Sodium-Ion Batteries

# KVOPO<sub>4</sub>: A New High Capacity Multielectron Na-Ion Battery Cathode

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Sodium ion batteries have attracted much attention in recent years, due to the higher abundance and lower cost of sodium, as an alternative to lithium ion batteries. However, a major challenge is their lower energy density. In this work, we report a novel multi-electron cathode material, KVOPO<sub>4</sub>, for sodium ion batteries. Due to the unique polyhedral framework, the  $V^{3+} \leftrightarrow V^{4+} \leftrightarrow V^{5+}$  redox couple was for the first time fully activated by sodium ions in a vanadyl phosphate phase. The KVOPO based cathode delivered reversible multiple sodium (i.e. maximum 1.66 Na<sup>+</sup> per formula unit) storage capability, which leads to a high specific capacity of 235 Ah kg<sup>-1</sup>. Combining an average voltage of 2.56 V vs. Na/Na<sup>+</sup>, a high practical energy density of over 600 Wh kg<sup>-1</sup> was achieved, the highest yet reported for any sodium cathode material. The cathode exhibits a very small volume change upon cycling (1.4% for 0.64 sodium and 8.0% for 1.66 sodium ions). Density functional theory (DFT) calculations indicate that the KVOPO<sub>4</sub> framework is a 3D ionic conductor with a reasonably, low Na<sup>+</sup> migration energy barrier of ≈450 meV, in line with the good rate capability obtained.

# 1. Introduction

Over the last 20 years, lithium ion battery (LIB) technologies have become the preferred advanced electrical energy storage systems.<sup>[1,2]</sup> However, as their use grows there is an increasing concern about the limited availability of lithium,<sup>[3]</sup> particularly if large scale grid storage becomes important.<sup>[4]</sup> Sodium, being much more abundant in nature is a natural alternative,

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battery safety.<sup>[14]</sup>

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and much research effort is again being directed at sodium-ion batteries (NIBs).<sup>[5–7]</sup> However, the larger sodium ion leads to a much more complex multiphasic behavior, which is expected to be detrimental to long-term capacity retention. Safety is also a concern because of sodium's low melting point.

A number of cathode materials have been reported for NIBs, including the layered oxides (e.g., NaMnO2),[8] tunnel oxides (e.g., Na<sub>0.44</sub>MnO<sub>2</sub>),<sup>[9]</sup> olivine (e.g., Na<sub>x</sub>Fe<sub>0.5</sub>Mn<sub>0.5</sub>PO<sub>4</sub>),<sup>[10]</sup> polyphosphates (e.g.,  $Na_2FeP_2O_7$ ),<sup>[11]</sup> NASICONS<sup>1</sup> (e.g.,  $Na_3V_2(PO_4)_3)$ ,<sup>[12]</sup> and fluorophosphates (e.g., NaVPO<sub>4</sub>F).<sup>[13]</sup> As the voltage of sodium couples is around 0.5 V less than lithium couples, it is important to increase the capacity to compensate. This might be achieved by investigating materials that can incorporate up to two sodium ions per redox active site, and in addition by looking at phosphates where the inductive effect of the PO<sub>4</sub><sup>3-</sup> polyanion increases

the voltage of the transition metal redox to higher values than

in the oxides.<sup>[5]</sup> In addition, the phosphate group decreases the

ease of oxygen release when fully charged, thus increasing the

above criteria as vanadium has multiple redox couples and has been shown to reversibly intercalate more than one Li ion.<sup>[15–23]</sup>

There are no reports of multiple Na or K ions being intercalated

The vanadyl phosphates, exemplified by LiVOPO<sub>4</sub>, fit the

into these VOPO<sub>4</sub> lattices. Goodenough and co-workers showed that 0.62 Na ions could be reversibly intercalated into NaVOPO<sub>4</sub> giving a capacity of 90 mAh g<sup>-1,[24]</sup> Very recently, Komaba and co-workers reported the reversible intercalatation of 0.63 K ions into KVOPO<sub>4</sub>.<sup>[25]</sup>

