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Investigation of Alkali-Ion (Li, Na, and K) Intercalation in K

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**Investigation of alkali-ion (Li, Na, and K) intercalation in VPO$_4$F**

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**Keywords:** Potassium, Sodium, Lithium, Batteries, Cathodes

**Abstract**

This work compares the intercalation of K, Na, and Li in VPO$_4$F. The VPO$_4$F cathode delivers reversible capacities of ~90–100 mAh g$^{-1}$ in K, Na, and Li cells, at an average voltage of ~4.33 V for K, ~3.98 V for Na, and ~3.96 V for Li. This is so far the highest average voltage known for a K-intercalation cathode. The lower voltage of Li insertion compared to Na is attributable to undercoordinated Li ions in the VPO$_4$F framework. While the material shows high rate capability for all the alkali ions, Li migration in VPO$_4$F is more difficult than Na and K. This work suggests that a large cavity is not always good for insertion of alkali-ions and cathode materials need to be suitably tailored to each intercalating ion species.

**1. Introduction**

Electrochemical energy storage of renewable energy is of considerable societal interest. Rechargeable batteries, including Li-ion (LIBs), Na-ion (NIBs), and K-ion batteries (KIBs) have been studied as potential energy
storage systems.[1-5] Among these, KIBs are particularly interesting because graphite can intercalate K ions reversibly, making it a standard anode for KIBs,[6-7] and because the standard redox potential of K/K$^+$ is lower than that of Na/Na$^+$ and even Li/Li$^+$ in non-aqueous electrolytes, translating into a potentially higher working voltage.[6]

Intense efforts have focused on the development of high-voltage cathodes for KIBs. In particular, many polyanionic compounds have been investigated as high-voltage cathodes for KIBs.[8-13] For example, Recham et al. reported KFeSO$_4$F as a cathode for KIBs; this material provides an average voltage of ~3.6 V vs. K/K$^+$ with a reversible capacity of ~100 mAh g$^{-1}$.[8] KVPO$_4$F and KVPO$_4$ were evaluated as K-cathodes by Chihara et al. and found to discharge ~92 mAh g$^{-1}$ at an average voltage of ~4.1 V vs. K/K$^+$ and ~80 mAh g$^{-1}$ with an average voltage of ~4.0 V vs. K/K$^+$, respectively.[9] We recently demonstrated that the performance of KVPO$_4$F can be improved to ~105 mAh g$^{-1}$ and ~4.33 V vs. K/K$^+$ through the synthesis of more stoichiometric KVPO$_4$F.[10] We also found that partial oxygen substitution in KVPO$_4$F disorders the anion sublattice, which reduces achievable capacity and voltage. [10]

In continuing our efforts to understand the structure-property relationship in electrode materials, we investigate and contrast in this work the alkali-ion (K, Na, and Li) intercalation properties of VPO$_4$F. We observe that the VPO$_4$F cathode can deliver reversible capacities of ~90-100 mAh g$^{-1}$ with high average voltages of ~4.3, ~3.98, and ~3.96 V in K, Na, and Li cells, respectively. We attribute the lowest voltage for Li, as compared to Na intercalation, to the large cavity size in the VPO$_4$F framework, which leads
to undercoordination for Li ions. The VPO₄F cathode exhibits stable cycling and high rate capability in K, Na, and Li cells. However, we find that Li insertion into VPO₄F is more difficult than Na and K despite its small ionic radius.

2. Results

2.1. Material characterization

Figure 1a presents an XRD pattern and refinement results for KVPO₄F. The refinement of the as-prepared KVPO₄F with Pna2₁ space group yields lattice parameters of \( a = 12.8174, b = 6.3955, \) and \( c = 10.6000, \) which agrees well with previous results in the literature.\(^{[10]}\) Figure 1b presents a SEM image of KVPO₄F. To obtain a better SEM image without effects of charging, the KVPO₄F particles were mixed with conductive carbon. The primary particle size of KVPO₄F is estimated to be \(~100-200\) nm. The small particles at the top of Figure 1b are the carbon additive.

