fully substantiating the corresponding claim in the manuscript.

We believe these supplementary theoretical calculations and mechanistic analyses have fully addressed all your concerns and strengthened the scientific rigor of this work. All the revised contents, including the newly supplemented data and mechanistic explanations, have been integrated into the revised manuscript and highlighted for your easy review. We sincerely thank you again for your professional guidance and careful evaluation.



Supplementary Fig. 6. Calculated bond dissociation energies of TMP, TBP, and TBXP molecules. (O-red, C-brown, P-dark green, H-white).

To identify the reactive sites on phosphate ester solvent molecules, stepwise bond dissociation energy calculations were performed on three phosphate solvents using DFT. The results indicate that the minimum BDE values for the TMP, TBP, and TBXP solvents are located on the side-chains, at 3.83, 3.79, and 3.63 eV, respectively. These BDE calculations verify that the side-chains are the major parasitic reaction sites in these phosphate solvents.

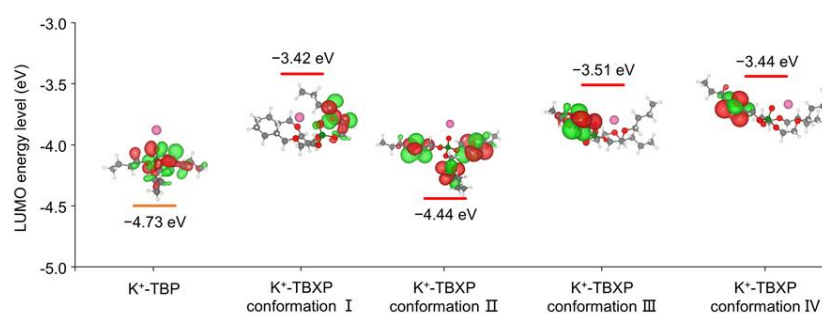


Fig. R1. Energy levels of TBP, and TBXP solvent molecules corresponding K⁺ ion pairs (K⁺-TBP and K⁺-TBXP). Color scheme of molecules: K, pink; O, red; P, green; C, grey; H, white.

Revisions:

Results and Discussion Section:

“Bond dissociation energy (BDE) calculations reveal that the major parasitic side reaction sites of phosphate solvents are concentrated on the side-chains (Supplementary Fig. 6).”

“The results demonstrate that when K⁺ coordination solely with the P=O site of TBXP solvent to form a divergent coordination configuration, the K⁺-TBXP conformation II exhibits a LUMO energy level of −4.44 eV (Supplementary Fig. 7). Notably, benefiting from the intrinsic side-chains coordination anchoring property of TBXP solvent, the additional coordination of K⁺ to the C-O-C site in its side-chains significantly enhances reductive stability, elevating the LUMO energy levels to the range of −3.42 eV (conformation I) to −3.51 eV (conformation III) (Fig. 2a and Supplementary Fig. 7). In contrast, TBP solvent exhibits severe steric hindrance from long alkyl side-chains structure, which restricts K⁺ coordination to the P=O site alone and forces the formation of a divergent coordination configuration. This unfavorable coordination mechanism results a much lower LUMO energy level of −4.50 eV for the K⁺-TBP conformation, indicating significantly poorer reductive stability (Fig. 2a).”

2. Line 200 describes TBXP as a strongly solvating solvent, a conclusion I can reasonably accept given its multidentate chelation property. However, Line 207 asserts that TBXP exhibits the weakest solvating capacity, creating an obvious contradiction. Regarding the ^{19}F NMR results: the observed downfield shift attributed to enhanced FSI⁻ anion coordination is actually a result of the fixed salt concentration (1 mol/L) used in your tests. Due to the large molar mass of TBXP, the actual salt-to-solvent molar ratio is higher, leading to more anions being passively coordinated with K⁺, which is analogous to the effect of high-concentration electrolytes. Similar contradictory statements appear elsewhere in the full manuscript and should be carefully reconsidered and revised.

Response:

We sincerely appreciate the reviewer's careful and professional comments, which have greatly helped us improve the quality of this manuscript. We apologize for the inappropriate description regarding the solvating ability of TBXP solvent. It is more appropriate to describe it as facilitating anion-reinforced solvation, and we have carefully revised the relevant statements throughout the manuscript accordingly.

At the molecular level, TBXP exhibits strong solvation of K⁺ owing to its multidentate chelating structure, as supported by binding energy calculations and NMR results. In the electrolyte system, the large molecular size of TBXP leads to a high effective salt-to-solvent molar ratio even at a low salt concentration (1 M), thereby promoting enhanced coordination between FSI⁻ anions and K⁺. This behavior is analogous to that observed in high-concentration electrolytes.

Following the reviewer's suggestion, we have carefully revised the analysis of the ^{19}F NMR results, as well as all relevant descriptions and Figures throughout the manuscript. The core viewpoint is clarified as the **formation of anion-reinforced solvation structures**, rather than the previously stated weak solvation ability of the TBXP solvent. We sincerely thank the reviewer again for these valuable and constructive comments, which have greatly improved the scientific rigor and presentation of this work.

Revisions:

Abstract Section:

“Here, we propose a molecular design strategy that integrates strong coordination capability with **anion-reinforced solvation structure**, thereby enabling the effective deployment of nonflammable phosphate solvents.”

“Concurrently, its large molecular structure effectively **increases the anion-to-solvent ratio** in the electrolyte, promoting the formation of stable electrode-electrolyte interphases, and resulting in exceptional compatibility with both the anode and cathode.”

Introduction Section:

“Here, we propose a molecular design concept for phosphate solvents, which integrates strong coordination and **anion-reinforced solvation** into a single molecule through via side-chain engineering.”

“Meanwhile, its large molecular structure effectively **increases the anion-to-solvent ratio, driving anions into the K^+ solvation sheath** and further facilitating the construction of a stable EEIs.”

Results and Discussion Section:

“This macromolecular solvent effectively **promotes the entry of more anions** into the K^+ solvation sheath (Supplementary Fig. 3).”

“As shown in Fig. 2d, contrary to the results under the fixed stoichiometric ratio condition, the TBXP-based electrolyte exhibits the most pronounced downfield chemical shift (**52.1 ppm**), indicating that TBXP solvent more efficiently promotes the **FSI⁻ anions into the primary K^+ solvation sheath.**”

“This finding provides compelling evidence for the feasibility of our design strategy, demonstrating that a solvent with both strong coordination and **anion-reinforced solvation** can be precisely achieved through side-chain engineering, thereby effectively enhancing the electrochemical performance of PIBs.”

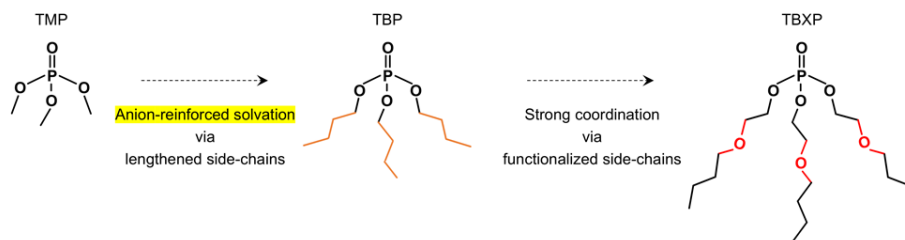


Fig. 1a. Logical flow, starting from the conventional TMP solvent, for the design of phosphate solvent molecules via side-chain engineering.

Conclusions Section:

“In this work, we conceived and reported a molecular design strategy that integrates strong coordination capability with anion-reinforced solvation characteristics to address the longstanding challenges of poor cycling stability and severe parasitic reactions in PIBs.”

3. In Line 239, you mention the average K-O distances. It would be advisable to present the average distances between K⁺ and specific coordinating oxygen species in TBXP, such as P=O and C-O-C moieties. Due to the obvious structural differences between these coordinating sites, directly comparing the coordination distances of all oxygen atoms may not be appropriate. The descriptions in lines 241–243 need to be reconsidered. Additionally, the statements in Lines 259–261 require re-evaluation.

Response:

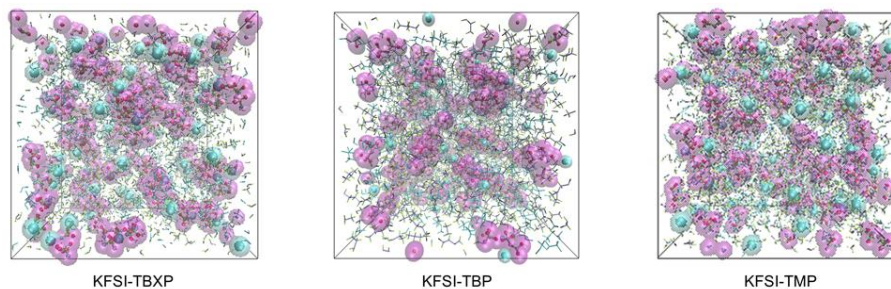
We sincerely appreciate the reviewer for their insightful and constructive comments, which have significantly facilitated the enhancement of the scientific rigor of our manuscript. In response, we have meticulously revised the relevant descriptions and supplemented detailed structural data and quantitative analyses, thereby improving the accuracy and rationality of the presented discussion.

The reviewer’s concern regarding the coordination environments of K⁺ in different electrolytes is highly professional and insightful, and we have addressed it meticulously with targeted revisions. To address this, we further extracted the top 20 most probable K⁺ solvation conformations from molecular dynamics (MD) simulations, which collectively account for approximately 90% of the total solvation

configurations (**Supplementary Figs. 20-23**). This approach enabled accurate quantification of the average distances between K^+ and each type of coordinating oxygen species, rather than adopting a single overall average. In particular, for the TBXP-based electrolyte, we explicitly distinguished and quantified the coordination contributions from the P=O and C-O-C sites to highlight its unique multi-site coordination characteristic. The results reveal that the weighted average $K^+-O_{P=O}$ distance is 2.89 Å in the KFSI-TMP electrolyte and 2.98 Å in the KFSI-TBP electrolyte (**Fig. 2f and Supplementary Fig. 24**). In the KFSI/TBXP electrolyte, the weighted average distances are 3.06 Å for $K-O_{P=O}$ and 3.04 Å for $K-O_{C-O-C}$, respectively (**Fig. 2f**).

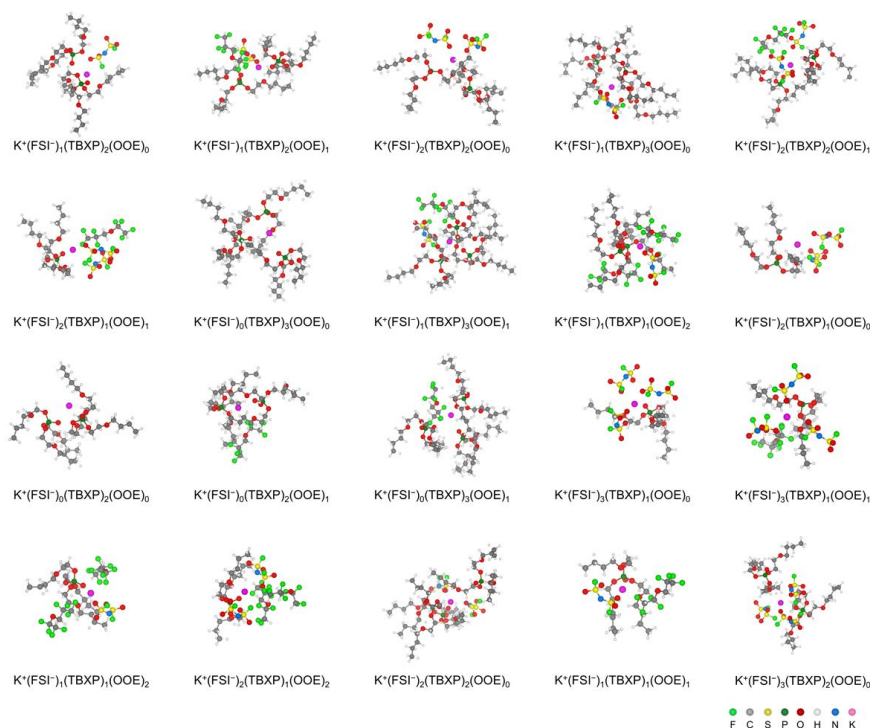
Correspondingly, the description in Lines 241-243 has been revised by replacing the general average $K^+-O_{solvent}$ distance with a rigorous comparison of site-specific $K^+-O_{solvent}$ distances, thereby rendering the structural comparison more rational and scientifically rigorous. Additionally, the statements presented in Lines 259-261 have been rigorously re-evaluated and systematically revised. To substantiate these claims, we have incorporated a comprehensive quantitative analysis that explicitly delineates the beneficial role of the unique solvation structure in promoting anion-cation coordination interactions (**Supplementary Fig. 27**). These modifications ensure complete consistency with the preceding solvation structure analysis and markedly enhance the logical integrity and coherence of the discussion section.

All revisions and supplementary data have been clearly annotated in the revised manuscript and supporting information, thereby effectively improving the scientific accuracy and rigor of the manuscript and addressing the reviewer's constructive suggestions.

