Computational and experimental search for potential polyanionic K-ion cathode materials†

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Introduction

Since the first commercialization of lithium-ion batteries (LIBs) by Sony in the early 1990s, LIBs have been the primary technology to provide energy storage in portable electronic devices and electric vehicles (EVs). However, the skyrocketing demand for energy storage, especially in the emerging EV market, raises concern about the availability and cost of lithium and other metals used in Li-ion cathodes.'–3 Na-ion batteries (NIBs) and K-ion batteries (KIBs) have been identified as potential low-cost alternatives to LIBs because of the natural abundance and wide distribution of Na and K resources. Compared to NIBs, KIBs are particularly attractive because (1) the standard redox potential of K/K+ (−2.93 V vs. standard hydrogen electrode (SHE)) is lower than that of Na/Na+ (−2.71 vs. SHE), translating into a higher operating voltage in an electrochemical cell; (2) the availability of stable K-graphite compounds enables the use of the well-developed graphite anode, while Na cannot intercalate into graphite; and (3) K+ has higher mobility than Li+ and Na+ in organic liquid electrolytes.'–9

In the early stage of K-ion cathode development, layered oxide compounds attracted significant attention given their success in LIBs and NIBs. Many K-containing layered oxides have shown reversible electrochemical (de)intercalation of K ions, including K-deficient KxMnO2, K1/2CrO2, KxFe0.5Mn0.5O2, and Kx/2Ni2/3Te1/3O2 (x < 1) and stoichiometric KCrO2.'–16 However, the average operating voltage is only in the range of 2.5 V vs. K/K+ in most K layered oxides; the exception is Kx/2Ni2/3Te1/3O2 in which electronegative TeO6 moieties increase the working voltage to ~3.3 V, but degrade the specific capacity. In recent work, we furthermore concluded that layered K-oxide compounds intrinsically have sloped voltage profiles regardless of the transition metal chemistry.'–18 In a layered structure, the large ionic radius of the K ion expands the alkali-ion layer and increases the interlayer distance, thereby making the screening from the adjacent oxygen layers less effective. The strong resulting K−K interaction increases the steepness of the voltage profiles in the sense that the (de)intercalation occurs over a much wider voltage range, which often exceeds the electrolyte stability window, therefore limiting the achievable capacity and lowering the average voltage.'–4,8,18–21

Because of these issues with layered oxide compounds, polyanionic compounds are of more interest for K cathodes.'–6,22–24
The larger K⁺-K⁺ distance in polyanionic compounds considerably reduces the effective K⁺-K⁺ interaction, generating a less sloped voltage profile and a generally operating voltage.¹⁹ In addition, polyanion groups further increase the voltage via the inductive effect.³⁵ Indeed, several K polyanion compounds have recently been investigated as high-voltage cathodes. For instance, the FeSO₄·F framework can intercalate K⁺ ions in a K half-cell at an average voltage of 3.6 V.²² Park et al. performed an extensive screening of K polyanion cathodes in the K-M-O and K-M-P-O spaces, and identified KVP₂O₇ as a candidate with reasonable electrochemical performance (55 mA h g⁻¹ at ~4.2 V).²⁶ In addition, the KVPO₄⁺ₓF₁⁻ₓ solid solution was investigated by Chihara et al.; this cathode material was shown to deliver a discharge capacity of 92 mA h g⁻¹ at an average voltage of 4.13 V.²⁷ Kim et al. later demonstrated that the operating voltage and specific capacity of the KVPO₄⁺ₓF₁⁻ₓ system could be further improved to 4.33 V and 105 mA h g⁻¹ by optimizing the synthesis route to obtain the end member KVPO₄F in which two oxygens in the VO₆ octahedra are fully substituted by fluorine.²⁸ Recently, KTIP₂O₇ was reported to have an average voltage of 3.6 V, which is extraordinarily high for Ti³⁺/⁴⁺ redox,³⁴ further demonstrating that K-containing polyanions have the potential to provide high energy density by upshifting the working voltage. In addition to compounds made by conventional solid-state or sol-gel synthesis, metastable polyanion compounds such as K₃V₂Cr(PO₄)₄ can be obtained from their Na counterparts by electrochemical ion exchange.²⁵