2.2. Electrochemical cycling of VPO₄F in K, Na, and Li cells

Figure 2a–c present the electrochemical charge and discharge profiles of VPO₄F electrodes in K, Na, and Li cells, respectively. Preceding the electrochemical measurements in Na and Li cells, the KVPO₄F cathode was fully charged to 5.0 V (vs. K/K⁺) in a K cell, and the charged VPO₄F cathode was reassembled in Na and Li cells. The specific capacity is calculated based on the weight of the KVPO₄F cathode. In the K cells, the VPO₄F cathode delivers capacities of 129 and 93 mAh g⁻¹ during the first charge.
and discharge, respectively, with an average voltage of ~4.33 V vs. K/K$^+$ (Figure 2a). The VPO$_4$F cathode exhibits a capacity of 122 mAh g$^{-1}$ for the first charge and 106 mAh g$^{-1}$ for the first discharge in Na cells (Figure 2b). An average voltage of ~3.98 V (vs. Na/Na$^+$) is observed in the Na cells. In the Li cells, the VPO$_4$F cathode achieves a capacity of ~119 mAh g$^{-1}$ and ~91 mAh g$^{-1}$ for the first charge and discharge, respectively, and average voltage of ~3.96 V (vs. Li/Li$^+$), as shown in Figure 2c. The charge and discharge voltage profiles of VPO$_4$F are unchanged during the electrochemical cycling in each cell, indicating reversible alkali-ion de/intercalation. This is confirmed by the cycling stability shown in Figure 2d. In K, Na, and Li cells, the VPO$_4$F cathode maintains respectively ~77%, ~77%, and ~79% of the initial discharge capacity after 100 cycles. We contrast the average voltage of the VPO$_4$F cathode in K, Na, and Li cells in Figure 2e, where we plot the average voltage of each cell vs. the standard hydrogen electrode (SHE) potential in propylene carbonate solvent.$^{[6]}$ The values in Figure 2e were obtained by adding the SHE potential of M/M$^+$ (M=Li, Na, and K) in carbonate solution to the average voltage of the cathode (vs. M/M$^+$). To eliminate the effect of polarization, we plot the average of the charge and discharge voltages. Insertion of K, Na, and Li in VPO$_4$F occurs at 1.45, 1.42, and 1.17 V (vs. SHE), respectively, indicating that the average voltage of VPO$_4$F decreases with decreasing intercalating ion size from K$^+$ to Li$^+$. As the charged state is the same in all the cases (VPO$_4$F), the electrochemical voltage is determined by the energetics of the discharged state alone (K$_x$VPO$_4$F vs. Na$_x$VPO$_4$F vs. Li$_x$VPO$_4$F). We expect that the large cavities for alkali ions in the VPO$_4$F framework preferentially
intercalate K and Na ions, forming more stable compounds and thus leading to a higher voltage than for Li intercalation. To understand in more detail how each ion intercalates, we compare the calculated crystal structures of KVPO$_4$F, NaVPO$_4$F, and LiVPO$_4$F. As presented in Figure S1, the K and Na ions are located in the same sites, K1 and K2, where they are coordinated by six O$^{2-}$ ions and two F$^-$ ions. In contrast, the Li ions prefer a site that has planar coordination with two O$^{2-}$ ions and two F$^-$ ions (Li1), and a site that has planar coordination with four O$^{2-}$ ions (Li2) (see Figure S2). The relative decrease of Li-insertion voltage compared to K-insertion is likely due to this unusual coordination of Li which usually prefers a tetrahedral or octahedral anion geometry. The calculated average voltages are 4.34 V (vs. K/K$^+$) for K intercalation, 3.88 V (vs. Na/Na$^+$) for Na intercalation, and 3.94 V (vs. Li/Li$^+$) for Li intercalation. These values translate to 1.46, 1.32, and 1.15 V vs. SHE, respectively, which is consistent with the experimental trend that the average voltage decreases with decreasing intercalating ion size.

