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Permalink
https://escholarship.org/uc/item/2qm6n845

Journal
Advanced Energy Materials, 8(26)

ISSN
1614-6832

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Publication Date
2018-09-14

DOI
10.1002/aenm.201801591

Peer reviewed
A new strategy for high voltage cathodes for K-ion batteries: stoichiometric KVPO$_4$F

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Keywords: K-ion battery, Cathode, Polyanion, Fluorophosphate

Abstract

The exploration of high-energy-density cathode materials is vital to the practical use of K-ion batteries. Layered K-metal oxides have too high voltage slope to be practical due to their large K$^+$-K$^+$ interaction, making 3D polyanion materials more relevant. Here, we develop stoichiometric KVPO$_4$F for use as a high-energy-density K-ion cathode. The KVPO$_4$F cathode delivers a reversible capacity of ~105 mAh g$^{-1}$ with an average voltage of ~4.3 V (vs. K/K$^+$), resulting in a gravimetric energy density of ~450 Wh kg$^{-1}$. During electrochemical cycling, the K$_x$VPO$_4$F cathode goes through various intermediate phases at $x = 0.75$, $0.625$, and $0.5$ upon K extraction and reinsertion, as determined by ex situ X-ray diffraction characterization and ab-initio calculations. This work further explains the role of oxygen substitution in KVPO$_{4+x}$F$_{1-x}$: the oxygenation of KVPO$_4$F leads to an anion-disordered
structure which prevents the formation of K⁺/vacancy orderings without electrochemical plateaus and hence to a smoother voltage profile.

1. Introduction
Li-ion batteries (LIBs) dominate the global market for portable and automotive energy storage technologies because of their high energy density. Their use is even expanding to large-scale applications such as grid-level energy storage systems. However, the question of whether Li reserves\(^1\) or the metal required for the cathode compounds\(^2\) can meet the demand for large-scale applications remains under debate. In response, Na-ion batteries (NIBs) and K-ion batteries (KIBs) have been studied as alternative energy storage technologies systems because of the global abundance of Na and K.\(^3\)\(^-\)\(^7\) When compared to NIBs, KIBs are particularly interesting because (i) K/K⁺ has a lower standard redox potential than Na/Na⁺, which can be translated into a higher working voltage,\(^5\) and (ii) graphite can intercalate K ions, forming a stable KC₈ compound, whereas no stable NaCₓ compounds are present in the Na–graphite system.\(^5\),\(^8\)\(^-\)\(^12\)

Layered transition metal oxides (TMOs) have been considered promising candidates for LIB and NIB cathodes because of their dense close-packed structure as well as their high Li and Na diffusivities.\(^13\)\(^-\)\(^15\) In this respect, K-TMOs, including KₓCoO₂ (x= 0.41, 0.6, and 0.67),\(^16\)\(^-\)\(^17\) KₓMnO₂ (x= 0.3 and 0.5),\(^18\)\(^-\)\(^19\) K₀.₇Fe₀.₅Mn₀.₅O₂,\(^2₀\) and K₀.₆₇Ni₀.₁₇Co₀.₁₇Mn₀.₆₆O₂,\(^2₁\) have been investigated as cathode materials for KIBs. However, the specific capacities and working voltage of K-TMOs are lower than those of Li- and Na-TMOs due to the strong K⁺-K⁺ interaction which is much larger than the corresponding Li⁺–Li⁺ or Na⁺–Na⁺ interactions.\(^16\)\(^-\)\(^2₁\) The strong K⁺-K⁺ interaction is due to the large size of K⁺ which increases the distance between the oxygen layers and reduces their effectiveness in screening the K⁺-K⁺ electrostatic repulsion. This strong interaction results in greater voltage slope and low specific capacity between set voltage limits for layered K-TMOs.
Polyanion compounds may be better cathode candidates because they exist in various structural frameworks in which the K ions are three-dimensionally arranged and separated by large polyanions, effectively reducing the strength of the K\(^+\)–K\(^+\) repulsion. The weaker K\(^+\)–K\(^+\) interaction can lead to a higher working voltage, as demonstrated in some polyanionic compounds such as K\(_3\)V\(_2\)(PO\(_4\))\(_3\),\(^{[22]}\) FeSO\(_4\)F,\(^{[23]}\) and KVP\(_2\)O\(_7\)\(^{[24]}\). Nevertheless, the achieved energy density of K-polyanionic compounds remains far below those of current LIB and NIB cathodes. Therefore, it is vital to explore new cathode materials for the development of high-energy-density KIBs.

Fluorophosphates, including AVPO\(_4\)F (A = Li and Na)\(^{[25-28]}\) and Li\(_2\)MPO\(_4\)F (M = Fe and Mn)\(^{[29-30]}\), continue to attract considerable attention as cathode materials for LIBs and NIBs because of their high working voltage. Recently, Fedotov et al. reported LiVPO\(_4\)F prepared by Li/K ion-exchange from KVPO\(_4\)F with a KTiOPO\(_4\)-type structure. This Li-ion cathode delivers operates at \(~4.0\) V (vs. Li/Li\(^+\)) with a specific capacity of \(~110\) mAh g\(^{-1}\).\(^{[31]}\) This recent discovery motivates our investigation of the structural and electrochemical properties of KVPO\(_4\)F for use as a KIB cathode. Specifically, in this work, we investigate the structure of as-synthesized KVPO\(_4\)F using \(^{31}\)P solid-state nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction (XRD), and the structural evolution of the material during K de/intercalation using \textit{ex situ} XRD and ab-initio calculations. Our findings demonstrate the consecutive occurrence of several two-phase reactions in the material upon K de/intercalation. We further explain how the fluorine:oxygen ratio in KVPO\(_{4+x}\)F\(_{1-x}\) affects its electrochemistry. The oxygenation of KVPO\(_4\)F results in a more disordered structure, leading to a smoother voltage profile. However, the oxygenation of KVPO\(_4\)F increases the initial V valence state and thus reduces the achievable specific capacity because of the more limited V redox availability. Oxygen substitution for fluorine also lowers the operating voltage because of the reduced inductive effect resulting from the lower fluorine concentration in the material.\(^{[32]}\)
2. Results