Vanadyl phosphates exist in a number of structural modifications, and they show a range of unit cell volumes from 83.7 Å<sup>3</sup> for  $\beta$ -LiVOPO<sub>4</sub>.<sup>[26]</sup> to 106.8 Å<sup>3</sup> for KVOPO<sub>4</sub>. The 27% expanded structural network of the KVOPO<sub>4</sub> lattice makes it particularly attractive for the intercalation of multiple alkali ions, like sodium. Thus, here we report a study of the KVOPO<sub>4</sub> phase as a host for a sodium battery. We show that it can indeed reversibly intercalate more than one sodium ion, and also that in addition it can cycle more than one Li or K ions. The sodium capacity found exceeds 235 mAh g<sup>-1</sup>, more than double that reported for the NaVOPO<sub>4</sub> phase.<sup>[24]</sup>

# 2. Results and Discussion

#### 2.1. Material Synthesis and Characterization

Phase-pure KVOPO4 was synthesized via a one-pot solidstate reaction route under a controlled reducing atmosphere. NH<sub>4</sub>VO<sub>3</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> were utilized as sources of vanadium and phosphorus, respectively. The NH<sub>3</sub> gas, generated by the decomposition of the precursors, yielded the V4+ by reducing the V<sup>5+</sup> source during the heating. Confirmation of phase pure material was determined by synchrotron X-ray diffraction, the full details of which are in Figure S1 and Tables S1-S4 of the Supporting Information, together with the CIF file. The determined unit cell dimensions, a = 12.7634(6) Å, b = 6.3672(3) Å, c = 10.5146(5) Å, V = 854.506(7) Å<sup>3</sup> are in very good agreement with those originally reported for single crystals: a = 12.7640(8) Å, b = 6.3648(4) Å, c = 10.5153(9) Å, V = 854.3(2),<sup>[27]</sup> and slightly different from the powders of Komaba and coworkers a = 12.7548(2) Å, b = 6.3656(1) Å, c = 10.5042(5) Å, V = 852.86(3) Å<sup>3</sup>.<sup>[25]</sup> However, in our powder we found no KVO<sub>3</sub> impurity. The volume per VOPO<sub>4</sub> unit (i.e., V/VOPO<sub>4</sub>) of KVOPO<sub>4</sub> is 106.8 Å<sup>3</sup>, which is 20–25% larger than those of the Li-/Na-VOPO<sub>4</sub> compounds.<sup>[26]</sup> The structure of KVOPO<sub>4</sub> is compared with that of  $\varepsilon$ -LiVOPO<sub>4</sub> in Figure 1. In both structures, the "VOPO4" framework is assembled by corner-sharing VO6 octahedra and PO4 tetrahedra, and it contains an assembly of parallel infinite VO<sub>3</sub> chains linked by single PO<sub>4</sub> tetrahedra. Whereas, in LiVOPO<sub>4</sub>, there are two four-sided 1D tunnels

along [110] as shown in Figure 1a.<sup>[28]</sup> For KVOPO<sub>4</sub>, as marked by the black dot rectangles, there are two intersecting six-side tunnels generated by the polyhedral blocks, which extended along *a* and *b* axis, respectively (Figure 1b).<sup>[27]</sup> The potassium ions align within these two tunnels. Compared to the VO<sub>3</sub> chains in LiVOPO<sub>4</sub> and NaVOPO<sub>4</sub> (Figure S2, Supporting Information), the VO<sub>3</sub> chains in KVOPO<sub>4</sub> exhibit a more distorted configuration due to the larger potassium ions.<sup>[29]</sup> These distorted VO<sub>3</sub> chains provide the much more wide-open VOPO<sub>4</sub> framework. This structure has many commonalities with the hexagonal tungsten bronzes, K<sub>x</sub>WO<sub>3</sub>, where the K ions are readily mobile.<sup>[30,31]</sup>

The 4+ oxidation state of the vanadium in the as-synthesized material was confirmed by an X-ray absorption near edge structure (XANES) analysis of the vanadium K-edge, and further details of the bonding were elucidated by extended X-ray absorption fine structure (EXAFS). These are fully described in Figures S3 and S4 and Tables S5 and S6 of the Supporting Information.

