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# Surface-substituted Prussian blue analogue cathode for sustainable potassium-ion batteries

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While lithium-ion batteries still dominate energy storage applications, aqueous potassium-ion batteries have emerged as a complementary technology due to their combined advantages in cost and safety. Realizing their full potential, however, is not without challenges. One is that among the limited choices of cathode materials, the more sustainable Prussian blue analogues suffer from fast capacity fading when manganese is present. Here we report a potassium manganese hexacyanoferrate  $K_{1.82}$ Mn[Fe(CN)<sub>6</sub>]<sub>0.96</sub>·0.47H<sub>2</sub>O cathode featuring an in situ cation engineered surface where iron is substituted for manganese. With this engineered surface, the cathode design exhibits a discharge capacity of 160 mAh g<sup>-1</sup> and 120 mAh g<sup>-1</sup> at 300 mA g<sup>-1</sup> and 2,500 mA g<sup>-1</sup>, respectively, and sustains 130,000 cycles (more than 500 days) with negligible capacity loss. Pairing the current cathode with a 3,4,9,10-perylenetetracarboxylic diimide anode yields a full potassium-ion cell that delivers an energy density as high as 92 Wh kg<sup>-1</sup> and retains 82.5% of the initial capacity after 6,500 cycles at 1,500 mA g<sup>-1</sup>. The unprecedented electrochemical performance could be attributed to the suppressed manganese dissolution as a result of the shielding surface layer. This work may open an avenue for the rational design of high-performance cathode materials with redox-active manganese for rechargeable batteries.

While the rapidly increasing number of portable electronics and a global push towards electric transportation and smart grids, the need for large-scale, sustainable, eco-friendly and safe high energy/power density electrochemical energy storage devices is ever increasing<sup>1-3</sup>. Though lithium-ion batteries are currently the most effective energy storage devices, the limited resource of lithium and flammable electrolytes have restricted the further applications of lithium-ion batteries<sup>4-7</sup>. Among the next-generation batteries<sup>8-11</sup>, rechargeable aqueous potassium-ion batteries (APIBs) are attractive because of their green, low-cost and simple assembly attributes for affordable, sustainable and safe large-scale energy storage<sup>12-15</sup>. In addition, APIBs can enable high power density<sup>16</sup>. Although the full APIBs have made some progress, their limited energy density and poor cycling stability are significant obstacles for practical applications<sup>17</sup>.

These challenges are largely due to the lack of cathode materials that simultaneously support high-discharge platforms, high capacity and long-term cycling stability. The high-discharge platform and high capacity are related to the elemental composition of the cathode material, and the cycling stability improves with structural/surface chemical stability. Prussian blue analogues (PBAs) are promising cathode materials due to their environmental friendliness and large channels for intercalation/deintercalation of ions<sup>13,14,18,19</sup>. Moreover, the chemical composition of PBAs can be tuned to facilitate desired capacities and discharge platforms. Among PBAs, the Mn-based PBAs are attractive cathode materials because of their non-toxicity, low cost and high energy density<sup>20,21</sup>. Unfortunately, the Mn-based PBAs usually suffer from capacity fading attributed to Mn dissolution. Once Mn dissolves into the electrolyte, Mn<sup>2+</sup> ions deposit on the surface of the anode, destroying the solid-electrolyte interphase, accelerating the electrolyte decomposition and blocking ion transport paths, resulting in the capacity decay<sup>22,23</sup>. Therefore, the suppression or elimination of Mn dissolution is essential to improve the cycle stability of Mn-based PBAs<sup>24</sup>, and extensive studies have been undertaken to alleviate this problem. The most effective methods propose either surface coating the cathode/anode, substituting manganese with iron, nickel or cobalt, using electrolyte additives and using a solid-state electrolyte as effective strategies to alleviate the manganese dissolution<sup>23-26</sup>. However, these approaches reduce the capacity and discharge platforms, sacrificing energy density.

Here we demonstrate an in situ electrochemical cation substitution approach that converts  $K_{1,82}Mn[Fe(CN)_6]_{0.96}$ ·0.47H<sub>2</sub>O (KMnF) to a modified electrode (KFe<sub>x</sub>Mn<sub>1-x</sub>F) through surface modification of the former in a modified electrolyte. Interestingly, our in situ surface-modification strategy significantly reduces Mn dissolution, thereby enhancing the electrode's structural and surface chemical stability. Consequently, the reversible capacity could reach about 160 mAh g<sup>-1</sup>. Notably, (1) high capacity retention of almost 100% after 130,000 cycles (more than 500 days) is achieved, and the full APIBs exhibit an energy density as high as 92 Wh kg<sup>-1</sup> with a durable cycle life; and the 15 mAh pouch-type APIBs could (2) operate over a wide temperature range (-20 °C to 50 °C) with high performance and could also (3) operate safely even when a third of it is cut off. This work provides a new pathway for the design of Mn-based cathodes with reduced Mn dissolution for energy storage applications.