2.1. Material characterization of KVPO$_4$F

Figure 1a presents a synchrotron-based XRD pattern of KVPO$_4$F powder and its Rietveld refinement result using the Pna$_2$1 space group. The crystal structure of KVPO$_4$F is isostructural with orthorhombic KTiOPO$_4$. However, the structures differ in the connectivity between the transition metal octahedra: TiO$_6$ units are connected to one another via O in KTiOPO$_4$, whereas VO$_4$F$_2$ units are connected via F in KVPO$_4$F. Refinement of the synchrotron XRD data (Table 1 in Supplementary Information) yields lattice parameters of $a = 12.8423(1)$ Å, $b = 6.40785(3)$ Å, and $c = 10.62974(6)$ Å. In the refinement, the calculated bond valence sum of the two vanadium sites is +2.98(2) and +2.97(2), suggesting the presence of V$^{3+}$ in the compound. Elemental analysis using inductively coupled plasma for K, V, P, and the ion selective electrode (ISE) method for F also indicates a K:V:P:F ratio of 1.04:1.00:0.96:0.96, which suggests that the composition of our KVPO$_4$F material is very close to the stoichiometric composition. Figures 1b and 1c present the crystal structure of KVPO$_4$F projected along the $b$- and $a$-axis, respectively. In the structure, VO$_4$F$_2$ octahedra are interconnected via corner-sharing PO$_4$ tetrahedra along the $a$ and $b$ axes. The F atom can occupy equatorial or axial positions around the V atom (V1 and V2 sites, respectively), and the VO$_4$F$_2$ octahedra share one F atom at the corner, forming zig-zag chains, which are then bridged via PO$_4$ tetrahedra as observed in Figure 1d. In the local vanadium environments, VO$_4$F$_2$ octahedra are surrounded by four PO$_4$ tetrahedra and two VO$_4$F$_2$ octahedra, as illustrated in Figure 1e. The V1 site is equatorially surrounded by four PO$_4$ tetrahedra and two VO$_4$F$_2$ octahedra (V2 site) at axial direction. In contrast, The V2 site is surrounded by three PO$_4$ tetrahedra and one VO$_4$F$_2$ octahedron (V1 site) in the equatorial plane and one PO$_4$ tetrahedron and VO$_4$F$_2$ octahedron (V1 site) in the axial direction. In the crystal structure of KVPO$_4$F, K ions occupy two 9-coordinate KO$_7$F$_2$ environments located at K1 and K2 sites with a three-dimensional arrangement, as shown in Figure 1b–c. The K1 site shares F with
two VO$_4$F$_2$ octahedra (Figure 1f), whereas the K2 site shares a F–F edge with one VO$_4$F$_2$ octahedron (Figure 1g). One should note that we compared our results of Rietveld refinements obtained using the structural models reported by Chihara et al.$^{[33]}$ and Fedotove et al.$^{[31]}$ and found a better agreement with the latter. In our refinement, K1 and K2 are both split between two sites, which are very close to each other, and thus, each has an occupancy factor of 0.5. The particle size of KVPO$_4$F is estimated from scanning electron microscopy analysis to be in the range of 20–200 nm (see Supplementary Figure 1). Thermogravimetric analysis reveals that the KVPO$_4$F material contains ~3.3% carbon by weight, as shown in Supplementary Figure 2.

2.2. Electrochemical K-storage properties of KVPO$_4$F

Figure 2a shows the voltage vs. capacity curves of KVPO$_4$F for the first two charge/discharge cycles between 3–5 V and a current rate of 5 mA g$^{-1}$. The first charge and discharge capacities are ~140 and ~105 mAh g$^{-1}$, respectively. Each charge and discharge voltage profile exhibits four distinct plateaus, indicating successive phase transitions as the K content changes. The identical voltage shape between charge and discharge curves demonstrates that K extraction and re-insertion processes are reversible. In turn, the differential capacity (dQ/dV$^{-1}$) curve in Figure 2b clearly displays four oxidation peaks at 4.04 (O1), 4.24 (O2), 4.41 (O3), and 4.87 (O4) V during charge and four reduction peaks at 3.97 (R1), 4.21 (R2), 4.34 (R3), and 4.72 V (R4) during discharge, demonstrating multiple reversible phase transitions upon cycling. Figure 2c shows the rate capability of KVPO$_4$F at current rates of 5, 10, 30, 50, 80, 100, 150, and 300 mA g$^{-1}$. KVPO$_4$F delivers a specific capacity of 102, 101, 92, 82, 72, 65, 56, and 44 mAh g$^{-1}$ at the respective rates. The capacity and coulombic efficiency of KVPO$_4$F as a function of cycle number at 5 mA g$^{-1}$ are plotted in Figure 2d. KVPO$_4$F maintains a reversible capacity of 78 mAh g$^{-1}$ (75% retention compared with that of the 1$^{st}$ discharge) after 30 cycles. The coulombic efficiency is low (~95%), leading to poor capacity retention. The low coulombic efficiency indicates that the anodic current is larger than the
cathodic current, which can result from decomposition of cathode materials and/or electrolyte degradation upon charging at high voltage (> 4.5 V). To rationalize the origin of capacity fading, we investigate the structural stability of KVPO$_4$F upon cycling using ex situ XRD and verify the health of the electrolyte upon charging using linear scan voltammetry. No noticeable structural change is observed in the ex situ XRD patterns of the KVPO$_4$F cathode after 30 cycles, as shown in Supplementary Figure 3. However, the linear scan voltage measurement of the K-electrolyte in Supplementary Figure 4 indicates that the anodic current starts to gradually increase at ~4 V and abruptly increases near 5.0 V (vs. K/K$^+$). Hence, the K-electrolyte is unstable at high voltage, which may be the origin of the low coulombic efficiency. It is likely that this leads to decomposition products on the cathode surface which increase impedance and thereby decrease effective capacity.

A plot of the average voltage vs. reversible capacity of various K-ion cathode materials as well as selected NIB and LIB cathodes is presented in Figure 3.$^{[16, 19-20, 22-24, 26, 33-38]}$ Our KVPO$_4$F electrode provides a high average discharge voltage of 4.33 V, which is the highest value among KIB cathode materials reported to date.$^{[16, 19-22, 24, 33-34]}$ Notably, the average voltage of KVPO$_4$F reported here is ~0.2-V higher than that reported by Chihara et al. for a similar compound.$^{[33]}$ This discrepancy is likely attributable to the different local structures and compositions of the two compounds, which will be discussed in more detail in the discussion section of this paper. Moreover, the voltage of KVPO$_4$F is also higher than that of other vanadium-containing polyanionic compounds for Li and Na systems such as NaVPO$_4$F, Na$_3$V$_2$(PO$_4$)$_2$F$_3$, Na$_7$V$_2$(PO$_4$)$_2$F$_3$, and LiVPO$_4$F.$^{[25, 35-38]}$

2.3. Structural evolution during charge and discharge of KVPO$_4$F

Figure 4a presents the formation energies of K$_x$VPO$_4$F ($x = 1, 0.875, 0.75, 0.625, 0.5, 0.375, 0.25, 0.125, 0$) phases obtained from first-principles DFT calculations. All symmetrically distinct K$^+$/vacancy orderings within the unit cell of K$_x$VPO$_4$F including 8 formula units were generated using the enumeration technique reported by Hart et al.$^{[39]}$ and the 50
configurations with the lowest electrostatic energy at each K content (0 ≤ x ≤ 1) were calculated using GGA+U. For the calculations, we used the crystal structure of KVPO₄F with two K (K1 and K2), both of which are split between two possible positions. These two positions are too close together to be occupied simultaneously, and thus, have partial occupancy. We find stable K⁺/vacancy orderings at x = 0.75 and 0.5 in KₓVPO₄F. At x = 0.625, the lowest energy configuration is ~ 6 meV per formula unit above the convex hull with respect to decomposition into K₀.₇₅VPO₄F and K₀.₅VPO₄F. Such a small energy difference makes it possible that K₀.₆₂₅VPO₄F is stabilized at room temperature by entropy. Overall, first-principles DFT calculations predict at least three two-phase reactions upon K extraction over the range of K contents: 1 > x > 0.75, 0.75 > x > 0.5, and 0.5 > x > 0. Figure 4b compares the calculated voltage to the experimental voltage curve obtained at a current rate of 5 mA g⁻¹. We note that the calculated voltage is shifted upwards by 0.35 V for better agreement with the experimental voltage curve. The calculated voltage plot shows phase transitions at x = 0.75 and 0.5 in KₓVPO₄F, which is consistent with our experimental observations of voltage steps at x = 0.75 and 0.5. The experimentally obtained voltage curve has an additional voltage step at x = 0.625, which suggests the formation of a stable intermediate phase, which may be the phase that is predicted to be close to the hull in the calculations (see Figure 4a).