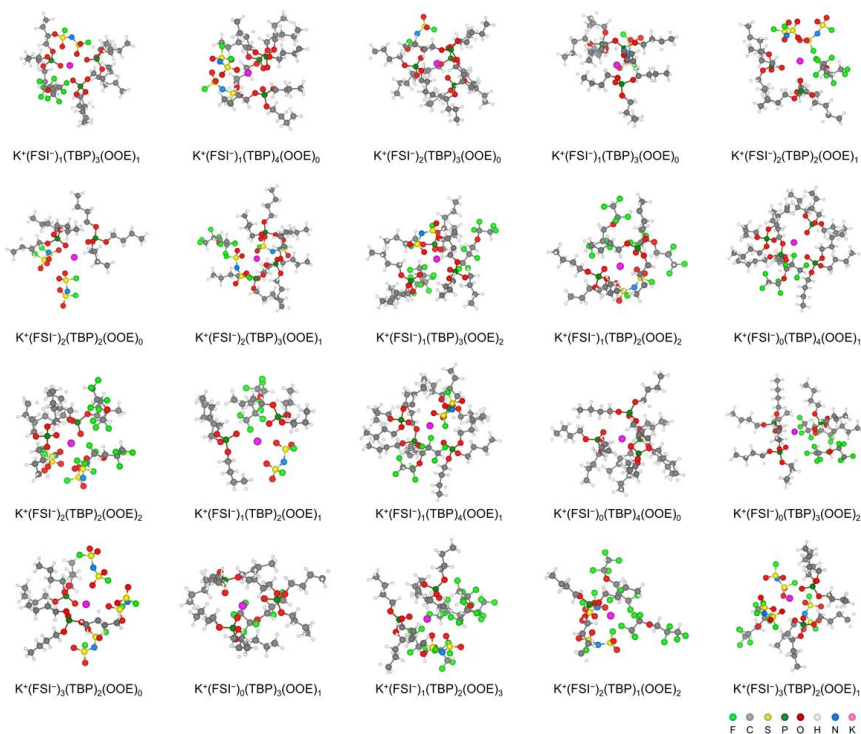


Supplementary Fig. 20. Snapshots of the MD simulated cells for different electrolytes.

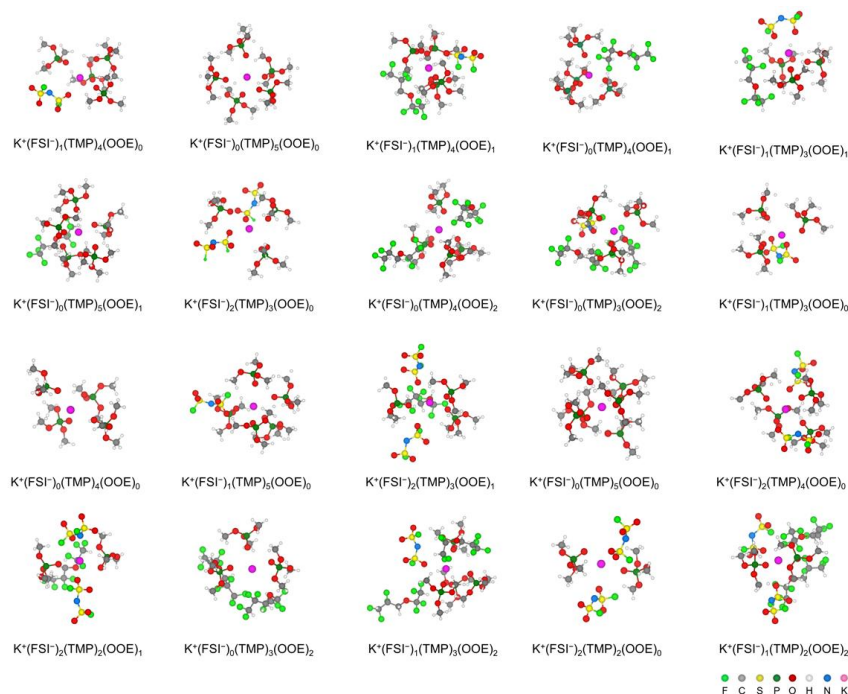
Classical MD simulations simulated the structures of the three electrolytes. The K^+ and FSI^- are depicted as ball-and-stick models, while solvent molecules are represented as wireframe models. As expected, these coordinated structures are uniformly dispersed in each electrolyte.



Supplementary Fig. 21. Representative K^+ solvation structures derived from MD simulations in the KFSI-TBXP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).



Supplementary Fig. 22. Representative K^+ solvation structures derived from MD simulations in the KFSI-TBP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).



Supplementary Fig. 23. Representative K^+ solvation structures derived from MD simulations in the KFSI-TMP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).

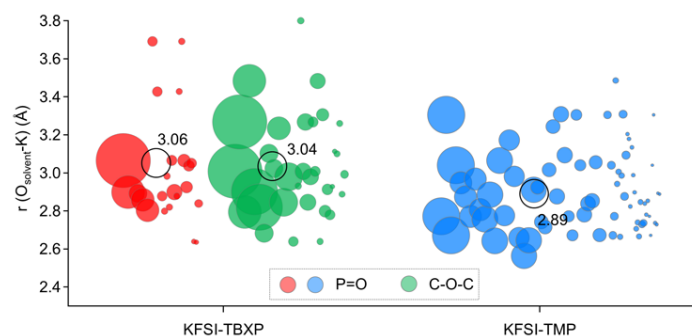
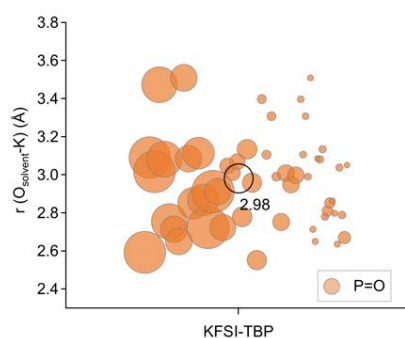
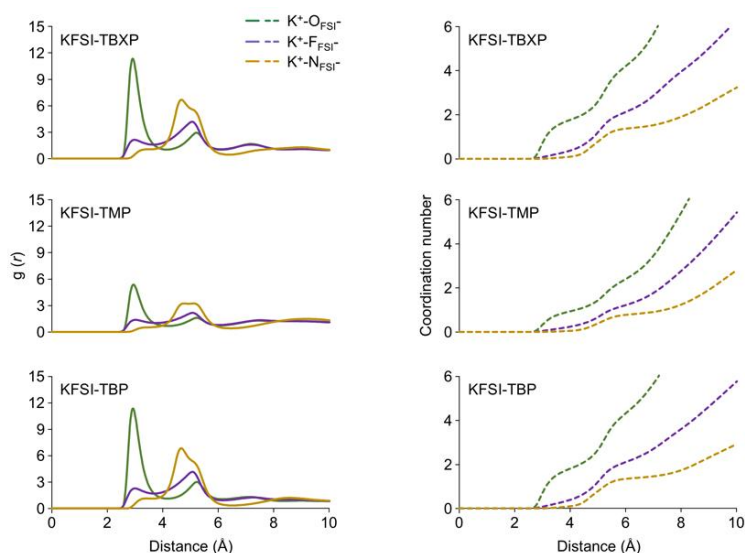


Fig. 2f. Coordination distances between K^+ and $O_{solvent}$ in KFSI-TBXP and KFSI-TMP electrolytes obtained from MD simulations. Shaded circular areas indicate the proportion.



Supplementary Fig. 24. Coordination distances between K^+ and $O_{solvent}$ in KFSI-TBP electrolyte by MD simulations. Shaded circular areas indicate the proportion.



Supplementary Fig. 27. The RDFs as deduced from the MD simulations. RDFs ($g(r)$, solid lines) and coordination numbers (CN, dashed lines) of FSI^- anions in different electrolytes.

From the FSI⁻ anion coordination perspective, the S=O group of FSI⁻ serves as the main coordination site. Quantitative analysis of CN shows that the CN of FSI⁻ anions in KFSI-TBXP, KFSI-TBP, and KFSI-TMP electrolytes are 2.03, 1.96, and 1.18, respectively. Notably, the CN of FSI⁻ anions in KFSI-TBXP and KFSI-TBP electrolytes is significantly higher than that in KFSI-TMP electrolyte, which facilitates the penetration of FSI⁻ anions into the K⁺ solvation sheath and contributes to the formation of an anion-reinforced solvation structure.

Revisions:

Results and Discussion Section:

“Molecular dynamics (MD) simulations were employed to examine the solvation structure characteristics of the three electrolytes (Supplementary Fig. 20). For each electrolyte, twenty representative coordination configurations were sampled to systematically compare the variations in their solvation structures (Supplementary Figs. 21-23). We first determined the distribution of distances between K⁺ and the primary coordinating oxygen atoms (the O_{solvent}, P=O and C-O-C sites are denoted as O_{P=O} and O_{C-O-C}, respectively), and calculated a weighted average across all data. The results reveal that the average K⁺-O_{P=O} distance in KFSI-TBXP electrolyte is 3.06 Å, which is greater than those in KFSI-TMP (2.89 Å) and KFSI-TBP (2.98 Å) electrolytes (Fig. 2f and Supplementary Fig. 24). Additionally, the average K⁺-O_{C-O-C} distance in the KFSI-TBXP electrolyte is 3.04 Å. The observed coordination involving both the P=O and C-O-C groups demonstrates the multi-site chelation characteristic of the TBXP solvent, and the longer K⁺-O_{solvent} distance may favor FSI⁻ anions into the K⁺ solvation sheath.”

“Furthermore, the RDFs analysis of FSI⁻ anions reveals a significantly higher CN in both the KFSI-TBXP and KFSI-TBP electrolytes compared to the KFSI-TMP electrolyte (Supplementary Fig. 27). Notably, despite the inherent multidentate and strong coordination characteristics of TBXP solvent, its pronounced molecular size effect still effectively facilitates the formation of an anion-reinforced solvation structure, which unambiguously corroborates the beneficial role of the molecular size effect in regulating the solvation structure of the electrolyte.”

4. In Figure 3a, KFSI-TMP exhibits the strongest reactivity. Calculated from the current and time, the side reaction capacity exceeds 1.2 mAh cm^{-2} , which is a considerably high value. However, in Figure 3b, KFSI-TMP still achieves an ICE of 78.1%, far superior to that of KFSI-TBP (50.3%). Additionally, why is the open-circuit voltage of the K||Cu cell with KFSI-TMP higher than 3 V in Figure 3a?

Response:

We greatly appreciate the reviewer for the meticulous and rigorous comments, and we sincerely apologize for the insufficient clarification and relevant errors of the abnormal open-circuit voltage and Coulombic efficiency discrepancy in the original manuscript. We have conducted systematic supplementary verification and mechanistic analysis to address the issues raised, and the detailed explanations are provided as follows.

During the initial measurements, an anomalous open-circuit voltage higher than 3.0 V was observed only in the K||Cu cell using the KFSI-TMP electrolyte. Given that this abnormality appeared reproducibly across multiple tests (**Fig. R2**), we overlooked this detail at that time, for which we sincerely apologize. Through subsequent step-by-step troubleshooting, we have confirmed that this abnormally high potential is caused by impurities adhering to the surface of the Cu current collector. These impurities induced a potential shift, leading to an anomalously high potential ($>3.0 \text{ V}$) reduction decomposition behavior. Importantly, this phenomenon does not reflect the intrinsic electrochemical properties of the KFSI-TMP electrolyte itself.

To address this, the Cu current collector was thoroughly cleaned with anhydrous ethanol and vacuum dried, and then Cyclic voltammetry (CV) and Chronopotentiometry (CP) tests were re-performed for this electrolyte system. The results show that the stabilized open-circuit voltage of the K||Cu cells returned to the normal level of approximately 2.5 V, and no reduction peak was observed at high potentials in the CV curves (**Supplementary Fig. 28**). This directly confirms that the previously observed anomalous high potential was solely caused by impurities on the Cu current collector. Meanwhile, the CV results clearly demonstrate that the reduction peak intensity of the KFSI-TMP electrolyte remains significantly higher than that of

the KFSI-TBP and KFSI-TBXP electrolytes, verifying its intrinsically more severe interfacial side reactions.

In addition, the extremely high side reaction capacity is attributed to the extremely low current density applied during the initial test. If the electrolyte fails to form a stable and dense SEI on the electrode surface, the small current used in the preliminary test will significantly prolong the electrochemical activation process, further aggravate the continuous side reactions, and ultimately result in severe electrolyte decomposition and the aforementioned ultra-high side reaction capacity. To better reflect the real SEI formation behavior and interfacial stability in the battery system, we increased the test current density to 0.1 mA cm^{-2} for verification (*Nat. Chem.* **2025**, *17*, 246-255), and the results consistently proved that the KFSI-TBXP electrolyte exhibits the weakest side reactions at the electrode interface, exhibiting superior interfacial stability (**Fig. 3a**).

Regarding the Coulombic efficiency issues, we also conducted quantitative analysis and targeted experimental verification. It should be clarified that the initial Coulombic efficiency (ICE) of K||graphite cells can be roughly calculated as: **ICE = K^+ deintercalation charge / (charge consumed for SEI formation + K^+ intercalation charge)**. The KFSI-TBP electrolyte exhibits a high K^+ intercalation overpotential, and the reductive decomposition of the electrolyte typically occurs at relatively high potentials (*Adv. Mater.* **2021**, *33*, 2006313). Consequently, only a small amount of K^+ can be intercalated into graphite at the K^+ intercalation **cut-off voltage of 0.01 V**. The low K^+ intercalation capacity is the core reason for its low ICE. To verify this deduction, we lowered the K^+ intercalation **cut-off voltage to -0.1 V** , even at this relatively low cut-off voltage, where K metal plating is likely to occur, no K metal plating plateau was observed in the galvanostatic cycling profiles, confirming that the boosted capacity is mainly contributed by enhanced K^+ intercalation into graphite. This lower cut-off voltage significantly promotes K^+ intercalation into graphite, thereby greatly improving cell capacity and increasing the initial Coulombic efficiency to 77.8%, directly confirming the validity of the above analysis.

Once again, we sincerely thank the reviewer for your professional and meticulous

comments, and we hope that these detailed responses and supplementary experimental evidence can fully address all your concerns and meet with your approval.