#### Results

In situ preparation and structure. In the synthesis of aqueous PBAs the nucleation and growth stages progress rapidly, making it impossible to control the particle size<sup>27</sup>. Here we demonstrate that PBAs with a narrow particle size distribution, high potassium content and crystallinity can be prepared by adding potassium citrate ( $C_6H_5K_3O_7$ ) to the aqueous solution of MnSO<sub>4</sub> (Methods). The different energies of potassium citrate inhibitors<sup>28</sup> control the crystallization of KMnF particles (Supplementary Figs. 1 and 2), leading to particles with hierarchically structured

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Fig. 1 | In situ substitution of Mn with Fe in KMnF. a, Schematic of our surface-modification strategy for mitigating structural instability due to Mn dissolution in the KMnF electrode. b, The 40th charge-discharge curves of KMnF in the pure (black traces) and modified electrolytes (red traces). c, The amounts of Fe and Mn in the pure and modified electrolytes at different cycles. The right and left black arrows indicate, respectively, the vertical coordinates for the grey and orange coloured data.

interfaces for rapid intercalation/deintercalation of potassium ions. Although particle size and aggregation vary, all particles exhibit a similar morphology with clear boundaries. The stoichiometric composition of these particles, as determined from the thermogravimetric and inductively coupled plasma-atomic emission spectrometry (ICP) analyses (Supplementary Fig. 3 and Supplementary Table 1, respectively), is  $K_{1.82}$ Mn[Fe(CN)<sub>6</sub>]<sub>0.96</sub>·0.47H<sub>2</sub>O (KMnF). The X-ray diffraction (XRD) Rietveld refinement revealed the structure of  $K_{1.82}$ Mn[Fe(CN)<sub>6</sub>]<sub>0.96</sub>·0.47H<sub>2</sub>O (Supplementary Fig. 4a and Supplementary Table 2) as monoclinic (M) in space group *P21/n* (*P* is primitive unit cell, *n* is the slip plane perpendicular to the *b* axis)<sup>21</sup>. Supplementary Fig. 4b shows the corresponding refined crystal structure in which Mn and Fe occupy the Mn–N and Fe–C positions in the regular octahedra, respectively.

The self-assembled particles with Fe-substituted octahedra are ideal for APIBs<sup>29,30</sup>. Figure 1a and Supplementary Fig. 5 depict in situ Fe-substitution Mn mechanisms during the charge-discharge process in the pure electrolyte and the modified electrolyte. During charging, Mn vacancies are generated on the surface

of the Mn-based cathode due to Mn dissolution (Supplementary Fig. 6 and related discussion). The continuous Mn dissolution caused the collapse of the structure and affected the cyclic stability of the electrode material. However, in the modified electrolyte, the Fe<sup>3+</sup> present in the electrolyte is introduced into the crystalline framework forming the Fe-N6 bonds during the discharge process, upholding the structural integrity. To confirm the mechanism for in situ Fe<sup>3+</sup> substitutions in the crystalline framework, ICP was performed using the pure and modified electrolytes following the charging/discharging process. The ICP study showed that the dissolution of Mn in the two electrolytes occurred mainly during the charging process, while the content of Fe in the modified electrolytes decreased during the discharge process due to Fe<sup>3+</sup> substitution in the crystalline framework (Supplementary Figs. 7-8 and Supplementary Table 3). The density functional theory calculations were also performed to calculate the free energy of the substituted Fe<sup>3+</sup> (Supplementary Fig. 9). The substitution of Fe<sup>3+</sup> ions is energetically favourable in the modified electrolyte when Mn vacancies exist. Therefore, Supplementary Figs. 7-9 collectively imply that

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**Fig. 2 | The K-storage performance of the KMnF electrode in the modified electrolyte. a**, The charge-discharge curves of the KMnF electrode in the modified electrolyte. **b**, The rate capability and corresponding Coulombic efficiency of the KMnF electrode in the modified electrolyte at various current densities. **c**, Comparison of the rate performance in this Article with previously reported PBA electrodes in aqueous batteries. **d**, The ultralong cycling stability of the KMnF electrode in the modified electrolyte. **e**, The Cyc (number), SCH (mAh g<sup>-1</sup>), SCL (mAh g<sup>-1</sup>), DP (V versus Ag/AgCl), CR (%) and FC (mAh g<sup>-1</sup>) for PBA cathodes of aqueous potassium-ion batteries reported in the literature are compared with those for the KMnF electrode in the modified electrolyte presented in this Article.

the Fe<sup>3+</sup> substitution in the crystalline framework mainly occurs during the discharge process. Furthermore, molecular simulations were also performed to investigate the solvation chemistry of the two electrolytes (Supplementary Figs. 10 and 11 and Supplementary Tables 4 and 5). The Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> participates in the solvation structure and the modified electrolyte can gain a wider window of electrochemical stability with decreased free-water-molecule content<sup>31</sup>.