As part of a continuous effort to develop high energy K-ion cathode materials, we conduct in the current study a computational materials screening through the Inorganic Crystal Structure Database (ICSD) and identify 10 potential polyanionic K-ion cathode materials with theoretical capacity >100 mA h g⁻¹. Among the 10 candidates, 4 compounds (K₃MnP₂O₇, K₃MnP₂O₇F₂, K₃Fe₃P₂O₇F₂, and K₆V₂(PO₄)₄), for which the theoretical average voltage is within a stable voltage window of the typical K-electrolytes (3.0–4.5 V), were synthesized and evaluated electrochemically. K₃Cr₃(PO₄)₄ also appeared in the screening as a K-ion cathode material; however, its predicted average voltage was too high (>4.5 V). To lower the operating voltage to a practical electrochemical window, we successfully substituted Cr with V and investigated the K-ion storage properties in the K₃V₃₋ₓCrₓ(PO₄)₄ (x = 0, 1, 2, 3) system. Among the K₃V₃₋ₓCrₓ(PO₄)₄ compounds, K₃V₂Cr(PO₄)₄ exhibits the highest reversible discharge capacity of ~42 mA h g⁻¹ with an average voltage of ~3.95 V and could maintain ~90% of the initial capacity after 50 cycles. The reversible structural evolution and V³⁺/⁴⁺ redox reaction in this compound family was investigated using in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS).

We find that redox potentials in many K-polyanion compounds sit on average at even higher voltage than in similar Li compounds. While this would benefit the specific energy of these cathode materials, combined with the poor K-ion mobility that we find, it will challenge the anodic limit of current K-ion electrolytes.

**Experimental**

**Solid-state synthesis**

K₃Fe₃P₂O₇F₂ was prepared by the solid-state reaction from a stoichiometric mixture of KF (>99%, Sigma-Aldrich) and Fe₃P₂O₇ in a sealed stainless steel tube at 600 °C for 16 h. To synthesize Fe₂P₂O₇, stoichiometric amounts of Fe₂O₃ (>96%, Sigma-Aldrich) and NH₄H₂PO₄ (98%, Alfa Aesar) were mixed and pre-heated at 350 °C before annealing at 900 °C under a continuous flow of H₂(2%)/Ar(98%) mixed gas for 12 h.

K₃MnP₂O₇F₂ was prepared by a solid-state reaction from a stoichiometric mixture of KF (>99%, Sigma-Aldrich) and Mn₂P₂O₇ in a sealed stainless steel tube at 650 °C for 12 h. Mn₂P₂O₇ was prepared by decomposition of MnPO₄·H₂O (99%, Alfa Aesar) at 600 °C under continuous Ar flow for 3 h.

K₃MnP₂O₇ was synthesized by a solid-state reaction from a stoichiometric mixture of K₂CO₃ (anhydrous, VWR), MnO (99%, Alfa Aesar), NH₄H₂PO₄ (98%, Alfa Aesar), and 5 wt% carbon black (Super P, Timcal). The precursors were homogeneously mixed by wet ball-milling using acetone as a solvent and then dried at 90 °C on a hot plate. The mixture was pre-heated at 350 °C before annealing at 600 °C under continuous Ar flow for 12 h.

K₃V₃(PO₄)₄ was prepared by a solid-state reaction from a homogeneous mixture of K₃PO₄ (98%, Sigma-Aldrich) and VPO₄ at 800 °C under continuous Ar flow for 8 h. VPO₄ was synthesized by reacting NH₄H₂PO₄ (98%, Alfa Aesar), V₂O₅ (>99.6%, Sigma-Aldrich), and 5 wt% carbon black (Super P, Timcal). The precursors were mixed using wet ball-milling in acetone for 12 h and dried overnight at 100 °C. The mixture was pelletized and then sintered at 750 °C for 4 h under continuous Ar flow.

To prepare K₃Vₓ₋ₓCrₓ(PO₄)₄ (x = 0, 1, 2, 3) compounds, VPO₄ and CrPO₄ were synthesized to be used as precursors. Stoichiometric amounts of V₂O₅ (98%, Sigma-Aldrich) and HN₄H₂PO₄ (98%, Alfa Aesar) were homogeneously mixed with 5 wt% carbon, and the mixture was pelletized and sintered at 750 °C under Ar flow for 4 h to produce VPO₄. For the synthesis of CrPO₄, Cr(NO₃)₃·9H₂O (99%, Sigma Aldrich) was dissolved in 60 mL of deionized water and NH₄H₂PO₄ (98%, Alfa Aesar) was dissolved in 10 mL of deionized water. The two solutions were mixed and dried. Then, the dried powder was pelletized and sintered at 1000 °C for 4 h in air. To synthesize K₃Vₓ₋ₓCrₓ(PO₄)₄ (x = 0, 1, 2, 3) compounds, a stoichiometric amount of K₃PO₄ (anhydrous, >98%, Sigma-Aldrich) was homogeneously mixed with VPO₄ and CrPO₄. The mixture powder was pelletized and then sintered at 900 °C for 4 h under a continuous flow of H₂(2%)/Ar(98%) mixed gas. After natural cooling to 300 °C, the samples were kept at this temperature and then transferred to an Ar-filled glovebox to prevent contamination from moisture.