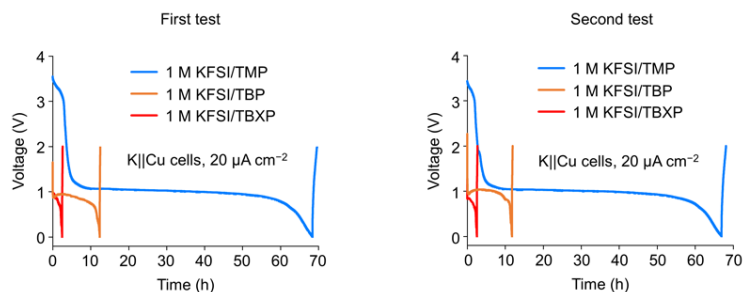
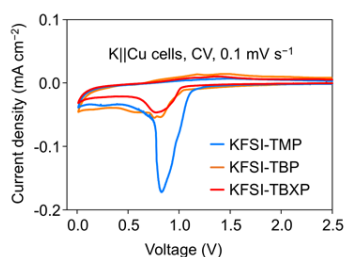


Fig. R2. The initial $E-t$ galvanostatic profiles of K||Cu cells in the three electrolytes under constant current, $|I| = 0.02 \text{ mA cm}^{-2}$.



Supplementary Fig. 28. CV profiles of K||Cu cells in three electrolytes at 0.1 mV s^{-1} . The CV profiles for K||Cu cells at 0.1 mV s^{-1} demonstrate marked differences in the reductive stability of the electrolytes. A prominent reduction peak is observed for the KFSI-TMP electrolyte, signifying substantial decomposition and the formation of an ineffective SEI. In contrast, both the KFSI-TBP and KFSI-TBXP electrolytes show significantly attenuated reduction currents. In the KFSI-TBXP electrolyte, exhibits the lowest current response, which underscores its excellent reductive stability and its ability to form a passivating SEI that effectively curtails sustained electrolyte decomposition.

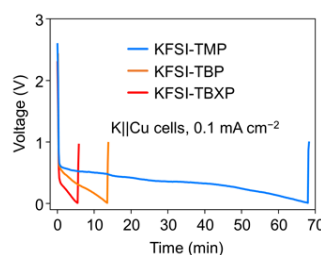
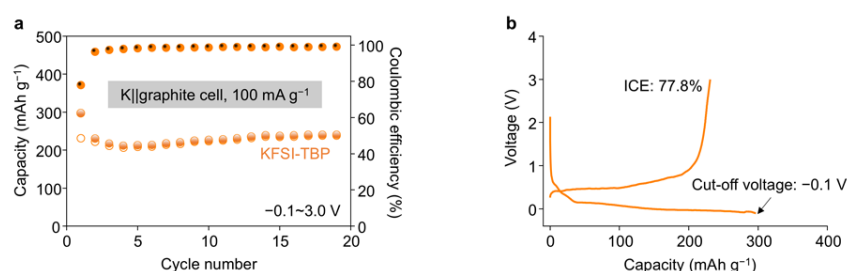


Fig. 3a. The initial $E-t$ galvanostatic profiles of K||Cu cells in the three electrolytes under constant current, $|j| = 0.1 \text{ mA cm}^{-2}$.



Supplementary Fig. 30. (a) Cycling performance of the graphite electrode in the KFSI-TBP electrolyte at 100 mA g^{-1} within a voltage range of -0.1 to 3.0 V and (b) corresponding charge-discharge profiles.

To elucidate the mechanism underlying the low ICE of graphite anodes in KFSI-TBP electrolyte, the K^+ intercalation cut-off voltage was lowered to -0.1 V to quantify intercalation-related capacity contributions. Electrochemical tests show this reduced cut-off markedly enhances K^+ intercalation capacity, delivering a reversible K^+ deintercalation capacity of 230 mAh g^{-1} and an ICE of 77.8% (Supplementary Fig. 30a). Moreover, no characteristic K metal plating plateau is observed in galvanostatic charge-discharge profiles, confirming the reversible capacity arises primarily from K^+ intercalation into graphite lattices (Supplementary Fig. 30b). The low ICE of graphite anodes in the KFSI-TBP electrolyte is mainly ascribed to two key factors. First, electrolyte decomposition at high potentials forms an SEI layer, causing severe initial irreversible capacity loss. Second, the large polarization potential severely hinders K^+ insertion into graphite, limiting reversible capacity and thereby further lowering the ICE.

Revisions:

Results and Discussion Section:

“We first investigated the formation of solid electrolyte interphase (SEI) on the Cu current collector surface in K||Cu cells using various electrolytes. Chronopotentiometry (CP) was applied at a constant current density of $|I| = 0.1 \text{ mA cm}^{-2}$ to cycle the K||Cu cells from 0.01 to 1.0 V. This protocol was designed to avoid bulk K metal deposition. A comparison of potential-time ($E-t$) profiles during galvanostatic cycling revealed that the K||Cu cells required the shortest time for the Cu electrode potential (E_{Cu}) drop to 0.01 V in the KFSI-TBXP electrolyte (Fig. 3a). An analysis of the integral charge (Q) during the first CP cycle showed that the $Q_{\text{discharge}}$ substantially exceeded the Q_{charge} , indicating significant irreversible reactions such as electrolyte decomposition, which is attributed to SEI formation. Subsequent cyclic voltammetry (CV) analyses further confirmed the mitigated reductive decomposition of the KFSI-TBXP electrolyte (Supplementary Fig. 28). This indicates that the designed electrolyte underwent the lowest extent of irreversible reductive decomposition during SEI formation, resulting in a stable SEI.”

“To assess graphite anode performance in the three electrolytes, K||graphite cells were cycled at 100 mA g^{-1} within a voltage window of 0.01-3.0 V. The K||graphite cell exhibited a high initial CE of 85.5% in KFSI-TBXP electrolyte, significantly outperforming KFSI-TMP (78.1%) and KFSI-TBP (62.3%) electrolytes (Fig. 3b). Furthermore, severe electrochemical polarization in the K||graphite cell with KFSI-TBP electrolyte not only resulted in diminished reversible capacity at the K^+ intercalation cut-off voltage of 0.01 V, but also accounted for its extremely low ICE under such constrained voltage conditions (Supplementary Figs. 29 and 30).”

Methods section:

“Specifically, LSV measurements were conducted on K||Al cells over a voltage window of 2.5-5.0 V at a scan rate of 1 mV s^{-1} , while CV measurements were performed on K||Cu cells over a range of 0.01-2.5 V at 0.1 mV s^{-1} and on K||PB cells over a range of 2.0-4.2 V at 0.05 mV s^{-1} .”

5. In Figure 3c, the cell with KFSI-TBP appears to exhibit a continuous capacity increase. What happens in the subsequent cycles that are not presented? And what is the underlying reason for this continuous capacity rise? Additionally, in Line 282, you mention that severe electrochemical polarization occurs in the K||graphite cell with KFSI-TBP electrolyte. Since KFSI-TBP shows comparable ionic conductivity to other electrolytes, what is the origin of this polarization?

Response:

We sincerely thank the reviewer for their careful review and valuable comments. Here, we provide detailed explanations and clarifications addressing the three key questions raised: the reason for not presenting the subsequent cycling performance of the K||graphite cell in the KFSI-TBP electrolyte, the underlying mechanism for the continuous capacity increase, and the origin of the severe electrochemical polarization observed.

Regarding the absence of subsequent cycling performance for the K||graphite cell with KFSI-TBP electrolyte, we initially did not perform long-term cycling tests on this cell due to its relatively low early cycle capacity; therefore, the corresponding long-cycle performance was not presented in the original manuscript. To clarify the underlying mechanism for the continuous capacity increase and understand its subsequent cycling performance evolution, we reassembled K||graphite cells with KFSI-TBP electrolyte and conducted full long-term cycling tests (**Fig. 3c**). The results align with those reported in the original manuscript, showing a continuous rise in the early cycles, and gradual stabilization after 100 cycles.

After in-depth analysis, we attribute this continuous capacity increase to a slow activation process of the graphite electrode in KFSI-TBP electrolyte, which fundamentally originates from the dynamic structural evolution of the graphite anode during cycling. As a typical intercalation-type potassium storage material, the interlayer spacing of graphite progressively expands with continuous K^+ intercalation, and such structural evolution facilitates K^+ diffusion and storage within graphite interlayers. However, the K||graphite cell suffers from substantial initial electrochemical polarization in KFSI-TBP electrolyte, which only allows a small

amount of K^+ to intercalate into the graphite interlayers. This significantly retards the structural evolution of the graphite anode, which is the primary reason for the slow and continuous capacity increase observed in this system. Further overpotential analysis directly validates this mechanism. The cell exhibits a high initial overpotential of 643.9 mV, which markedly decreases to 212.7 mV after 100 cycles, indicating substantial polarization mitigation that correlates well with the trend of capacity increase and electrode activation (**Supplementary Fig. 31**). In addition, lowering the discharge cut-off voltage is an effective strategy to promote efficient K^+ intercalation into graphite, avoiding the inhibition of K^+ intercalation caused by high overpotential. The results reveal that when the K^+ intercalation cut-off voltage is reduced to -0.1 V, the K||graphite cell maintains a high initial capacity and the continuous early capacity increase is significantly alleviated, further verifying the rationality of the aforementioned activation mechanism (**Supplementary Fig. 30**).

Regarding the origin of the severe electrochemical polarization observed at the graphite anode in the KFSI-TBP electrolyte, we consider the primary cause is not the intrinsic ionic conductivity of the electrolyte, but rather the properties of the solid-electrolyte interphase (SEI) at the electrode surface. As a typical intercalation-type potassium storage material, the electrochemical polarization behavior of the graphite anode is highly sensitive to interfacial characteristics. Numerous studies have demonstrated that intrinsic properties of the SEI, such as thickness and ionic conductivity, directly dominate the overall electrode polarization behavior. (*Nat Energy* 2023, 8, 1365-1374; *Adv. Funct. Mater.* 2025, 35, 2504576) Therefore, under the condition of comparable ionic conductivity among different electrolytes, the difference in intrinsic properties of the SEI is the fundamental source of the discrepancy in electrochemical polarization.

We greatly appreciate the reviewer's suggestions, which have greatly helped to improve our manuscript. Accordingly, we have made the corresponding revisions in the revised manuscript.

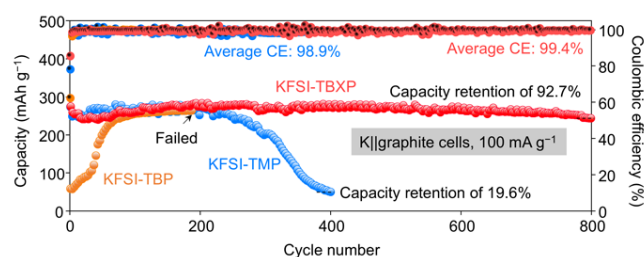
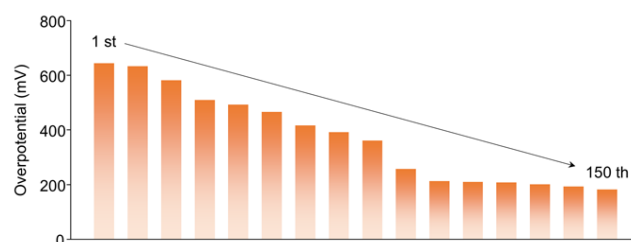
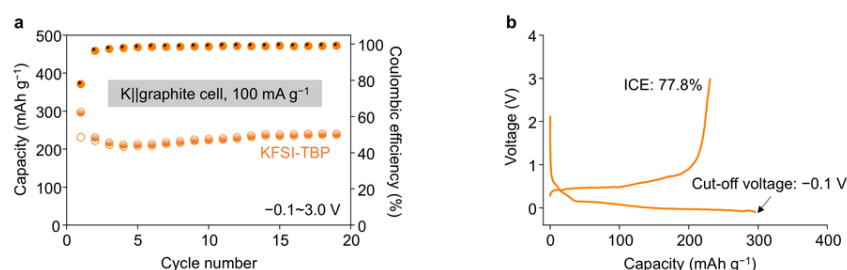


Fig. 3c. Cycling stability of graphite anodes in different electrolytes.



Supplementary Fig. 31. Overpotential analysis of the graphite electrode in the KFSI-TBP electrolyte.

Overpotential analysis of the graphite electrode in the KFSI-TBP electrolyte shows an initial overpotential of 643.9 mV. This high initial polarization is the key factor hindering effective K^+ intercalation into the graphite interlayers, and directly accounts for the low capacity observed during the early cycles. As cycling proceeds, the overpotential gradually decreases, stabilizing at 212.7 mV after 100 cycles. Concurrently, the cell capacity increases significantly and also stabilizes. These results indicate that the sustained capacity increase during the initial cycles of the graphite anode in the KFSI-TBP electrolyte is primarily attributable to a slow electrode activation process.



Supplementary Fig. 30. (a) Cycling performance of the graphite electrode in the KFSI-TBP electrolyte at 100 mA g⁻¹ within a voltage range of -0.1 to 3.0 V and (b) corresponding charge-discharge profiles.

Revisions:**Results and Discussion Section:**

“When using KFSI-TBP electrolyte, the low initial capacity and its subsequent rise are attributed to severe electrochemical polarization and sluggish electrode activation (Supplementary Fig. 31). The capacity gradually stabilizes at approximately 255 mAh g⁻¹ after 100 cycles, and the cell fails at the 189 cycle (Fig. 3c and Supplementary Fig. 29).”

6. The KFSI-TBP electrolyte enables the K||PB cell to cycle stably for over 500 cycles at 100 mA g⁻¹. However, in Supplementary Figure 31, obvious overcharge occurs in the cell after the rate capability test. How to understand this inconsistent phenomenon?

Response:

We sincerely appreciate the reviewer’s careful question and insightful observation. We have thoroughly investigated this phenomenon and provide the following explanation.

