

Supplementary Information

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

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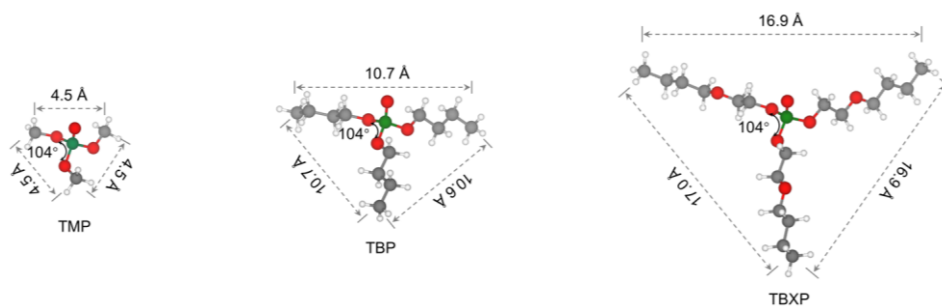
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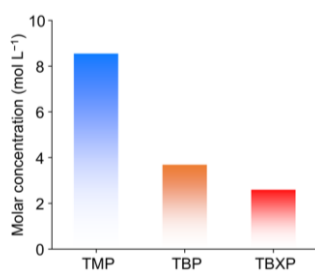
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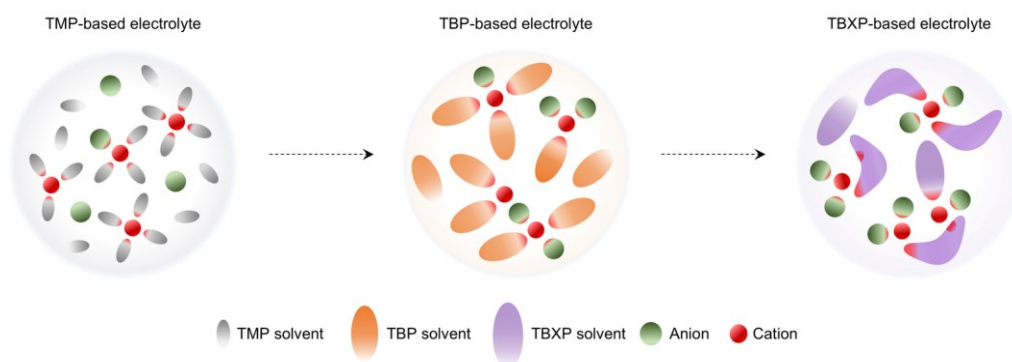
Supplementary Fig. 1. Molecular sizes of phosphate solvents. Color scheme of molecules: P, green; O, red; C, grey; H, white.

End-to-end distances between terminal C atoms with the O-P-O bond angle (θ) constrained at 104° . The terminal C atoms distances are measured as ~ 4.5 Å, 10.6 Å, and 16.9 Å for TMP, TBP, and TBXP, respectively, reflecting the progressive increase in molecular dimensions.

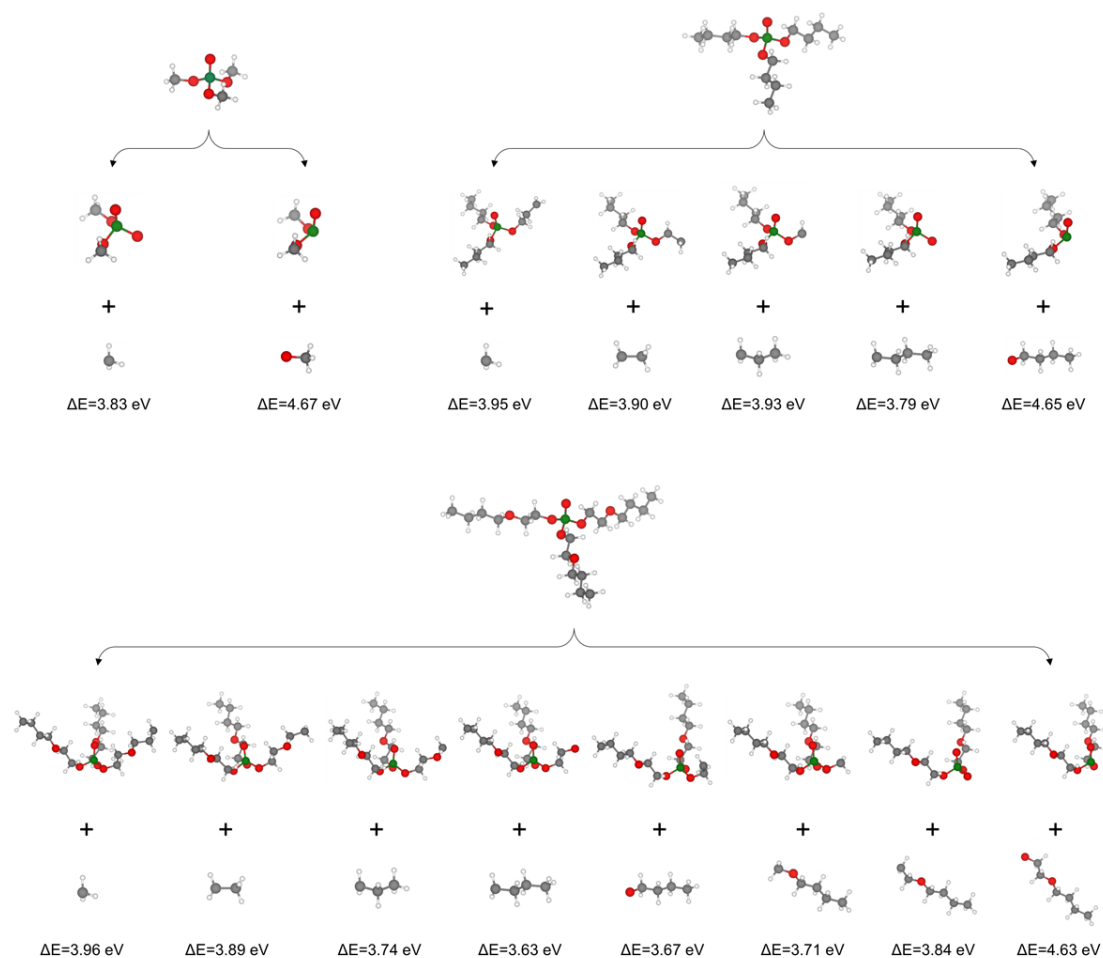


Supplementary Fig. 2. Molar concentration of phosphate-based solvents.

With increasing molecular side chain length, the solvents TMP, TBP, and TBXP exhibit sequentially decreasing molar concentrations of 8.55 mol L⁻¹, 3.68 mol L⁻¹, and 2.58 mol L⁻¹, respectively.

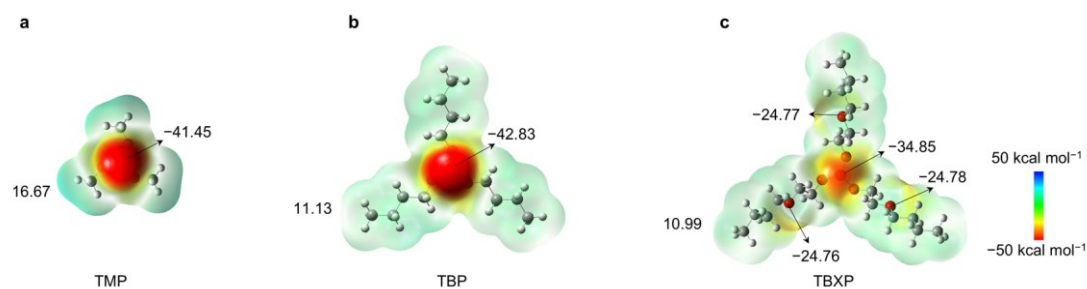


Supplementary Fig. 3. Schematic illustration of different solvation structures constructed by tuning the solvent molecular size in the electrolyte.



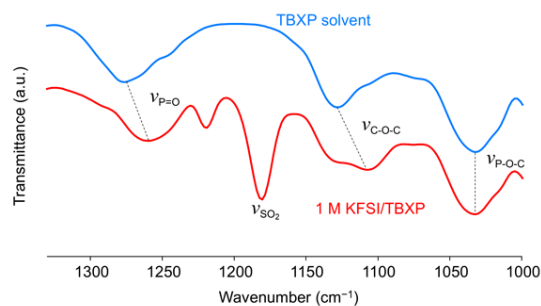
Supplementary Fig. 4. Calculated BDEs of TMP, TBP, and TBXP molecules. (O-red, C-brown, P-dark green, H-white).

To identify the reactive sites on phosphate ester solvent molecules, stepwise bond dissociation energy (BDE) 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 computational results imply that the side-chains may represent the most susceptible sites for parasitic reactions in these phosphate solvents.



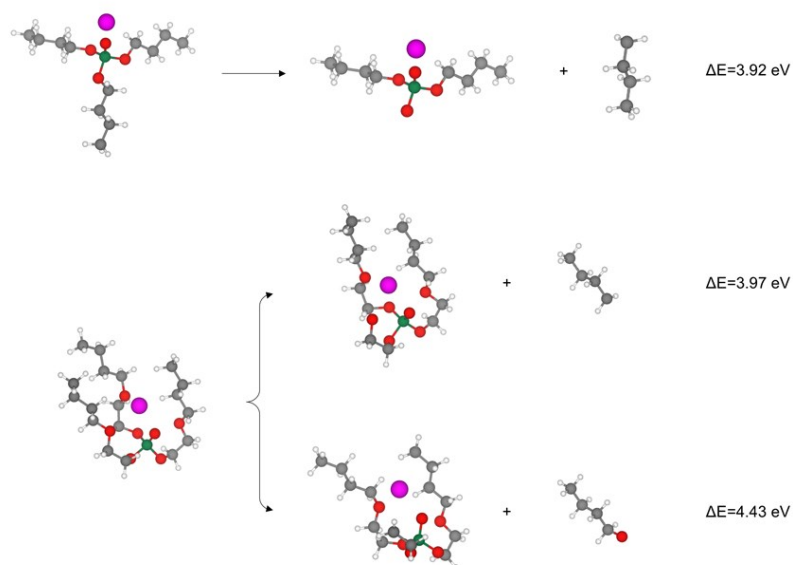
Supplementary Fig. 5. Calculated ESP maps of (a) TMP, (b) TBP, and (c) TBXP solvent molecules.

Electrostatic potential (ESP) characterizes the surface charge distribution of solvent molecules. Regions of negative ESP typically indicate potential electron-rich sites that may coordinate with K^+ . As shown in Supplementary Fig. 5, the negative ESP in TMP and TBP solvent molecules is predominantly localized around the phosphoryl (P=O) group, suggesting that this group likely serves as the primary site for K^+ coordination. In contrast, the TBXP molecule exhibits negative ESP at both the backbone P=O group and the side-chain ether oxygen (C-O-C) groups. This multi-site negative charge distribution facilitates the formation of a multi-site strong coordination configuration, thereby enhancing the binding strength with K^+ .



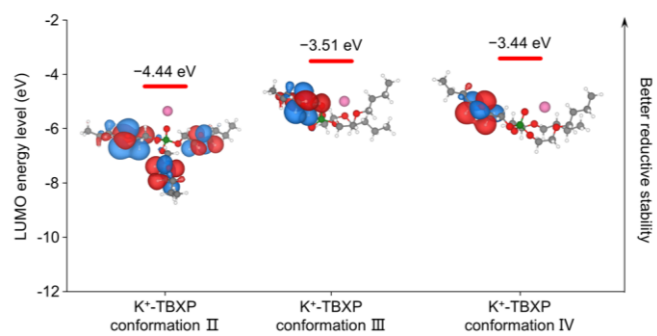
Supplementary Fig. 6. FT-IR spectra of the TBXP solvent and the 1 M KFSI/TBXP electrolyte, respectively.

As shown in Supplementary Fig. 6, 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 contributes only weakly to K^+ coordination. These spectral observations are consistent with the multi-site chelation design of the TBXP solvent molecule.