2.3. Rate capability
The rate capability of VPO$_4$F in K, Na, and Li cells in discharge was tested by charging at 30 mA g$^{-1}$ and discharging at various current rates ranging from 30 to 2000 mA g$^{-1}$. The results are shown in Figure 3a-c. In K cells, VPO$_4$F cathode delivers 92.14, 90.65, 88.5, 85.7, 82.8, 79.4, 75.5, 72.4, and 62.2 mAh g$^{-1}$ at 30, 50, 100, 200, 500, 800, 1000, and 2000 mA g$^{-1}$, respectively (Figure 3a). In Na cells, VPO$_4$F cathode provides 99.1, 97.5, 93.8, 90.3, 86.6, 82.9, 80, 77, and 66.4 mAh g$^{-1}$ at 30, 50, 100, 200, 500, 800, 1000, 2000 mA g$^{-1}$, respectively, as observed in Figure 3b. Capacities of 90.4, 88.4, 85, 81, 78, 75, 72, 66, and 40.4 mAh g$^{-1}$ are observed for the
VPO$_4$F cathode in Li cells at 30, 50, 100, 200, 500, 800, 1000, 2000 mA g$^{-1}$, respectively (Figure 3c). Figure 3d–e compares the capacity retention of VPO$_4$F with increasing current in K, Na, and Li cells. At a high current of 2000 mA g$^{-1}$ (~15C, where 1C = 128 mA g$^{-1}$), VPO$_4$F retains 67.5% (K), 67% (Na), and 44.69% (Li) of its low-rate capacity. Interestingly, once the current density is higher than 800 mA g$^{-1}$ (6.25C), worse rate capability is observed for Li intercalation than for Na and K despite its smaller ionic radius. These results indicate that Li migration in VPO$_4$F is more difficult than for K and Na, the origin of which we investigate in the next section.

2.4. **K, Na, and Li migration barriers in VPO$_4$F cathode**

Figure 4 shows the *ab-initio* calculated K-ion migration barriers of three possible paths in the KVPO$_4$F structure. Each path starts and ends in an equivalent site so that it can percolate through the extended crystal. In a pristine KVPO$_4$F structure (without vacancies), K ions are located at two distinct sites, namely K1 and K2. The K ion at the K1 site shares two F ions with two VO$_4$F$_2$ octahedra, whereas at the K2 site, K shares two F ions with a single VO$_4$F$_2$ octahedron.$^{[10]}$ Interestingly, when a vacancy is formed in the KVPO$_4$F structure, the K ion adjacent to the vacancy spontaneously moves to a new site (K3), which is located between the K1 and K2 sites (Figure S3). This ‘spontaneous K3 migration’ participates in K-ion diffusion along path3, as discussed later. As there is spontaneous K ion migration into the new K3 site in both initial and final structures and they have the equivalent site occupancy in our K migration calculations, the energy of these structures are the same although the K1 and K2 site energies are different. (Figure 4).
Figure 4a shows the migration energy for K along path 1 which goes between K1 site and through a K2 site, illustrated in Figure 4b. This path (path 1) involves two hops. In the first hop (pink trajectory), the K ion at the K1 site hops to a K2 site. In the second hop (blue trajectory), the K ion moves from this K2 to another K1 site. The overall diffusion direction of this path is along the a-axis and has a migration barrier of 421 meV. Path 2 is an alternative pathway between two K1 sites through K2, but this time along the bc diagonal direction. The energy and visualization is shown in Figure 4c and 4d for half of the path as the second half is symmetric. The very high migration energy along this path (> 1 eV) as compared to path 1 is related to the hexagonal voids K-ion has to pass through. At the transition states of path 1 and path 2 (asterisks in Figure 4a and 4c, respectively), the K ion passes through hexagonal void 1 and void 2, respectively. The two hexagonal voids are shown in Figure S4. Four VPO$_4$F$_2$ octahedra and two PO$_4$ tetrahedra bound hexagonal void 1 while hexagonal void 2 is composed of three VPO$_4$F$_2$ octahedra and three PO$_4$ tetrahedra. Because the K ion gets close to a V ion in these voids, they constitute the bottlenecks for the two K-migration paths. For path 2, the distance between the hopping K ion and the nearest V ion at the hexagonal void is only 3.12 Å, which is shorter than that for path 1 (3.36 Å). This increased electrostatic interaction likely contributes to the higher K migration barrier along path 2 than along path 1.