#### 2.2. Potassium Extraction and Intermediate K<sub>x</sub>VOPO<sub>4</sub> Phases

In order to intercalate sodium or lithium into the "VOPO4" framework of KVOPO<sub>4</sub>, the potassium must first be removed. Immersion of KVOPO<sub>4</sub> for 6 h into the sodium electrolyte showed no ion exchange, as measured by chemical analysis of the solid material (Table S7, Supporting Information). Thus, the potassium was extracted in an electrochemical cell by charging the material up to 4.5 versus Na/Na<sup>+</sup> at C/15 and holding there for 10 h, similar to our earlier formation of  $\varepsilon$ -VOPO<sub>4</sub> from H<sub>2</sub>VOPO<sub>4</sub>.<sup>[32]</sup> Figure 2a shows the charging profile and the cyclic voltammogram (CV) curve for the potassium extraction process (i.e., the first charge). The top and bottom x-axis correlates to the current values of the CV test and the time used for the galvanostatic charging, respectively. Several plateaus (highlighted in cyan rectangles) can be easily distinguished in the charging curve, which corresponds to the distinct peaks in the CV curve. The plateau/peak indicates the existence of K<sub>v</sub>VOPO<sub>4</sub> intermediate phases and the two-phase reaction between them. To determinate the structure of the K<sub>x</sub>VOPO<sub>4</sub> phase, we selected the ex situ samples (i.e., point b, c, d, e) between the plateaus and collected synchrotron X-ray diffraction (SXRD) data. Figure 2b showed the evolution of the SXRD upon charging, where we can easily distinguish the reflections ascribed to the new intermediate phase 1, 2, and 3. XANES



K<sup>+</sup>/Na<sup>+</sup> tunnels

Figure 1. a) Crystal structure of  $\varepsilon$ -LiVOPO<sub>4</sub>, and b) crystal structure of KVOPO<sub>4</sub>, highlights the intersecting K<sup>+</sup>/Na<sup>+</sup> ion tunnels and one VO<sub>3</sub> chain.



Figure 2. a) Galvanostatic charge profile and the CV curve of the potassium extraction process. b) The evolution of the ex situ SXRD data upon potassium extraction revealing the appearance of intermediate phases. c) V K-edge XANES spectra of KVOPO4 cathode upon potassium extraction. d-f) Rietveld refinement of the SXRD data collected at points of b, c, e in (a). The reflections marked with \* are ascribed to the aluminum signal from the current collector.

analysis of the vanadium K-edge revealed that the K, VOPO4 intermediate phase became more potassium deficient upon higher charging voltage. As shown in Figure 2c, the shift of both the pre-edge and main edge toward higher energy region upon charge indicates the oxidization of V4+ to V5+ associated with the potassium extraction. For the spectra collected at point *c* and *e*, the pre-edge region exhibits apparent doublet shapes which can be ascribed to a combination of V<sup>4+</sup> and V<sup>5+</sup>. The V<sup>4+</sup> component indicates some potassium remaining in the structure. At higher voltage, the V<sup>5+</sup> component grew in intensity at the expense of the V<sup>4+</sup> component intensity.

We determined the crystal structures of the intermediate phases 1, 2, and 3 using high resolution ex situ SXRD data. The structure information of the phases is listed in Table S8 of the Supporting Information. The intermediate phases inherit the "VOPO<sub>4</sub>" polyhedron framework (e.g., space group, symmetry) of the pristine phase, but with different potassium deficiency. The appearance of these K<sub>x</sub>VOPO<sub>4</sub> intermediate phases is likely due to the strong long-range ordering of the potassium vacancies at specific potassium concentrations. Similar behavior was also observed in the sodium-based compounds.<sup>[33,34]</sup> As shown in Figure 2d-f, the ex situ SXRD patterns were then refined based on the structures of the K<sub>x</sub>VOPO<sub>4</sub> intermediate phases and a KClO<sub>4</sub> impurity. The KClO<sub>4</sub> came from K<sup>+</sup> extracted from KVOPO<sub>4</sub> and the ClO<sub>4</sub><sup>-</sup> in the NaClO<sub>4</sub>-based electrolyte. As the electrode was charged to higher voltage, the material contained a larger proportion of a low potassium content phase. Based on the formula of the intermediate phases and the ratio between them, the final product obtained at point *e* has the formula  $K_{0.36}$ VOPO<sub>4</sub>; this was used as the cathode material for the following reversible Na intercalation. Additional potassium could not be removed in the cell, because electrolyte decomposition becomes the dominant reaction when the cell voltage reached 4.5 V.