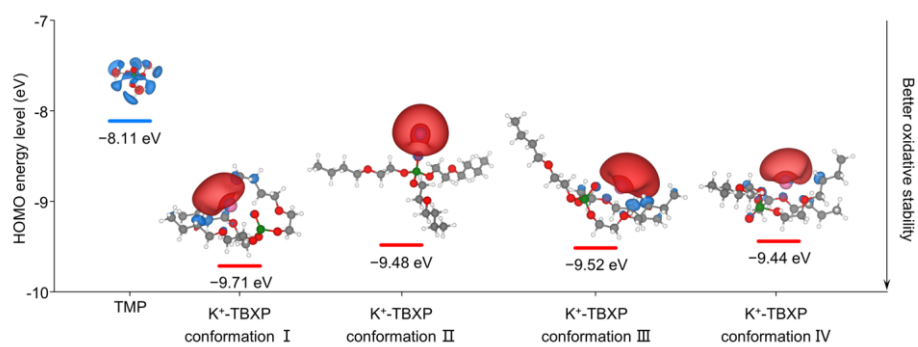


Supplementary Fig. 7. Calculated BDEs of the K^+ -TBP and K^+ -TBXP ion pairs. Color scheme of molecules: K-pink, O-red, C-brown, P-dark green, H-white.

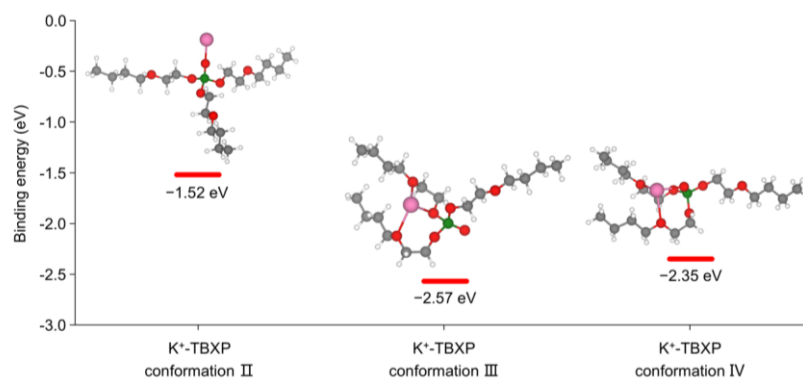
To evaluate the stability of ion-solvent clusters in the electrolyte system, we performed BDE calculations for both K^+ -TBP and K^+ -TBXP ion pairs. All calculations were specifically targeted at the lowest BDE sites previously identified in the isolated single solvent molecules. The results show a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



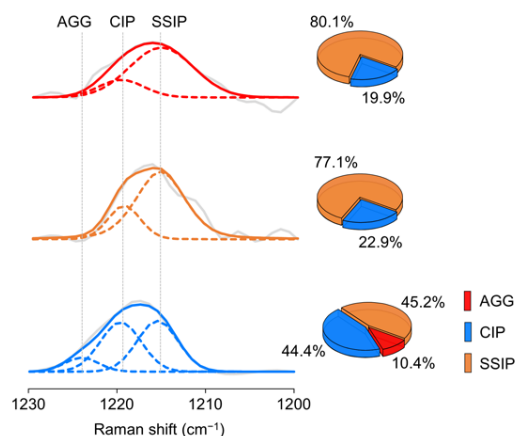
Supplementary Fig. 8. LUMO energy levels of K⁺-TBXP in different conformations.



Supplementary Fig. 9. HOMO energy levels of the TMP solvent molecule and K⁺-TBXP in different conformations.

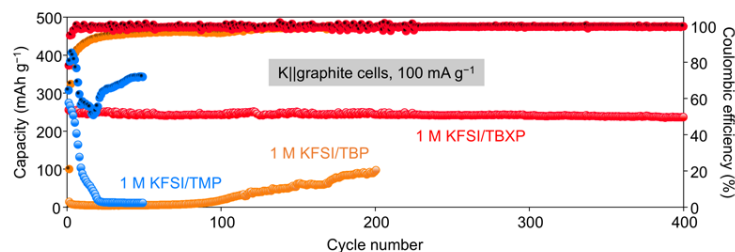


Supplementary Fig. 10. The binding energies of different configurations between K⁺ and TBXP (K⁺-TBXP) and the corresponding structures.



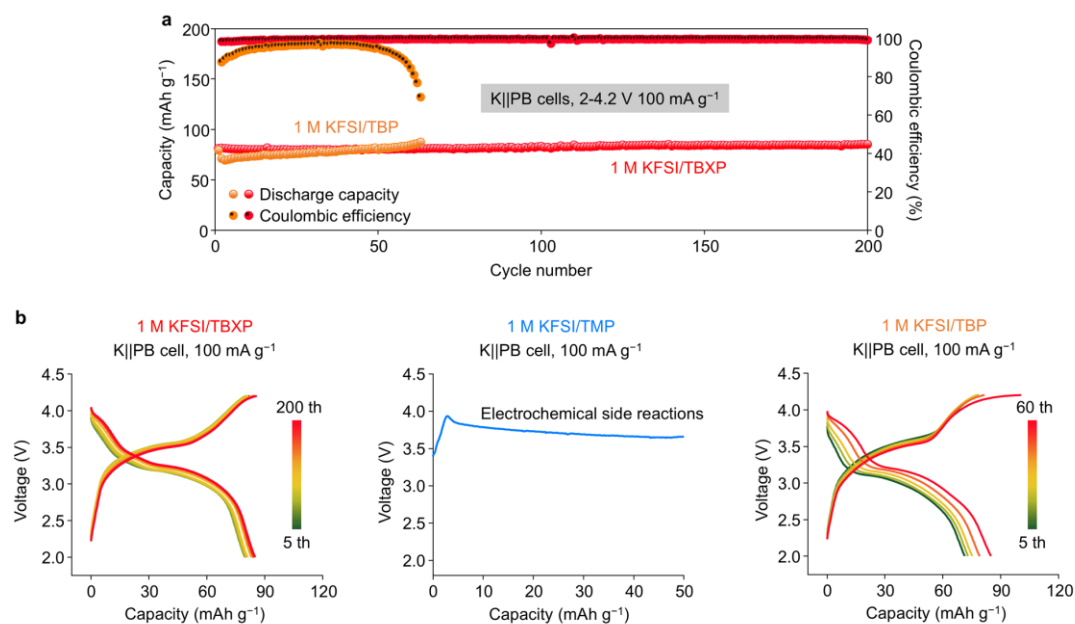
Supplementary Fig. 11. Raman spectra of electrolytes with identical salt to solvent molar ratios.

The coordination interactions between K^+ and FSI^- in the electrolytes were investigated by Raman vibrational modes in the range of 1200-1230 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.



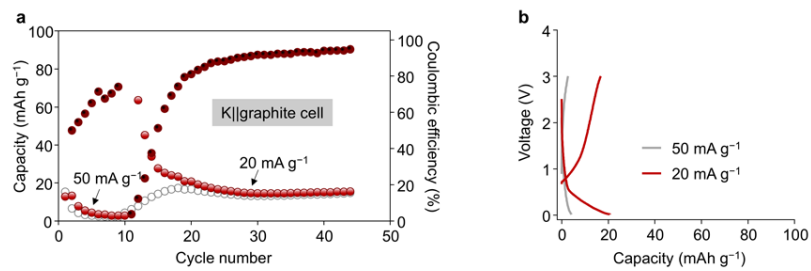
Supplementary Fig. 12. Cycling performance of K||graphite cells in the three electrolytes at 100 mA g^{-1} and at $28 \pm 1 \text{ }^{\circ}\text{C}$.

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 improved cycling stability, delivering a reversible capacity of 236.6 mAh g^{-1} after 400 cycles with a capacity retention of 90.7%.

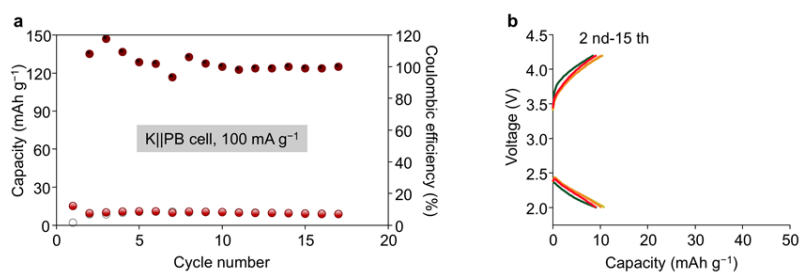


Supplementary Fig. 13. (a) Cycling performance and (b) corresponding charge-discharge profiles of K||PB cells in the three electrolytes at 28 ± 1 °C.

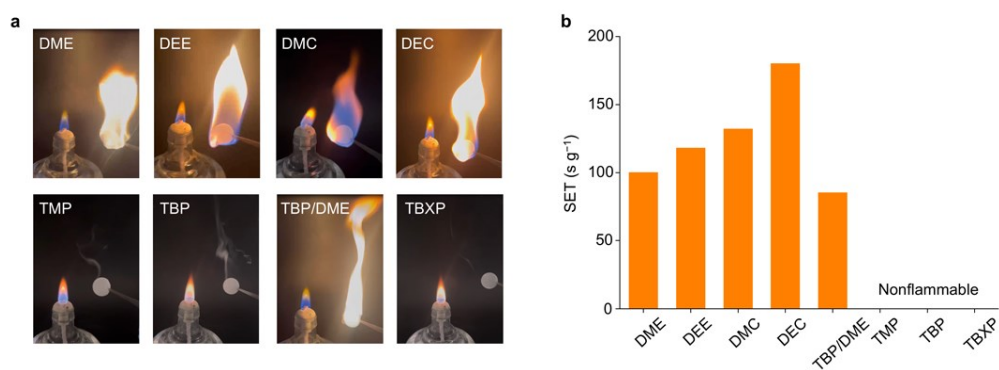
To evaluate the cycling performance of K||PB cells using 1 M KFSI in single-solvent electrolytes, the cells were tested at a cut-off voltage of 4.2 V at 100 mA g^{-1} . The results show that the 1 M KFSI/TBXP electrolyte enables cycling stability, with negligible capacity decay after 200 cycles and an 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.



Supplementary Fig. 14. (a) Cycling performance and (b) corresponding charge-discharge profiles of K||graphite cell in the 1 M KFSI/THP electrolyte at 28 ± 1 °C.



Supplementary Fig. 15. (a) Cycling performance and (b) corresponding charge-discharge profiles of K||PB cell in the 1 M KFSI/THP electrolyte at 28 ± 1 °C.

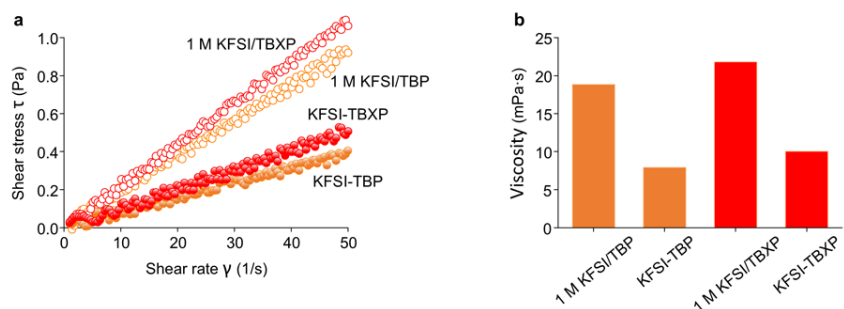


Supplementary Fig. 16. (a) Flammability analysis and (b) self-extinguishing time (SET) of various solvents.



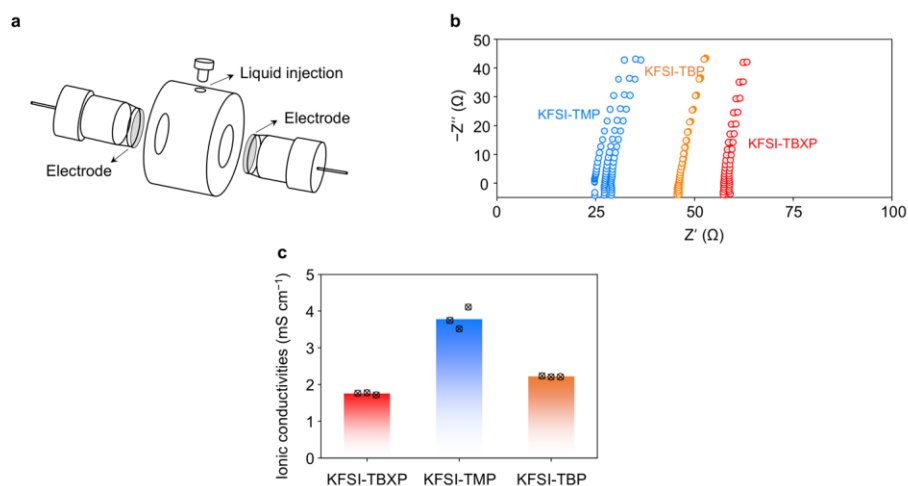
Supplementary Fig. 17. Wettability tests of the separator in different solvents.