The K-storage competence of the KMnF electrode was evaluated in the pure and modified electrolytes. It delivers a discharge capacity of 119 mAh g<sup>-1</sup> with a low initial Coulombic efficiency of 56% in the pure electrolyte (Supplementary Fig. 12). Clearly, the discharge voltage deteriorates sharply with increasing charge-discharge cycles. For comparison, Fig. 1b displays the 40th chargedischarge curves of the KMnF electrode at 300 mA g<sup>-1</sup> in pure and modified electrolytes. The observed specific capacity of the KMnF electrode after 40 cycles is about 85 mAh g<sup>-1</sup> in the pure electrolyte. In contrast, the KMnF electrode can deliver nearly twice as much (160 mAh g<sup>-1</sup>) in the modified electrolyte. In addition, Supplementary Figs. 13 and 14 show the poor cycling stability and Coulombic efficiency of the KMnF electrode in the pure electrolyte; it exhibits a reversible capacity of 41.65 mAh g<sup>-1</sup> after 300 cycles under a current density of 300 mA g<sup>-1</sup>. The most notorious cause for poor electrochemical performance is Mn dissolution<sup>32</sup>. In contrast, Supplementary Figs. 13 and 14 show the excellent K-storage performance of KMnF electrodes in the modified electrolyte; it delivers a capacity of 160 mAh g<sup>-1</sup> with negligible capacity attenuation over 300 cycles under a current density of 300 mA g<sup>-1</sup>. Moreover, the 10th, 100th and 300th charge-discharge curves (CDCs) of the KMnF electrode in the modified electrolyte recorded at a current density of 300 mA g<sup>-1</sup> overlap (Supplementary Fig. 15) and steadily deliver a high reversible capacity of 160 mAhg<sup>-1</sup> and an initial Coulombic efficiency of 82% (Supplementary Figs. 13 and 14).

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It is worth noting that the CDCs of the 10th, 100th and 300th cycles display similar capacity and voltage plateaus, highlighting a stable phase transformation (Supplementary Figs. 15 and 16), which also indirectly suggests that Fe substitution occurs in the first few cycles (~10 cycles) and then stabilizes the structure for subsequent efficient cycling. We also investigated the effect of including varying concentrations of additives in the modified electrolyte on the cycle stability of the KMnF electrode. The results show that different concentrations of additives (between 0.01 M and 0.2 M) could enable the KMnF electrode to achieve stable cycling (Supplementary Fig. 17).

This observation is also consistent with the data shown in Fig. 1c, suggesting that the KMnF electrode undergoes Fe substitution in the first few cycles in the modified electrolyte. After ten cycles, the amounts of Fe and Mn in the modified electrolyte remain steady, highlighting the critical role of a favourable structural modification caused by the Fe salt. Supplementary Fig. 18 shows the transmission electron microscopy images of the KMnF particles before and after 200 cycles in the modified electrolyte, which confirm that the KMnF framework remains intact after 200 cycles. Thus, outstanding cycle stability and a high capacity is achieved in the Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> modified electrolyte.

Electrochemical performance of modified cathode. Figure 2 shows the electrochemical performance of the KMnF cathode in the modified electrolyte from 0V to 1.25V (versus Ag/AgCl). As shown in Fig. 2a, the 10th and 40th CDCs fully overlap, implying a reversible and stable cycling performance. Note that the voltage curves for the first cycle differ from the subsequent ones due to the electrode's restructuring and accompanying chemical composition change during the first ten cycles. After the 10th cycle, the KMF electrode delivers a reversible capacity of 149 and 95 mAhg<sup>-1</sup> at a



**Fig. 3 | Investigation of the reaction mechanism and in situ Fe substitution. a**, Contour plot of in situ XRD collected during the first to fifth cycles of KMnF in the modified electrolyte. **b**, Rietveld refinement of the modified electrode. **c**, Raman spectrum of the initial electrode and modified electrode. The black dashed line marks the appearance of a new peak. **d**, Mn 2*p* XPS of the initial and modified electrodes (full discharge to 0.01V versus Ag/AgCl). The black dashed line visually shows the migration of the peak. 2*p* is the electron orbital of Mn. **e**,**f**, STEM line scan of the initial electrode (**e**) and the modified electrode after the first fully discharged state (**f**). Insets show the STEM image of initial KMnF. The shaded area indicates the boundary of initial KMnF particles and the green arrow indicates the direction of line scanning.