The KFSI-TBP electrolyte enables the K||PB cell to cycle stably for more than 500 cycles at 100 mA g⁻¹, and no obvious overcharge occurs under this low current density. Under such mild current condition, the structural evolution of the cathode material is sufficiently slow and controllable, helping maintain lattice integrity and suppress severe interfacial side reactions. In contrast, the obvious overcharge observed after the rate capability test is mainly attributed to the severe structural degradation and particle cracking of the cathode material under high current densities (*Angew. Chem. Int. Ed.* 2025, 64, e202518712; *ACS Nano* 2025, 19, 33202-33211), which the KFSI-TBP electrolyte cannot prevent. These structural damages continuously expose fresh active surfaces, aggravating interfacial parasitic reactions. As a result, part of the charge is consumed in irreversible side reactions rather than in reversible potassium-ion storage, which directly accounts for overcharge and the pronounced decrease in Coulombic efficiency.

To further verify this mechanism, we performed high rate cycling tests on K||PB cell

in KFSI-TBP electrolyte at 500 mA g^{-1} (2-4.2 V). As shown in **Fig. R3**, the cell maintains a Coulombic efficiency of $\sim 99\%$ in the initial cycles, but after 25 cycles, the Coulombic efficiency drops to $\sim 80\%$, accompanied by an obvious overcharge behavior where the charge capacity exceeds the discharge capacity. To clarify this point, we have reinforced the relevant discussion in the revised manuscript and supplemented appropriate literature citations to support this interpretation.

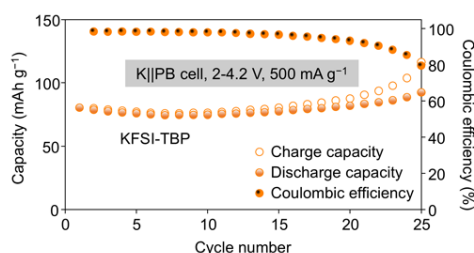


Fig. R3. Cycling performance of K||PB cell in the KFSI-TBP at 500 mA g^{-1} .

Revisions:

Results and Discussion Section:

“In contrast, the K||PB cells using KFSI-TMP and KFSI-TBP electrolytes experienced overcharging failure upon returning to 100 mA g^{-1} , which could be attributed to severe interfacial side reactions induced either from intrinsic parasitic reactions within the electrolytes or from structural evolution of the electrode material (Supplementary Figs. 48 and 49).⁴⁹”

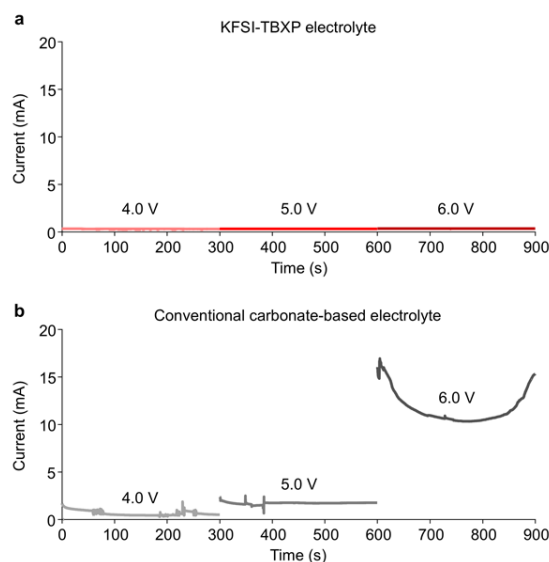
References Section:

[49] Mo Y, et al. Polarity Gradient CEI Driven Rapid Desolvation for Extreme Fast-Charging Potassium-Ion Batteries. *Angew. Chem. Int. Ed.* **64**, e202518712 (2025).

7. What do the "abusive conditions" specifically refer to in Figure 5i? Experimental testing methods and related details should be clearly included in the Methods section. Additionally, complete details about the tested batteries need to be provided, such as cycling conditions before the tests and the state of charge (SOC) during the test.

Response:

We appreciate the reviewer’s constructive comment, which has helped improve the completeness and clarity of our manuscript. In the revised manuscript, the “abusive conditions” corresponding to **Fig. 5i** have been clearly defined, and the required details about the tested batteries have been added to the Methods section. Specifically, prior to the abusive tests, the cells were subjected to five charge-discharge cycles. During testing, the cells were charged to 4.0 V (corresponding to 100% state of charge, SOC), and abusive conditions were constant-voltage overcharge at 4.0 V, 5.0 V, and 6.0 V respectively, for 5 minutes each, with temperature variation recorded. Corresponding *I-t* profiles have also been added to support experimental results (**Supplementary Fig. 58**). All relevant details are supplemented in the revised manuscript to ensure experimental clarity and address the reviewer’s concerns.



Supplementary Fig. 58. Current-time profiles of pouch cells under constant-voltage charging at various voltages. (a) KFSI-TBXP electrolyte and (b) conventional carbonate-based electrolyte.

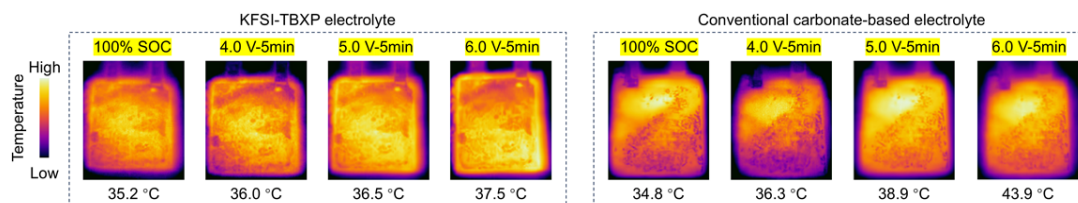


Fig. 5i. Infrared thermography images of pouch cells.

Revisions:**Results and Discussion Section:**

“Moreover, to evaluate the thermal behavior of the pouch cell under abusive conditions, the pouch cell with our designed electrolyte was charged to 4.0 V (100% state of charge, SOC) and then maintained under various overvoltage conditions via constant-voltage charging for 5 minutes, during which thermal imaging analysis was performed (Supplementary Fig. 58). The results revealed absence of thermal runaway and a smaller temperature change (Fig. 5i).”

Methods section:

“A thermal imager (FOTRIC 285) recorded the pouch cells’ temperatures after each constant-voltage overcharge test. Briefly, the pouch cells were first subjected to 5 cycles, then charged to 4.0 V (100% SOC), followed by constant-voltage overcharge tests at 4.0 V, 5.0 V, and 6.0 V (each lasting 5 minute). After the 5 minutes test under each voltage, the thermal imager recorded the cells’ temperature.”

8. All cells tested have excessively low mass loading ($1\text{--}1.5\text{ mg cm}^{-2}$). It is strongly recommended that full-cell performance tests under high mass loading conditions (cathode mass loading should exceed 20 mg cm^{-2}). In addition, details of the pouch cell, including electrode information (e.g., active material loading, electrode area, and thickness) and total capacity, are lacking and should be supplemented for evaluation.

Response:

We greatly appreciate the reviewer for their insightful comments. We fully acknowledge the importance of evaluating full cell performance under high cathode mass loading conditions to reflect practical applications. In response to these comments, we have performed additional experimental tests and made targeted revisions and thorough clarifications as outlined below.

Potassium-ion batteries remain are still in the early stages of research and development, especially compared with mature lithium-ion battery systems. Although

Prussian blue (PB) cathode has been relatively extensively investigated in potassium-ion batteries, their overall performance still cannot match that of commercial lithium-ion battery cathodes. The core bottlenecks lie in their relatively low electronic conductivity and low compaction density (**Fig. R4a**), which impose substantial challenges for the fabrication of high-mass-loading, large-area electrodes via conventional slurry-coating techniques (*ACS Energy Lett.* **2025**, *10*, 1751-1761). Specifically, high mass loading readily gives rise to electrode cracking during electrode preparation and calendaring. Furthermore, nearly all advanced cathode materials for potassium-ion batteries suffer from insufficient active potassium inventory (**Fig. R4b**). Due to a shortage of sufficient active potassium sources, graphite anodes must be pre-potassiated prior to full cell assembly, which also makes the current pouch full cell manufacturing process difficult to commercialize. Nevertheless, to realize full cell testing at high mass loading ($>20 \text{ mg cm}^{-2}$), we have successfully fabricated coin-type full cells with a cathode mass loading of $\sim 21.5 \text{ mg cm}^{-2}$ via repeated coating and calendaring. These cells exhibit stable cycling for more than 80 cycles with an area capacity of $\sim 1.71 \text{ mAh cm}^{-2}$ (**Supplementary Fig. 56**). We believe this result provides a preliminary demonstration of the feasibility of our electrolyte under high mass loading conditions.

As requested, detailed parameters of the pouch cell, including active material loading, electrode area, electrode thickness, and total capacity, as well as the corresponding pouch cell fabrication procedures, have been supplemented in the main text and Methods section for further evaluation (**Supplementary Fig. 57**). We are grateful for the reviewer's understanding of this inherent limitation. To promote the practical application of potassium-ion batteries, we are actively developing novel cathode materials with high compacted density, high specific capacity, and superior ionic and electronic conductivity, while optimizing electrode and pouch cell fabrication processes. In future work, we will focus on evaluating high-mass-loading, high-capacity potassium-ion battery devices.

We hope that these revisions and clarifications adequately address the reviewer's concerns and provide a clearer perspective on the current status of research on PIBs.

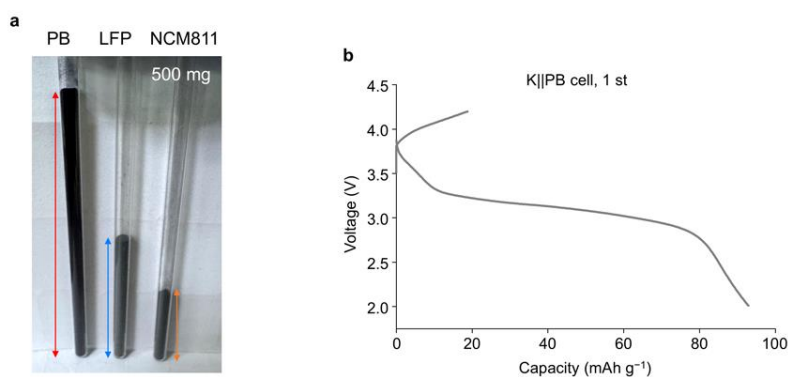
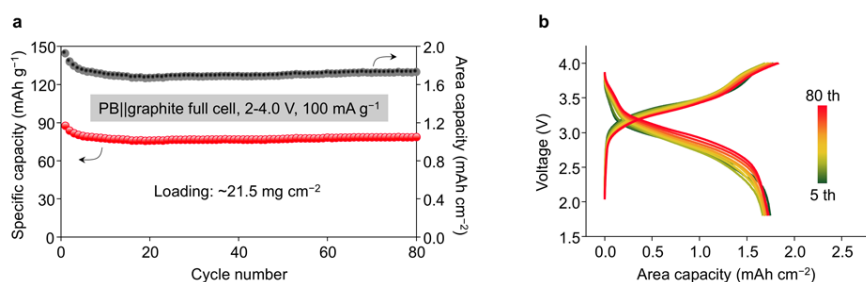


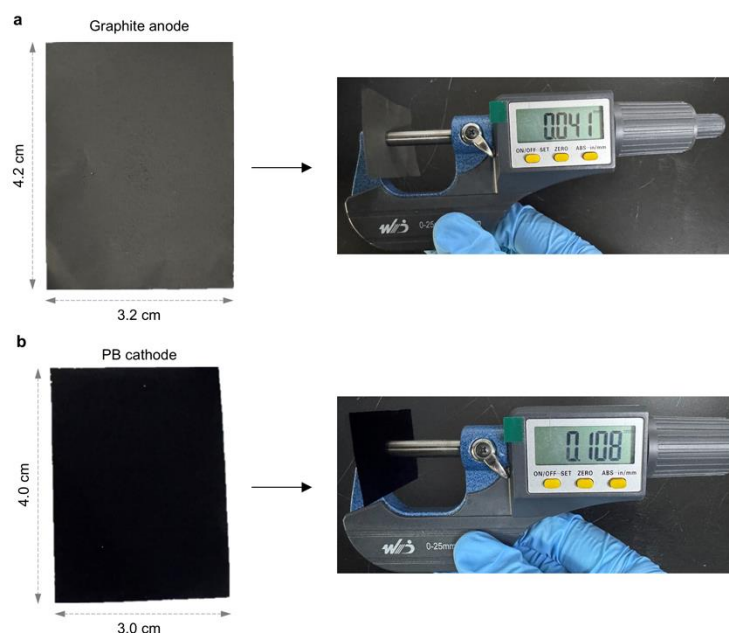
Fig. R4. (a) Photographs of PB, LFP, and NCM811 powders under equal mass conditions. (b) Initial charge-discharge profile of K||PB cell.

Compared with commercial cathode materials widely used in lithium-ion batteries, such as LFP and NCM811, the Prussian blue (PB) cathode in potassium-ion batteries delivers a relatively low compaction density (**Fig. R4a**). This characteristic imposes significant constraints on the construction and fabrication of high-areal-loading electrodes. Furthermore, analysis of the initial charging profile of the K||PB cell reveals a severe shortage of active potassium sources in the PB cathode, which necessitates a pre-potassiation treatment for the graphite anode prior to full cell assembly (**Fig. R4b**).



Supplementary Fig. 56. (a) Cycling performance and (b) corresponding charge-discharge profiles of high mass loading PB||graphite full cell at 100 mA g⁻¹.

High mass loading PB electrodes were successfully fabricated via repeated coating and calendaring processes, followed by the assembly of PB||graphite full cell. Electrochemical cycling results reveal that the full cell exhibits stable cycling for more than 80 cycles in the KFSI-TBXP electrolyte, with an areal capacity of approximately 1.74 mAh cm⁻².