Various solvents (TBP and TBXP) exhibit high viscosity, which compromises wettability and prevents uniform spreading on the separator, manifesting as localized aggregation. In contrast, the addition of 30 vol% low-viscosity OOE co-solvent lowers the viscosity, thereby facilitating rapid electrolyte diffusion and homogeneous wetting across the separator.



Supplementary Fig. 18. Rheological characterisation of electrolytes. (a) Curves of shear stress versus shear rate for different electrolytes, and (b) corresponding steady-state viscosity values.

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.



Supplementary Fig. 19. Ionic conductivity of electrolytes. (a) Schematic diagram of the ionic conductivity measurement device. (b) Electrochemical impedance spectroscopy (EIS) Nyquist plots for different electrolytes (triplicate measurements) at 25 °C. (c) Calculated ionic conductivity of different electrolytes.

The formula for ionic conductivity of electrolytes is as follows:

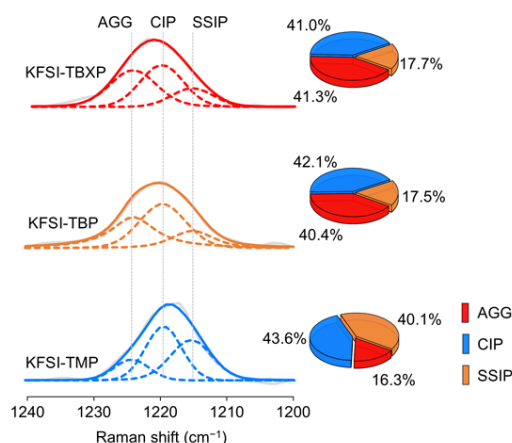
$$\sigma = \frac{d}{S \times R}$$

where R is the resistance measured by EIS, and S and d denote the area of the electrode and the distance between the two electrodes, respectively.

Supplementary Table 1. Ionic conductivity of various electrolytes

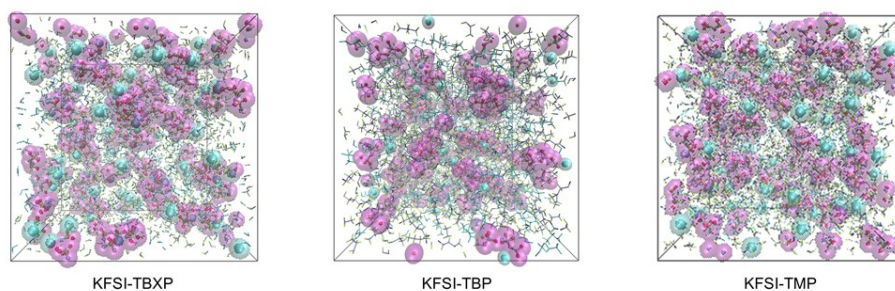
Electrolyte	Cell#1	Cell#2	Cell#3
KFSI-TBXP	1.76	1.78	1.72
KFSI-TMP	3.75	3.52	4.11
KFSI-TBP	2.24	2.21	2.21

*The unit of ionic conductivity is mS cm⁻¹.



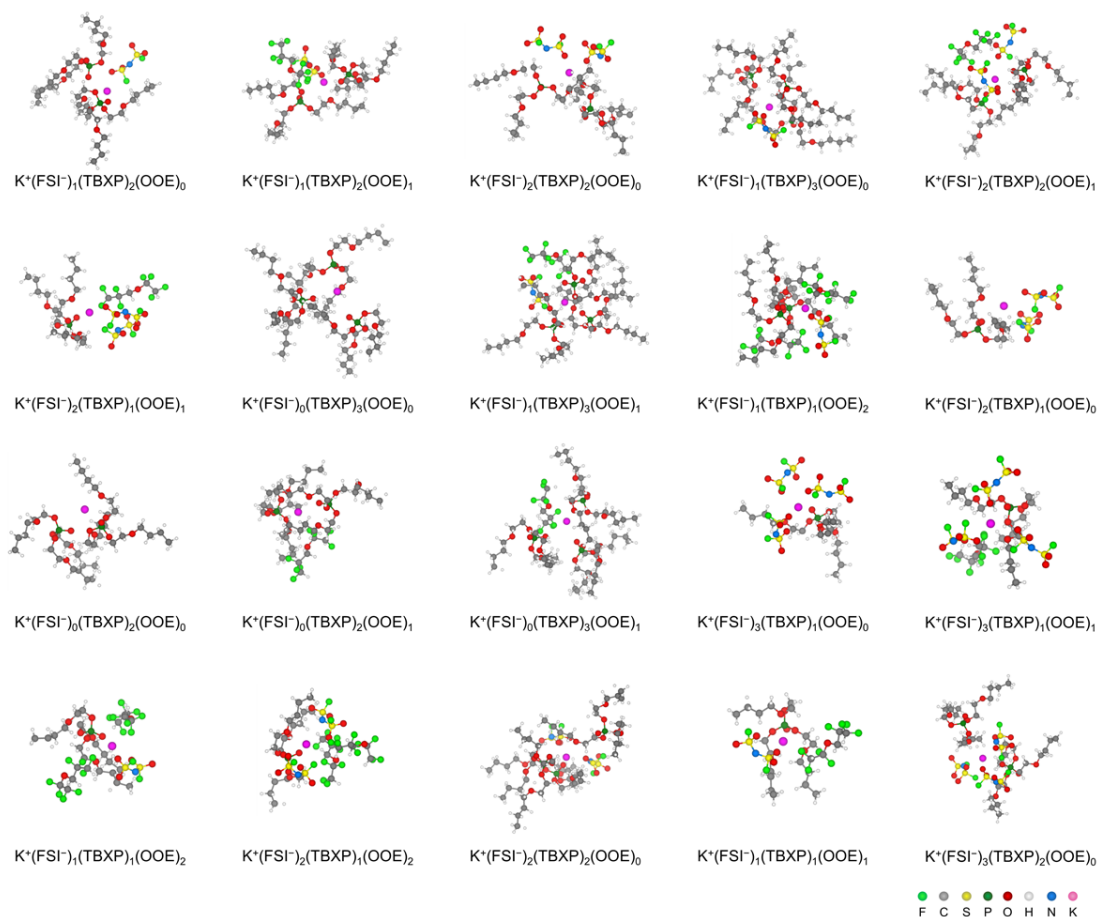
Supplementary Fig. 20. Raman spectra in the 1200-1240 cm^{-1} region corresponding to the S=O stretching mode of FSI^- for mixed electrolytes containing 30 vol% OOE (denoted as KFSI-TMP, KFSI-TBP, and KFSI-TBXP).

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.

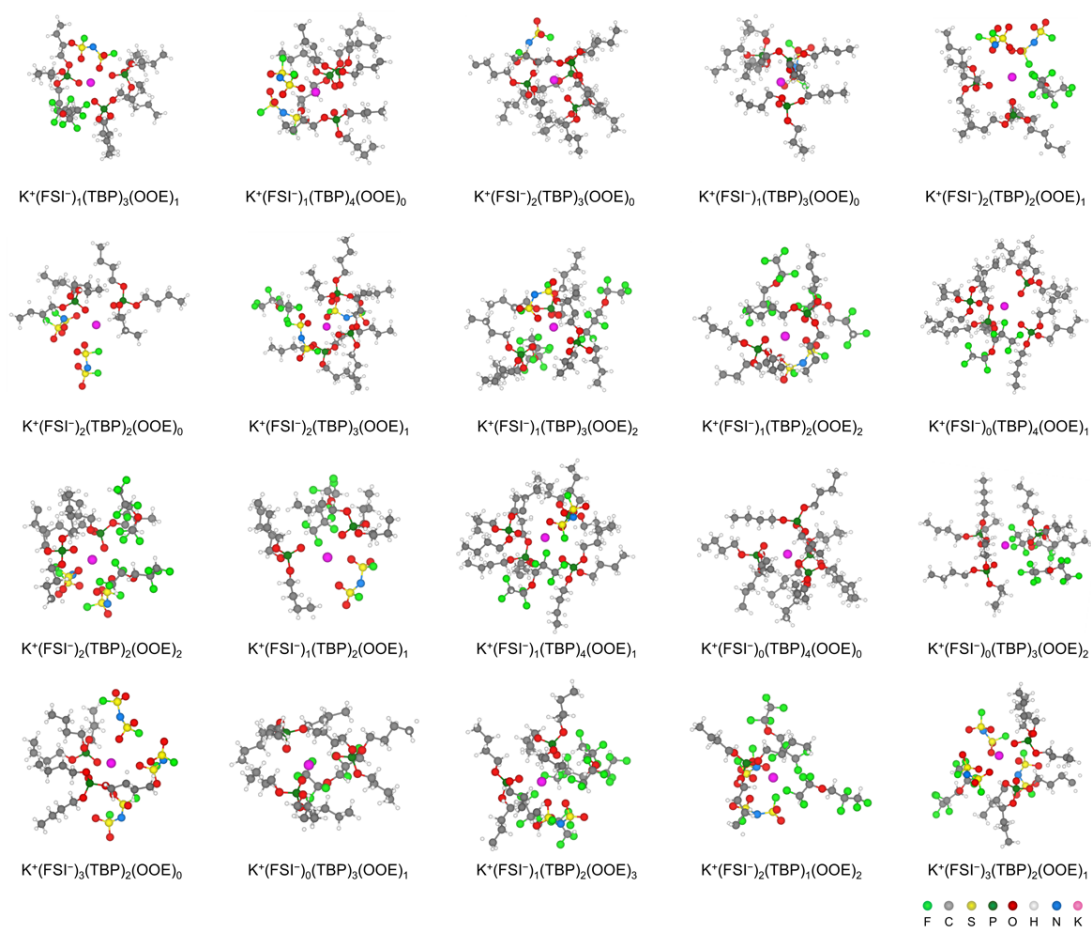


Supplementary Fig. 21. Snapshots of the MD simulated cells for different electrolytes.