To better understand the structural evolution of KₓVPO₄F upon cycling, ex situ XRD data are collected from samples at different states of charge and discharge. Figure 5a presents a representative charge/discharge profile, with the points indicating the states at which the ex situ XRD patterns in Figure 5b–d are obtained. The K concentration is estimated by normalizing the experimentally determined specific capacity to the theoretical value. When the K content, x, decreases from 1 to 0.86, the XRD peaks at 16.6°, 26.9°, 29.3°, and 33.1°, which belong to KVPO₄F, slightly shift to higher angle and no additional peak evolution is observed. This indicates that K extraction occurs through a solid-solution reaction in
$K_xVPO_4F$ when $x$ is between 1 and 0.86. A new set of XRD peaks start to appear at 16.8°, 29.4° and 33.4° at the expense of the peak at 26.3° and 29.3° when $x = 0.79$. This new diffraction peaks are fully formed in the diffraction patterns for $x = 0.72$, which is indicative of the new ordered phase being formed around $x \sim 0.72$. This is consistent with the voltage step at $x = 0.75$ in both the experimental and calculated curves in Figure 4b. In the range of 0.72 > $x > 0.63$, another set of peaks appears at 16.9°, 29.5°, and 33.7°, indicating the formation of the second new phase. This result agrees well with the formation of a compound at $x \sim 0.625$ in $K_xVPO_4F$, as discussed earlier. Further K extraction to $x \sim 0.5$ generates new XRD peaks at 17.1°, 29.7°, 33.1°, and 44.0°, which indicates an additional phase transition from $K_{0.625}VPO_4F$ to $K_{0.5}VPO_4F$, consistent with the voltage step at $x \sim 0.5$ in $K_xVPO_4F$ in both the experimental and DFT calculations (Figure 4b). As the K content further decreases from $x \sim 0.5$ to $x \sim 0.0$, the VPO$_4$F phase is formed with XRD peaks at 17.2°, 29.8°, 33.5°, and 34.2° in Figure 5b–d. After discharge, the XRD pattern of the pristine KVPO$_4$F phase is fully recovered, which indicates that the structural changes occurring upon cycling are reversible.

Supplementary Figure 5 presents the predicted structures of $K_xVPO_4F$ for $x = 1, 0.75, 0.625, 0.5, \text{and } 0$, which reveal that K ions in K1 sites that share F with two different VO$_4$F$_2$ octahedra (see Figure 1f) are extracted first until the K content reaches $x = 0.5$. Potassium ions in K2 sites that share an F–F edge with one VO$_4$F$_2$ octahedron (see Figure 1g) are removed later. DFT calculations shows that the extraction of K ions from the K2 sites leads to a slight distortion of the PO$_4$ tetrahedra due to the shrinking ionic radius of V upon oxidation. Supplementary Figure 6 presents the simulated XRD patterns of $K_xVPO_4F$ ($x = 1, 0.75, 0.625, 0.5, \text{and } 0$) based on the lowest energy structures obtained from first-principles DFT calculations. When the K concentration ($x$) decreases from 1 to 0.75, new XRD peaks appear near 16.2° and 32.2° at the expense of the peak at ~25.2° in the simulated XRD patterns. At the $K_{0.625}VPO_4F$ composition, XRD peaks appear at 16.15°, 28.5°, and 32.65°. Further K extraction to $x \sim 0.5$ generates a new set of XRD peaks near 16.3°, 28.6°, and 32.9°. The
simulated XRD pattern of VPO₄F exhibits new peaks at 16.6°, 28.8°, 32.8°, and 33.5°. Overall, the evolution of the simulated XRD patterns with K content is similar to that of the *ex situ* XRD data (see Figure 5) and confirms the experimentally observed sequence of phase transitions as K is extracted/re-inserted from KₓVPO₄F, with stable intermediate phases forming at x = 0.75, 0.625, and 0.5. We note that the predicted peak positions differ slightly from the experimentally determined positions as DFT using GGA+U slightly over-predicts the lattice parameters.¹⁹, ₄₀-₄² We further performed a full-pattern-matching procedure to compare the experimentally obtained *ex situ* XRD patterns with the simulated XRD patterns at specific K concentrations. Supplementary Table 2 lists the refined lattice parameters of KₓVPO₄F at x = 1.0, 0.75, 0.625, 0.5, and 0 using the computed structural model. The results demonstrate that the volume of KVPO₄F shrinks by ~6.54% upon full K extraction, which is most likely attributable to the shrinkage of the V octahedra as V³⁺ is oxidized to V⁴⁺ as well as to the removal of large K ions. Notably, the magnitude of the volume change observed here upon K extraction is similar to that observed upon Li removal from LiFePO₄ (~6.8%).⁴³

2.4. Effect of oxygenation in KVPO₄F

Fluorophosphates have been extensively studied as cathode materials for LIBs and NIBs because of their high operating voltage and, thus, high energy density.²⁶-³⁰, ³⁷ In fluorophosphates, F⁻ can often be substituted with some O²⁻ (oxygenation), in which case charge compensation is achieved by changing the oxidation state of nearby transition metals. In these compounds, the fluorine:oxygen ratio generally plays an important role in determining the electrochemical properties, including the working voltage and reversible capacity.⁴⁴-⁴⁵ For example, in tavorite LiVPO₄ₓF₁₋ₓ compounds, the average voltage and reversible specific capacity at practical current rates decrease as the fluorine content decreases. Moreover, the voltage plateaus that appear in pure oxyphosphate LiVPO₄O become less pronounced with mixed fluorine-oxygen compositions.⁴⁴-⁴⁵ To better understand the role of the fluorine:oxygen ratio in KVPO₄F, we prepared an oxygen-substituted composition,
KVPO_{4+x}F_{1-x}, in a mildly reducing environment (see Methods section). Supplementary Figure 7 presents the synchrotron-based XRD analysis of the oxygen-substituted phase. The refinement of the synchrotron XRD data (Table 3 in Supplementary Information) gives lattice parameters of $a = 12.8235$ (1) Å, $b = 6.39630$ (6) Å, and $c = 10.5860$ (1) Å, which are in a good agreement with the values in the literature\textsuperscript{[31, 33]} but slightly smaller than the values obtained for our stoichiometric KVPO$_4$F sample, as shown in Figure 1a and Supplementary Table 1. The smaller lattice parameters are consistent with oxidation of V to compensate for the increased nominal negative charge due to the O$^{2-}$ substituting for F$^-$. The bond valence sum results indicate that the oxidation states of the two V sites are $+3.24(1)$ and $+3.04(9)$ in KVPO$_{4+x}F_{1-x}$, which suggests partial oxidation of V during synthesis upon oxygenation.

Elemental analysis using inductively coupled plasma for K, V, P, and the ISE method for F indicates a K:V:P:F ratio of 1:1:1:0.64 in KVPO$_{4+x}F_{1-x}$. Based on the elemental analysis, the composition of the oxygen-substituted sample is estimated to be KVPO$_{4.36}F_{0.64}$. Figures 6a–b present the XANES spectra of KVPO$_4$F and KVPO$_{4.36}F_{0.64}$ with reference spectra containing V$^{3+}$, V$^{4+}$, V$^{5+}$, and V metal. The inset of Figure 6a presents the V K-edge XANES spectra, where the normalized intensity is 0.5 (near the inflection point); the pre-edge region of the spectra is shown in Figure 6b. The photon energies of KVPO$_4$F at the inflection point and the pre-edge position are similar to those observed for Li$_3$V$_2$(PO$_4$)$_3$ only containing V$^{3+}$. Therefore, the oxidation state of V in KVPO$_4$F is trivalent. In contrast, the photon energies of KVPO$_{4.36}F_{0.64}$ at its inflection point and pre-edge position lie between those of Li$_3$V$_2$(PO$_4$)$_3$ (V$^{3+}$) and V$_2$O$_4$ (V$^{4+}$), indicating partial oxidation of V, which is in a good agreement with the XRD refinement results.