**Characterization**

The crystal structures of the obtained materials were analyzed using XRD (Rigaku Miniflex 600) with Cu Kα radiation. In situ XRD was performed on a Bruker D8 Advance X-ray diffractometer using Mo Kα radiation. A homemade in situ cell with a Be
window was galvanostatically cycled at 3 mA g⁻¹ between 2.5 and 5.0 V using a Maccor potentiostat, and XRD patterns were collected from 13° to 22° 2θ every 30 min at room temperature. The particle morphology was verified using field-emission scanning electron microscopy (FE-SEM; Zeiss Gemini Ultra-55).

X-ray absorption spectroscopy (XAS) measurements were performed in transmission mode at room temperature at beamline 20-BM at the Advanced Photon Source, Argonne National Laboratory. The prepared XAS samples were sealed with polyimide tape (Kapton, DUPONT) to prevent contamination from air exposure. The incident energy was selected using a Si(111) monochromator, and the beam intensity was reduced by 15% using a Rh-coated mirror to minimize high-order harmonics. Reference spectra of V and Cr were collected using pure V and Cr metal foils. The XAS data were analyzed using Athena software, and the spectral energies were calibrated by referencing the first inflection points in the spectra of V and Cr metal foils.

Electrochemical tests

Cathodes were prepared by mixing KₓVₓ₋₃₋ₓCrₓ(PO₄)₄ (70 wt%), Super P carbon (Timcal, 20 wt%), and polytetrafluoroethylene binder (DUPONT, 10 wt%) in an Ar-filled glovebox. Cathodes with a loading density of ~3.7 mg cm⁻² were assembled in a two-electrode configuration using a K-metal anode and glass fiber separator (Whatman, GF/F) in a 2032 coin cell. The electrolyte was custom-made using 0.7 M KPF₆ (Sigma-Aldrich) in anhydrous ethylene carbonate/proplylene carbonate (EC/PC) (1:1 by volume, Sigma-Aldrich). Electrochemical tests were performed on a battery testing station (Arbin Instruments) at room temperature in galvanostatic mode. All the other electrodes were also tested under the same conditions.

Computational details

The DFT calculations were performed using the Vienna ab initio simulation package (VASP) and projector-augmented wave (PAW) method. For each of the structural optimization calculations, a reciprocal space discretization of 25 Å⁻¹ was applied, and the convergence criteria were set to 10⁻⁶ eV for electronic loops and 0.02 eV Å⁻¹ for ionic loops. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional with the rotationally averaged Hubbard U correction was applied to obtain more accurate DFT energetics; the U parameters were taken from a previously reported calibration to oxide formation energies. For each of the compounds, multiple K-vacancy orderings were enumerated at different K concentrations, with the 20 configurations with the lowest electrostatic energy selected for DFT calculations. For compounds with mixing of cation or anion sites, the lowest energy cation/anion ordering in the pristine state was first determined. For other K contents, the enumeration was only performed on K/Vac sites with the cation/anion ordering fixed. The voltage profile was calculated from the DFT energies of materials on the pseudo-binary convex hull with the pristine compound and full depotassiated compound as the end compounds. The average between two K compositions x₁ and x₂ was determined as specified by Aydinol et al.: ³⁹

\[
V = -\frac{E(K_{x_1}X) - E(K_{x_2}X) - (x_2 - x_1)E(K)}{(x_2 - x_1)F}
\]

where \(E(K_{x_1}X)\) and \(E(K)\) are the DFT energies of the most stable \(E(K_{x_2}X)\) and bcc K metal (space group: Im3m), respectively, and \(F\) is the Faraday constant. Climbing image nudged elastic band (ci-NEB) calculations are performed to evaluate the K diffusion barrier for selected compounds. ³¹ For all calculations, the force convergence criterion is set to 0.05 eV Å⁻¹.

Results

Computational materials screening of ICSD for potential polyanionic K-ion cathodes