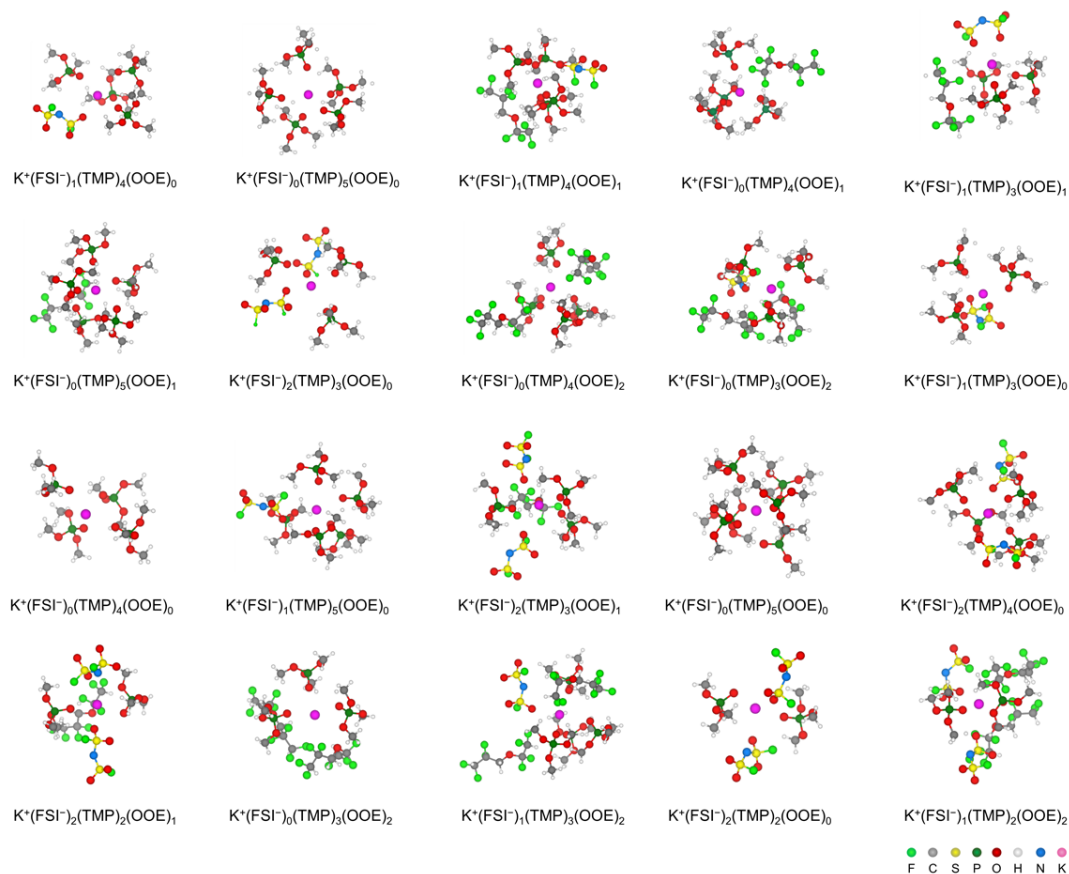
Classical MD simulations simulated the structures of the three electrolytes. The K^+ and FSI^- are depicted as ball-and-stick models, while solvent molecules are represented as wireframe models. As expected, these coordinated structures are uniformly dispersed in each electrolyte.



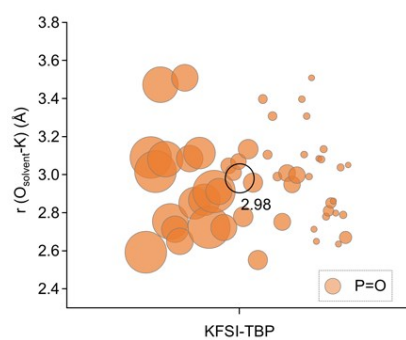
Supplementary Fig. 22. Representative K^+ solvation structures derived from MD simulations in the KFSI-TBXP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).



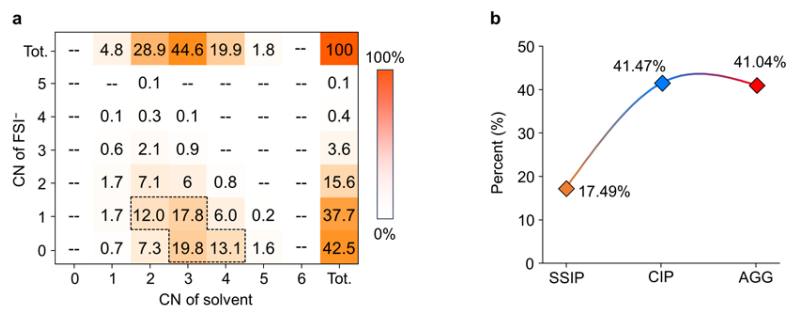
Supplementary Fig. 23. Representative K^+ solvation structures derived from MD simulations in the KFSI-TBP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).



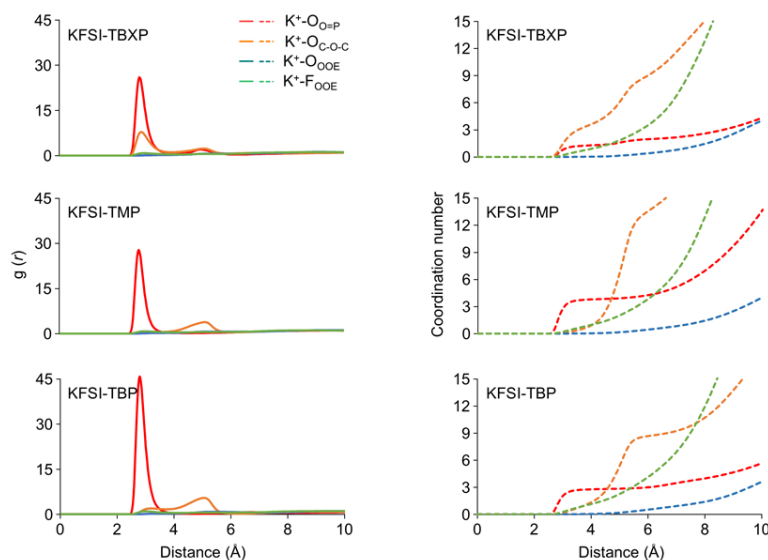
Supplementary Fig. 24. Representative K^+ solvation structures derived from MD simulations in the KFSI-TMP electrolyte. (K-pink, N-blue, O-red, S-yellow, C-brown, F-light green, P-dark green, H-white).



Supplementary Fig. 25. Coordination distances between K^+ and $\text{O}_{\text{solvent}}$ in KFSI-TBP electrolyte by MD simulations. Shaded circular areas indicate the proportion.

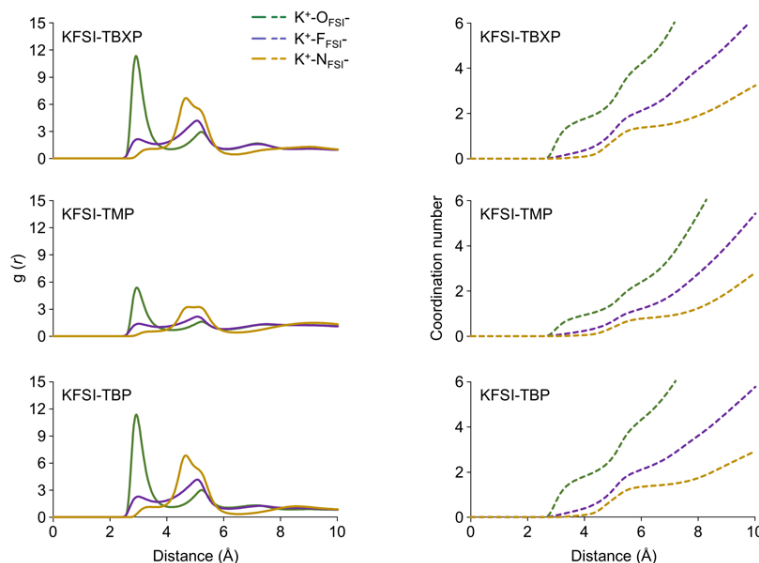


Supplementary Fig. 26. (a) Coordination number distribution isosurfaces of K^+ -solvent and K^+ -FSI $^-$ by the MD simulations. (b) Distribution of primary solvation sheath compositions in the KFSI-TBP electrolyte.



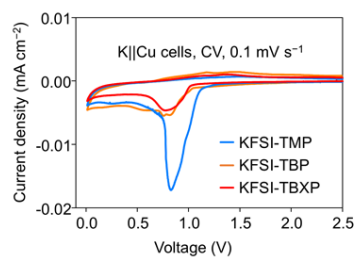
Supplementary Fig. 27. The RDFs as deduced from the MD simulations. RDFs ($g(r)$, solid lines) and coordination numbers (CN, dashed lines) of solvent molecules in different electrolytes.

Solvation structure analysis at the atomic scale by $g(r)$ and CN calculations. Solvent coordination analysis indicates that K^+ primarily coordinates with the P=O (main-chain) and C-O-C (side-chains) sites of the TBXP solvent in KFSI-TBXP electrolyte. In contrast, K^+ mainly coordinates with the P=O group in KFSI-TMP and KFSI-TBP electrolytes. This difference in coordination sites and coordination numbers suggests the contribution of the side-chain C-O-C sites to coordination in the KFSI-TBXP electrolyte, likely leading to the formation of a multidentate, strong coordination structure that differs from the coordination mechanisms of the KFSI-TMP and KFSI-TBP electrolytes.



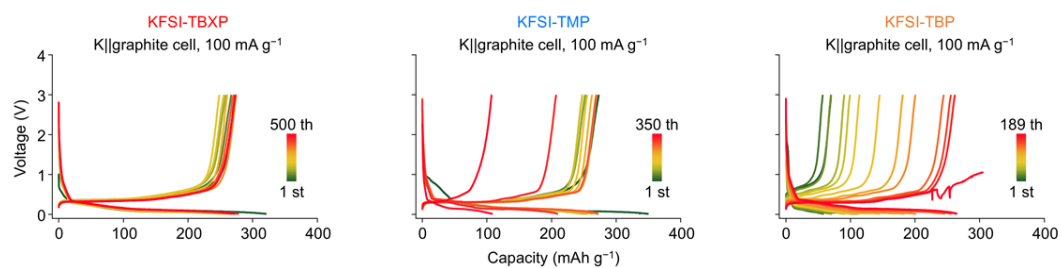
Supplementary Fig. 28. The RDFs as deduced from the MD simulations. RDFs ($g(r)$, solid lines) and coordination numbers (CN, dashed lines) of FSI^- anions in different electrolytes.

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 higher CN of FSI^- anions in KFSI-TBXP and KFSI-TBP electrolytes, compared to KFSI-TMP electrolyte, suggests that FSI^- anions may more readily enter the K^+ solvation sheath, potentially contributing to the formation of an anion-reinforced solvation structure.

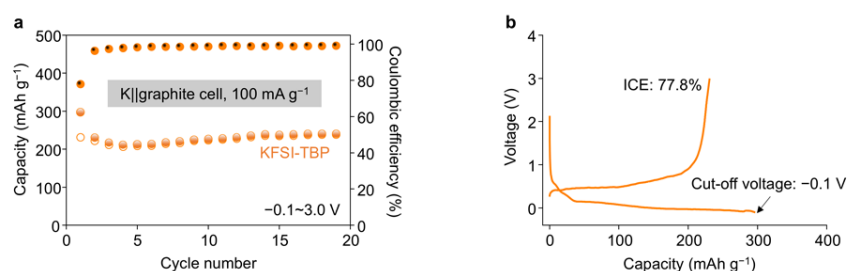


Supplementary Fig. 29. CV profiles of K||Cu cells in three electrolytes under 28 ± 1 °C at 0.1 mV s^{-1} .

The CV profiles for K||Cu cells at 0.1 mV s^{-1} reveal 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 attenuated reduction currents. In the KFSI-TBXP electrolyte, exhibits the lowest current response, which underscores its reductive stability and ability to form a passivating SEI that effectively curtails sustained electrolyte decomposition.

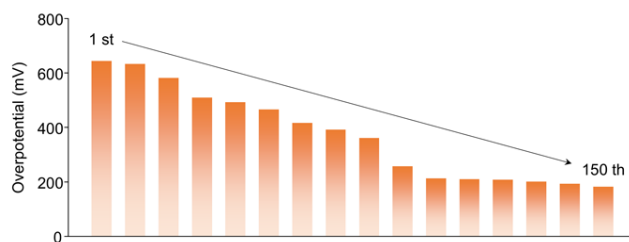


Supplementary Fig. 30. Charge-discharge profiles of K||graphite cells using different electrolytes under 28 ± 1 °C at 100 mA g⁻¹.



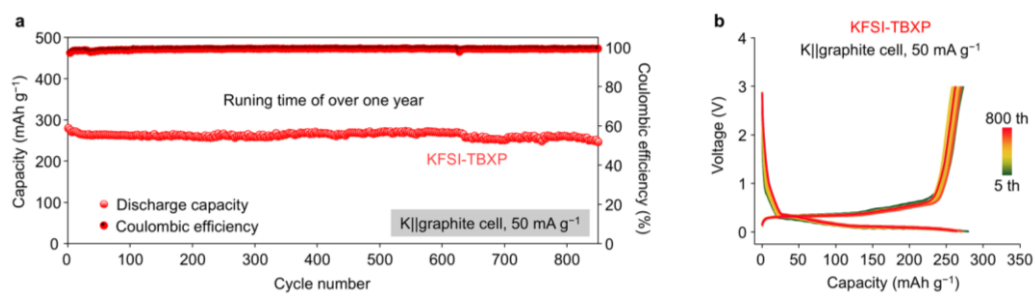
Supplementary Fig. 31. (a) Cycling performance of the graphite negative electrode in the KFSI-TBP electrolyte at 100 mA g⁻¹ within a voltage range of -0.1 to 3.0 V at 28 ± 1 °C, and (b) corresponding charge-discharge profiles.