Figure 6c presents the $^{31}$P solid-state NMR double-adiabatic spin-echo spectra collected for KVPO$_4$F and KVPO$_{4.36}F_{0.64}$. Both materials are paramagnetic, and the major source of the $^{31}$P chemical shift is the hyperfine (paramagnetic) interactions between unpaired $d$ electrons from
V$^{3+}$ ($d^2$) and V$^{4+}$ ($d^1$) and the P nucleus through space and via V–O–P and V–F–P bond pathways. There are two forms of paramagnetic interactions: isotropic Fermi contact interactions and anisotropic electron–nuclear dipolar coupling. Both interaction types lead to a shift of the $^{31}$P resonance frequency, although the pseudo-contact shift due to electron–nuclear dipolar interactions was observed to be a lot smaller than the Fermi contact shift in related olivine-type LiTMPO$_4$ (TM = Fe, Mn, Co)$^{[46-48]}$ such that the overall chemical shift can be approximated by the Fermi contact shift ($\delta_{FC}$) here. A fit of the $^{31}$P spectrum of KVPO$_4$F indicates two broad $^{31}$P resonances at ~4600 and ~3400 ppm, consistent with the presence of two P crystallographic sites (P1 and P2) in the structure. To assist in the assignment of the $^{31}$P NMR spectrum of KVPO$_4$F, hybrid DFT/ HF calculations of the $^{31}$P NMR parameters were performed on a fully optimized KVPO$_4$F structure (after relaxation of the atomic positions and lattice parameters) using two hybrid functionals with 20% (HYB20) and 35% (HYB35) HF exchange. The comparison of the experimental spectrum and first-principles results in Supplementary Table 4 indicates an ~1200- ppm shift difference between the two experimental peaks, which is in good agreement with the difference between the Fermi contact shifts computed for P1 and P2 ($\Delta \delta_{FC}$), ranging from 1187 ppm (HYB35 calculations) to 1471 ppm (HYB20 calculations). We note that the shifts and shift differences obtained using the HYB35 functional are in better agreement with the experimental data than those obtained with HYB20; however, the absolute $\delta_{FC}$ values computed for P1 and P2 are still larger than those observed experimentally by at least ~800 ppm. This discrepancy may be attributed to spin-orbit coupling resulting from the non-zero orbital angular momentum of V$^{3+}$ ($t_{2g}^2e_{g}^0$ electronic configuration), not accounted for in our NMR calculations. Spin-orbit coupling leads to both g-tensor anisotropy and zero field splitting and affects the $\delta_{FC}$. It was recently demonstrated that spin-orbit coupling corrections (via the isotropic g shift) to the $\delta_{FC}$ of $^{31}$P in olivine-type LiFePO$_4$ ($t_{2g}^4e_{g}^2$), LiCoPO$_4$ ($t_{2g}^5e_{g}^2$), LiNiPO$_4$ ($t_{2g}^5e_{g}^2$) are comprised
between ~800 ppm and ~1400 ppm, while the $\delta_{\text{FC}}$ itself is comprised between ~1600 and ~3200 ppm.\textsuperscript{[48]} Hence, it is not unlikely that corrections of a similar order of magnitude may need to be applied to our calculation results on KVPO$_4$F, but this should not significantly affect the shift differences $\Delta \delta_{\text{FC}}$ in Supplementary Table 4. Our calculations indicate a larger shift for P1 than for P2, leading us to assign the ~4600 ppm peak to P1 and the ~3400 ppm peak to P2. We note that anisotropic electron–nuclear dipolar interactions are only partially averaged out by fast spinning of the powder sample at the MAS and result in additional peaks (sidebands) in the $^{31}$P NMR spectrum obtained for KVPO$_4$F, as indicated by the asterisk. The sharp signal at 0 ppm is attributed to a diamagnetic impurity present in both KVPO$_4$F and KVPO$_{4.26}$F$_{0.64}$.

The $^{31}$P spectrum of KVPO$_{4.36}$F$_{0.64}$ exhibits more resonances than that of KVPO$_4$F, indicating a larger number of effective P environments in the material. Although all the P sites are surrounded by four V$^{3+}$ in their first metal coordination shell in KVPO$_4$F, partial oxidation of V in KVPO$_{4.36}$F$_{0.64}$ can create additional P environments surrounded by (1) three V$^{3+}$ and one V$^{4+}$, (2) two V$^{3+}$ and two V$^{4+}$, (3) one V$^{3+}$ and three V$^{4+}$, or (4) V$^{4+}$ only in the first metal coordination shell. Because V$^{3+}$ and V$^{4+}$ lead to different shift contributions to the total $^{31}$P paramagnetic shift and because the individual contributions from the four V in the first coordination shell are additive, the progressive oxidation of one, two, three, and four V$^{3+}$ to V$^{4+}$ in the first metal coordination shell of P results in discrete changes in the two resonant frequencies observed in the KVPO$_4$F spectrum. In fact, the resonances observed at ~5400, ~4600, ~3400, ~2200, and ~1200 ppm in the KVPO$_{4.36}$F$_{0.64}$ spectrum are almost all separated by ~1200 ppm, suggesting that these different resonances correspond to P environments surrounded by varying numbers of V$^{3+}$ and V$^{4+}$ cations in the first metal coordination shell. We speculate that fewer unpaired electrons for V$^{4+}$ result in a smaller shift contribution than for V$^{3+}$ and tentatively assign the higher resonant frequencies (5400 and 4600 ppm) to P local environments with a majority of V$^{3+}$ neighbors. In contrast, the lower resonant frequencies
(2200 and 1200 ppm) likely correspond to P sites with mostly $V^{4+}$ neighbors. Furthermore, the broad peaks at 5400, 4600, 3400, 2200, and 1200 ppm in the KVPO$_{4.36}$F$_{0.64}$ $^{31}$P NMR spectrum correspond to overlapping signals from $^{31}$P sites with a particular $V^{3+}$/$V^{4+}$ metal coordination (as discussed above) but with slightly different $V$–O, $V$–F, O–P, and F–P bond lengths and $V$–O–P and $V$–F–P bond angles, leading to slightly different resonant frequencies. Unlike for KVPO$_4$F, spinning sidebands cannot be distinguished in the spectrum obtained for KVPO$_{4.36}$F$_{0.64}$ because of the large number of P signals and the broad, overlapping resonances. Overall, the $^{31}$P NMR data indicate a more disordered structure for KVPO$_{4.36}$F$_{0.64}$ than for KVPO$_4$F with a larger range of bond distances and bond angles and a greater number of local P environments with various numbers of $V^{3+}$ and $V^{4+}$ cations in the first metal coordination shell.