high current density of 700 and 7,000 mA  $g^{-1}$ , respectively. When the current density is ramped down from 7,000 to 4,000, 2,500, 1,500 and 700 mA  $g^{-1}$ , the capacities are recovered as 95, 108, 116, 129 and 149 mAh  $g^{-1}$ , respectively (Fig. 2b). Supplementary Fig. 19 shows the CDCs at various current densities, and the low overpotential only reaches ~0.2 V when the current density increases from 700 to 7,000 mA  $g^{-1}$ , implying a rapid transfer of ions. We use voltammetric sweep data from 0.1 to  $30 \text{ mV s}^{-1}$  to further confirm the fast kinetics and the low overpotential exhibited by the KMnF electrode (Supplementary Fig. 20 and related discussion). Figure 2c and Supplementary Table 6 compare the rate performance with previously reported PBA electrodes in aqueous batteries<sup>12,28,33–35</sup>. Clearly, the rate performance of our KMF electrode is the highest among previously reported PBA electrodes, which highlights



Fig. 4 | Elemental content across the cross-sectional areas of the initial and modified electrodes. **a**, Image of the selected cross-sectional area, intensity contour map and elemental content obtained from the STEM-EELS line scan of the initial electrode. **b**, The same as in **a** for the modified electrode. Note that the scan direction in **a** is from the surface to the interior of the crystal, while it is from the interior to the surface of the crystal in **b**. The black arrows show the direction of scanning.

the influence of the  $Fe(CF_3SO_3)_3$  modified electrolyte. Next, the ultralong cycling stability of the KMnF electrode was evaluated at a current density of 2,500 mA g<sup>-1</sup>. It maintains a capacity of around 120 mAh g<sup>-1</sup> after 130,000 cycles and no discernable capacity fade per cycle (Fig. 2d). Notably, compared with previous aqueous battery studies, this electrode has been stably operating for an unprecedented time (over 500 days). Furthermore, it is also noteworthy that the KMnF cathode supersedes the KCoHCF, KFeHCF, KNiHCF and the KFeMnHCF-3565 electrodes in cyclability (Cyc), specific capacity at high/low rate (SCH/SCL), discharge plateau (DP), capacity retention (CR) and final capacity (FC) (Fig. 2e and Supplementary Table 7), demonstrating its excellent overall electrochemical performance<sup>12,13,15,28</sup>.

**Storage mechanism and local bonding configuration.** It is well known from previous reports on aqueous and nonaqueous batteries that Li/Na/KMnF undergoes three phase transitions from the M to cubic (C) to tetragonal (T) phases<sup>15,18</sup>. To elucidate the role of the modified electrolyte in the structure optimization of the KMnF electrode, in situ XRD was used to characterize the structural changes of the KMnF electrode during charge–discharge processes. A contour plot of in situ XRD of KMnF in the pure electrolyte is shown in Supplementary Fig. 21. During charging from 2.1 to 2.2 V, the intensity of X-ray peaks of the KMnF electrode at around 17.4°, 24.7° and 35.4° continually vanish. New peaks appear at 16.5°, 23.5° and 33.7°, indicating a phase transition from the M phase to the C phase due to the restructuring of MnN<sub>6</sub> and FeC<sub>6</sub> octahedra in the framework<sup>32</sup>. With further charging from 2.2 to 2.5 V, the peaks at 16.5°, 23.5° and 33.7° shift to 16.9°, 24.1° and 34.2°, which corre-

sponds to the second phase change of KMnF from the C phase to the T phase caused by the cooperative Jahn–Teller distortion of  $Mn^{3+}$  in the  $MnN_6$  octahedron<sup>36</sup>. The entire charging process is reversible. In the subsequent discharge process, the electrode structure returns from the T phase to the C phase and then to the M phase. In contrast to the above trend, in the modified electrolyte, the peaks corresponding to the M crystal phase shift slightly to the left, and new weak peaks manifest at 16.5°, 23.5° and 33.6° when charged to 2.5 V, implying a phase transition from the M phase to the C phase (Fig. 3a and Supplementary Fig. 22). The C-to-T phase transition is absent. Therefore, the KMnF electrode in the modified electrolyte exhibits a mild phase transition and improved electrochemical performance.