To elucidate the mechanism underlying the low ICE of graphite negative electrodes in the 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 voltage enhances K⁺ intercalation capacity, delivering a reversible K⁺ deintercalation capacity of 230 mAh g⁻¹ and an ICE of 77.8% (Supplementary Fig. 31a). 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. 31b). The low ICE of graphite negative electrodes 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.

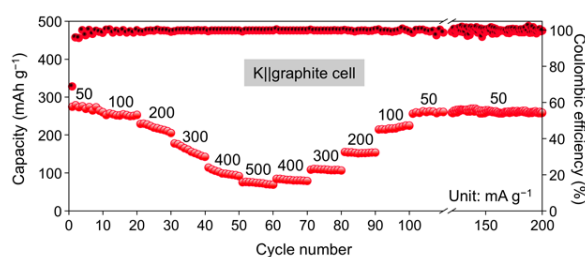


Supplementary Fig. 32. Overpotential analysis of K||graphite cell in the KFSI-TBP electrolyte.

Overpotential analysis of the K||graphite cell 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 and also stabilizes. These results indicate that the sustained capacity increase during the initial cycles of the K||graphite cell in the KFSI-TBP electrolyte is primarily attributable to a slow electrode activation process.

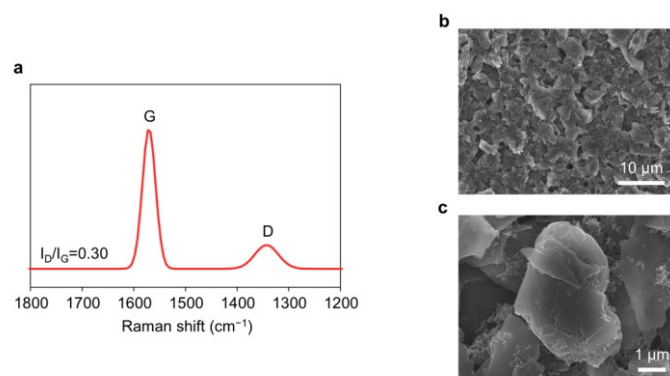


Supplementary Fig. 33. Electrochemical performance of K||graphite cell in the KFSI-TBXP electrolyte under 28 ± 1 °C at 50 mA g^{-1} . (a) Cycling performance and (b) corresponding charge-discharge profiles of K||graphite cell.



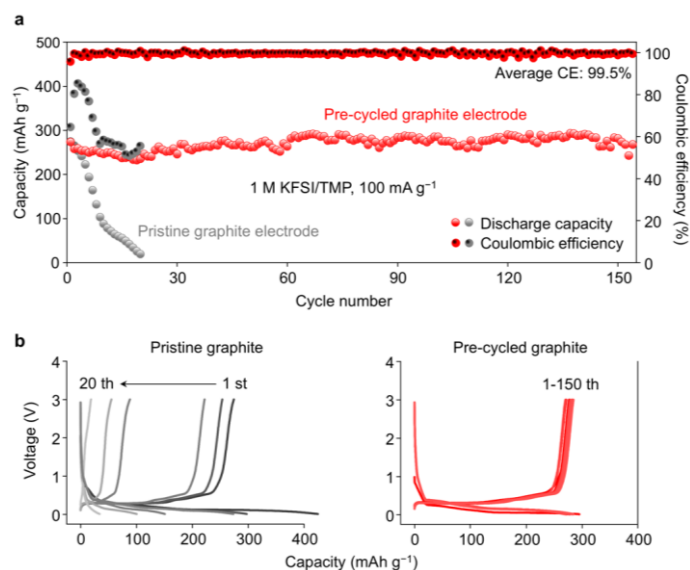
Supplementary Fig. 34. Rate performance of K||graphite cell in the KFSI-TBXP electrolyte at 28 ± 1 °C.

The rate capability of K||graphite cells in the KFSI-TBXP electrolyte was evaluated at specific current 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 specific current 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 specific current, demonstrating rate recovery and cycling stability.



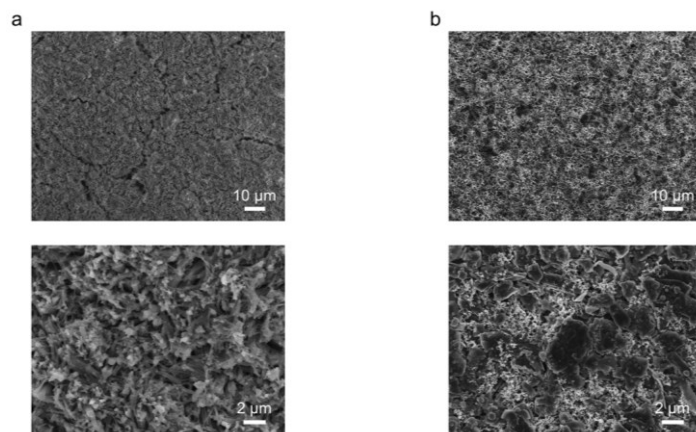
Supplementary Fig. 35. Structure characterization. (a) Raman spectra of the graphite negative material. (b, c) Typical SEM images of a pristine graphite negative electrode.

The I_D/I_G ratio of the graphite material was determined by Raman spectroscopy. Based on peak area integration, the measured ratio is 0.29 (Supplementary Fig. 35a). The graphite material exhibits a flake microstructure with micron-sized dimensions, as observed by SEM characterization (Supplementary Figs. 35b, c).



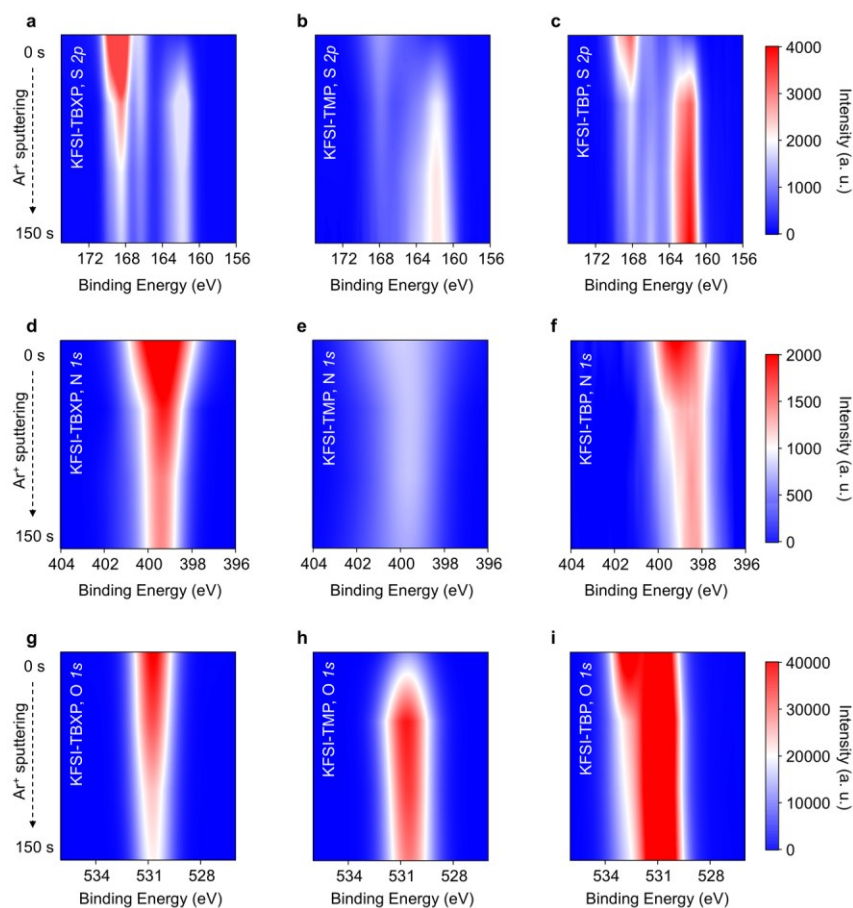
Supplementary Fig. 36. Verification of SEI formed stability on graphite negative electrodes in the KFSI-TBXP Electrolyte. (a) Cycling performance and (b) corresponding charge-discharge profiles of pristine and pre-cycled graphite negative electrodes in the 1 M KFSI/TMP electrolyte under 28 ± 1 °C at 100 mA g^{-1} .

To verify the stability of the SEI formed on graphite negative electrode in the KFSI-TBXP electrolyte, graphite negative electrodes were first pre-cycled for 30 cycles to establish an SEI coating. These pre-cycled electrodes were then transferred to the 1 M KFSI/TMP electrolyte for performance comparison. The results show that pristine graphite negative electrodes exhibit an ICE of only 64.5% in 1 M KFSI/TMP electrolyte. In contrast, the pre-cycled electrodes achieve a higher ICE of 95.7%, demonstrating that the pre-formed SEI effectively suppresses electrolyte decomposition and reduces irreversible charge loss. Furthermore, the pre-cycled electrodes maintain stable capacity over 150 cycles in 1 M KFSI/TMP electrolyte with an average CE of 99.5%. Conversely, the pristine graphite negative electrodes exhibit rapid capacity decay after only 20 cycles, with CE consistently below 86% throughout cycling. These findings confirm that KFSI-TBXP electrolyte enables the formation of a stable SEI on graphite negative electrodes, thereby effectively suppressing continuous electrolyte decomposition and electrode structural degradation.

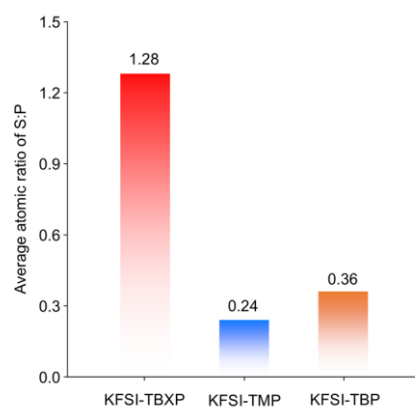


Supplementary Fig. 37. Typical SEM images of graphite negative electrodes cycled in the 1 M KFSI/TMP electrolyte. (a) Initial graphite negative electrode (100 mA g^{-1} , 20 cycles, $28 \pm 1 \text{ }^{\circ}\text{C}$). (b) Graphite negative electrode pre-cycled in the KFSI-TBXP electrolyte (100 mA g^{-1} , 20 cycles, $28 \pm 1 \text{ }^{\circ}\text{C}$).

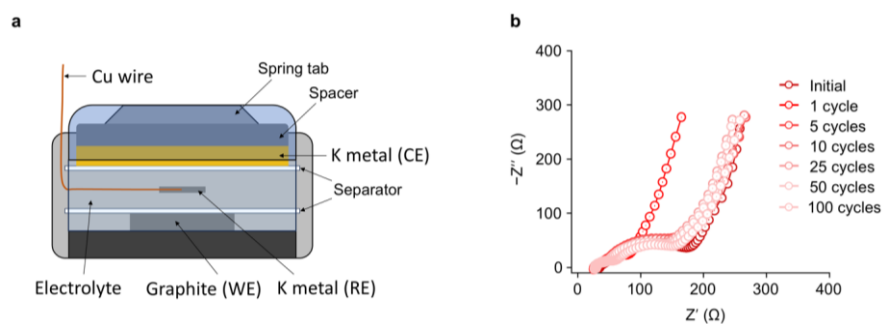
The structural evolution of graphite negative electrodes was investigated using SEM. The pristine graphite negative electrode developed cracks and exhibited severe degradation of its flake-like structure after 20 cycles in 1 M KFSI/TMP electrolyte (Supplementary Fig. 37a), with virtually no intact flake structure remaining. In contrast, the graphite negative electrode pre-cycled in KFSI-TBXP electrolyte to form an SEI retained its structural integrity; the electrode morphology and graphite flakes remained intact during subsequent cycling (Supplementary Fig. 37b), demonstrating enhanced structural stability of graphite negative electrodes afforded by the SEI derived from pre-cycling in KFSI-TBXP electrolyte.