Figure 7a shows the galvanostatic charge/discharge profiles of KVPO$_4$F and KVPO$_{4.36}$F$_{0.64}$ in the second cycle at a current rate of 5 mA g$^{-1}$. KVPO$_{4.36}$F$_{0.64}$ delivers a reversible capacity of ~85 mAh g$^{-1}$ with an average discharge voltage of ~4.2 V. In contrast, KVPO$_4$F provides a reversible specific capacity of ~100 mAh g$^{-1}$ and an average discharge voltage of ~4.3 V. The smaller capacity of KVPO$_{4.36}$F$_{0.64}$ than KVPO$_4$F is attributable to its higher average V oxidation state in KVPO$_{4.36}$F$_{0.64}$ than in KVPO$_4$F which leaves less $V^{3+}$ to be oxidized. The lower F concentration also results in a lower working voltage for KVPO$_{4.36}$F$_{0.64}$ than for KVPO$_4$F likely because of the reduced inductive effect.$^{[32]}$ The differences in the voltage curves of the two materials are highlighted in Figure 7b: the voltage profiles of KVPO$_4$F and KVPO$_{4.36}$F$_{0.64}$ are replotted as a function of relative capacity normalized by the obtained capacities. KVPO$_4$F exhibits multiple plateaus, whereas the voltage profile of KVPO$_{4.36}$F$_{0.64}$ is smooth without plateau-like features. This difference reflects the disordered local structure in KVPO$_{4.36}$F$_{0.64}$, as revealed by $^{31}$P NMR (Figure 6c). To obtain a better understanding of the effect of oxygenation in KVPO$_4$F on its local structure, we predict the most stable structures of KVPO$_4$F and KVPO$_{4.375}$F$_{0.625}$ using DFT calculations. Here, we calculated the structure of
KVPO$_{4.375}$F$_{0.625}$, which has a composition similar to that of KVPO$_{4.36}$F$_{0.64}$ with a reasonable unit cell size. Supplementary Figure 8 and 9 show the local K and V environments in KVPO$_4$F and KVPO$_{4.375}$F$_{0.625}$, respectively. As mentioned previously, KVPO$_4$F exhibits two 9-coordinate K sites with local coordination KO$_7$F$_2$ and two octahedral V sites with coordination VO$_4$F$_2$. In contrast, KVPO$_{4.375}$F$_{0.625}$ has a greater range of K and V environments: three 9-coordinate K sites with local coordination of one KO$_7$F$_2$, one KO$_8$F, and one KO$_9$ and four octahedral V sites with local coordination including two VO$_4$F$_2$, one VO$_5$F, and one VO$_6$. The various K and V sites present in the KVPO$_{4.375}$F$_{0.625}$ structure can lead to more continuous energy changes upon K extraction, which can be translated into a more sloped voltage profile compared with that for KVPO$_4$F.

3. Discussion
Layered K-TMO$_2$ compounds exhibit sloped voltage curves upon charge and discharge because the two-dimensional arrangement of large K ions in the alkali metal layer leads to short K$^+$–K$^+$ distances, resulting in strong interaction between the K ions.$^{[16, 19]}$ For example, the extraction of 0.33 K$^+$ from K$_{0.6}$CoO$_2$ leads to a voltage change of 2.2 V, i.e., the average voltage slope is 6.67 V per 1 K$^+$ transfer.$^{[16]}$ Similarly, 0.45 K$^+$ can be extracted from the K$_{0.5}$MnO$_2$ cathode as the potential is increased by 2.4 V, corresponding to an average voltage slope of 5.33 V per 1 K$^+$ transfer.$^{[19]}$ Supplementary Figure 10 presents a simplified schematic of the voltage curves of K-TMO$_2$ compounds with different voltage slopes. Within a reasonable voltage window (4.0–1.5 V) and considering the stability range of layered K-TMO$_2$ upon K extraction, the achievable specific capacity substantially depends on the average slope of the voltage vs. capacity profile. In addition, the sloped voltage curves generally lead to an average voltage lower than 3.0 V in the range of 4.0–1.5 V (vs. K/K$^+$), as observed in the plot. Overall, the large slopes of the K-TMO$_2$ voltage curves limit both the achievable specific capacity and voltage and, therefore, the energy density of these materials. In contrast, ~1.0 K$^+$ can be extracted from KVPO$_4$F in the voltage range of ~1.0 V. In this
case, the average voltage slope is \(~\)1 V per 1 K\(^{+}\) transfer, which is 5–7 times smaller than the slopes of reported layered K-TMO\(_2\) compounds. This finding suggests that the K\(^{+}\)–K\(^{+}\) interactions in KVPO\(_4\)F are substantially weaker than those in the layered K-TMO\(_2\) compounds because of the three-dimensional arrangement of K ions in the fluorophosphate framework that allows for a longer K\(^{+}\)–K\(^{+}\) distance (\(~3.8\) Å in KVPO\(_4\)F vs. \(~2.8\) Å in K\(_{0.6}\)CoO\(_2\)). \(^{16}\) The size of the voltage steps in the electrochemical curve is another indicator of the strength of the K\(^{+}\)–K\(^{+}\) interactions in the host material. K\(_x\)VPO\(_4\)F exhibits a voltage step of \(~\)0.35 V at \(x = 0.5\), whereas a much larger voltage step of \(~\)0.5 V is observed for K\(_x\)CoO\(_2\) at the same K content, \(^{16}\) confirming the smaller K\(^{+}\) interaction in KVPO\(_4\)F than in layered K-TMO\(_2\). As a result, the KVPO\(_4\)F cathode delivers a respectable capacity of 105 mAh g\(^{-1}\) with an exceptionally high discharge voltage of \(~4.33\) V (vs. K/K\(^{+}\)), thereby providing a high gravimetric energy density of 454 Wh kg\(^{-1}\). This is remarkably larger than that of layered K-TMO\(_2\) compounds (see Figure 3). Overall, this study demonstrates that KVPO\(_4\)F with a polyanionic framework can provide a higher working voltage and exhibits a voltage curve with a smaller slope than that of layered K-TMO\(_2\) compounds. In this respect, our work demonstrates that it is crucial to explore new cathode materials with polyanionic frameworks for KIBs, as they can provide a high working voltage and, thus, a high energy density.

The stoichiometric KVPO\(_4\)F exhibits multiple plateaus as K is extracted because of the formation of the stable intermediate phases at \(x = 0.75, 0.625,\) and 0.5 in K\(_x\)VPO\(_4\)F (Figure 4 and 5). The formation of intermediate phases is attributable to the formation of K\(^{+}\)/vacancy orderings at specific K contents to reduce the strength of K\(^{+}\)–K\(^{+}\) interactions. Oxygen substitution for fluorine in KVPO\(_4\)F is effective in reducing K\(^{+}\)/vacancy ordering because the locally disordered fluorine–oxygen anion distribution makes the K site energies different, disrupting the K\(^{+}\)/vacancy ordering. Therefore, the oxygenation will wipe out the voltage steps from the KVPO\(_{4+x}\)F\(_{1-x}\) cathode, as shown in Figure 7. In fact, the shape of the voltage curve of our non-stoichiometric KVPO\(_{4.36}\)F\(_{0.64}\) is almost identical to that reported by Chihara
These findings strongly suggest that their material is likely the anion-disordered KVPO$_{4+x}$F$_{1-x}$ compound rather than stoichiometric KVPO$_4$F. In addition, the refinement results obtained by Chihara et al. indicate that the bond valence sums of V1 and V2 are +3.2 and +3.4, respectively, presumably due to partial oxygenation. As a result, their compound delivers ~80 mAh g$^{-1}$ with an average voltage of ~4.1 V, similar to the properties of our oxygen-substituted KVPO$_{4.36}$F$_{0.64}$. Consequently, we argue that the synthesis of stoichiometric KVPO$_4$F needs to be delicately tuned to achieve high energy density.