The XRD Rietveld refinement revealed an M phase for the modified electrode structure in space group P21/n (Fig. 3b). Supplementary Fig. 23 and Supplementary Table 8 show the corresponding refined crystal structure in which Mn and Fe occupy the Mn/Fe-N and Fe-C positions in the regular octahedra, respectively. By comparing the structural parameters of the KMnF electrode (Supplementary Table 2) and the modified electrode (Supplementary Table 8) it is evident that the Fe-N bonds exist in the modified electrode. The results directly confirm the presence of substituted Fe in the structural framework. Raman spectra were collected from the initial and modified electrodes (Fig. 3c) to gain insight into the electronic structure modification of KMnF with cycling in the modified electrolyte. In the Raman spectrum of the initial electrode, two peaks at ~2,076 and ~2,116 cm<sup>-1</sup> are present, which correspond to the  $Mn^{2+}-N\equiv C-Fe^{2+}$  and Mn<sup>3+</sup>−N≡C−Fe<sup>2+</sup> vibrations, respectively<sup>37</sup>. These peaks shift to ~2,078 and ~2,118 cm<sup>-1</sup>, respectively in the modified electrode's



**Fig. 5** | **First-principle calculations and Fe/Mn element content. a**, The  $K_2MnF$  and  $K_2Fe_{0.15}Mn_{0.85}F$  model structures corresponding to the state density. The dashed green line is the Fermi energy ( $E_F$ ). The position of the dashed grey line is the bottom of the conduction band of  $K_2MnF$ . The position of the dashed orange line is the bottom of the conduction band of  $K_2Fe_{0.15}Mn_{0.85}F$  **b**, K-ion diffusion in the  $K_2MnF$  and  $K_2Fe_{0.15}Mn_{0.85}F$  model structures. **c**, The lattice constants and volume change of  $K_{2-x}Fe_{0.15}Mn_{0.85}F$  at different charging states. *a*, *b* and *c* are the three crystal axes of unit cell. The blue arrow indicates that the vertical coordinate of the blue line is the right *y* axis. **d**,**e**, Density of states projected on Fe (**d**) and Mn (**e**) columns at different charging states. The dashed grey line is the Fermi energy. **f**, The energy-dispersive X-ray spectroscopy-determined contents of Mn and Fe in the KMnF electrode after 0, 5, 100 and 200 cycles in the modified electrolyte.

Raman spectrum. Moreover, a shoulder peak is observed at 2,083 cm<sup>-1</sup> and assigned to Fe<sup>3+</sup>–N $\equiv$ C–Fe<sup>2+</sup> vibrations<sup>37</sup>. The substitution causes a right shift of the peak and the appearance of a new peak; in other words, different transition metals near the N $\equiv$ C group exhibit different electron cloud distributions, which affect the change of vibration frequency.

The X-ray photoelectron spectroscopy (XPS) shows that the binding energy of the Fe 2p3/2 peak shifts from 707.8 eV (discharge to 0.01 V versus Ag/AgCl) to a higher value of 708.7 eV (initial electrode) and the Mn 2p3/2 peak also shifts from 640.6 eV to a higher value of 641.6 eV, suggesting that the average valence states of Fe and Mn increase after the Fe metal ion is substituted in the framework (Fig. 3d and Supplementary Fig. 24). A KF-rich cathodic electrolyte interphase (CEI) was found on the surface of the modified electrode (Supplementary Figs. 25 and 26), which further explains the first Coulombic efficiency (82%)38. The existence of the CEI membrane presumably inhibits the Mn dissolution by blocking the electrolyte contact with soluble Mn. In addition, the spherical aberration-corrected scanning transmission electron microscopy (STEM) line scan of discharged KMnF shows that the content of Fe in KMnF is more than that of Mn, and this phenomenon predominantly occurs at the surface of KMnF. At the same time, its interior is consistent with the composition of the initial electrode (Fig. 3e,f).

To gain further insights into the electrode compositions, STEM– electron energy-loss spectroscopy (EELS) line scan and elemental mapping of the cross-sectional areas of the initial and modified electrodes were performed. As is evident in Fig. 4a, the intensity contour map and elemental content show a uniform presence of Fe and Mn in the interior of the initial electrode, consistent with the results shown in Supplementary Video 1. Because the brightness across the modified electrode's cross-sectional area does not change, it is inferred that the Fe and Mn elemental distribution is the same as in the initial electrode (Fig. 4b). However, at the surface of the modified electrode, the relative content of Fe increases sharply compared with Mn, confirming that  $Fe^{3+}$  ions are introduced into the electrode's framework when cycled in the modified electrolyte (Supplementary Fig. 27 and Supplementary Videos 1 and 2).

Collectively, XRD Rietveld refinement, Raman spectroscopy, XPS, STEM line scans and STEM-EELS cross-sectional surface line scans demonstrate that Fe present in the modified electrolyte in situ fills the vacancies created by Mn in the KMnF framework. The creation of vacancies due to Mn dissolution and subsequent filling of vacancies with Fe<sup>3+</sup> can also be inferred from the behaviour of the CDCs, which entirely overlap except for the first ten cycles, indicating that the Mn dissolution and Fe substitution only occurs in the first few cycles.