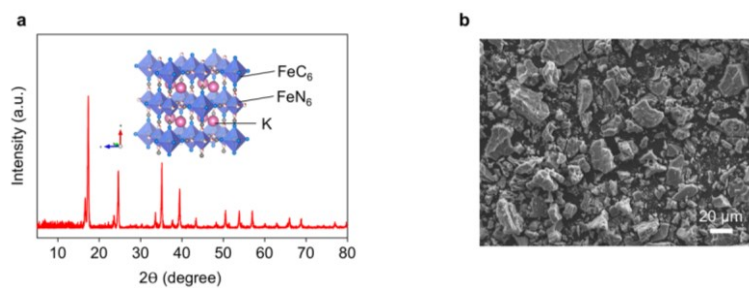
Supplementary Fig. 38. Elemental composition analysis of the SEI on graphite negative electrodes. Ex-situ XPS spectral contour maps of (a-c) S $2p$, (d-f) N $1s$, and (g-i) O $1s$ of formed SEI on graphite negative electrodes in the three electrolytes (100 mA g^{-1} , 20 cycles, $28 \pm 1 \text{ }^{\circ}\text{C}$).



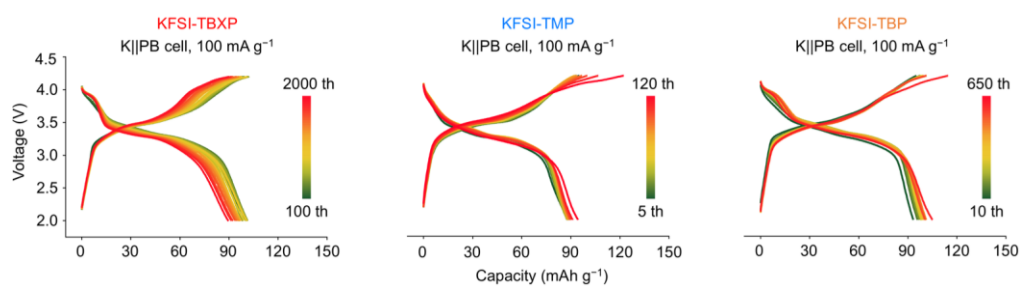
Supplementary Fig. 39. The average atomic ratio of S:P on graphite negative electrodes after cycling in different electrolytes.



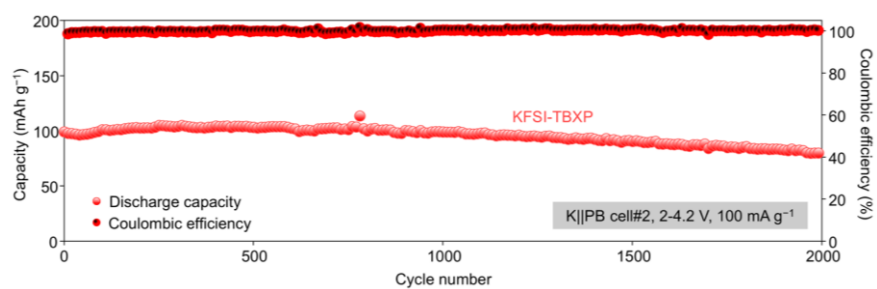
Supplementary Fig. 40. (a) Cell configuration for three-electrode EIS measurements. (b) Nyquist plots of the graphite negative electrodes in the KFSI-TBXP electrolyte at 28 ± 1 °C.



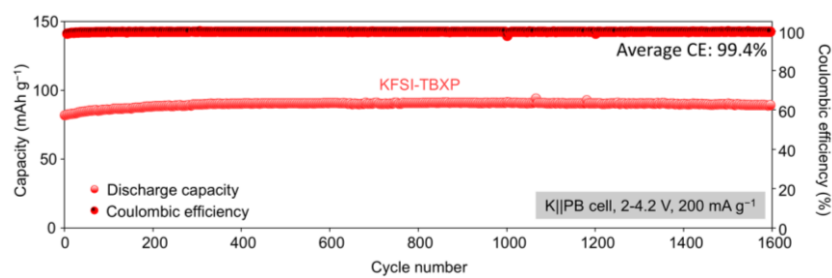
Supplementary Fig. 41. Structural characterization of the PB positive material. (a) XRD pattern and crystal structure of the PB positive material. (b) Typical SEM image of the pristine PB positive material.



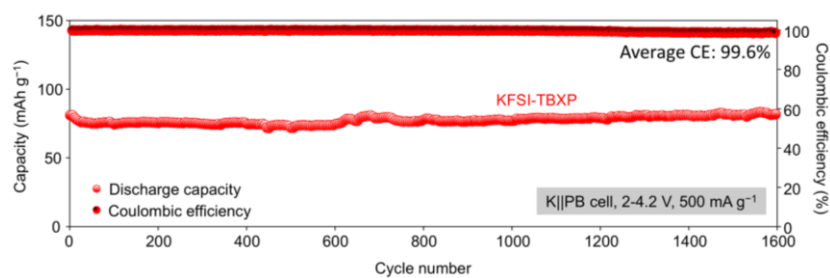
Supplementary Fig. 42. Charge-discharge profiles of PB positive electrodes using different electrolytes under 28 ± 1 °C at 100 mA g^{-1} .



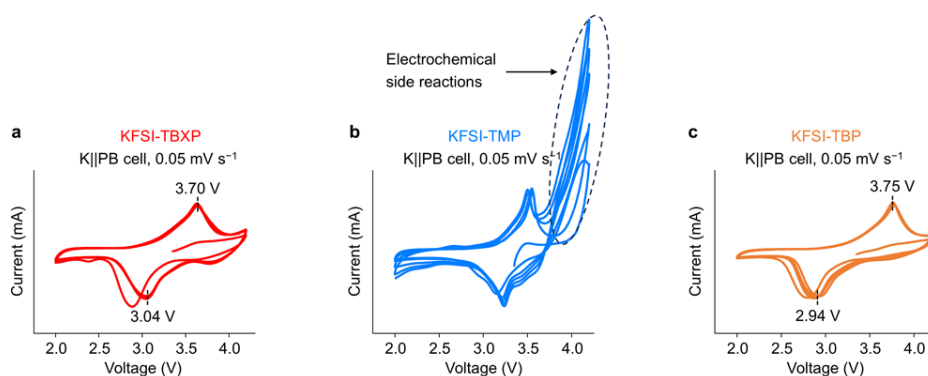
Supplementary Fig. 43. Cycling performance of K||PB cell in the KFSI-TBXP electrolyte under 28 ± 1 °C at 100 mA g^{-1} .



Supplementary Fig. 44. Cycling performance of K||PB cell in the KFSI-TBXP electrolyte under 28 ± 1 °C at 200 mA g^{-1} .

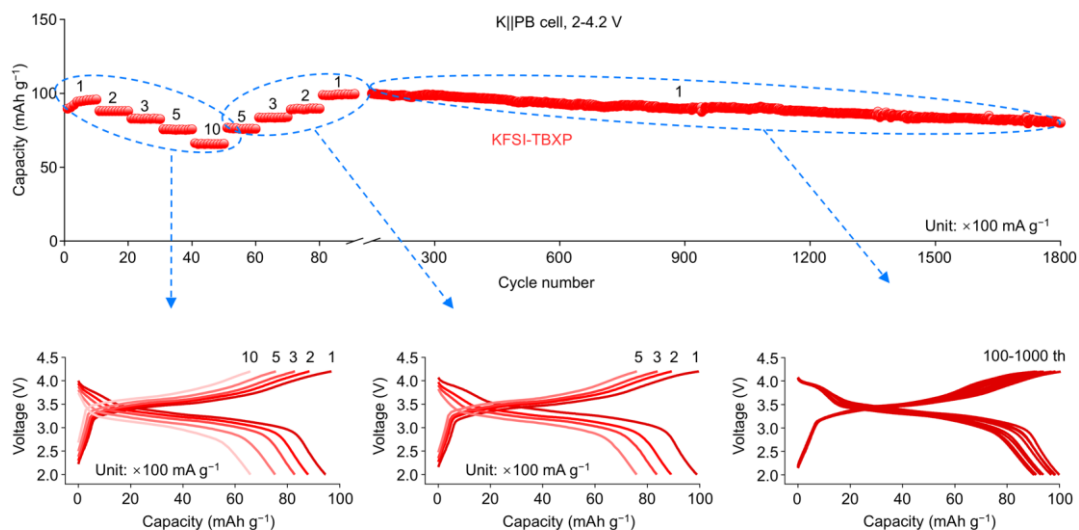


Supplementary Fig. 45. Cycling performance of K||PB cell in the KFSI-TBXP electrolyte under 28 ± 1 °C at 500 mA g^{-1} .



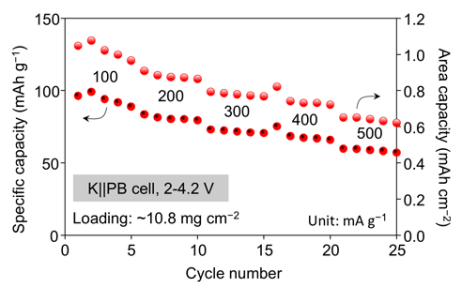
Supplementary Fig. 46. CV profiles of K||PB cells in (a) KFSI-TBXP, (b) KFSI-TMP, and (c) KFSI-TBP electrolytes under 28 ± 1 °C at 0.05 mV s^{-1} .

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) of the K||PB cell in the KFSI-TBXP electrolyte exhibit a high degree of overlap (Supplementary Fig. 46a). 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. 46b). Meanwhile, the KFSI-TBP electrolyte shows relatively poorer CV profile overlap, suggesting inferior cycling stability compared to the KFSI-TBXP electrolyte (Supplementary Fig. 46c). 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.



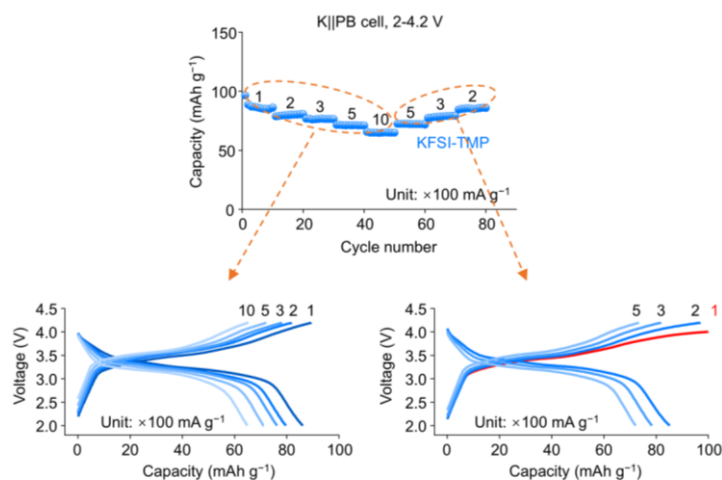
Supplementary Fig. 47. Rate performance of the PB positive electrode using KFSI-TBXP electrolyte and its corresponding charge-discharge profiles at 28 ± 1 °C.

As shown in Supplementary Fig. 47, when the KFSI-TBP electrolyte was employed, rate performance testing of the K||PB cell revealed a decrease in discharge capacity from 94.6 to 65.8 mAh g⁻¹ as the specific current was progressively increased from 100 to 1000 mA g⁻¹. Subsequently, when the specific current is reduced to 100 mA g⁻¹, the cell delivers a discharge capacity of 99.0 mAh g⁻¹ with a CE of 99.2%, and maintains stable cycling for over 1800 cycles.



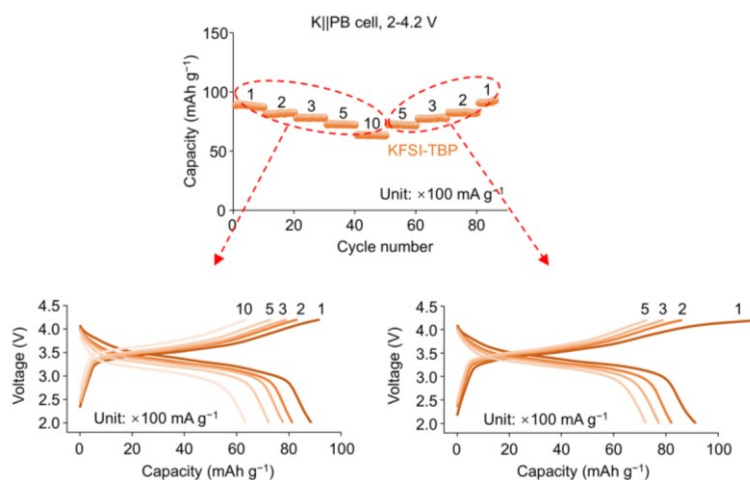
Supplementary Fig. 48. Rate performance of high mass loading K||PB cell in the KFSI-TBXP electrolyte at 28 ± 1 °C.