4. Conclusion
In this study, stoichiometric KVPO$_4$F was synthesized and evaluated as a cathode material for KIBs. The KVPO$_4$F cathode delivers a reversible capacity of ~105 mAh g$^{-1}$ with an average voltage of ~4.33 V (vs. K/K$^+$), resulting in a gravimetric energy density of ~454 Wh kg$^{-1}$. Reversible K extraction from and reinsertion into K$_x$VPO$_4$F is confirmed by ex situ XRD characterization combined with DFT calculations, revealing the formation of stable intermediate compounds at $x = 0.75, 0.625, \text{and } 0.5$. This work further explains how the F/O ratio in KVPO$_{4+x}$F$_{1-x}$ affects its electrochemical properties. The oxygenation of KVPO$_4$F leads to a more disordered structure around the K and V sites and thus a smooth voltage profile without voltage plateaus. In addition, oxygen substitution for fluorine in KVPO$_4$F reduces the achievable specific capacity as well as the operating voltage. These effects can be explained by partial V$^{3+}$ oxidation in the oxygenated compound and by a reduced inductive effect as the F content is decreased, respectively.

5. Experimental Section

Synthesis of stoichiometric KVPO$_4$F and non-stoichiometric KVPO$_{4.36}$F$_{0.64}$

KVPO$_4$F was prepared using a two-step reaction. In the first step, VPO$_4$ was synthesized by reacting NH$_4$H$_2$PO$_4$ (11.5 g, 98%, Alfa Aesar), V$_2$O$_5$ (9.05 g, >99.6%, Sigma–Aldrich), and carbon black (1.2 g, super P, Timcal). The precursors were mixed using a wet ball-milling method with zirconia balls and an acetone solvent in a polypropylene jar for 12 h and then...
dried overnight at 100 °C. The mixture was pelletized and then sintered at 750 °C for 4 h with Ar flow. In the second step, stoichiometric amounts of KF (99.9%, Sigma–Aldrich) and VPO$_4$ were homogeneously mixed using a planetary ball mill (Retsch PM200) at 300 rpm for 4 h. The powder was then pelletized and sintered at 650 °C for 8 h with Ar flow. The carbon black was used as a reducing agent to control the fluorophosphate stoichiometry, ensuring the trivalency of V. Non-stoichiometric KVPO$_{4.36}$F$_{0.64}$ was prepared using a similar process as KVPO$_4$F but without carbon, and the nominal composition was determined using inductively coupled plasma technique (Luvak, USA). For the synthesis of KVPO$_{4.36}$F$_{0.64}$, VPO$_4$ and KF (99.9%, Sigma–Aldrich) were homogeneously mixed using a planetary ball mill (Retsch PM200) at 300 rpm for 4 h. The mixture was pelletized and then sintered at 600 °C for 1 h with flow of a H$_2$(2%)/Ar(98%) mixture gas.

**Electrochemical measurements**

Electrodes were prepared by mixing the active material (KVPO$_4$F or KVPO$_{4.36}$F$_{0.64}$) (80 wt%), Super P carbon black (Timcal, 10 wt%), and PTFE (DuPont, 10 wt%) binder in an Ar-filled glovebox. Test cells were assembled into 2032 coin-cells in the glovebox with a two-electrode configuration using K-metal counter electrodes. A separator of grade GF/F (Whatman, USA) and an electrolyte of 0.7 M KPF$_6$ in ethylene carbonate/diethyl carbonate (EC/DEC; anhydrous, 1:1 volume ratio) were used. The electrochemical tests were performed using a battery testing station (BT-2000, Arbin Instruments) with cathode films with a loading density of ~5.1 mg cm$^{-2}$.

**Synchrotron-based X-ray diffraction analysis**

High-resolution synchrotron powder diffraction data were collected at beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory, using an average wavelength of 0.457 Å. Discrete detectors covering an angular range from −6° to 16° 2θ were scanned over a 34° 2θ range, with data points collected every 0.001° 2θ and a scan speed of 0.01°/s. The samples were sealed in polyimide (Kapton, Cole-Parmer) capillaries and measured for 1
h. Rietveld refinement\cite{49} of the data was performed using the Fullprof program,\cite{50} and structure visualization was performed with VESTA.\cite{51}

X-ray absorption near-edge structure analysis

Vanadium K-edge X-ray absorption near-edge structure (XANES) experiments were performed in transmission mode at room temperature in an Ar gas-ionization chamber using a Si(111) double-crystal monochromator detuned to \(~70\%\) of its original intensity to eliminate higher-order harmonics at the 10C beamline at Pohang Light Sources-II (PLS-II). A reference spectrum of V metallic foil was collected simultaneously for the energy calibration. The XANES data were handled and processed using the Athena program.

Magnetic susceptibility measurements

Field-cooled (FC) and zero-field-cooled (ZFC) DC magnetic susceptibility data of the as-synthesized KVPO\textsubscript{4}F were recorded using a commercial magnetic property measurement system (MPMS) over the temperature range of 2 K to 390 K under an external field of 1000 Oe.

\textsuperscript{31}P NMR analysis

\textsuperscript{31}P NMR data were obtained at room temperature using a Bruker Avance 500 MHz (11.7 T) wide-bore NMR spectrometer at a Larmor frequency of 202.5 MHz. The data were obtained under 60-kHz magic angle spinning (MAS) using a 1.3-mm double-resonance probe. The \textsuperscript{31}P chemical shifts were referenced against phosphoric acid (85 wt\% H\textsubscript{3}PO\textsubscript{4} in a deuterated solution, $\delta = 0$ ppm). To effectively excite the broad range of \textsuperscript{31}P resonant frequencies present in paramagnetic KVPO\textsubscript{4}F and KVPO\textsubscript{4.36}F\textsubscript{0.64}, a double-adiabatic spin-echo experiment, previously used on closely related LiFe\textsubscript{x}Mn\textsubscript{1−x}PO\textsubscript{4} compounds,\cite{46} was conducted. This pulse sequence employs a pair of tanh/tan short high-power adiabatic pulses (SHAPs),\cite{52} each sweeping through a 5-MHz frequency range in 50 $\mu$s with an RF amplitude of 312.5 kHz (300 W). The double-adiabatic spin-echo spectra were obtained using a 90° RF pulse of 0.8 $\mu$s at 300 W, followed by two high-power 180° SHAPs described above. A recycle delay of 0.1 s
was used throughout the experiment. Lineshape analysis was performed using the SOLA lineshape simulation package within the Bruker Topspin software.