**Calculations.** The density of states and K<sup>+</sup> ion diffusion barriers in the K<sub>2</sub>MnF and K<sub>2</sub>Fe<sub>0.15</sub>Mn<sub>0.85</sub>F electrodes were investigated by first-principles calculations to elicit the fundamental mechanism of the K storage in the K<sub>2</sub>Fe<sub>x</sub>Mn<sub>1-x</sub>F electrode. As shown in Fig. 5a,b, K<sub>2</sub>Fe<sub>0.15</sub>Mn<sub>0.85</sub>F shows a relatively smaller bandgap (1.08 eV versus 1.58 eV) and a lower K<sup>+</sup> ion diffusion barrier (0.30 eV versus 0.49 eV) than K<sub>2</sub>MnF, implying that in situ substitutions of Fe into vacancies created by Mn in the PBAs improves the electronic conductivity and K<sup>+</sup> ion diffusion rate. Figure 5c shows the lattice constants and volume change of the K<sub>2</sub>Fe<sub>0.15</sub>Mn<sub>0.85</sub>F electrode at different charging states. The lattice change results in only 9.8% volume shrinkage and presumably mitigates the Jahn–Teller distortion during cycling.



**Fig. 6 | The electrochemical performance of the KMnF//modified electrolyte//PTCDI full battery. a**, Rate capability of the full battery. **b**, The charge-discharge curves of the full battery at various current densities. The numbers represent the current density and the corresponding colours represent the charge-discharge curves. **c**, The ultralong cycling stability of the coin-type full cell. **d**, Comparison of various electrochemical data for the full cell with previous reports for aqueous K/Na-ion full cells. NTP, NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. **e**, Performance of the APIB pouch-type full battery at different temperatures (–20 °C to 50 °C) and 800 mA g<sup>-1</sup>. The inset figure shows two photographs of the APIB pouch battery before and after a third of the APIB pouch battery is cut off. The data in the black dashed oval represent the electrochemical performance of the pouch battery after cutting.

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Figure 5d,e presents the Fe and Mn density of states, respectively, in K<sub>2</sub>Fe<sub>0.15</sub>Mn<sub>0.85</sub>F, K<sub>1</sub>Fe<sub>0.15</sub>Mn<sub>0.85</sub>F and Fe<sub>0.15</sub>Mn<sub>0.85</sub>F at different charging states. During extraction of the first potassium ion, a change in the density of states is observed for Fe and Mn ions with a portion of their unoccupied spin-up states moving above the Fermi level, which corresponds to the redox of the high-spin state for Fe/Mn-N. During extraction of the second potassium ion, a significant change in the density of states is observed for Fe ions, with it moving above the Fermi level. At the same time, the main characteristics of the Mn electronic structure are primarily unaltered. This change corresponds to the low-spin state for Fe-C, and the calculated Fe<sup>2+</sup>/Mn<sup>2+</sup>-N and Fe<sup>2+</sup>-C to Fe<sup>3+</sup>/Mn<sup>3+</sup>-N and Fe<sup>3+</sup>-C energy transformation agrees well with previously reported values<sup>18</sup>. Moreover, these atomic and electronic properties can lead to the high structural stability of the electrode under long cycling and high rate conditions. In addition, to further determine whether the Fe and Mn elements used in the calculation are consistent with the experiment, we performed energy-dispersive X-ray spectroscopy analysis of the electrodes after a different number of cycles (Fig. 5f and Supplementary Fig. 28). After five cycles in the modified electrolyte for KMnF, the ratio of Fe to Mn on the N bond is maintained at about 0.16:0.84 (the total amount of iron minus the original amount of iron is equal to the amount of iron on the N bond), which is consistent with the ratio of Fe to Mn used in the calculation. Supplementary Fig. 29 shows that the Mn distribution at the edge of KMnF particles is much lower than the Fe distribution, while the Fe and Mn elemental distributions in the interior are the same, which further verifies the fact that the in situ substitution of Mn with Fe occurs predominantly at the surface of the particles. To further understand the influence of Fe substitution, we performed first-principles calculations to investigate the Mn-N bond changes of the K<sub>2</sub>MnF and the K<sub>2</sub>Fe<sub>x</sub>Mn<sub>1-x</sub>F electrodes during charge processes (Supplementary Fig. 30 and related discussion).