Supplementary Fig. 57. Parameters of (a) graphite anode and (b) PB cathode for pouch cell assembly.

Revisions:

Results and Discussion Section:

“To further verify the feasibility of the KFSI-TBXP electrolyte under high mass loading conditions, a high-loading PB||graphite full cell was fabricated with a PB cathode mass loading of 21.5 mg cm^{-2} . This cell delivers a high areal capacity of $\sim 1.74 \text{ mAh cm}^{-2}$ at 100 mA g^{-1} and exhibits stable cycling for more than 80 cycles (Supplementary Fig. 56).”

“To better assess scalability under realistic conditions, the monolayer PB||graphite pouch full cell using the KFSI-TBXP electrolyte was evaluated (Supplementary Fig. 57).”

Methods section:

“Prior to pouch cell assembly, the graphite anode underwent a contact pre-potassiation treatment. Specifically, bulk K metal was rolled into a $300 \text{ }\mu\text{m}$ -thick K foil, and the graphite-electrolyte-K foil was assembled into a sandwich structure, which was then left standing for 4 h to obtain the pre-potassiated graphite electrode. The monolayer pouch cells with a capacity of 1.3 mAh were assembled. The PB cathode dimensions

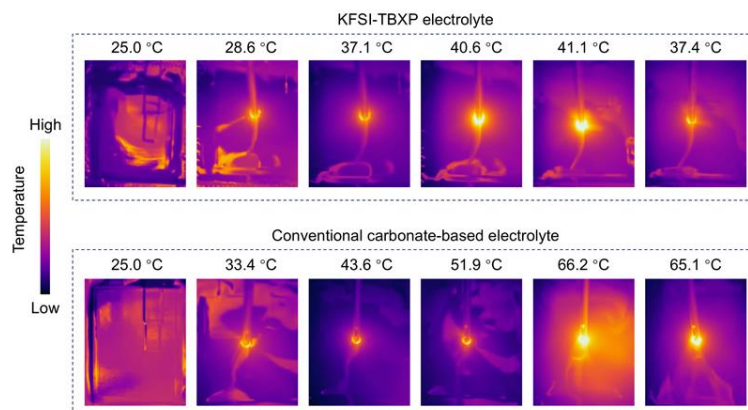
are 3 cm × 4 cm with a total mass loading of approximately 13.5 mg, while the graphite anode measured 3.2 cm × 4.2 cm. An electrolyte injection volume of 0.6 mL per cell.”

9. Given that the core goal of this work is to design a non-flammable electrolyte for KIBs to enhance safety, supplementary safety tests (e.g., needle penetration test of pouch cells) are recommended to demonstrate the strategy's practicality.

Response:

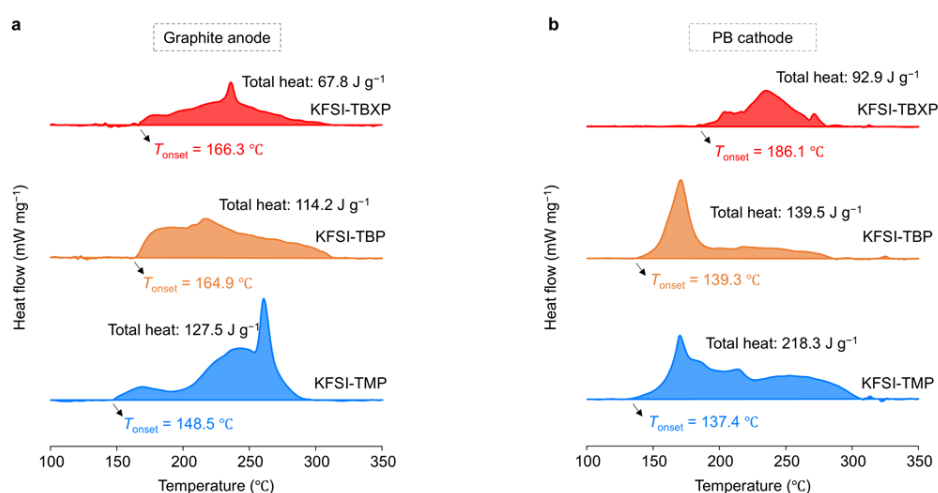
We greatly appreciate the reviewer's valuable and constructive suggestion. In response to your comment on supplementary safety validation, we have added needle penetration tests on monolayer PB||graphite pouch cells, combined with infrared thermography to monitor temperature evolution during the piercing process (**Supplementary Fig. 59**). All tests were performed under a fully charged conditions (100% SOC). The results demonstrate that the monolayer pouch cell with the KFSI-TBXP electrolyte exhibits a maximum temperature of only 41.1 °C during the needle penetration, which is markedly lower than 66.2 °C measured for the conventional carbonate-based electrolyte counterpart. These supplementary data further verify the superior thermal safety of our non-flammable electrolyte design for KIBs. The relevant results and discussion have been incorporated into the revised manuscript.

Furthermore, to provide a more rigorous, quantitative safety evaluation, we also performed differential scanning calorimetry (DSC) measurements to assess the thermal stability of the electrolyte in contact with the electrode materials. Specifically, DSC analysis was conducted on electrolyte-PB cathode (charged to 4.2 V) and electrolyte-graphite anode (potassiated graphite) mixtures. The results demonstrate that the TBXP-based electrolyte exhibits a higher onset temperature for exothermic reactions and a lower total heat release compared to the other electrolyte systems (**Supplementary Fig. 60**). These findings further confirm the ability of the TBXP-based electrolyte to suppress heat-generating reactions, thereby improving battery safety.



Supplementary Fig. 59. Infrared thermography images of the pouch cell during the nail penetration short-circuit test.

All pouch cells were fully charged to 100% SOC before the nail penetration short-circuit test, then placed in a constant-temperature chamber for 30 min of thermal equilibration. The infrared thermal imaging results demonstrate that the maximum temperature of the pouch cell with the KFSI-TBXP electrolyte reaches only 41.1 °C throughout the nail penetration and short-circuit process, which is significantly lower than the peak temperature of 66.2 °C recorded with the conventional carbonate-based electrolyte.



Supplementary Fig. 60. DSC profiles of (a) potassiated graphite anodes (0.01 V) and (b) fully charge-state PB cathodes (4.2 V) mixed with relevant electrolyte.

The thermal compatibility of the graphite anode and PB cathode in different electrolytes was evaluated using differential scanning calorimetry (DSC). For the

potassiated graphite anode, the mixture with KFSI-TBXP electrolyte exhibited an exothermic reaction onset temperature (T_{onset}) of 166.3 °C and a total heat release of 67.8 J g⁻¹. In comparison, the anode mixed with KFSI-TBP electrolyte showed a T_{onset} = 164.9 °C with a total heat release of 114.2 J g⁻¹, while the KFSI-TMP electrolyte showed the lowest T_{onset} (148.5 °C) and the highest total heat release (127.5 J g⁻¹). Notably, although the T_{onset} of KFSI-TBXP and KFSI-TBP were similar, KFSI-TBXP significantly suppressed the total heat release, demonstrating superior thermal stability. For the charge-stare PB cathode (4.2 V), the mixture with KFSI-TBXP electrolyte delivered a T_{onset} = 186.1 °C and a total heat release of 92.9 J g⁻¹, markedly outperforming the KFSI-TBP (139.3 °C, 139.5 J g⁻¹) and KFSI-TMP (137.4 °C, 218.3 J g⁻¹) counterparts. These results indicate that the KFSI-TBXP electrolyte effectively suppresses exothermic reactions between the electrodes and electrolyte, thereby enhancing battery safety under thermal runaway conditions.

Revisions:

Results and Discussion Section:

“Subsequently, nail penetration short circuit test combined with infrared thermography imaging further confirmed its superior thermal safety. The pouch cell using KFSI-TBXP electrolyte maintained a much lower temperature during the short-circuit penetration process compared with the conventional carbonate-based electrolyte (Supplementary Fig. 59). Furthermore, differential scanning calorimetry (DSC) was employed to assess the thermal abuse tolerance of both the potassiated graphite-electrolyte and charged PB cathode-electrolyte mixtures. Compared to the KFSI-TBP and KFSI-TMP electrolytes, the KFSI-TBXP electrolyte exhibited a higher exothermic onset temperature and lower total heat release, indicating superior capability in mitigating thermal runaway (Supplementary Fig. 60).”

Methods section:

“Differential scanning calorimetry (DSC) measurements were performed on a thermal analyzer (China-DZ-DSC300C). Potassiated graphite anodes were retrieved from cells discharged to 0.01 V at 20 mA g⁻¹ in the corresponding electrolytes, while

charged PB cathodes were obtained from cells charged to 4.2 V at 100 mA g⁻¹. Both electrodes were carefully rinsed with dimethyl carbonate (DMC) three times to remove residual electrolyte. After overnight drying, the electrode powders were mixed with the selected electrolyte solutions and sealed in 100 µL high-pressure gold DSC capsules. The DSC profiles were recorded from 30 to 400 °C at a heating rate of 10 °C min⁻¹.”

Minor notes

Line 297, TBP should be TBXP.

In the title, "strong coordination and weak solvation" needs revision to avoid misunderstanding, as TBXP does not exhibit weak solvating ability.

Response:

We sincerely appreciate the reviewer’s careful and professional comments, which have significantly improved the accuracy and precision of our results presented in our manuscript.

We offer our sincere apologies for the oversight in our manuscript, in which “TBXP” was incorrectly written as “TBP” on Line 297. This writing error has been corrected in the revised manuscript, and we thank the reviewer for bringing this to our attention. Regarding the title, we agree with the reviewer that the original phrasing “strong coordination and weak solvation” could be misleading, as TBXP does not inherently possess weak solvating ability. Following the reviewer’s valuable suggestion, we have revised the title to “***Reconciling Strong Coordination and Anion-Reinforced Solvation Structure Enables Nonflammable Electrolytes for Potassium-Ion Batteries***”. This revision eliminates the potential ambiguity, enhances the scientific rigor and accuracy of the manuscript, and allows the core findings and mechanistic insights of this work to be presented more precisely.

We sincerely thank the reviewer again for these constructive suggestions, which have significantly enhanced the scientific rigor and readability of our manuscript. All revisions have been clearly marked in the revised manuscript.

Revisions:

Results and Discussion Section:

“Compared to the pristine graphite electrode (Supplementary Fig. 34), no discernible cracking was observed on flake graphite cycled in the KFSI-TBXP electrolyte (Fig. 3d).”

Title:

“Reconciling Strong Coordination and Anion-Reinforced Solvation Structure Enables Nonflammable Electrolytes for Potassium-Ion Batteries”

Once again, we sincerely thank the reviewer for their insightful feedback and constructive suggestions, which have significantly strengthened the clarity and academic depth of our analysis and elevated the overall quality of the manuscript. We greatly appreciate the reviewer’s time and expertise devoted to this work, and sincerely hope that the revised version meets with their approval.

Reviewer #4:

This manuscript reports the design of a nonflammable phosphate solvent (TBXP) that simultaneously enables multidentate coordination and molecular-size effects through side-chain engineering, leading to high-voltage stability, long cycle life, and enhanced safety in potassium-ion batteries. The concept of electrolyte molecular design is both novel and progressive.

However, the current manuscript lacks (1)direct evidence of the mechanism, (2)quantitative evaluation of safety tests, (3)quantification of the solvation structure, and (4)evaluation for practical use. Therefore, I recommend major revision before the manuscript can be considered for publication.

Response:

Thank you very much for your recognition of the novelty and progressiveness of our electrolyte molecular design strategy based on nonflammable TBXP solvent, with multidentate coordination and molecular-size effects, as well as for your constructive and professional comments on the mechanism, quantitative characterization, and practical evaluation. We highly appreciate these valuable suggestions, which have greatly helped us improve the scientific rigor and practicability of this manuscript. Our point-by-point responses to all detailed concerns are provided below. We have carefully revised the manuscript in accordance with your comments and have supplemented it with corresponding experimental evidences.

(1) Direct evidence of the mechanism

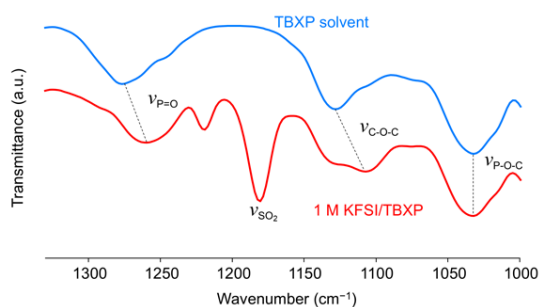
While the manuscript claims that ether oxygen atoms in side-chains coordinate with K^+ , the direct experimental evidence is lacking. Highly recommended techniques would include, for example, IR/Raman or ^{17}O -NMR measurements focusing on the TBXP molecule itself, which would show coordination-induced vibrational shifts or electronic shielding corresponding to the ether oxygen atoms in side-chains. Alternatively, it is also preferable to add experimental data using triheptyl phosphate that does not contain -O- groups in side-chains as a comparative example.

Response:

Thank you for your insightful and rigorous comments. We fully agree that direct experimental evidence is essential to verify the coordination between the ether oxygen atoms in the side-chains of TBXP and K^+ . We also recognize the critical value of employing a structurally analogous phosphate solvent without ether groups as a comparative example, to highlight the unique role of the side-chain ether oxygen atoms. In response to your highly valuable suggestions, we have conducted targeted supplementary experiments to provide convincing experimental support.