**Hybrid DFT/HF calculations of paramagnetic NMR parameters**

Spin-unrestricted hybrid density functional theory/Hartree Fock (DFT/HF) calculations were performed on stoichiometric KVPO₄F, starting from the structure obtained from Rietveld refinement and reported in Supplementary Table 1. The CRYSTAL14 all-electron linear combination of atomic orbitals (LCAO) code was used, and two spin-polarized exchange-correlation functionals based upon the B3LYP form were applied, with weights of the HF exchange of 20% (B3LYP or H20) and 35% (H35). Electron-nuclear hyperfine NMR parameters were obtained in ferromagnetically aligned cells (at 0 K) using a method identical to that described elsewhere[47, 54]. Briefly, the Fermi contact shift ($\delta_{FC}$) is computed from the spin density at the nuclear position. $\delta_{FC}$ is subsequently scaled to a value consistent with the room-temperature paramagnetic state in which the experiments were performed by multiplication with the so-called magnetic scaling factor $\phi$: $^{[54]}$

$$\phi(T) = \frac{B_0\mu_{eff}^2}{3k_Bg_e\mu_BS(T - \Theta)}$$

Here, $B_0$ is the external magnetic field strength, $\mu_{eff}$ is the effective magnetic moment per V site, $k_B$ is Boltzmann’s constant, $g_e$ is the electron $g$-factor, $\mu_B$ is the Bohr magneton, $S$ is the formal spin of the transition metal species ($S_{\gamma2+} = 1$), $T$ is the temperature of the sample (assumed to be 320 K to account for frictional heating caused by fast (60-kHz) rotation of the NMR rotor), and $\Theta$ is the Weiss constant. $\mu_{eff}$ and $\Theta$ were determined from magnetic susceptibility measurements of the as-synthesized stoichiometric KVPO₄F. The $\Theta$ and $\mu_{eff}$ values used to compute the scaling factor $\phi$ are the average values determined from the FC and ZFC data obtained on the as-synthesized KVPO₄F: $\Theta = 6 \pm 3$ K and $\mu_{eff} = \sqrt{18} \times C = 2.55 \mu_B$, where $C$ is the Curie constant. Using the equation above, the
scaling factor at 320 K is $\Phi(320K) = 0.0262$. Full details of the calculations, including the basis sets and numerical parameters, are provided in the Supplementary Information.

**DFT calculation of phase stability and voltage profile**

First-principles DFT calculations on $K_xVPO_4F$ were performed with the spin-polarized generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. The projector augmented-wave approach was used as implemented in the Vienna ab initio simulation package (VASP). The Hubbard U correction to GGA (GGA+U) was employed to correct the self-interaction error of GGA. A U value of 4 eV was used for V, as employed in previous computational studies of vanadium fluorophosphates. A plane-wave energy cutoff of 520 eV and a gamma-centered $3 \times 2 \times 2$ $k$-point grid were used. All symmetric distinct K-vacancy orderings within the unit cell of $K_xVPO_4F$ including 8 formula units were generated using the enumeration technique reported by Hart et al., and the 50 configurations with the lowest electrostatic energy at each K content were calculated using GGA+U. The voltage profile was calculated from the DFT energies of the most stable configurations at each K content as

$$V = -\frac{E(K_{x2}VPO_4F) - E(K_{x1}VPO_4F) - (x_2 - x_1)E(K)}{(x_2 - x_1)F},$$

where $E(K_xVPO_4F)$ and $E(K)$ are the DFT energies of the most stable $K_xVPO_4F$ and bcc K metal (space group: Im-3m), respectively, and $F$ is the Faraday constant. To find reasonable configurations for $KVPO_{4.375}F_{0.625}$, all fluorine–oxygen orderings for additional oxygen at F sites of $KVPO_4F$ were generated using the same enumeration technique as previously discussed, and the 10 configurations with lowest electrostatic energy were calculated using GGA+U.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was supported by (i) the Laboratory Directed Research and Development Program of Lawrence Berkeley National Laboratory under U.S. Department of Energy (Contract No. DE-AC02-05CH11231). Work at the Molecular Foundry was supported by (ii) the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. (iii) This work was also supported by the BIC (Battery Innovative Contest) program of LG Chem, Ltd. under Contract No. 20181787. This work used (iv) the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant no. ACI-1053575, and (v) resources of the National Energy Research Scientific Computing Center (NERSC), a DOE Office of Science User Facility supported by the Office of Science of the US Department of Energy under contract no. DE-C02-05CH11231. (vi) Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. (vii) The authors would like to acknowledge the California NanoSystems Institute (CNSI) at the University of California Santa Barbara (UCSB) for experimental time on the 500 MHz NMR spectrometer. The NMR experimental work reported here made use of the shared facilities of the UCSB MRSEC (NSF DMR 1720256), a member of the Material Research Facilities Network.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))
References


Figure 1. Structural analysis of KVPO₄F. a. Rietveld refinement of X-ray diffraction pattern of KVPO₄F (wavelength = 0.457 Å). (Inset: Enlarged X-ray diffraction pattern from 20° to 30°.) The crystal structure of KVPO₄F projected along b. b-axis and c. a-axis. d. Connectivity of vanadium octahedrons. e. Local vanadium octahedral environment. f. K1 site and g. K2 site.
Figure 2. K-storage properties of KVPO$_4$F cathode. a. Charge/discharge profiles of KVPO$_4$F at 5 mA g$^{-1}$. b. Differential capacity (dQ dV$^{-1}$) curves of KVPO$_4$F for 1$^{st}$ and 2$^{nd}$ cycles. c. Rate capability of KVPO$_4$F at various current densities ranging from 5 to 300 mA g$^{-1}$. d. Capacity retention of KVPO$_4$F at 5 mA g$^{-1}$. 
Figure 3. Performance comparison of KVPO$_4$F and various cathode materials for LIBs, NIBs, and KIBs. Capacity–voltage plots of various cathode materials for LIBs, NIBs, and KIBs. Here, the plotted voltages are the average experimental discharge voltages reported in the literature.$^{16, 19-20, 22-24, 26, 33-38}$ (Green: KIB cathodes, Purple: NIB cathodes, Brown: LIB cathodes, and Red: KVPO$_4$F)
Figure 4. **a.** Formation energy of $K_xVPO_4F$ as a function of K content ($x$) obtained using first-principles DFT calculations. **b.** Calculated voltage plot (dashed line) compared with experimentally obtained charge/discharge profiles (solid line). The red dashed line in (a) is the convex hull of the formation energy. We note that the calculated voltage plot is shifted upwards by 0.35 V for better agreement with the experimental voltage curve.
Figure 5. Structural evolution of $K_xVPO_4F$ upon K extraction and reinsertion. a. Galvanostatic charge/discharge profile and b–d. XRD patterns of $K_xVPO_4F$ samples obtained at different states of cycling.
Figure 6. XANES and $^{31}$P-NMR results of KVPO$_4$F and KVPO$_{4.36}$F$_{0.64}$. a. V K-edge XANES spectrum of KVPO$_4$F and KVPO$_{4.36}$F$_{0.64}$ with reference compounds of Li$_3$V$_2$(PO$_4$)$_3$, V$_2$O$_4$, V$_2$O$_5$, and V metal as references. (Inset: XANES spectrum near the inflection point of 0.5) b. Pre-edge region of XANES spectra c. $^{31}$P double-adiabatic spin-echo solid-state NMR spectra collected on KVPO$_4$F and KVPO$_{4.36}$F$_{0.64}$ at 60-kHz magic angle spinning and an external field of 11.7 T. (Inset: diagram of the 31P site)
Figure 7. Galvanostatic charge/discharge profiles of KVPO$_4$F and KVPO$_{4.36}$F$_{0.64}$ in the 2$^{nd}$ cycle. a. Capacity vs. voltage plot and b. relative capacity vs. voltage plot.
This work reports the stoichiometric KVPO₄F cathode, which delivers a reversible capacity of ~105 mAh g⁻¹ with an average voltage of ~4.3 V (vs. K/K⁺), resulting in a gravimetric energy density of ~450 Wh kg⁻¹. This work further investigates the structural evolution of KₓVPO₄F and oxygen substitution effect on its electrochemistry.