The computational materials search followed the criteria summarized in Fig. 1. K-containing polyanionic materials with composition A-TM-XO-C, where A represents K, TM represents one or more transition metals with multi-electron redox capability (from the group of V, Cr, Mn, Fe, and Ni), XO represents a polyion group (including PO₄³⁻, SO₄²⁻, SiO₄⁴⁻, and BO₄³⁻), and C represents the counter anion F⁻ or O²⁻ (the presence of a counter anion was not required), were first identified in the ICSD,⁴⁴ resulting in a total of 74 K-containing polyanion compounds. Of these compounds, 20 compounds having a K/TM ratio < 1 were excluded as they were unlikely to deliver high capacity. To ensure active redox centers, the remaining 54 candidates were reduced to 21 compounds by requiring that the transition metal is in octahedral coordination and has an appropriate valence state (i.e., V⁴⁺, Cr³⁺/⁴⁺, Mn²⁺/³⁺, Fe²⁺/³⁺, and Ni²⁺/³⁺). We did not consider cobalt as a redox center due to its high cost and low abundance. Notably, the electrochemistry of 19 of these 21 compounds has not previously been reported (except for KₓVₓ(PO₄)₄ which was published while we conducted this study). Next, a capacity filter (>100 mA h g⁻¹ based on K and TM oxidation ability) was applied, and 10 compounds with promising theoretical capacity were identified and are listed in Table 1. The approximate voltage profiles of the 10 entries were calculated, and only four of them were found to have an average voltage < 4.5 V. Our experimental investigation therefore first focused on these four compounds. Note that only the compounds with multi-electron redox capability during the screening process. In principle one can also search for poly-anion compounds with redox inactive metals such as Al, Zn, etc. and then evaluate the possibility of synthesizing their structure with redox active metals as has been done in some previous more elaborate high-throughput searches. However, in this work we limit ourselves to compounds which have already been reported in the ICSD database.

Experimental exploration of four potential K-ion cathodes with reasonable voltage

The four potential K-ion cathode materials of interest were successfully synthesized using conventional solid-state methods (Experimental section) and characterized using XRD. As shown in Fig. 2a, the diffraction patterns match well with the simulated ones with no or little evidence of any impurity phases. Fig. 2b summarizes the calculated voltage profiles of the
four compounds, i.e., K₂MnP₂O₇, K₂Mn₂P₂O₇F₂, K₂Fe₂P₂O₇F₂, and K₆V₂(PO₄)₄, all which exhibit promising theoretical capacity (>100 mA h g⁻¹) at a reasonable operating voltage (<4.5 V). The electrochemical properties of these four compounds as K-ion cathodes were then tested in K metal half-cells with the results plotted in Fig. 2c. For K₂MnP₂O₇, K₂Mn₂P₂O₇F₂, and K₂Fe₂P₂O₇F₂, K ions could be extracted electrochemically; however, the deintercalation process is irreversible with almost no capacity observed during the subsequent discharge. Even when charged to a lower cut-off voltage, no discharge capacity is observed. In contrast, K₆V₂(PO₄)₄ delivers about 17% of the charged capacity back in discharge. By decreasing the charge voltage cutoff to 4.0 V, the electrochemical performance of K₆V₂(PO₄)₄ can be improved, as shown in Fig. 2d. Although the first-cycle coulombic efficiency is approximately 50%, a reversible capacity of ~42 mA h g⁻¹ with high coulombic efficiency could be obtained during the second cycle. Further lowering the cut-off voltage to 3.75 or 3.25 V significantly reduces the capacity (Fig. S2†).

### Table 1

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>Potential redox couple</th>
<th>Theoretical capacity (mA h g⁻¹)</th>
<th>Average voltage (V)</th>
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<tr>
<td>1</td>
<td>K₂MnP₂O₇</td>
<td>Mn²⁺/⁴⁺</td>
<td>171.2</td>
<td>4.08</td>
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<tr>
<td>2</td>
<td>K₂Mn₂P₂O₇F₂</td>
<td>Mn²⁺/³⁺</td>
<td>131.4</td>
<td>4.19</td>
</tr>
<tr>
<td>3</td>
<td>K₂Fe₂P₂O₇F₂</td>
<td>Fe²⁺/³⁺</td>
<td>130.7</td>
<td>3.56</td>
</tr>
<tr>
<td>4</td>
<td>K₆V₂(PO₄)₄</td>
<td>V⁵⁺/⁴⁺</td>
<td>149.8</td>
<td>3.36</td>
</tr>
<tr>
<td>5</td>
<td>K₃Cr₃(PO₄)₄</td>
<td>Cr³⁺/⁴⁺</td>
<td>120.7</td>
<td>4.85</td>
</tr>
<tr>
<td>6</td>
<td>K₂Mn₄(SO₄)₃</td>
<td>Mn²⁺/³⁺</td>
<td>110.4</td>
<td>4.74</td>
</tr>
<tr>
<td>7</td>
<td>K₂Ni₄(SO₄)₃</td>
<td>Ni²⁺/³⁺</td>
<td>108.6</td>
<td>5.19</td>
</tr>
<tr>
<td>8</td>
<td>KCrPO₄F</td>
<td>Cr³⁺/⁴⁺</td>
<td>128.2</td>
<td>4.88</td>
</tr>
<tr>
<td>9</td>
<td>KFePO₄F</td>
<td>Fe³⁺/⁴⁺</td>
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<td>5.27</td>
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<tr>
<td>10</td>
<td>KMnPO₃F₃</td>
<td>Mn³⁺/⁴⁺</td>
<td>114.3</td>
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practical application. The operating voltage in a polyanion system can be tailored by either polyanion substitution or transition-metal substitution.\textsuperscript{46–48} In an effort to use these tools, one of the proposed high-voltage compounds, K\textsubscript{3}Cr\textsubscript{3}(PO\textsubscript{4})\textsubscript{4}, was further investigated in an attempt to lower its voltage. According to the calculated voltage profiles in Fig. S1,\textsuperscript{†} the extraction of the last two K ions occurs above 5 V in this compound. We evaluated the effect of V substitution because V\textsuperscript{3+/4+} redox typically occurs at lower voltage than Cr\textsuperscript{3+/4+} redox in polyanion compounds,\textsuperscript{46,47,49} and several V-based polyanionic K cathodes have shown reasonable working voltage.\textsuperscript{20,23,25–28,30,31} Indeed, we observe a decreased voltage in the calculated voltage profiles of the V-substituted K\textsubscript{3}Cr\textsubscript{x}(PO\textsubscript{4})\textsubscript{4} compounds (Fig. S3†). Therefore, V\textsuperscript{3+} substitution for Cr\textsuperscript{3+} was performed experimentally and a series of K\textsubscript{3}V\textsubscript{3–x}Cr\textsubscript{x}(PO\textsubscript{4})\textsubscript{4} (x = 0, 1, 2, 3) compounds were successfully synthesized via solid-state method and electrochemically evaluated.