Figure 4e and 4f show the K migration barrier and corresponding trajectory of path 3. Each K site in Figure 4f is labeled for clarity, namely B and E are K1-type sites, A and D are K2 sites, and C is a K3 site. Path 3 consists of
two hops, each of which involves concerted migration. The first hop (0% of the path coordinate in Figure 4e) starts with site C (K3) vacant because the adjacent B (K1) and D (K2) sites are occupied. The first hop (pink trajectory) migrates the K ion from site B to A, forming a vacancy at B. At the same time, the K ion at site D spontaneously moves to site C (K3) because the vacancy formed at the adjacent B site has lowered the energy of that site. The second hop (blue trajectory) migrates the K ion at site E to the vacant D site, while the K ion at site C is simultaneously pushed to site B because of the repulsion between the two K ions. This concerted migration enables K ions to move along the c-axis with a migration barrier of 195 meV. The reason the path3 has a low migration barrier is that the K ion passes through larger cavities, composed of eight polyhedra (Figure S5), without traversing the hexagonal voids. The shortest K–V distance in the transition state along path3 is 3.74 Å, which is much longer than that along path1 (3.36 Å) or path2 (3.12 Å). Because the migration barrier of path2 is too high for K ions to migrate, diffusion of K is limited to migration along path1 and path3.

**Figure 5** investigates the migration of Na in VPO₄F. Similar to the pristine KVPO₄F structure, there are two sites (Na1 and Na2) in NaVPO₄F, with the Na1 and Na2 sites corresponding to the K1 and K2 sites, respectively. However, in the NaVPO₄F structure, there is no locally stable K3 site and corresponding concerted migration, but path2 passes through the local K3 environment. We speculate that this is because Na ions are undercoordinated in the K3 site, which is even larger than the K1 and K2 sites. Figure 5a and 5b show the Na migration barrier and corresponding
trajectory for path1. For path1, the Na ion at the Na1 site moves to the Na2 site in the first hop (pink trajectory). In the second hop (blue trajectory), the Na ion migrates from the Na2 to the Na1 site through the hexagonal void1 (Figure S4a), which is represented by a black dashed line. The overall migration direction of path1 is along the a-axis with a barrier of 222 meV. Along path2, the Na ion migrates the Na1 to Na2 through the hexagonal void2 (Figure S4b), which is represented as a black dashed line in Figure 5d, followed by another hop back to a Na1 position. The overall migration direction of path2 is along the b-axis, and the migration barrier is 297 meV. Along these paths, the energy at the Na2 site (50% of the path coordinate) is approximately 200-meV higher than at the Na1 site (0% or 100% of the path coordinate), which is likely attributable to the shorter Na–V distance at the Na2 site (3.18 Å) compared with that at the Na1 site (3.44 Å). Along path1, the Na ion passes through the hexagonal void1 where the shortest Na–V distance is 3.30 Å, which is larger than that at the Na2 site (3.18 Å). Thus, Na migration through the hexagonal void1 does not result in a significant Na migration barrier and most of the barrier is accounted for by the Na1-Na2 site energy difference. Along path2, however, the energy is highest when the Na ion traverses the hexagonal void2 where Na is only 3.03 Å away from a V ion.

For comparison, Figure 6 shows the Li-ion migration barriers for three possible migration paths in LiVPO$_4$F. (path1, path2, and path3) The two Li sites in LiVPO$_4$F are different than the K or Na sites: Li ions have planar coordination with 2O$_2^-$ and 2F$^-$ (Li1) shown in Figure S2a or with 4O$_2^-$ (Li2) (see Figure S2b). The K site coordinated by 7O$_2^-$ ions and 2F$^-$ ions is likely
too large for Li to occupy. In LiVPO$_4$F, the Li1 site is about 240 meV higher in energy than the Li2 site. There are several reasons for this energy difference. The Li1 site has more V neighbors than the Li2 site. Whereas the Li2 site is coordinated by 4O$^{2-}$ which screen the electrostatic repulsion with the surrounding V ions, the Li1 site is coordinated by 2O$^{2-}$ and 2F$^-$ creating less effective screening of the interaction with V.