**Keyword:** K-ion battery, Cathode, Polyanion, Fluorophosphate

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A new strategy for high voltage cathodes for K-ion batteries: stoichiometric KVPO₄F
Supporting Information

A new strategy for high voltage cathodes for K-ion batteries: stoichiometric KVPO$_4$F

Haegyeom Kim, Dong-Hwa Seo, Matteo Bianchini, Raphaële J. Clément, Hyunchul Kim, Jae Chul Kim, Won-Sub Yoon, Gerbrand Ceder*

Additional details on hybrid DFT/HF calculations of paramagnetic NMR parameters

$^{31}$P paramagnetic NMR parameters were computed within the CRYSTAL14 all-electron linear combination of atomic orbitals (LCAO) code.[1] Two spin-polarized exchange-correlation functionals based upon the B3LYP form, with weights of Hartree-Fock (HF) exchange of 20% (B3LYP or H20) and 35% (H35), were chosen for their satisfactory performance in determining the electronic structure, band gaps and properties of transition metal compounds (H20),[2, 3] and for their accurate determination of the magnetic coupling constants of related materials (H35).[4, 5, 6]. Moreover, previous studies on transition metal phosphates have demonstrated that the experimental NMR shift generally lies within the shift range set by the HYB20 and HYB35 computed shifts.[7, 8, 9] Two types of basis sets were employed, a smaller basis set (BS-I) was used for structural relaxations, and a larger basis set (BS-II) was used to calculate the NMR parameters, requiring an accurate description of the core electronic states. For BS-I, individual atomic basis sets were of the form (21s13p)/[1s4sp] for K, as used by Civalleri et al.[10], (20s12p4d)/[1s4sp2d] for V, (16s8p1d)/[1s3sp1d] for P, (14s6p1d)/[1s3sp1d] for O, and (10s6p1d)/[4s3p1d] for F, where the values in parentheses denote the number of Gaussian primitives and the values in square brackets the contraction scheme. All BS-I were obtained from the CRYSTAL repository and were unmodified from their previous use in a broad range of compounds.[11] For BS-II, modified IGLO-III sets were adopted for P, O and F, of the form (11s7p3d)/[7s6p3d] for P
and (10s6p2d)/[6s5p2d] for O and F,[12] a flexible and extended TZVP-derived (17s11p1d)/[6s4p1d] set was used for K, modified from [13] by increasing the exponent of the d shell, and an Ahlrichs DZP-derived (13s9p5d)/[7s5p3d] set was applied to V\cite{14}.

Hyperfine NMR parameters were computed in the fully optimized (atomic positions and cell parameters) KVPO₄F structure. All first principles structural optimizations were carried out in the ferromagnetic (FM) state, after removal of all symmetry constraints (P1 space group). Structural optimization was pursued on an 8 formula unit supercell using the quasi-Newton algorithm with RMS convergence tolerances of 10⁻⁷, 0.0003, and 0.0012 au for total energy, root-mean-square (rms) force, and rms displacement, respectively. Tolerances for maximum force and displacement components were set to 1.5 times the respective rms values. Sufficient convergence in total energies and spin densities was obtained by application of integral series truncation thresholds of 10⁻⁷, 10⁻⁷, 10⁻⁷, and 10⁻¹⁴ for Coulomb overlap and penetration, exchange overlap, and g- and n-series exchange penetration, respectively, as defined in the CRYSTAL documentation.[11] An isotropic Monkhorst-Pack[15] reciprocal space mesh with shrinking factor 4 was used for structural relaxation and paramagnetic NMR calculations of the cuboid cell (12.9 x 6.4 x 10.7 Å after relaxation). The final total energies and spin and charge distributions were obtained in the absence of any spin and eigenvalue constraints.

References


Supplementary Table 1. Structural parameters for KVPO$_4$F obtained from Rietveld refinement of synchrotron XRD data. z/c of V1 was fixed due the floating origin along c of the Pna21 space group.

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<td>0.798(2)</td>
<td>0.312(2)</td>
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<td>1.8(1)</td>
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<tr>
<td>K1’</td>
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<td>0.374(1)</td>
<td>0.759(2)</td>
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<tr>
<td>K2’</td>
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<td>0.690(3)</td>
<td>0.079(2)</td>
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<td>1.8(1)</td>
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Supplementary Figure 1. Scanning electron microscopy image of KVPO₄F.
Supplementary Figure 2. TGA analysis of KVPO$_4$F.
Supplementary Figure 3. *Ex situ* XRD patterns of KVPO$_4$F after the 1$^{st}$, 15$^{th}$ and 30$^{th}$ cycle.
Supplementary Figure 4. Linear scan voltage measurement of the electrolyte. 0.7 M KPF$_6$ in EC/DEC is used as the electrolyte and K metal is used as the counter electrode.
Supplementary Figure 5. Simulated crystal structure of $K_xVPO_4F$ when $x = 1.0$, 0.75, 0.625, 0.5, and 0.0, as obtained from DFT calculations.
Supplementary Figure 6. Simulated XRD patterns of $K_xVPO_4F$ when $x = 1.0$, 0.75, 0.625, 0.5, and 0.0 based on the crystal structures obtained from DFT calculations.
**Supplementary Table 2.** Refined lattice parameters of K\(_x\)VPO\(_4\)F (\(x = 1.0, 0.75, 0.625, 0.5,\) and 0.0) of *ex situ* XRD using structures obtained from DFT calculations.

<table>
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<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å(^3))</th>
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Supplementary Figure 7. Synchrotron-based X-ray diffraction analysis of KVPO$_{4.36}$F$_{0.64}$ (wavelength = 0.457 Å). (Inset: Enlarged X-ray diffraction pattern from 20º to 30º.)
**Supplementary Table 3.** Structural parameters for KVPO$_{4.36}$F$_{0.64}$ structure obtained from Rietveld refinement of synchrotron XRD data. The relative O and F occupancies were not refined due their light weight and the impossibility to distinguish them with X-Rays. z/c of V1 was fixed due the floating origin along c of the Pna21 space group.

Space group: Pna2$_1$; Z = 8

a = 12.8235(1) Å, b = 6.39630(6) Å, c = 10.5860(1) Å

V = 868.30(1) Å$^3$, V/Z = 108.54(1) Å$^3$  

$\chi^2 = 10.9$, $R_{\text{bragg}} = 5.39\%$, $R_{\text{wp}} = 20.5\%$

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<th>atom</th>
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Supplementary Table 4. First principles $^{31}$P Fermi contact NMR shifts ($\delta_{\text{FC}}$) for the two P sites present in KVPO$_3$F. The difference ($\Delta \delta_{\text{FC}}$) between the shifts of P1 and P2 is reported for comparison with the shift difference between the two signals observed in the $^{31}$P NMR spectrum. $\delta_{\text{FC}}$ values were derived from the spin density at the $^{31}$P nucleus obtained from hybrid DFT/HF calculations using the HYB20 and HYB35 functionals (containing 20 and 35% Hartree-Fock exchange, respectively). The spin density was scaled by a magnetic scaling factor $\Phi = 0.0262$ further discussed in the methods section. $\delta_{\text{FC}}$ values reported in this table are averages over all P1 and P2 sites in the cell.

<table>
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<td>5425</td>
</tr>
<tr>
<td>$\delta_{\text{FC}}(P_2)$ / ppm</td>
<td>5217</td>
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<tr>
<td>$\Delta \delta_{\text{FC}} = \delta_{\text{FC}}(P_1) - \delta_{\text{FC}}(P_2)$ / ppm</td>
<td>1471</td>
<td>1187</td>
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Supplementary Figure 8. Local K and V environments in KVPO$_4$F.
Supplementary Figure 9. Local K and V environments in KVPO_{4.375}F_{0.625}. 
Supplementary Figure 10. Schematic voltage curves of K-TMO$_2$ cathodes with different voltage slopes.