Full APIBs. The ultralong cycling stability and outstanding rate performance of the modified KMnF electrode motivated us to explore a suitable anode for assembling and evaluating full batteries for possible practical applications. Organic 3,4,9,10-peryl enetetracarboxylic diimide (PTCDI) anodes exhibit outstanding performance in APIBs and aqueous potassium dual-ion batteries<sup>15</sup>. Note that the modified electrolyte still possesses a stabilization window of 3.0 V, meaning that for PTCDI anodes it can reach a lower redox potential (Supplementary Figs. 31 and 32). The PTCDI anode delivers a reversible capacity around 108 mAh g<sup>-1</sup> after 200 cycles at 1,000 mA g<sup>-1</sup> (Supplementary Fig. 33). The PTCDI anode and KMnF cathode were activated for five cycles in a three-electrode system to ensure optimal electrochemical performance by full batteries. The KMnF//PTCDI full batteries display a superior rate capability at various current densities  $(300-2,000 \text{ mA g}^{-1})$  and deliver reversible capacities of 75, 69, 59 and 56 mAh  $g^{-1}$  (Fig. 6a). The full batteries can still output a capacity of 75 mAh g<sup>-1</sup> when the current density suddenly drops from 2,000 to 300 mA g<sup>-1</sup>. The charge-discharge curves are shown in Fig. 6b, with a discharge plateau of 1.32 V at 300 mA g<sup>-1</sup>. Notably, two coin-full or pouch-full cells could power an LED screen (Supplementary Fig. 34).

The full cell exhibits excellent cycling stability with a capacity retention of 82.5% over 6,500 cycles, and average Coulombic efficiency is close to 100% (Fig. 6c). Finally, Fig. 6d and Supplementary Table 10 compare the performance of our APIBs with previously reported aqueous potassium/sodium-ion batteries<sup>15,39-45</sup>. In contrast, our full cell APIB, which relies on in situ substitutions of Fe for Mn-created vacancies in PBAs, exhibits the best energy density and cycling stability. Furthermore, the pouch battery could operate over a wide temperature range (-20 °C to 50 °C) with 78% retention of its capacity at 800 mA g<sup>-1</sup> when its temperature was decreased from 25 °C to -20 °C and increased to 50 °C (Fig. 6e). Interestingly, when

1/3 of the pouch battery was cut off, it continued to operate safely at a reduced capacity of 64% of its original capacity (the orange dots in the dotted circle in Fig. 6e). Overall, the pouch-cell measurement indicates the high safety of APIBs.

#### Discussion

The dissolution of Mn<sup>2+</sup> ions and the Jahn-Teller distortion of the host lattice framework are well-known issues in the Mn-based Prussian blue analogues, which is also the case in our KMnF. This study demonstrates that the cation engineered surface on the KMnF electrode favourably tunes the lattice parameters and redox properties to alleviate the Jahn-Teller distortion and the dissolution of Mn<sup>2+</sup> ions. It is noteworthy that (1) such substitution reactions are not straightforward and typically require several comparative tests to find a suitable proportion of the transition metal and (2) the redox activation of all elements typically reaches a maximum capacity of only ~70% of the theoretical capacity. Thus, this study is novel in that a significantly improved electrochemical performance of APIBs is demonstrated using a modified electrolyte in which a PBA cathode is suitably modified in situ at the atomic scale. Specifically, because of the in situ substitution of Fe at the Mn-N sites and the CEI formation, further dissolution of Mn<sup>2+</sup> ions and the Jahn-Teller distortion are largely alleviated. Furthermore, the in situ XRD scans recorded the phase transitions of KMnF in the pure and modified electrolytes during the depotassiation/potassiation process and confirmed that the modified electrolyte does inhibit the cubic to the tetragonal phase transition due to the favourable substitution of Fe. This finding is also consistent with the results from STEM line scans and Raman spectroscopy. Additionally, our first-principles calculations confirmed that the in situ substituted Fe effectively inhibits the movement of the Mn-N bond compared with that in traditional K<sub>2</sub>MnF. As a result, the KMnF electrodes exhibited a high capacity (160 mAh g<sup>-1</sup>) and ultralong stability (over 130,000 cycles) in the modified electrolyte. The assembled APIBs also showed excellent electrochemical performance and revealed their great potential for sustainable large-scale applications. Thus, the in situ modification of PBA cathodes could bring battery research a step closer to the commercial realization of improved alkali metal ion storage.

#### Methods

**Synthesis of electrodes.** The PTCDI anode was purchased from Sigma–Aldrich. The KMnF cathode was prepared by a simple precipitation method. About 6 mmol potassium ferrocyanide trihydrate ( $K_4Fe(CN)_6$ - $3H_2O$ ) was added into 200 ml of deionized water to form a transparent light-yellow liquid. Then, 6 mmol of manganese (II) sulfate monohydrate ( $MnSO_4$ - $H_2O$ ) and 8 g of potassium citrate were dissolved into 200 ml of deionized water. Afterward, the  $MnSO_4$  solution was slowly added to the former solution and stirred at 60 °C for 12 hours. After 12 hours, the mixed solution was aged for 24 hours at 60 °C. A white precipitate was obtained by centrifugation, which was cleaned thrice with deionized water and alcohol to remove impurities. Finally, the cathode material needed for the experiment was obtained by vacuum drying at 80 °C.