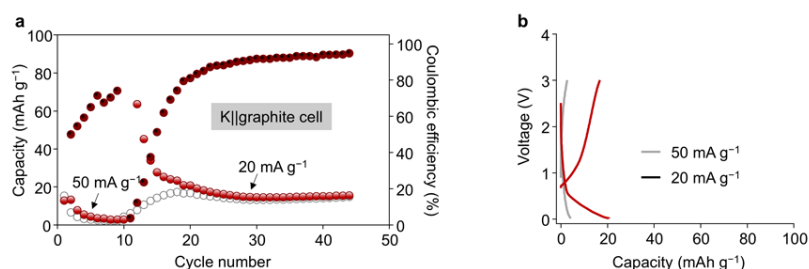
We performed FT-IR spectroscopy on the TBXP solvent and on the 1 M KFSI/TBXP electrolyte, respectively. As shown in **Supplementary Fig. 5**, the characteristic stretching vibrations of both the P=O group and the C-O-C group show obvious shifts in the 1 M KFSI/TBXP electrolyte. These spectral variations serve as direct evidence that both the main-chain P=O and side-chain C-O-C moieties are actively involved in K^+ coordination, consistent with the multi-site chelation design of the TBXP molecule (*Energy Environ. Sci.* 2026, 19, 969981).

Following the reviewer's suggestion for a comparative example, we selected triheptyl phosphate (THP) as a structural analog of TBXP solvent, which has the same alkyl chain length but no C-O-C ether groups in its side-chains. Owing to the large molecular weight and strong steric hindrance of THP, the introduction of OOE promotes salt precipitation, resulting in limited solubility of KFSI in the mixed solvent. We therefore prepared the 1 M KFSI/THP electrolyte for electrochemical performance evaluation. As shown in **Supplementary Figs. 13 and 14**, the THP-based electrolyte exhibits negligible reversible capacity in both K||graphite and K||PB cells, even at low current densities.

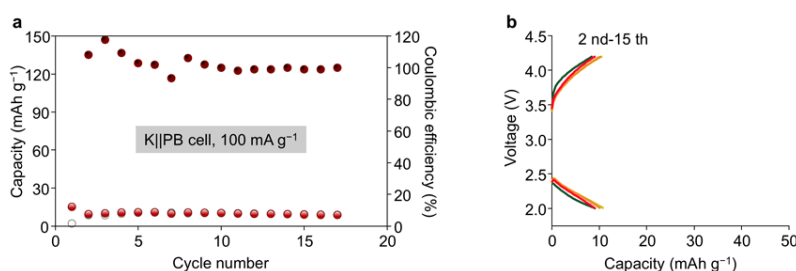


Supplementary Fig. 5. FT-IR spectra of the TBXP solvent and the 1 M KFSI/TBXP electrolyte, respectively.

As shown in Supplementary Fig. 5, the FT-IR spectrum of the TBXP solvent exhibits characteristic stretching vibrations corresponding to the P=O (1277 cm^{-1}), C-O-C (1129 cm^{-1}), and P-O-C (1033 cm^{-1}) groups. Upon the addition of KFSI to formulate the 1 M KFSI/TBXP electrolyte, both the P=O and C-O-C stretching vibrations shift toward lower wavenumbers, indicating their active participation as primary coordination sites for the potassium ion¹. In contrast, the P-O-C stretching vibration remains virtually unchanged, suggesting that this group does not significantly contribute to K^+ coordination. These spectral observations are consistent with the multi-site chelation design of the TBXP solvent molecule.



Supplementary Fig. 13. (a) Cycling performance and (b) corresponding charge-discharge profiles of K||graphite cell in the 1 M KFSI/THP electrolyte.



Supplementary Fig. 14. (a) Cycling performance and (b) corresponding charge-discharge profiles of K||PB cell in the 1 M KFSI/THP electrolyte.

Revisions:

Results and Discussion Section:

“To clarify the respective contributions of the coordination sites, electrostatic potential (ESP) maps and Fourier-transform infrared (FT-IR) spectroscopy were performed (Supplementary Figs. 4 and 5). The results confirm that both the

main-chain P=O and side-chain C-O-C sites in TBXP serve as primary coordination sites of K^+ , consistent with the multi-site chelation design of the TBXP solvent molecule.”

“To identify the critical role of C-O-C groups in the side-chains of TBXP solvent, we further introduced triheptyl phosphate (THP) solvent with identical side-chain length but without C-O-C groups as a control analogue. The results demonstrate that the THP-based electrolyte exhibits negligible reversible capacity in both the graphite anode and the PB cathode, even at low current densities (Supplementary Figs. 13 and 14).”

(2) Quantitative evaluation of safety tests

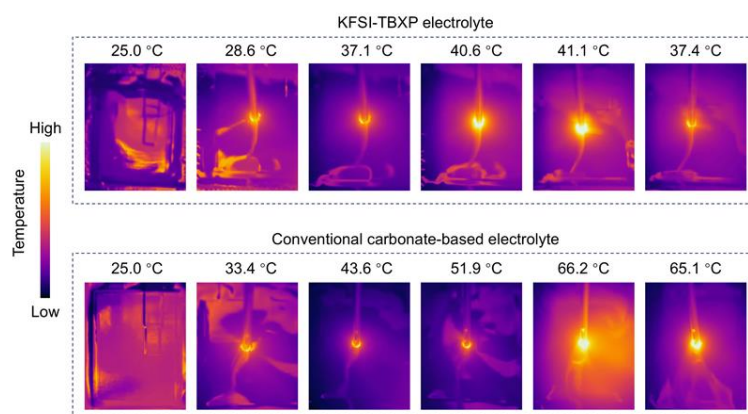
Battery safety (thermal tests, overcharge tests, and nail penetration tests, etc.) is strongly linked to the thermal stability of the electrodes. For safety measures, it is more important to improve the heat resistance of the electrode interface than to make it flame retardant. It is strongly recommended to carry out the above safety tests on pouch cells or to perform DSC measurements on the electrodes (cathode and anode) using electrolytes with TMP, TBP, and TBXP.

Response:

We greatly appreciate the reviewer’s insightful and professional suggestion on the quantitative evaluation of battery safety performance. We fully agree with the reviewer that the thermal stability of the electrode interface plays a more critical role in battery safety than mere electrolyte flame retardancy, and that comprehensive safety characterization is essential to validate the practical reliability of the developed electrolyte system.

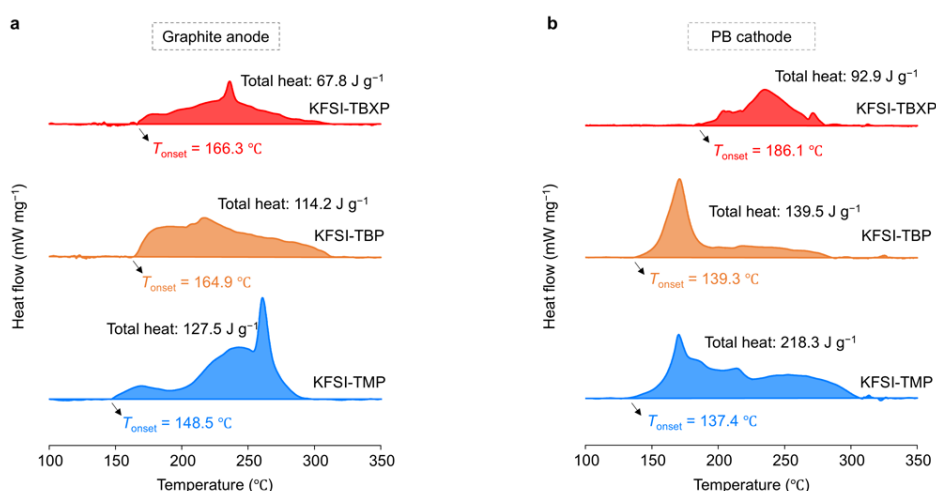
In response to your recommendation, we have supplemented thermal imaging coupled nail penetration tests on pouch cells to clarify the practical thermal safety performance. All pouch cells were fully charged to 100% SOC and kept at a constant temperature for thermal equilibration before testing (**Supplementary Fig. 59**). The thermal imaging results clearly confirmed that the KFSI-TBXP electrolyte effectively suppressed the temperature rise during the nail penetration process, exhibiting a much

lower peak temperature compared with the conventional carbonate-based electrolyte. Furthermore, we have carried out DSC measurements on the charged PB cathode and potassiated graphite anode electrodes after cycling TMP-, TBP-, and TBXP-based electrolytes, respectively, to quantitatively assess the thermal stability of the electrode interfaces (**Supplementary Fig. 60**). The newly supplemented DSC results clearly reveal the superior heat resistance (**higher exothermic onset temperature and lower total heat release**) of the electrode interphases formed in the TBXP electrolyte, which further corroborates the enhanced safety characteristics of our designed electrolyte. We have integrated these additional experimental results into the revised manuscript to support the quantitative safety analysis. The detailed data and corresponding discussions are presented in the revised main text and the supporting information to provide a more comprehensive and convincing safety evaluation.



Supplementary Fig. 59. Infrared thermography images of the pouch cell during the nail penetration short-circuit test.

All pouch cells were fully charged to 100% SOC before the nail penetration short-circuit test, then placed in a constant-temperature chamber for 30 min of thermal equilibration. The infrared thermal imaging results demonstrate that the maximum temperature of the pouch cell with the KFSI-TBXP electrolyte reaches only 41.1 °C throughout the nail penetration and short-circuit process, which is significantly lower than the peak temperature of 66.2 °C recorded with the conventional carbonate-based electrolyte.



Supplementary Fig. 60. DSC profiles of (a) potassiated graphite anodes (0.01 V) and (b) fully charge-state PB cathodes (4.2 V) mixed with relevant electrolyte.

The thermal compatibility of the graphite anode and PB cathode in different electrolytes was evaluated using differential scanning calorimetry (DSC). For the potassiated graphite anode, the mixture with KFSI-TBXP electrolyte exhibited an exothermic reaction onset temperature (T_{onset}) of 166.3 °C and a total heat release of 67.8 J g⁻¹. In comparison, the anode mixed with KFSI-TBP electrolyte showed a T_{onset} = 164.9 °C with a total heat release of 114.2 J g⁻¹, while the KFSI-TMP electrolyte showed the lowest T_{onset} (148.5 °C) and the highest total heat release (127.5 J g⁻¹). Notably, although the T_{onset} of KFSI-TBXP and KFSI-TBP were similar, KFSI-TBXP significantly suppressed the total heat release, demonstrating superior thermal stability. For the charge-state PB cathode (4.2 V), the mixture with KFSI-TBXP electrolyte delivered a T_{onset} = 186.1 °C and a total heat release of 92.9 J g⁻¹, markedly outperforming the KFSI-TBP (139.3 °C, 139.5 J g⁻¹) and KFSI-TMP (137.4 °C, 218.3 J g⁻¹) counterparts. These results indicate that the KFSI-TBXP electrolyte effectively suppresses exothermic reactions between the electrodes and electrolyte, thereby enhancing battery safety under thermal runaway conditions.

Revisions:

Results and Discussion Section:

“Subsequently, nail penetration short circuit test combined with infrared thermography imaging further confirmed its superior thermal safety. The pouch cell using KFSI-TBXP electrolyte maintained a much lower temperature during the

short-circuit penetration process compared with the conventional carbonate-based electrolyte (Supplementary Fig. 59). Furthermore, differential scanning calorimetry (DSC) was employed to assess the thermal abuse tolerance of both the potassiated graphite-electrolyte and charged PB cathode-electrolyte mixtures. Compared to the KFSI-TBP and KFSI-TMP electrolytes, the KFSI-TBXP electrolyte exhibited a higher exothermic onset temperature and lower total heat release, indicating superior capability in mitigating thermal runaway (Supplementary Fig. 60).”

Methods section:

“Differential scanning calorimetry (DSC) measurements were performed on a thermal analyzer (China-DZ-DSC300C). Potassiated graphite anodes were retrieved from cells discharged to 0.01 V at 20 mA g⁻¹ in the corresponding electrolytes, while charged PB cathodes were obtained from cells charged to 4.2 V at 100 mA g⁻¹. Both electrodes were carefully rinsed with dimethyl carbonate (DMC) three times to remove residual electrolyte. After overnight drying, the electrode powders were mixed with the selected electrolyte solutions and sealed in 100 μL high-pressure gold DSC capsules. The DSC profiles were recorded from 30 to 400 °C at a heating rate of 10 °C min⁻¹.”

(3) Quantification of the solvation structure

A central argument of the manuscript is that reduced free solvent content promotes anion-derived, inorganic-rich SEI/CEI formation. Therefore, quantification of the free solvent ratio and solvent-ion species (SSIP/CIP/AGG) is required. For example, peak separation analysis of Raman measurements, detailed shift analysis of NMR results, and chemical potential measurements using a ferrocene reference electrode conducted by Prof. Yamada et al. Furthermore, in the evaluation of KFSI-TMP, KFSI-TBP, and KFSI-TBXP, the molecular weights of the solvents differ significantly, so the discussion should be based on fixed stoichiometry (molar ratio) rather than molar concentration; otherwise it would be unfair.

Response:

We sincerely thank the reviewer for their highly insightful and constructive comments,

which have provided critical guidance for help substantially enhance the quantitative rigor and reliability of our solvation structure analysis. In response, we have performed systematic peak separation analysis of Raman measurements and detailed shift analysis of NMR results, following the methodology reported by Prof. Yamada et al. (*Nat. Energy* 2022, 7, 1217-1224). These references have now been appropriately cited in the revised manuscript.

To further optimize the solvation structure analysis, we have re-evaluated the relevant results from two complementary and representative perspectives, which effectively enhances the comprehensiveness of our findings: (i) a fixed salt-to-solvent molar ratio, which reflects the elucidation of the intrinsic solvation characteristics of individual solvent molecules (**Fig. 2c and Supplementary Fig. 10**); and (ii) a fixed molar concentration of 1 M, which represents practical electrolyte formulations (**Figs. 2d, 2e and Supplementary Fig. 19**). This dual approach provides a comprehensive understanding of both fundamental solvation behavior and practical electrolyte performance.