Fig. 3a presents the XRD pattern of K\textsubscript{3}V\textsubscript{3}(PO\textsubscript{4})\textsubscript{4} together with the refinement results. The refined structure of K\textsubscript{3}V\textsubscript{3}(PO\textsubscript{4})\textsubscript{4} belongs to the orthorhombic space group Cmca, and is isostructural to K\textsubscript{3}Cr\textsubscript{x}(PO\textsubscript{4})\textsubscript{4}.\textsuperscript{50} The refined lattice parameters are \(a = 10.734\) (5) Å, \(b = 20.41\) (1) Å, and \(c = 6.502\) (3) Å. The XRD patterns of K\textsubscript{3}V\textsubscript{2}Cr(PO\textsubscript{4})\textsubscript{4}, K\textsubscript{3}VCr\textsubscript{2}(PO\textsubscript{4})\textsubscript{4}, and K\textsubscript{3}Cr\textsubscript{3}(PO\textsubscript{4})\textsubscript{4} are similar to that of K\textsubscript{3}V\textsubscript{3}(PO\textsubscript{4})\textsubscript{4}, as shown in Fig. 3b, except for a slight, non-uniform shift of the diffraction peaks (inset of Fig. 3b). Fig. 3c–f summarize the refined volume and lattice

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**Fig. 2** XRD patterns and electrochemical properties of four potential K-ion cathodes. (a) Experimentally observed (top line) and simulated XRD patterns (bottom line). (b) Calculated approximate voltage profiles. The plateaus reflect the fact that only an average voltage between each two successive K-contents is calculated. Voltage profiles of all predicted compounds are shown in Fig. S1.\textsuperscript{†} (c) Electrochemical voltage profiles in K-metal half-cells between 2.5 and 5 V at a current density of 5 mA g\textsuperscript{−1}. (d) 1st and 2nd cycle voltage profiles of K\textsubscript{6}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{4} with cut-off voltage of 4.25 and 4.0 V.
parameters for $K_3V_3-xCr_x(PO_4)_4$ ($x = 0, 1, 2, 3$). A continuous change with respect to the $V:Cr$ ratio can be clearly observed, indicating the successful incorporation of $V^{3+}$. As expected, the $a$ and $c$ lattice parameters monotonically decrease by 2.36% and 1.73%, respectively, with the increasing content of the smaller-sized $Cr^{3+}$. In contrast, the $b$ lattice parameter remains relatively
constant (0.44% change). As a result, the overall volume decreases by 3.63%. Detailed refinement results are presented in Fig. S4.† In all four compounds, there is no noticeable formation of any impurity phase. In addition, Fig. 4 shows the elemental distributions in as-synthesized particles obtained from energy dispersive X-ray spectroscopy (EDS), further confirming that K, V, and Cr are homogenously distributed within particles without any phase segregation. The particle size of K$_3$V$_x$Cr$_{3-x}$(PO$_4$)$_4$ ($x$ = 0, 1, 2, 3) as determined from scanning electron microscopy (SEM) images (Fig. S5†) are similar around a few microns (1–5 μm).