Supplementary Fig. 48 shows the rate performance of a K||PB cell with a high PB active material 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 specific current 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.



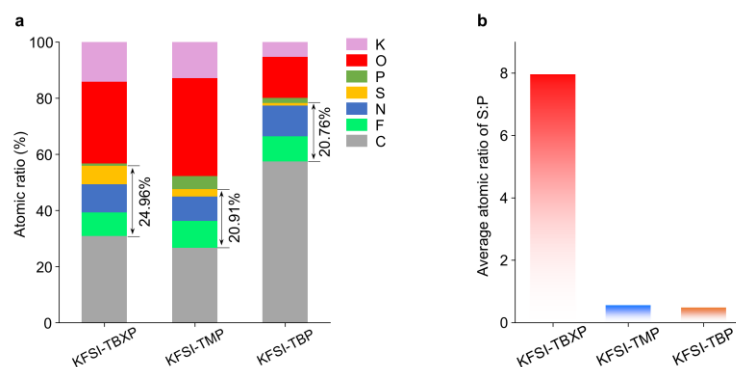
Supplementary Fig. 49. Rate performance of the PB positive electrode using KFSI-TMP electrolyte and its corresponding charge-discharge profiles at 28 ± 1 °C.

As shown in Supplementary Fig. 49, when the KFSI-TMP electrolyte was employed, rate performance testing of the K||PB cell revealed a decrease in discharge capacity from 86.1 to 64.9 mAh g⁻¹ as the specific current was progressively increased from 100 to 1000 mA g⁻¹. Subsequently, during the cycling step in which the specific current was reduced back to 100 mA g⁻¹, the cell failed to charge normally due to severe side reactions from electrolyte oxidative decomposition.

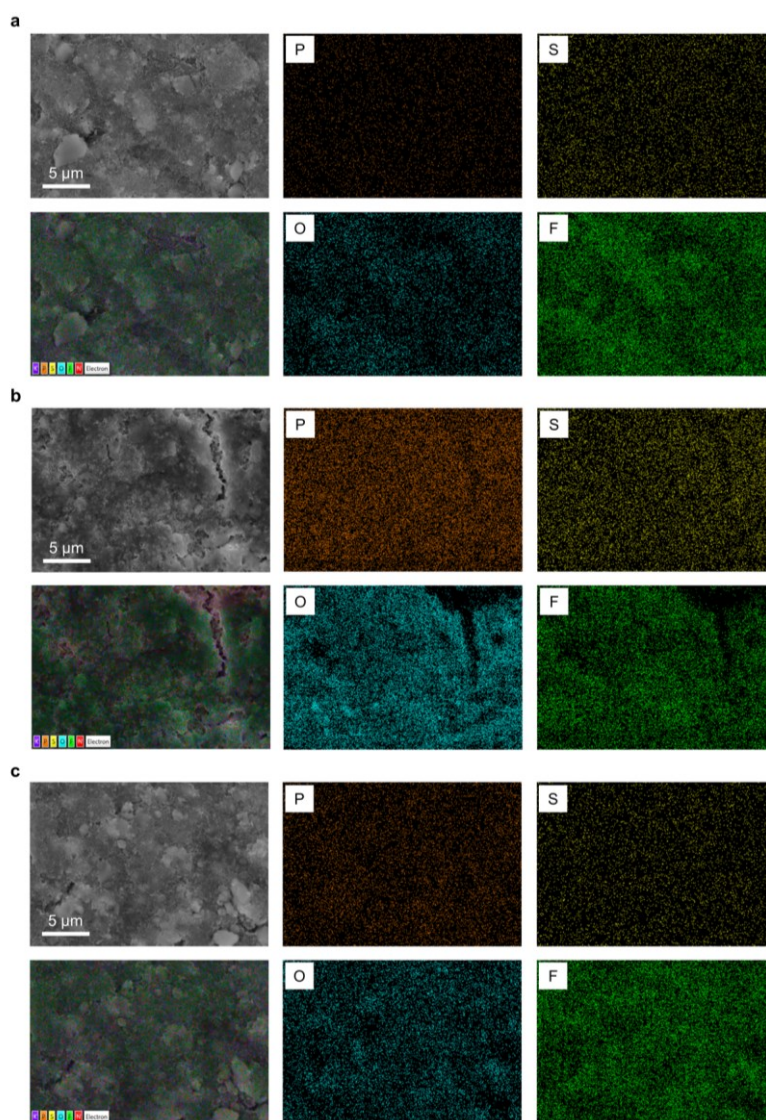


Supplementary Fig. 50. Rate performance of the PB positive electrode using KFSI-TBP electrolyte and its corresponding charge-discharge profiles at 28 ± 1 °C.

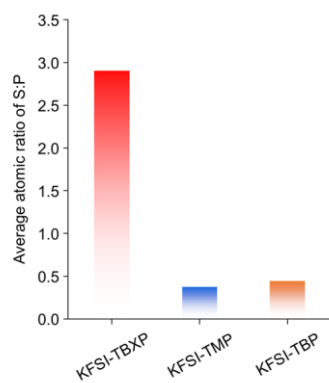
As shown in Supplementary Fig. 50, when the KFSI-TBP electrolyte was employed, rate performance testing of the K||PB cell revealed a decrease in discharge capacity from 88.5 to 63.5 mAh g⁻¹ as the specific current was progressively increased from 100 to 1000 mA g⁻¹. Subsequently, during the cycling step in which the specific current was reduced back to 100 mA g⁻¹, a notable irreversible oxidative side reaction occurred, leading to a reduction in CE to 75%.



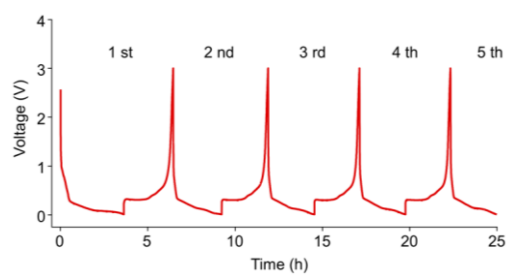
Supplementary Fig. 51. Elemental composition analysis of the CEI on PB positive electrodes. (a) Atomic ratios of the CEI formed on PB positive electrodes in different electrolytes. (b) The average atomic ratio of S:P on PB positive electrodes after cycling in different electrolytes.



Supplementary Fig. 52. SEM elemental mappings of PB positive electrodes after 100 cycles in (a) KFSI-TBXP, (b) KFSI-TMP, and (c) KFSI-TBP electrolytes.

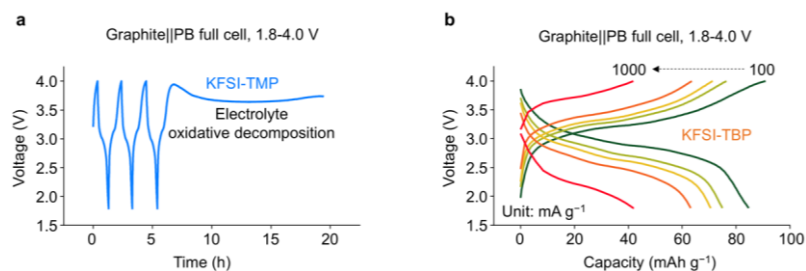


Supplementary Fig. 53. The average atomic ratio of S:P on the PB positive electrodes after cycling in the three electrolytes.



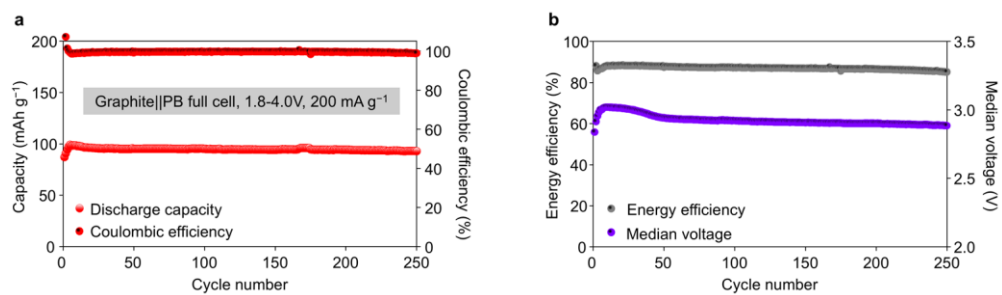
Supplementary Fig. 54. Time-voltage profiles of graphite negative electrode during pre-potassiation.

The graphite negative electrode was pre-potassiated by discharging the K||graphite cell to 0.01 V after 5 cycles under 28 ± 1 °C at 100 mA g^{-1} .

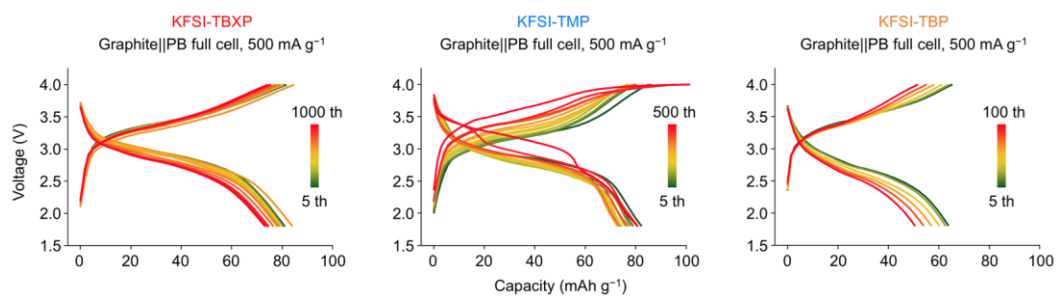


Supplementary Fig. 55. (a) Time-voltage curve of graphite||PB full cell in the KFSI-TMP electrolyte under 28 ± 1 °C at 100 mA g^{-1} . (b) Charge-discharge profiles corresponding to the rate performance of the graphite||PB full cell in the KFSI-TBP electrolyte at 28 ± 1 °C.

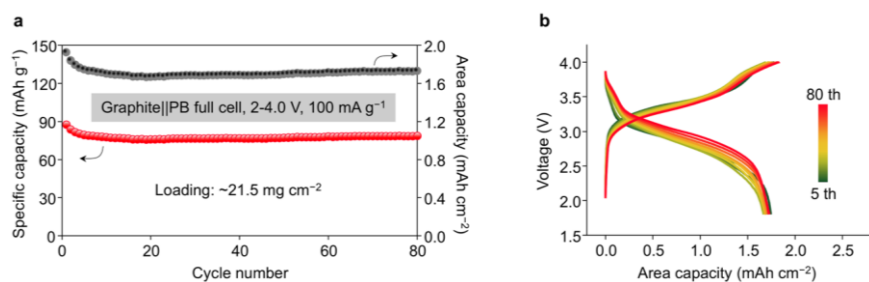
When using the KFSI-TMP electrolyte, the graphite||PB full cell failed to operate after only 3 cycles at 100 mA g^{-1} due to continuous oxidative decomposition of the electrolyte (Supplementary Fig. 55a). In contrast, although the full cell using the KFSI-TBP electrolyte remained functional, it exhibited poor rate performance, delivering discharge capacities of 84.7, 74.9, 70.6, 63.1, and 42.0 mAh g⁻¹ at specific current of 100, 200, 300, 500, and 1000 mA g⁻¹, respectively (Supplementary Fig. 55b).



Supplementary Fig. 56. (a) Cycle performance of a graphite||PB full cell in the KFSI-TBXP electrolyte under 28 ± 1 °C at 200 mA g^{-1} . (b) Energy efficiency and discharge median voltage of graphite||PB full cell in the KFSI-TBXP electrolyte under 28 ± 1 °C at 200 mA g^{-1} .