It should be noted that the characteristic Raman peak of phosphate ester solvents is located at approximately 730 cm^{-1} , which heavily overlaps with the characteristic peak of the FSI^- anion (*Nat. Energy* 2018, 3, 674-681). This spectral overlap leads to a compromise the accuracy of peak separation. To overcome this technical limitation, we selected the characteristic peak of the FSI^- anion at around 1210 cm^{-1} (S=O stretching mode of FSI^-) for quantitative analysis of ion coordination configurations. This peak has been validated as an effective and reliable method for quantifying ion coordination states in phosphate-based electrolyte systems (*Energy Environ. Sci.* 2024, 17, 9100; *Adv. Funct. Mater.* 2025, 35, 2504367). To better visualize and present the key analytical results, we have updated **Figs. 2c, 2d and 2e** to display the quantitative solvation structure analysis based on Raman and NMR characterizations. We sincerely appreciate the reviewer's recommendation to conduct chemical potential measurements using a ferrocene reference electrode, which is a classical and widely adopted technique in lithium-based electrolyte research. However, potassium metal is markedly more chemical reactivity than lithium metal and prone to spontaneous,

vigorous side reactions with nearly all common organic electrolytes. Even in 1,2-dimethoxyethane (DME), a solvent widely recognized for its favorable compatibility with alkali metal anodes, potassium metal undergoes rapid parasitic reactions (*Nat. Commun.* 2023, 14, 6006), which would severely compromise the reliability and reproducibility of chemical potential test data. Moreover, to the best of our knowledge, no reliable method for measuring chemical potential in potassium-based electrolyte systems has been reported in the peer-reviewed literature to date, primarily due to the intrinsic ultra-high reactivity of potassium metal. We sincerely hope the reviewer understands this technical limitation.

Once again, we thank the reviewer for these valuable suggestions, which have effectively improved the quality and rigor of this manuscript. All corresponding revisions have been marked and updated in the revised manuscript.

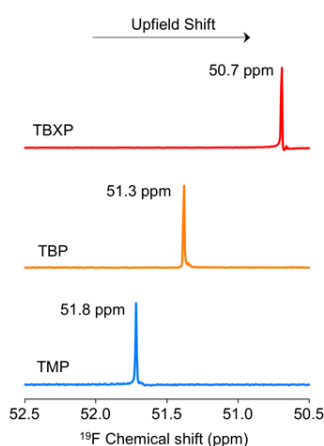
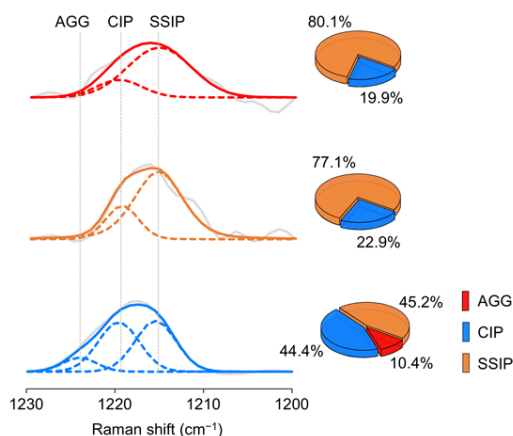


Fig. 2c. ^{19}F NMR spectra of $\text{K}^+\text{-FSI}^-$ ion pairs in electrolytes of identical salt to solvent molar ratios.



Supplementary Fig. 10. Raman spectra of electrolytes with identical salt to solvent molar ratios.

The coordination interactions between K^+ and FSI^- in the electrolytes were investigated by Raman vibrational modes in the range of $1200\text{--}1230\text{ cm}^{-1}$, where the spectral bands correspond to the $S=O$ stretching vibrations of FSI^- anions^{2,3}. In the 1 M KFSI-TMP electrolyte, the proportion of AGGs was 10.4%. In contrast, in the TBP- and TBXP-based electrolytes with the same molar ratio of salt to solvent as the 1 M KFSI-TMP electrolyte, ions predominantly exist as solvent-separated ion pairs (SSIP, solvated K^+ without FSI^- coordination). This indicates that abundant solvent molecules participate in K^+ solvation in the TBP- and TBXP-based electrolytes, further hindering the incorporation of FSI^- anions into the K^+ solvation sheath.

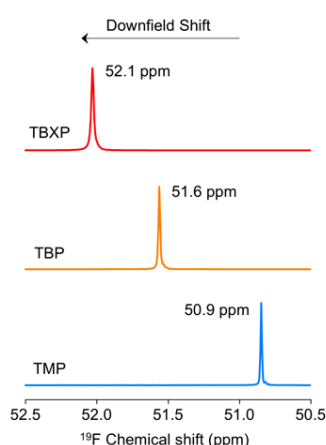


Fig. 2d. ^{19}F NMR spectra of K^+ - FSI^- ion pairs in electrolytes of 1 M KFSI salt with various solvents.

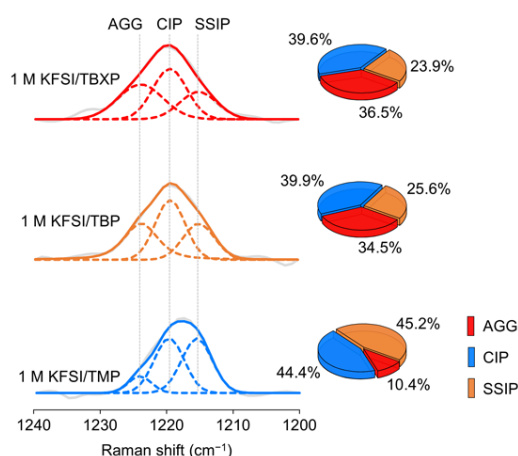
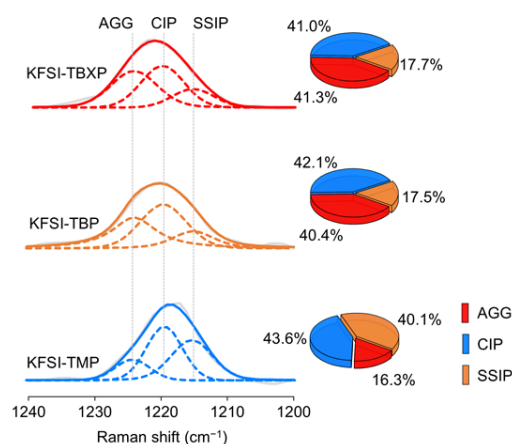


Fig. 2e. Raman spectra in the $1200\text{--}1240\text{ cm}^{-1}$ region corresponding to the $S=O$

stretching mode of FSI^- for single-solvent electrolytes (1 M KFSI in TMP, TBP, and TBXP).



Supplementary Fig. 19. Raman spectra in the 1200-1240 cm^{-1} region corresponding to the S=O stretching mode of FSI^- for mixed electrolytes containing 30 vol% OOE (denoted as KFSI-TMP, KFSI-TBP, and KFSI-TBXP).

Raman spectroscopy was further employed to examine the solvation structures of the electrolytes containing 30 vol% OOE co-solvent. The results show that the introduction of OOE co-solvent leads to a slight increase in the proportion of AGGs across all three electrolyte systems, indicating a modest promotion of FSI^- participation in the K^+ solvation sheath. Specifically, the AGG fraction increases from 36.5% to 41.3% for the TBXP-based electrolyte, from 34.5% to 40.4% for the TBP-based system, and from 10.4% to 16.3% for the TMP-based electrolyte. Notably, even after the introduction of OOE co-solvent, the TBXP-based electrolyte maintains the highest AGG proportion among the three electrolyte systems. This demonstrates that the TBXP solvent intrinsically facilitates the incorporation of FSI^- anions into the inner solvation sheath of K^+ more effectively than TBP and TMP under comparable electrolyte formulations. This characteristic promotes the formation of an anion-derived inorganic-rich interphase.

Revisions:

Results and Discussion Section:

“To evaluate the intrinsic solvation capability of solvent molecules, we conducted ^{19}F nuclear magnetic resonance (NMR) analysis under a fixed stoichiometric ratio of bis(fluorosulfonyl)imide potassium (KFSI) to solvent. The strength of K^+ - FSI^- interaction correlates directly with the magnitude of the observed ^{19}F NMR peak field chemical shift.^{36, 37} As shown in Fig. 2c, at the same molar ratio of salt to solvent (FSI^- :solvent = 1:5), the TBXP-based electrolyte exhibited an apparent shielded effect toward upfield shift (50.7 ppm), which was in sharp contrast to that of the TMP-based electrolyte (51.8 ppm). This result indicates that the TBXP solvent has stronger coordination capability, thereby reducing the free solvent content in the electrolyte. This characteristic was also confirmed by the corresponding Raman spectra (Supplementary Fig. 10). To further probe insight into the influence of molecular size effects on electrolyte solvation structures, we conducted ^{19}F NMR analysis on various electrolyte systems with an identical KFSI salt concentration (1 M). As shown in Fig. 2d, contrary to the results under the fixed stoichiometric ratio condition, the TBXP-based electrolyte exhibits the most pronounced downfield chemical shift (52.1 ppm), indicating that TBXP solvent more efficiently promotes the FSI^- anions into the primary K^+ solvation sheath. Raman spectroscopy results further corroborated this conclusion. Fig. 2e shows the Raman spectra and peak positions of FSI^- anions, indicating K^+ - FSI^- ion-pairing behavior.^{38, 39} Fitting analysis of the Raman peaks in this range showed that the TBXP-based electrolyte has a higher fraction of ion aggregates (AGGs, an anion coordinating to two or more K^+) at 36.5%, compared to 10.4% for the TMP-based electrolyte.”

“Furthermore, Raman analysis revealed that the solvation structure evolution trend remained largely unchanged after the introduction of the OOE co-solvent, whereas the AGG ratio increased only slightly (Supplementary Fig. 19).”

References Section:

[38] Wang J, et al. Boosting ultra-fast charging in lithium metal batteries through enhanced solvent-anion interaction via conjugation effect. *Energy Environ. Sci.* **17**, 9100-9111 (2024).

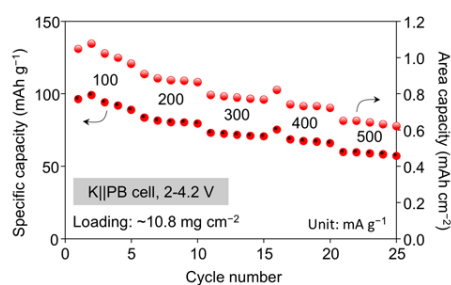
[39] Ko S, et al. Electrode potential influences the reversibility of lithium-metal anodes. *Nat. Energy* 7, 1217-1224 (2022).

(4) Evaluation for practical use

Considering the practical use of batteries, the ionic conductivity of the KFSI-TBXP electrolyte at 25°C (1.75 mS cm^{-1}) is extremely low. The ionic conductivity of current electrolytes must be at least 7 mS cm^{-1} at 25°C, even for prismatic and pouch-type cells. It is necessary to evaluate low-temperature performance (e.g., -20 to 0 deg.C) or rate performance when the amount of electrode loading is increased.

Response:

We sincerely thank the reviewer for this constructive and application-oriented comment. In response to your suggestion, we conducted additional experiments to verify the rate performance of the battery at a higher PB cathode mass loading. The cell using KFSI-TBXP electrolyte delivers favorable rate capability ($100\text{-}500 \text{ mA g}^{-2}$) even at a high PB cathode areal mass loading of $\sim 10.8 \text{ mg cm}^{-2}$ (**Supplementary Fig. 47**). The corresponding rate performance data and updated figures have been added and clearly marked in the revised manuscript. We greatly appreciate your valuable advice, which enhances the practical significance of this work.



Supplementary Fig. 47. Rate performance of high mass loading K||PB cell in the KFSI-TBXP electrolyte.

Supplementary Fig. 47 shows the rate performance of a K||PB cell with a high PB cathode mass loading of $\sim 10.8 \text{ mg cm}^{-2}$, using the KFSI-TBXP electrolyte within a voltage window of 2-4.2 V. The cell delivers an initial capacity of $\sim 93.9 \text{ mAh g}^{-1}$, corresponding to an area capacity of $\sim 1.01 \text{ mAh cm}^{-2}$. Upon stepwise increases in the current density to 200, 300, 400, and 500 mA g^{-1} , the capacity gradually declines to

80.9, 71.6, 67.1, and 58.6 mAh g⁻¹, respectively.

Revisions:

Results and Discussion Section:

“Encouragingly, the K||PB cell with the KFSI-TBXP electrolyte also presents favorable rate performance at a high mass loading of ~10.8 mg cm⁻² at 100 to 500 mA g⁻¹ (Supplementary Fig. 47).”

Once again, we sincerely thank the reviewer for their insightful feedback and constructive suggestions, which have significantly strengthened the clarity and academic depth of our analysis and elevated the overall quality of the manuscript. We greatly appreciate the reviewer’s time and expertise devoted to this work, and sincerely hope that the revised version meets with their approval.

Point-by-point Response to the Reviewers' Comments

Nature Communications manuscript NCOMMS-25-97130A

Title: Reconciling Strong Coordination and Anion-Reinforced Solvation Structure

Enables Nonflammable Electrolytes for Potassium-Ion Batteries

Dear Referees:

We hereby submit our revised manuscript in response to the second round of reviews for our manuscript (Manuscript number: **NCOMMS-25-97130A**). We extend our deepest gratitude to the Editor and the four reviewers. We thank the Editor for your professional guidance, rigorous oversight and consistent support throughout the review process, and the four reviewers for your dedicated time, professional expertise and insightful constructive feedback to refine our work. We have fully addressed all comments raised in this round with targeted revisions, all clearly highlighted in the manuscript for ease of reference. Our detailed point-by-point responses to all comments are presented in the subsequent sections. We sincerely hope this revised manuscript will receive your full approval and be accepted for publication in “*Nature Communications*”.