X-ray absorption near edge structure (XANES) spectroscopy was performed to identify the oxidation states of vanadium and chromium in the as-synthesized K$_3$V$_{3-x}$Cr$_x$(PO$_4$)$_4$ ($x$ = 0, 1, 2, 3) system. Fig. 5a presents the V K-edge spectra of K$_3$V$_3$(PO$_4$)$_4$, K$_3$V$_2$Cr(PO$_4$)$_4$, and K$_3$Cr$_3$(PO$_4$)$_4$. In addition to the identical edge positions and pre-edge features in all three samples, the obtained spectra also overlap with that of the Li$_3$V$_2$(PO$_4$)$_3$ (V$^{3+}$) reference, confirming that all the K$_3$V$_{3-x}$Cr$_x$(PO$_4$)$_4$ ($x$ = 0, 1, 2) compounds contains V$^{3+}$ in the pristine structure. For the Cr K-edge, no noticeable differences were observed among K$_3$V$_2$Cr(PO$_4$)$_4$, K$_3$VCr$_2$(PO$_4$)$_4$, and K$_3$Cr$_3$(PO$_4$)$_4$, and the edge position of all the samples is similar to that of Cr$_2$O$_3$, as shown in Fig. 5b. Notably, Cr$^{3+}$ with d$^2$ electron configuration usually has a distorted octahedral symmetry, which results in a prominent pre-edge peak, as shown by the XAS spectra of CrO$_2$.

![XANES spectra of K$_3$V$_3$(PO$_4$)$_4$, K$_3$V$_2$Cr(PO$_4$)$_4$, K$_3$VCr$_2$(PO$_4$)$_4$, and K$_3$Cr$_3$(PO$_4$)$_4$.](image)

Fig. 5 XANES spectra of K$_3$V$_3$(PO$_4$)$_4$, K$_3$V$_2$Cr(PO$_4$)$_4$, K$_3$VCr$_2$(PO$_4$)$_4$, and K$_3$Cr$_3$(PO$_4$)$_4$. (a) V K-edge (b) Cr K-edge. Li$_3$V$_2$(PO$_4$)$_3$, Cr$_2$O$_3$, and CrO$_2$ are used as references for V$^{3+}$, Cr$^{3+}$, and Cr$^{4+}$, respectively.

Fig. 5 XANES spectra of K$_3$V$_3$(PO$_4$)$_4$, K$_3$V$_2$Cr(PO$_4$)$_4$, K$_3$VCr$_2$(PO$_4$)$_4$, and K$_3$Cr$_3$(PO$_4$)$_4$. (a) V K-edge (b) Cr K-edge. Li$_3$V$_2$(PO$_4$)$_3$, Cr$_2$O$_3$, and CrO$_2$ are used as references for V$^{3+}$, Cr$^{3+}$, and Cr$^{4+}$, respectively.

![Electrochemical properties of K$_3$V$_{3-x}$Cr$_x$(PO$_4$)$_4$ (x = 0, 1, 2, 3).](image)

Fig. 6 Electrochemical properties of K$_3$V$_{3-x}$Cr$_x$(PO$_4$)$_4$ (x = 0, 1, 2, 3). First and second charge–discharge profiles between 2.5 and 5.0 V at 10 mA g$^{-1}$ for (a) K$_3$V$_3$(PO$_4$)$_4$, (b) K$_3$V$_2$Cr(PO$_4$)$_4$, (c) K$_3$VCr$_2$(PO$_4$)$_4$, and (d) K$_3$Cr$_3$(PO$_4$)$_4$. (e) Voltage profiles of K$_3$V$_2$Cr(PO$_4$)$_4$ at room temperature and 45 °C. (f) Cycling stability of K$_3$V$_2$Cr(PO$_4$)$_4$ at room temperature and 45 °C.
half cells, with K metal and 0.7 M KPF6 in EC/PC (1 : 1 vol.) used that Cr is present as Cr³⁺ in all the samples.

3.46 V). In Fig. 6e, the K₃V₂Cr(PO₄)₄ cathode exhibits smaller polarization followed by K₃V₃(PO₄)₄ (17 mA h g⁻¹/C₂⁴) charge capacity of 34 mA h g⁻¹/C₁⁴ when the temperature increases to 45 °C, as shown in Fig. 6a-d. During the first charge all the samples exhibit some irreversible capacity which may originate from the electrolyte decomposition because of the high cut-off voltage (5.0 V vs. K/K⁺). For discharge, K₃V₂Cr(PO₄)₄ delivers the highest discharge capacity of ~5469 eV decreases to close to that of the pristine K₃V₂Cr(PO₄)₄, indicating a reversible but incomplete reduction of V⁵⁺ to V⁴⁺. In the second cycle, reversible V oxidation and reduction are also observed. In contrast, no change is observed in the Cr K-edge, as reference. However, no such pre-edge feature is observed for any of the K₃Vₓ₋₃Crₓ(PO₄)₄ (x = 1, 2, 3) compounds, indicating that Cr is present as Cr³⁺ in all the samples.