Figure 6a-b show the Li migration barrier and trajectory along path1. A Li ion at a Li2 site first moves through a Li1 site (pink trajectory) into another Li2 site (blue trajectory). This trajectory along the bc diagonal direction has a migration barrier of 442 meV. Figure 6c-6d and Figure 6e-f show the migration energy and corresponding trajectory of path2 and path3, respectively. Similar to path1, the Li ion moves from Li2 to Li1 (pink trajectory) and then migrates to another Li2 site (blue trajectory) along path2 and path3. The migration barriers of path2 and path3 are 470 and 629 meV, respectively. At the transition state for each path, the hopping Li ion is coordinated by only two anions, whereas it is coordinated by four anions at the Li1 and Li2 sites. The fact that Li$^+$ has to squeeze through this anion-anion dumbbell where it is highly undercoordinated creates a high Li migration barrier. Of the three paths, the migration barrier of path1 is the lowest because the shortest Li–V distance (3.35 Å) at the transition state is longer than that for path2 (2.68 Å) or path3 (2.80 Å). Path3 has a higher migration barrier than path2, although the shortest Li–V distance for path3 is longer than that for path2. This result is likely attributed to the anion species, encountered along the trajectory. At the transition state, the hopping Li ion is coordinated by 2O$^{2-}$ ions along path2 but by 1O$^{2-}$ ion
and $1\text{F}^-$ ion along path3. Moreover, the second shortest Li-V distance for path3 (3.51 Å) is shorter than that for path2 (4.40 Å). These factors may contribute to the higher migration barrier for path3. The migration barriers in LiVPO$_4$F are relatively high compared with those in KVPO$_4$F and NaVPO$_4$F, which is likely responsible for the inferior rate capability of LiVPO$_4$F at 2000 mA g$^{-1}$ observed in Figure 3d–e.

3. Discussion

This work demonstrates that the VPO$_4$F framework can function as a versatile cathode for alkali ions, including K, Na, and Li. In all the K, Na, and Li cells, the VPO$_4$F cathode delivers good cycling stability and a high discharge rate (Figure 2 and Figure 3, respectively). The stable cycle life and high rate capability of the VPO$_4$F cathode likely result from the large cavity size for alkali ions, which can accommodate alkali-ion intercalation and enable fast alkali-ion migration. Our NEB calculations reveal that KVPO$_4$F, NaVPO$_4$F, and LiVPO$_4$F have migration barriers of 195, 222, and 442 meV, respectively. The K and Na migration barriers are even lower than that for the NASICON-type Na$_3$V$_2$(PO$_4$)$_3$ cathode (353 meV),$^{[14]}$ and the Li migration barrier in the VPO$_4$F cathode is comparable to that for tavorite LiVPO$_4$F (418 meV), a high-rate cathode.$^{[15]}$ These results indicate the VPO$_4$F is a framework for fast alkali-ion intercalation. Interestingly, both experiments and NEB calculations show that the insertion of Li into VPO$_4$F is more difficult than Na and K. The higher Li migration barrier is attributable to the different site occupancy which leads to a different migration path and transition state where it is only coordinated by two anions. Our work illustrates how different alkali ions can have different migration paths in the same host, and demonstrates that large alkali-ion
migration channels are not always good for fast ion diffusion, something that has been earlier observed when comparing Na and Li migration in β-alumina. To achieve high-rate capability, one needs to design electrode materials in which void space and transition states are suitably tailored to each migrating ion species.

In Figure 7, we show the average voltage of the VPO₄F cathode in K, Na, and Li cells compared with that of other vanadium-redox-based polyanion cathode materials. The working voltage of K-VPO₄F is the highest for all reported K cathodes and higher than KVPO₄₋ₓFₓ⁻¹[9-10] and KVOPO₄[9]. In the Na cell, VPO₄F provides a high voltage of 3.98 V (vs. Na), which is the highest ever reported voltage in a vanadium-based polyanion cathode for NIBs, including Na₃V₂(PO₄)₃,[22] Na₃V₂(PO₄)₂F₃,[23] NaVPO₄F,[24] and NaVOPO₄.[25] The voltage of 3.96 V (vs. Li) in a VPO₄F/Li cell is comparable to that of LiVPO₄F[26] and Li₃V₂(PO₄)₃[27]. Given the higher standard redox potential of Na/Na⁺ than Li/Li⁺, it is interesting that VPO₄F has a higher voltage in the Na cell than in the Li cell.[6] The lower voltage for Li likely originates from the relatively small ionic size of Li⁺ compared to Na⁺ or K⁺, which makes it less stable in the large Na site of the VPO₄F framework. This work suggests that the relative size of the intercalating ion species and the cavity plays an important role in determining the voltage of the alkali ion intercalation.