**Electrochemical measurements.** Active materials (70%), Ketjen black (20%) and carboxymethylcellulose sodium (10%) were mixed in a mixture of deionized water and ethanol (4:1) to obtain a slurry. Using carbon cloth  $(1 \times 1 \text{ cm}^2)$  as a collector, the slurry evenly coated on its surface and vacuum dried overnight. Each carbon cloth was loaded with about 3.0 mg of active material. Using a three-electrode system, the electrochemical performances of these cathodes were evaluated. Both pure (21 M KCF<sub>3</sub>SO<sub>3</sub> aqueous electrolyte) and modified (0.01–0.2 M Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> per 21 M KCF<sub>3</sub>SO<sub>3</sub> aqueous solution) electrolytes were used in this study. The additive concentration used in the electrochemical tests is 0.2 M, unless mentioned otherwise. The full battery was assembled in coin and pouch-cell formats. Before assembling the coin battery, the cathode and anode were charged and discharged five times in the three-electrode system (pre-potassiated) and then washed with deionized water and dried. The mass loading of the KMnF cathode and the PTCDI anode were around 3.5 mg cm<sup>-2</sup> for the coin cells and around 20 mg cm<sup>-2</sup> for the pouch cells.

**Materials characterization.** ICP and thermogravimetric analyses analysed the approximate content of each element in the KMnF material. The electrolyte's Fe and Mn concentration trends were investigated by ICP (~0.01 M Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> per 21 M KCF<sub>3</sub>SO<sub>3</sub> aqueous electrolyte). Ex-situ XRD, Raman and in situ XRD were

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used to investigate the crystal structure and crystal phase evolution of KMnF during charge and discharge. STEM and STEM-EELS line scan and elemental mapping of the cross-sectional areas of the initial and modified electrodes were performed to gain insight into the electrode compositions.

**Computational methods.** We employed a first-principle calculation based on the density functional theory calculations<sup>46</sup> within the generalized gradient approximation using the Perdew–Burke–Ernzerhof<sup>47</sup> formulation. In our calculation, the projected augmented wave potential<sup>48</sup> was used to describe the ionic cores for all atoms. We took valence electrons into account using a plane-wave basis set with a kinetic energy cutoff of 400 eV. A 0.05 eV width and the Gaussian smearing method were used to describe the Kohn–Sham orbitals' partial occupancies. In addition, if the energy change was lower than  $10^{-6}$  eV, the electronic energy was considered self-consistent. In addition, for the Mn and Fe atoms, the *U* (Hubbard) schemes were applied and the *U* was set as 3.2 and 2.9 eV. In all the calculations, the  $3 \times 3 \times 2$  for the Monkhorst–Pack k-point in the periodic interface model was used. Additionally, the K-ion migration-barrier energies were evaluated using the climbing nudged elastic band methods.

Molecular simulations were performed to study the structural behaviour of the 21 M KCF<sub>3</sub>SO<sub>3</sub>, 0.2 M Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> and 21 M KCF<sub>3</sub>SO<sub>3</sub> systems. Our simulation calculation was conducted on four structures with an integration timestep of 1 fs. The periodic boundary conditions were applied for cells in the x-y plane. The supercell size is  $24 \times 24 \times 24$  nm<sup>3</sup>. The relaxed structures were obtained using the conjugate gradient algorithm methods under energy minimization. Using the NPT (the isothermal-isobaric ensemble) ensemble, the equilibrium structure was achieved with the 300 K under the 20 ns. Furthermore, a potential cutoff radius of 2.25 nm was applied in the calculation of the non-bonded interaction and the particle-particle mesh was used to describe the electrostatic interactions. The Andersen feedback thermostat and Berendsen barostat algorithm were used in the system with NVT (canonical ensemble). As the interaction between molecules is very weak, the binding energy  $(E_b)$  between anions and electrode was defined as  $E_{\rm b} = E_{\rm ad/sub} - E_{\rm ad} - E_{\rm sub}$ , where  $E_{\rm ad/sub}$ ,  $E_{\rm ad}$  and  $E_{\rm sub}$  are the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure and the clean substrate, respectively.

#### Data availability

The data that support the plots depicted in this manuscript and other findings of this study are available upon request from the corresponding author.

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#### Author contributions

B.L. conceived the project. J.G. and B.L. developed the concept. J.G. conducted the experiments and data analysis. J.G., B.L. and A.M.R wrote the manuscript. All authors discussed and commented on the manuscript.

#### **Competing interests**

The authors declare no competing interests.

#### Additional information

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