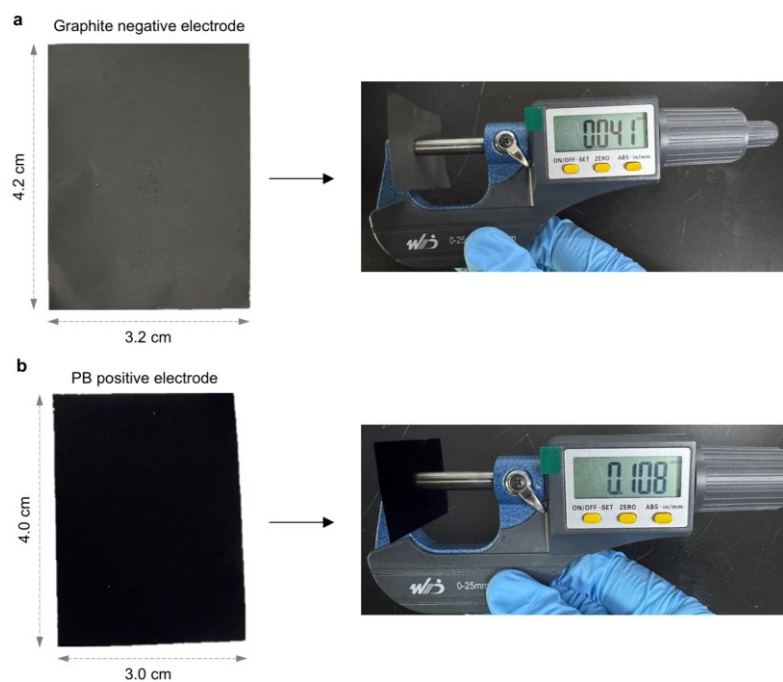


Supplementary Fig. 57. Charge-discharge profiles of the graphite||PB full cells in the three electrolytes under 28 ± 1 °C at 500 mA g⁻¹.

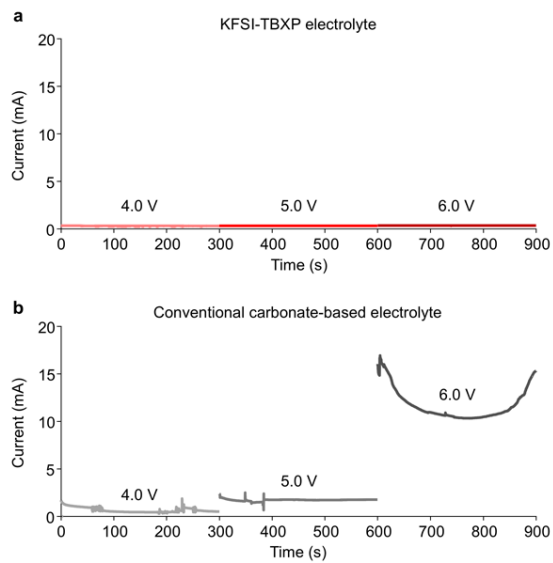


Supplementary Fig. 58. (a) Cycling performance and (b) corresponding charge-discharge profiles of high mass loading graphite||PB full cell under 28 ± 1 °C at 100 mA g^{-1} .

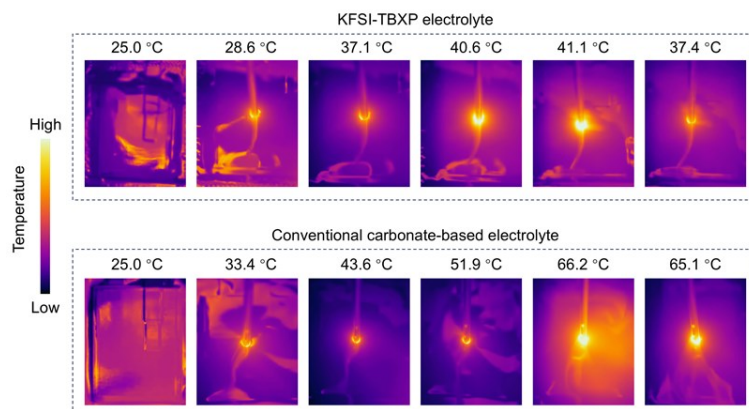
High mass loading PB positive electrodes were successfully fabricated via repeated coating and calendaring processes, followed by the assembly of graphite||PB full cell. Electrochemical cycling results reveal that the full cell exhibits stable cycling for more than 80 cycles in the KFSI-TBXP electrolyte,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



Supplementary Fig. 59. Parameters of (a) graphite negative electrode and (b) PB positive electrode for pouch cell assembly.

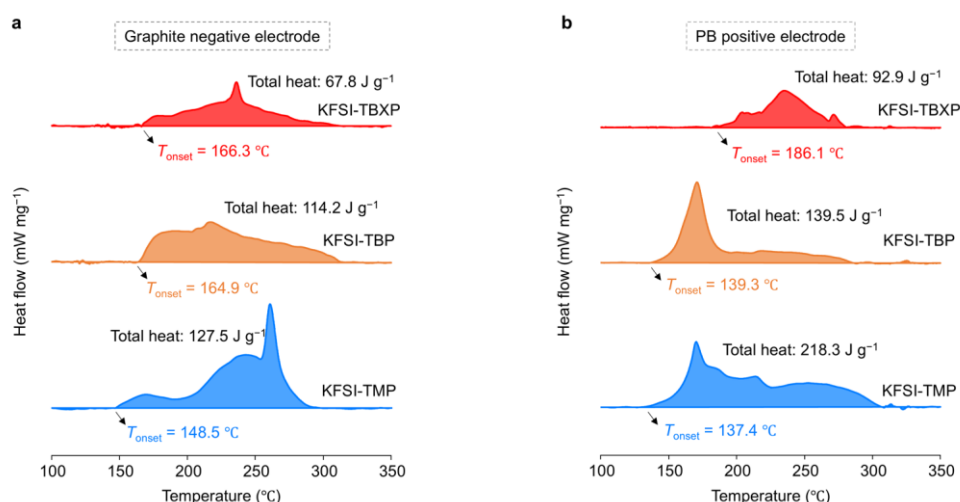


Supplementary Fig. 60. Time-current curves of pouch cells under constant-voltage charging at various voltages. (a) KFSI-TBXP electrolyte and (b) conventional carbonate-based electrolyte.



Supplementary Fig. 61. 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 lower than the peak temperature of 66.2 °C recorded with the conventional carbonate-based electrolyte.



Supplementary Fig. 62. DSC profiles of (a) potassiated graphite negative electrodes (0.01 V) and (b) fully charge-state PB positive electrodes (4.2 V) mixed with relevant electrolyte.

The thermal compatibility of the graphite negative electrode and PB positive electrode in different electrolytes was evaluated using differential scanning calorimetry (DSC). For the potassiated graphite negative electrode, 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 graphite negative electrode 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 suppressed the total heat release, demonstrating greater thermal stability. For the charge-state PB positive electrode (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, 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.

Supplementary Table 2. Comparison of the cycling performance of K||PB cells with various electrolytes at room temperature.

Electrolyte	Cycle number	Specific current (mA g ⁻¹)	Operation window (V)	Specific capacity (mAh g ⁻¹)	Electrolyte volume (μL)	Mass loading (mg cm ⁻²)	Capacity retention	Ref.
								<i>Angew. Chem. Int. Ed.</i> 62 , e202312973 (2023).
1 M KFSI/DMM ⁴	200	100	2-4.2	75	120	~1.0	98.9	<i>Energy Environ. Sci.</i> 17 , 274-283 (2024).
4 M KFSI/PC ⁵	110	100	2.5-4.2	105	/	1.0-2.0	81.7	<i>ACS Nano</i> 17 , 20, 20325-20333 (2023).
KFSI/DME-TTE (1:2:1 by mol) ⁶	130	100	1.5-4.0	67	80	0.8-1.0	98	<i>J. Am. Chem. Soc.</i> 139 , 9475-9478 (2017).
KFSI/DME (3:5 by mol) ⁷	55	100	2.0-4.0	65	/	/	99	<i>Nat. Sustain.</i> 7 , 326-337 (2024).
1 M KFSI/DME-MME-OOE ⁸	105	100	2.0-3.8	78	80	1.0-1.5	95	<i>Nat. Commun.</i> 12 , 7184 (2021).
1 M KPF ₆ /EC-DEC ⁹	150	100	2.0-4.2	75	60	~1.5	90	<i>Appl. Phys. Lett.</i> 124 , 063901 (2024).
1 M KFSI-TPP ¹⁰	650	100	2.0-4.2	85	90	0.8-1.0	72.4	<i>Natl. Sci. Rev.</i> 11 , nwae359 (2024).
1.5 M KFSI/DGM-DBE ¹¹	700	200	2.0-4.5	70	80	0.8-2.0	91.9	<i>Joule</i> 2 , 736-746, (2018).
0.8 M KPF ₆ -PC + 5v% FEC ¹²	510	200	2.0-4.5	80	/	0.5-0.8	69	<i>Adv. Funct. Mater.</i> 27 , 1604307 (2017).
0.8 M KPF ₆ /EC-DEC ¹³	55	50	2.0-4.0	75	/	~1.5	90	<i>Adv. Mater.</i> 34 , 2202685 (2022).
4 M KFSI-DME ¹⁴	60	200	1.5-3.7	80	120	/	98	<i>Adv. Energy Mater.</i> 9 , 1902618 (2019).
2.76 M KFSI/DME-HFE ¹⁵	210	133	2.0-4.0	70	/	~1.5	85.7	This work
KFSI-TBXP	3200	100	2.0-4.2	100	80	1.0-1.5	88.6	

Supplementary Table 3. Comparison of the cycling performance of graphite||PB full cells with various electrolytes at room temperature.

Electrolyte	Cycle number	Specific current (mA g ⁻¹)	Operation window (V)	Specific capacity (mAh g ⁻¹)	Electrolyte volume (μL)	Mass loading (mg cm ⁻²)	Ref.
1 M KFSI/EC-DEC + kaolin ¹⁶	650	300	1.5-3.5	61	70	~1.0	<i>Joule</i> 9 , 101952, (2025).
1 M KFSI/DMM ⁴	150	100	1.5-3.5	60	120	~1.0	<i>Angew. Chem. Int. Ed.</i> 62 , e202312973 (2023).
1 M KFSI/EC-DEC + DTD@CAPE ¹⁷	600	300	1.3-3.6	66	100	~1.0	<i>Adv. Funct. Mater.</i> 34 , 2407867 (2024).
1 M KFSI/AVIMFSI ¹⁸	700	200	1.3-3.6	70	100	~1.0	<i>Energy Environ. Sci.</i> 16 , 1166 (2023).
1 M KFSI/DME-MME-OOE ⁸	100	100	1.5-3.6	75	80	1.0-1.5	<i>Nat. Sustain.</i> 7 , 326-337 (2024).
1 M KFSI/TPP-TFP-OHE ¹⁹	200	200	1.0-3.8	80	80	1.0-2.0	<i>Angew. Chem. Int. Ed.</i> 63 , e20240515 (2024).
0.8 M KPF ₆ /EC-DEC ¹³	50	100	1.0-3.8	75	/	~1.5	<i>Adv. Funct. Mater.</i> 27 , 1604307 (2017).
2.76 M KFSI/DME-HFE ¹⁵	100	133	2.0-4.0	45	/	~1.5	<i>Adv. Energy Mater.</i> 9 , 1902618 (2019).
4 M KFSI/PC ⁵	1000	200	2.0-4.2	100	/	1.0-2.0	<i>Energy Environ. Sci.</i> 17 , 274-283 (2024).
0.8 M KFSI/EC-DEC-Pyr13FSI ²⁰	300	200	1.5-4.0	60	100	1.5-2.5	<i>Angew. Chem. Int. Ed.</i> 64 , e202502016 (2025).
1 M KPF ₆ /DEGDME ²¹	500	500	1.5-4.0	50	/	1.0-2.0	<i>Angew. Chem. Int. Ed.</i> 60 , 13050-13056 (2021).
KFSI-TBXP	1500	500	1.8-4.0	82	80	1.0-1.5	This work

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