5. Conclusion
This work investigated the alkali-ion (K, Na, and Li) intercalation properties of VPO₄F. The VPO₄F cathode discharges ~90–100 mAh g⁻¹ in K, Na, and Li cells, and for K provides the highest voltage (~4.33 V) observed in a poly-
anion cathode. The relatively lower Li intercalation voltage is attributable to the large cavity size in the VPO₄F framework, which destabilizes the Li site. The VPO₄F cathode also provides stable cycle life and high rate capability in all the K, Na, and Li cells.

6. Experimental Section

Synthesis

KVPO₄F was prepared using a solid-state method. First, VPO₄ was synthesized by reacting NH₄H₂PO₄ (11.5 g, 98%, Alfa Aesar), V₂O₅ (9.05 g, >99.6%, Sigma-Aldrich), and carbon black (1.2 g, 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. Stoichiometric amounts of KF (99.9%, Sigma-Aldrich) and VPO₄ were homogeneously mixed using a planetary ball mill (Retsch PM200) at 300 rpm for 4 h. The mixture was pelletized and sintered at 650 °C for 8 h with continuous Ar flow.

Structure analysis

The structure of each sample was analyzed using X-ray diffraction (XRD; Rigaku Miniflex 600) with Cu Kα radiation, and the structural parameters were determined using the Rietveld method and Highscore Plus software. Scanning electron microscopy (SEM) images were collected on a Zeiss Gemini Ultra-55 Analytical Field Emission SEM in the Molecular Foundry at Lawrence Berkeley National Laboratory.

Electrochemical measurements

Electrodes were prepared by mixing the active material (70 wt%), Super P carbon black (Timcal, 20 wt%), and polytetrafluoroethylene (PTFE; DuPont,
10 wt%) binder in an Ar-filled glovebox. Test cells were assembled into 2032 coin-cells in a glovebox with a two-electrode configuration using K, Na, and Li metal counter electrodes. A grade GF/F separator (Whatman, USA) and an electrolyte of 0.7 M KPF$_6$ in ethylene carbonate/diethyl carbonate (EC/DEC; anhydrous, 1:1 volume ratio), 1 M NaPF$_6$ in EC/DEC, or 1 M LiPF$_6$ in EC/DEC were used. The electrochemical tests were performed on a battery testing station (Arbin Instruments) using cathode films with a loading density of $\sim$4.9 mg cm$^{-2}$.

**Computational methods**

Density functional theory (DFT) calculations were performed using the projector augmented-wave (PAW) approach$^{[28]}$ as implemented in the Vienna ab initio simulation package (VASP)$^{[29-31]}$. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional$^{[32]}$ was adopted for all the calculations. To compensate for the self-interaction errors of the generalized gradient approximation (GGA), the Hubbard U correction was employed$^{[33]}$. The U value for vanadium was set to 5.0 eV, as used in a previous study of KVPO$_4$F.$^{[10]}$ A gamma-centered 2 × 3 × 2 k-point grid was used, and the planewave cutoff energy was set to 520 eV. The structures of NaVPO$_4$F and LiVPO$_4$F were constructed by substituting K in KVPO$_4$F with the corresponding alkali elements. Because the alkali-ion sites are partially occupied in the original structural data, all the K-vacancy orderings within a unit cell (8 formula units) were generated, and the 50 configurations with the lowest electrostatic energies were selected using the Pymatgen package.$^{[34]}$ The most stable configurations were then determined from the
DFT calculations. The average voltage was calculated using the following equation:\[^{[35]}\]

\[
V = -\frac{E(\text{AVPO}_4F) - E(\text{VPO}_4F) - E(A)}{F},
\]

where \( E(\text{AVPO}_4F) \), \( E(\text{VPO}_4F) \), and \( E(A) \) are the calculated energies of AVPO\(_4\)F, VPO\(_4\)F, and metallic A (K, Na, or Li), respectively, and \( F \) is the Faraday constant.