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#### 2.3. Electrochemistry of K<sub>x</sub>Na<sub>v</sub>VOPO<sub>4</sub>

Sodium intercalation into the above K<sub>0.36</sub>VOPO<sub>4</sub> phase cathode was studied using a Na metal anode. Figure 3a shows the galvanostatic charge/discharge profiles of K<sub>0.36</sub>VOPO<sub>4</sub> at a current density of C/20 (the C value was normalized by one Na+ per formula unit, i.e., 133 mAh g<sup>-1</sup>) in the voltage window of 1.3-4.5 V. The profiles exhibit a distinct two redox-region feature for both charge and discharge, which is analogous to that of the multielectron vanadyl phosphates in lithium cells (e.g.,  $\varepsilon$ -,  $\beta$ -LiVOPO<sub>4</sub>).<sup>[22,35]</sup> The high and low redox-regions exhibit average voltages of  $\approx$ 3.8 and  $\approx$ 1.9 V, respectively. These values agree well with the density functional theory (DFT) calculated voltages of the  $V^{5+}/V^{4+}$  and  $V^{4+}/V^{3+}$  redox couples (magenta dashed line). As discharged to 1.3 V versus Na/Na<sup>+</sup>, the electrode delivered discharge capacity of 235 mAg h<sup>-1</sup>. The carbon phase in the composite may contribute a small capacity ( $\approx 10 \text{ mAh g}^{-1}$ ) in the same voltage window, as shown in Figure S5 of the Supporting Information. The amount of sodium intercalated is thus around 1.66 sodium per formula unit, which clearly shows that both the  $V^{5+} \leftrightarrow V^{4+}$  and the  $V^{4+} \leftrightarrow V^{3+}$  couples are electrochemically active in this vanadyl phosphate structure. Cyclic voltammetry (CV), shown in Figure 3b, shows the complexity of the reactions in each of the redox couples, consistent with the ordering of the alkali ions in the tunnels suggested by the

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**Figure 3.** a) Galvanostatic charge/discharge profiles of the  $K_{0.36}$ VOPO<sub>4</sub> cathode in sodium anode cell. The magenta dashed line is the calculated voltage profile of Na<sub>x</sub>VOPO<sub>4</sub> (x = 0, 1, 2) and b) CV curves of the  $K_{0.36}$ VOPO<sub>4</sub> cathode.

X-ray diffraction data. They also show the reversibility of the reactions.

Based on the capacity and voltage in Figure 3a, K<sub>0.36</sub>VOPO<sub>4</sub> has an energy density of 600.6 Wh kg<sup>-1</sup> at an average potential of 2.56 V. This compares very favorably with other sodium cells. Figure 4 summarizes the published capacity, average voltage, and observed energy density for a range of sodium ion battery cathodes calculated by exactly the same method, including layered oxides,<sup>[36-40]</sup> olivine phosphates.<sup>[10]</sup> NASICON,<sup>[41,42]</sup> vanadyl phosphates,<sup>[16,24]</sup> pyrophosphate,<sup>[11,43]</sup> and sulfate.<sup>[44]</sup> The multiple sodium storage capability of the  $K_{\nu}VOPO_4$  cathode gives it the highest capacity of any of these reported materials, even if there is a minor contribution from the carbon additive; this latter might reduce the contribution from the  $K_{0.36}$ VOPO<sub>4</sub> component to 580 Wh kg<sup>-1</sup>, which is still the highest value in Figure 4. Moreover, the excellent thermal stability of phosphates makes the KVOPO<sub>4</sub> a highly promising candidate for the cathode of a high energy density sodium ion battery, which area is presently dominated by the layered oxides.<sup>[45]</sup>