The K₃Vₓ₋₃Crₓ(PO₄)₄ (x = 0, 1, 2, 3) samples were tested in K-half cells, with K metal and 0.7 M KPF₆ in EC/PC (1 : 1 vol.) used as the anode and electrolyte, respectively. The first and second charge-discharge profiles of all four compounds are presented in Fig. 6a-d. During the first charge all the samples exhibit some irreversible capacity which may originate from the electrolyte decomposition because of the high cut-off voltage (5.0 V vs. K/K⁺). For discharge, K₃V₂Cr(PO₄)₄ delivers the highest discharge capacity of ~43 mA h g⁻¹ with an average voltage of 3.95 V, followed by K₃V₃(PO₄)₄ (~34 mA h g⁻¹ and 3.85 V), KₓVCr₂(PO₄)₄ (~17 mA h g⁻¹ and 3.77 V), and KₓCr₃(PO₄)₄ (~3 mA h g⁻¹ and 3.46 V).

When the temperature increases to 45 °C, as shown in Fig. 6e, the K₃V₂Cr(PO₄)₄ cathode exhibits smaller polarization and delivers a higher discharge capacity of ~57 mA h g⁻¹, indicating that poor K-ion diffusion may limit the room temperature performance. Although the electrochemical cycling at 45 °C increases the specific capacity, the cycling stability becomes worse: only 63% of the discharge capacity remains after 50 cycles compared with 90% at room temperature (Fig. 6f), which can likely be attributed to the accelerated electrolyte decomposition at higher temperature.²²

As it shows the highest capacity among the KₓV₃₋₃Crₓ(PO₄)₄ systems, the structure of K₃V₂Cr(PO₄)₄ was monitored by in situ XRD upon K (de)intercalation. Fig. 7 presents the in situ XRD patterns obtained from K₃V₂Cr(PO₄)₄ cycled between 2.5 and 5.0 V in a K-half cell. Upon the first charge, the peaks at 14.0° and 14.5° merge into one peak at 14.3°. Further charge shifts the peaks at 14.3° and 15° to higher angle, consistent with a shrinkage of the lattice upon K extraction. After the continuous peak shift, no additional peak evolution is observed, indicating that K-extraction from K₃V₂Cr(PO₄)₄ occurs via a solid solution. Upon discharge, the peaks at 14.7° and 15.2° shift to lower angle, corresponding to an expansion of the lattice by K insertion. However, at the end of the discharge, the peak at 14.3° does not split into two peaks as in the XRD pattern of the pristine structure. This irreversible structural behavior could be the result of low K diffusivity in the discharged state, which is often observed in the literature. During the second cycle, a continuous peak shift is again observed, demonstrating that, after the first cycle, K extraction and reinsertion occur reversibly in K₃V₂Cr(PO₄)₄.

To understand the redox mechanism in K₃V₂Cr(PO₄)₄ during K (de)intercalation, we monitored the valence change of V and Cr during charge-discharge via ex situ XANES spectroscopy. Fig. 8a shows the V K-edge, and the inset shows the enlarged pre-edge feature. The intensity of the pre-edge peak at ~5469 eV significantly increases when the cathode is charged to 4.5 V and further increases at 5.0 V, clearly indicating the oxidation of V⁵⁺ to V⁴⁺. After discharging, the pre-edge peak intensity at ~5469 eV decreases to close to that of the pristine K₃V₂Cr(PO₄)₄, indicating a reversible but incomplete reduction of V⁴⁺ to V⁵⁺. In the second cycle, reversible V oxidation and reduction are also observed. In contrast, no change is observed in the Cr K-edge, as
shown in Fig. 8b. This finding implies that Cr does not participate in the redox reaction in this compound.

We found that $K_3V_{3-x}Cr_x(PO_4)_4$ ($x = 0, 1, 2, 3$) compounds are easily hydrated, as demonstrated by the difference in the XRD patterns after hydration and dehydration in Fig. 9a. When exposed to air or water, the XRD peak at $\sim 31^\circ$ disappears and a new peak emerges at $\sim 30.5^\circ$. After dehydration at 600 $^\circ$C, the pristine diffraction pattern could be recovered. Fig. 9b presents the weight change of the hydrated compound upon heating; $\sim 2.66\%$ weight loss is observed, corresponding to 1H$_2$O per formula unit of $K_3V_3(PO_4)_4$. Moreover, the crystal structure of the hydrated compound $K_3V_3(PO_4)_4\cdot$H$_2$O was further analyzed, and the refinement result is presented in Fig. 9c. An orthorhombic $K_3Fe_3(PO_4)_4\cdot$H$_2$O (space group: $Pnma$) was used as a model structure and shows good agreement with the observed XRD pattern. The XRD pattern of the hydrated phase also fits well with a very recent report of orthorhombic $K_3V_3(PO_4)_4\cdot$H$_2$O. Similarly, all the $K_3V_{3-x}Cr_x(PO_4)_4$ ($x = 0, 1, 2, 3$) compounds exhibit such hydration behavior, as evidenced by the peak change at approximately 30$^\circ$ after 5 h air exposure (Fig. 9d). The moisture sensitive nature of $K_3V_{3-x}Cr_x(PO_4)_4$ ($x = 0, 1, 2, 3$) requires an inert storage environment of these materials, which might lead to difficulty in applications.