The migration barriers for alkali ions in AVPO\(_4\)F were calculated using the climbing image nudged elastic band (CI-NEB) method.\[^{[36]}\] For these calculations, 1 × 2 × 1 supercells containing 16 formula units with a gamma-centered 1 × 1 × 2 k-point grid were used. The standard GGA functional was employed as it is difficult to achieve convergence for NEB calculations using GGA + U because of possible metastability of the electronic states along the migration path.\[^{[37]}\]

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

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References

**Figure 1. Structure and morphology of KVPO₄F.**

- **a.** Rietveld-refined XRD profile obtained from as-prepared KVPO₄F using the Pna₂₁ space group which provides a good fit ($R_{wp} = 5.5$).
- **b.** SEM image of KVPO₄F.
Figure 2. Electrochemical measurements of VPO₄F in K, Na, and Li cells. Charge/discharge profiles of VPO₄F in a. K, b. Na, and c. Li cells. d. Cycling stability of VPO₄F in K, Na, and Li cells. e. Average voltage of VPO₄F vs. standard hydrogen electrode (SHE).
Figure 3. Discharge rate capability of VPO₄F in K, Na, and Li cells.

Discharge profiles of VPO₄F in a. K, b. Na, and c. Li cells at different current rates (30–2,000 mA g⁻¹). d. Discharge capacity of VPO₄F at different current rates. e. Normalized capacity of VPO₄F at different current rates.
Figure 4. K-ion migration barriers and paths in KVPO₄F. a. K-ion migration barrier and b. K migration path1; c. K-ion migration barrier and d. K migration path2; and e. K-ion migration barrier and f. K migration path3. The asterisks represent transition states. The value of the migration barriers is shown at the top right corner of each plot in a, c, and e. The pink and blue trajectories correspond to the migration barriers of the same color. K1, K2, and K3 denote symmetrically distinct K sites, and the black dashed lines represent cross sections of the hexagonal voids. The K sites along path3 are labeled with A–E for clarity.
Figure 5. Na-ion migration barriers and migration paths in NaVPO$_4$F. a. Na-ion migration barrier and b. Na migration path1; c. Na-ion migration barrier and d. Na migration path2. The asterisks represent transition states. The value of the migration barriers is shown at the top right corner of each plot in a and c. The pink and blue trajectories correspond to the migration barriers of the same color. Na1 and Na2 denote symmetrically distinct Na sites, and the black dashed lines represent cross sections of the hexagonal voids.
Figure 6. Li-ion migration barriers and migration paths in LiVPO$_4$F.

a. Li-ion migration barrier and b. Li migration path1; c. Li-ion migration barrier and d. Li migration path2; and e. Li-ion migration barrier and f. Li migration path3. The asterisks represent transition states. The value of the migration barriers is shown at the top right corner of each plot in a, c, and e. The pink and blue trajectories correspond to the migration barriers of the same color. Li1 and Li2 denote symmetrically distinct Li sites.
Figure 7. Average voltage of VPO$_4$F in K, Na, and Li cells and comparison with V-based polyanion cathodes from the literature.\cite{9, 10, 22-27}
**Keyword** Potassium, Sodium, Lithium, Batteries, Cathodes

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**Investigation of alkali-ion (Li, Na, and K) intercalation in VPO$_4$F**

This work investigates and compares the K, Na, and Li intercalation properties in VPO$_4$F cathode. It demonstrates that large alkali-ion migration channels are not always good for fast ion diffusion and thus cathode materials need to be suitably tailored to each intercalating ion species.
Supporting Information

Investigation of alkali-ion (Li, Na, and K) intercalation in VPO$_4$F

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Figure S1. Calculated structures of a, b KVPO$_4$F, c, d NaVPO$_4$F, and e, f LiVPO$_4$F.
**Figure S2.** a. Li1 and b. Li2 site coordinations in calculated LiVPO$_4$F structure.
Figure S3. K-ion migration to K3 site during DFT structural relaxation. The K ion adjacent to a vacancy spontaneously moves to a K3 site.
Figure S4. Two types of hexagonal voids in VPO$_4$F framework. a. Void1 is composed of four VPO$_4$F$_2$ octahedra and two PO$_4$ tetrahedra. b. Void2 is composed of three VPO$_4$F$_2$ octahedra and three PO$_4$ tetrahedra. The dashed lines denote the shortest V–V or V–P distance.
Figure S5. Large voids composed of (a) four VO$_4$F$_2$ octahedra and four PO$_4$ tetrahedra and (b) five VO$_4$F$_2$ octahedra and three PO$_4$ tetrahedra. The K ion in KVPO$_4$F passes through these large voids along path3.