Instructions.

Blue: comments from Reviewers;

Black: our response to reviewer's comments;

Highlighted text in yellow: revisions made in the revised manuscript.

Reviewer #1 (Remarks to the Author):

The authors have thoroughly addressed the reviewer comments and provided clear, well-reasoned revisions that substantially strengthen the manuscript. The additional experiments and clarifications regarding the electrolyte formulation, solvation structure, and interfacial interpretation have improved both the mechanistic clarity and the scientific rigor of the work. The revised manuscript now presents a coherent and convincing case for the proposed molecular design strategy for nonflammable electrolytes in potassium-ion batteries. In its current form, the manuscript is suitable for publication in this journal.

Response:

Thank you very much for your positive and encouraging comments on our revised manuscript. We are truly grateful that you have found our previous revisions, additional experiments, and mechanistic clarifications to be clear and well-reasoned. We are delighted to know that the improved manuscript now presents a coherent and convincing case for our proposed molecular design strategy, and that you consider it suitable for publication in this journal. Once again, thank you for your time and expert guidance throughout the review process.

Reviewer #2 (Remarks to the Author):

The authors have addressed my comments. I don't have further questions.

Response:

Thank you very much for your time and effort in reviewing our manuscript. We are glad to know that our revisions have properly addressed your comments and that you have no further questions. Your positive feedback is greatly appreciated.

Reviewer #3 (Remarks to the Author):

Following substantial revisions, the authors have evidently devoted considerable effort to enhancing the manuscript across multiple aspects.

Most of my concerns have been adequately addressed. The only remaining issue is that the side chain in TBXP shows the lowest BDE value, corresponding to the worst stability. Is this inconsistent with the main claim of the manuscript?

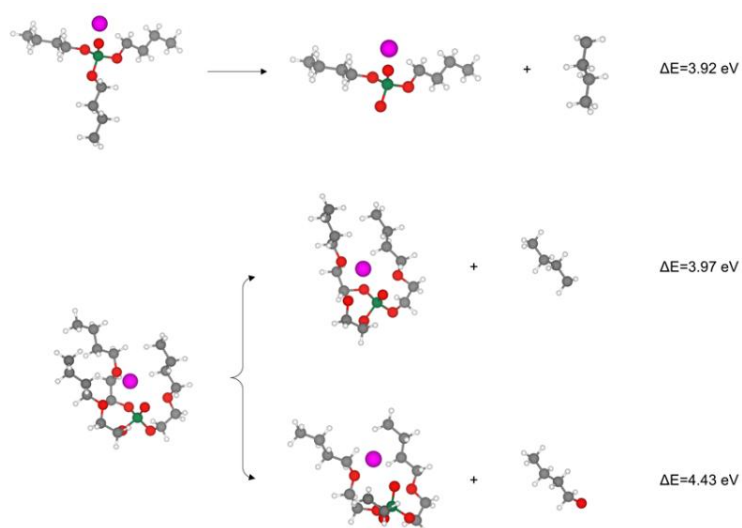
Response:

We sincerely appreciate the reviewer for recognizing our comprehensive revision efforts and acknowledging that most of the previously raised concerns have been well addressed. We also sincerely thank the reviewer for raising this valuable question, which has allowed us to further supplement and clarify the mechanistic discussion in the manuscript.

Importantly, for TMP-based electrolytes, the stability is generally dominated by the properties of individual solvent molecules, as these systems contain abundant free, uncoordinated solvent molecules. In contrast, for the larger-molecular phosphate ester (TBP and TBXP) electrolytes, an exceptionally high salt-to-solvent molar ratio is maintained even at low salt concentrations. This high salt-to-solvent molar ratio forms a coordination mechanism analogous to that of high-concentration electrolytes, where the actual stability of the system is primarily governed by K^+ -solvent clusters rather than that of isolated single solvent molecules.

To verify this mechanism, we further performed targeted BDE calculations in the K^+ -coordinated solvation environment mimicking our actual electrolyte system. The results show that, unlike the divergent coordination of TBP solvent, the anchoring coordination of the TBXP side-chain significantly increases its BDE in the solvated state, effectively suppressing side-chain cleavage (**Supplementary Fig. 7**). This contrast between intrinsic single-molecule instability and superior solvated-state stability precisely demonstrates the advantage of our design strategy, which is fully consistent with the core claim of the manuscript.

Thank you again for your constructive feedback. We hope this clarification fully addresses your concern.



Supplementary Fig. 7. Calculated bond dissociation energies of the K^+ -TBP and K^+ -TBXP ion pairs. Color scheme of molecules: K-pink, O-red, C-brown, P-dark green, H-white.

To evaluate the stability of ion-solvent clusters in the electrolyte system, we performed BDE calculations for both K^+ -TBP and K^+ -TBXP ion pairs. All calculations were specifically targeted at the lowest BDE sites previously identified in the isolated single solvent molecules. The results show a striking contrast to the stability of individual solvent molecules, as the K^+ -TBXP ion pair exhibits a significantly higher BDE than the K^+ -TBP ion pair. This finding clearly demonstrates that the multidentate strong coordination of the TBXP side-chain effectively enhances the stability of its own side-chains.

Revisions:

Results and Discussion Section:

“Specifically, using conventional phosphate solvent trimethyl phosphate (TMP) as the backbone, we constructed the tributyl phosphate (TBP) solvent molecule by lengthening phosphate molecular backbones (Fig. 1a). Bond dissociation energy (BDE) calculations demonstrate that the major parasitic reaction sites of phosphate solvents reside predominantly on the side-chains, and the BDE values decrease progressively with increasing side-chains length (Supplementary Fig. 4).”

“The results confirm that both the main-chain P=O and side-chain C-O-C sites in TBXP serve as primary coordination sites of K^+ , consistent with the multi-site chelation design of the TBXP solvent molecule. The combined effect of the large molecular size and the multi-site strong coordination mechanism significantly reduce the proportion of free solvent molecules in the electrolyte system. Notably, BDE calculations of K^+ -solvent cluster reveal that, compared with TBP which exhibits a divergent coordination structure, the side-chain anchoring coordination of TBXP significantly enhances the stability of its side-chains (Supplementary Fig. 7).”

Reviewer #4 (Remarks to the Author):

This manuscript presents an interesting and well-designed electrolyte concept based on combining multidentate coordination and molecular-size effects. The revised version has been significantly improved, and I appreciate the authors' efforts in addressing the previous comments. In particular, the added mechanistic evidence, comparative experiments, and quantitative safety evaluations substantially strengthen the manuscript.

I have one remaining concern regarding the practical applicability of the electrolyte. The ionic conductivity ($\sim 1.75 \text{ mS cm}^{-1}$ at 25°C) is relatively low compared to typical practical systems, which may impose limitations under realistic conditions. Although higher mass loading data are now provided, the areal capacity and cycle life remain somewhat limited, suggesting non-negligible transport constraints.

In addition, low-temperature performance has not been evaluated, which is relevant given the expected decrease in conductivity at reduced temperatures. The manuscript also uses terms such as “practical” (e.g., in the Abstract) or implies applicability to realistic battery systems; however, given the relatively low ionic conductivity, the scope of such applicability should be more clearly defined.

I recommend the authors briefly clarify these points and specify the applicable operating conditions to avoid overgeneralization.

Overall, I believe this can be addressed within a minor revision.

Response:

We sincerely appreciate the reviewer's positive recognition of our electrolyte design concept, high praise for our previous revisions, and the valuable and constructive comments provided to further elevate the overall quality of this manuscript.

In response to the remaining concerns raised in this round of review, we have implemented targeted revisions to the manuscript as detailed below. First, regarding the ionic conductivity issue, we have supplemented additional clarification in the revised manuscript. Second, following your insightful suggestions, we have explicitly defined the applicable scope of this electrolyte system and revised the relevant content to avoid overgeneralization and potential misunderstandings. In addition, we have

supplemented and expanded the low-temperature performance evaluation of the electrolyte system. Owing to the low melting point of the TBXP solvent, the TBXP-based electrolyte maintains a liquid state at $-20\text{ }^{\circ}\text{C}$ (**Fig. R1a**). As the reviewer correctly noted, reduced temperature inevitably leads to a decrease in ionic conductivity. Specifically, the electrolyte exhibits an ionic conductivity of only 0.38 mS cm^{-1} at $-20\text{ }^{\circ}\text{C}$ (**Fig. R1b**), which significantly restricts its low-temperature electrochemical performance. Accordingly, although the K||PB cell delivers a reversible capacity of $\sim 60\text{ mAh g}^{-1}$ under $-20\text{ }^{\circ}\text{C}$ at 50 mA g^{-1} (**Fig. R1c**), these tests were conducted under limited mass loading, and the cell exhibits a relatively large polarization under this low-temperature operating condition. (**Fig. R1d**).

As the reviewer commented, this manuscript proposes an interesting and well-designed electrolyte design concept. In our future work, we will further advance the electrolyte regulation strategy, enhance the low-temperature adaptability of the electrolytes, and optimize the comprehensive electrochemical performance under high-mass-loading conditions.

Overall, we have comprehensively revised the manuscript in strict accordance with your constructive comments. All modifications have been clearly marked in the revised manuscript for your convenient inspection. We sincerely appreciate your rigorous review, professional comments and valuable guidance, which have greatly facilitated the improvement and rationalization of this work. We sincerely hope that the revised manuscript can meet your approval and the requirements for formal publication.

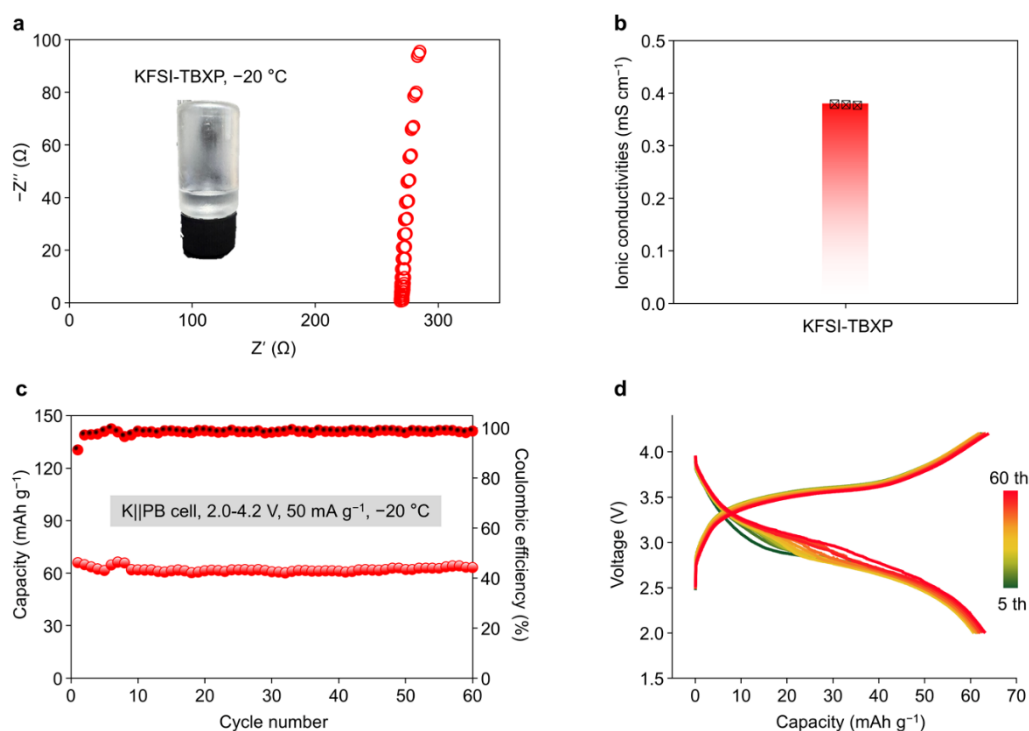


Fig. R1. (a) Electrochemical impedance spectroscopy (EIS) Nyquist plots (triplicate measurements). An optical photograph of the electrolyte at $-20\text{ }^{\circ}\text{C}$ is shown as an inset. (b) Ionic conductivity of the KFSI-TBXP electrolyte under $-20\text{ }^{\circ}\text{C}$. (c) Cycling performance and (d) corresponding charge-discharge profiles of K||PB cell under $-20\text{ }^{\circ}\text{C}$ at 50 mA g^{-1} .

Revisions:

Abstract Section:

“This work demonstrates an innovative strategy for electrolyte design in PIBs.”

Introduction Section:

“This molecular design concept offers a promising strategy for developing electrolytes for PIBs.”

Results and Discussion Section:

“At $25\text{ }^{\circ}\text{C}$, the ionic conductivities were measured at 3.8 mS cm^{-1} for KFSI-TMP, 2.22 mS cm^{-1} for KFSI-TBP, and 1.75 mS cm^{-1} for KFSI-TBXP electrolytes (Supplementary Fig. 18 and Supplementary Table 1). Notably, the generally inferior ionic conductivity of PIBs electrolytes fundamentally stems from the limited

dissociation degree of potassium salts. Although the TBXP-based electrolyte exhibits the lowest ionic conductivity, it is still sufficient to meet the requirements for battery operation at room temperature.”

“To assess graphite anode performance in the three electrolytes, K||graphite cells were cycled at 100 mA g⁻¹ within a voltage window of 0.01-3.0 V. All electrochemical tests were conducted at room temperature.”

Conclusions Section:

“This work presents a novel approach to molecular engineering, offering new insights into electrolyte design for PIBs.”

Methods Section:

“Unless otherwise noted, the average mass loading of the PB cathode is approximately ~1.0-1.5 mg cm⁻².”