**Discussion**

The average voltage of several K layered and polyanion cathodes as well as their experimentally reported Li or Na analogous are plotted in Fig. 10. Due to the steepness of the voltage profiles, K layered oxides suffer a significant voltage lowering when
Table 2  DFT-calculated volume change and energy above the hull of the four predicted compounds upon K extraction

<table>
<thead>
<tr>
<th>Compound</th>
<th>Volume change (%)</th>
<th>E_{\text{null}} (meV per atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Half extraction</td>
<td>Full extraction</td>
</tr>
<tr>
<td>K_2MnPO_7</td>
<td>−11.3</td>
<td>−21.5</td>
</tr>
<tr>
<td>K_2MnPO_3F_2</td>
<td>−5.9</td>
<td>−12.4</td>
</tr>
<tr>
<td>K_6V_2(PO_4)_4</td>
<td>−4.2</td>
<td>−9.6</td>
</tr>
<tr>
<td>K_6V_2(PO_4)_4</td>
<td>−3.7</td>
<td>−6.0</td>
</tr>
</tbody>
</table>

compared with their Li counterparts: for example, LiCoO_2 exhibits an average voltage of approximately 4 V, which is ~1.3 V higher than that of K_0.8CoO_2. Moreover, the voltage of K layered oxides is also lower than that of Na layered oxides, which makes K layered oxides even less competitive in terms of energy density. In contrast, our work confirms the general finding that polyanion systems have less sloped voltage profile compared to that of layered oxide, which makes higher operating voltage in K polyanion systems possible. Despite their more optimal voltage profile, the K_3V_3Cr(PO_4)_4 systems are not satisfactory from an energy density perspective because of the low specific capacity.

K-containing polyanion systems seem to have a remarkably high voltage for a given redox couple. As shown in Table 1, only 4 of the 10 predicted materials have a reasonable average voltage. Although most of the reported K polyanion cathodes are based on V^{3+/4+}, Fe^{2+/3+}, or Ti^{3+/4+} redox couples, which one would expect to have relatively low redox potential, their operating voltage approaches or even surpasses 4 V. In particular, as shown in Fig. 10, the voltages of KFeSO_4F, KVPO_4, KVPO_4F, KTiPO_4F, and KVP_2O_7 are even higher than that of several reported working K polyanion cathodes. For example, the voltage above the hull of K_3V_3Cr(PO_4)_4 is 1.3 V lower than that of K_0.8CoO_2, which may be worthwhile to understand better how structure and composition engineering in the future.

In conclusion, ten potential K polyanion cathodes with >100 mA h g\(^{-1}\) theoretical capacity are identified from the computational screening of the ICSD, among which four compounds (K_2MnPO_7, K_2MnPO_3F_2, K_2FePO_2F_2, K_6V_2(PO_4)_4) and a family of K_3−xCr_x(PO_4)_4 (x = 0, 1, 2, 3) compounds are synthesized and explored electrochemically. Among these, K_6V_2Cr(PO_4)_4 delivers the largest reversible capacity, and the redox mechanism and structural evolution are further investigated via X-ray absorption and diffraction techniques, respectively. Though K polyanion compounds presented in this work indeed show less sloped voltage profiles compared to layered oxides, other issues such as high K ions migration barrier, high oxidation voltage bring up new challenges, which calls for more in-depth electrochemical investigation and composition engineering in the future.
Author contributions

H. K. initiated the project. H. K. and G. C. supervised the research in all aspects. H. K. and J. W. synthesized, characterized and tested the compounds. B. O. performed the DFT calculation. H. K. acquired and analysis the XAS data. Y. T. acquired the SEM images. J. W. wrote the manuscript. B. O., H. K. and G. C. revised the manuscript. J. W. and B. O. contributed equally to this work.

Conflicts of interest

The authors declare no conflicts of interests.

Acknowledgements

This work was supported by the BIC (Battery Innovative Contest) program of LG Chem, Ltd under Contract No. 20181787. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. 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. The computational analysis was performed using computational resources supported by the Department of Energy’s Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory. Computational resources were also provided by the Extreme Science and Engineering Discovery Environment (XSEDE), supported by National Science Foundation grant number ACI1053575, and the National Energy Research Scientific Computing Center (NERSC), a DOE Office of Science User Facility supported by the Office of Science and the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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