We have evaluated the stability of the host lattice to multiple intercalation and removal of the sodium ions over both redox couples and just over the upper voltage couple. The results are shown in Figure 5; an average 97 mAh g<sup>-1</sup> were cycled over 400 cycles in the higher voltage regime, and for both redox couples an initial 205 mAh g<sup>-1</sup> slowly decayed to 180 mAh g<sup>-1</sup> for the 100th cycle. These results clearly indicate that the VOPO<sub>4</sub> lattice is very stable, even when multiple ions are repeatedly intercalated and removed. This is without doubt related to the less than 10% change in the lattice volume on reaction, which was measured on ex situ samples (see Figure S6, Supporting Information). As expected removal of potassium causes contraction of the lattice, and as sodium is intercalated the lattice expands. The volume of the hosts KVOPO<sub>4</sub> and K<sub>0.36</sub>VOPO<sub>4</sub> are 106.8 and 103.2 Å3/VOPO4, respectively, and those of  $[Na,K]_1VOPO_4$  and  $[Na,K]_2VOPO_4$  are 104.6 and 112.2 Å<sup>3</sup>/ VOPO<sub>4</sub>, respectively. It is computationally impractical to model the exact composition of K<sub>0.36</sub>Na<sub>x</sub>VOPO<sub>4</sub>, which would require excessively large supercells. Instead, we have simulated  $Na_x VOPO_4$  (x = 0, 1, 2), derived from the fully depotassiated KVOPO<sub>4</sub>, to evaluate the volume change upon sodiation



Figure 4. Energy density comparison of various cathode materials for sodium ion batteries.



**Figure 5.** Discharge and charge capacity of  $K_{0.36}VOPO_4$  in a sodium cell for (top) over both redox couples and (bottom) over the V<sup>5+</sup>/V<sup>4+</sup>. Rate of reaction 0.054 mA cm<sup>-2</sup> (= C/10).







**Figure 6.** a) V K-edge XANES spectra of the  $K_{0.36}$  VOPO<sub>4</sub> electrodes at different discharged states. b) V K-edge XANES spectra of the  $K_{0.36}$ VOPO<sub>4</sub> electrodes at different charged states. c) V K-edge EXAFS spectra of the pristine KVOPO<sub>4</sub> and  $K_{0.36}$ VOPO<sub>4</sub> electrodes at states of discharged to 2.7 V, charged back to 3.7 V. d) V K-edge EXAFS spectra of the  $K_{0.36}$ VOPO<sub>4</sub> electrodes at the original, fully discharged and fully charged back states.

(Figure S7 and Table S9, Supporting Information). The volume changes for the first and second Na insertion into VOPO<sub>4</sub> are  $\approx$ 1.4% and  $\approx$ 8.8%, respectively. This is in excellent agreement with the observed small volume changes of  $\approx$ 1.4% and  $\approx$ 8% after 0.64 and 1.66 Na insertion into K<sub>0.36</sub>VOPO<sub>4</sub>.

The change in valence state of vanadium upon reversible sodiation was tracked by XANES. As illustrated in Figure 6a, starting from the  $K_{0,36}VOPO_4$  after potassium extraction, the pre-edge of the Dis. 3.8 V sample shifts toward lower energy and the high-energy shoulder almost disappears, which indicates the reduction of V<sup>5+</sup> to V<sup>4+</sup> on Na intercalation. As discharged to 2.7 V, the pre-edge became very similar to that of the pristine state in term of energy, indicating a pure V<sup>4+</sup> and approximately one [K+Na] per formula unit in the material, which agrees well with the capacity value. On intercalation of the 2nd Na when discharged to 1.8 V, the V K-edge shifts more toward lower energy and the intensity of the pre-edge region begins to decrease, suggesting the reduction of  $V^{4+}$  to  $V^{3+}$ . With further discharge down to 1.3 V, the V K-edge exhibits the largest shift toward lower energy, while the pre-edge has the lowest intensity with the appearance of a shoulder toward low-energy side of the pre-edge, similar to that of the V<sub>2</sub>O<sub>3</sub> reference. As shown in Figure 6b, the valence state fully reverses back on Na extraction, i.e., the pre-edge continuously shifts toward the higher energy and increased in intensity during the charging. At 4.5 V, the pre-edge again exhibits a  $V^{4+}/V^{5+}$  doublet shape which is almost identical to that of the original  $K_{0.36}VOPO_4$ . The XANES data reveal the reversible redox reaction among  $V^{3+} \leftrightarrow V^{4+} \leftrightarrow V^{5+}$ , which agrees well with the electrochemistry data. The evolution of the vanadium local coordination is revealed by the EXAFS data. Figure 6c shows the EXAFS data of the states with [Na+K]

concentration near one per formula unit (i.e., pristine KVOPO<sub>4</sub>, Dis. 2.7 V, and 2nd Chg. 3.7 V). These spectra have a very close resemblance in terms of both the V–O shell and the V–P/O/V shell. This phenomenon agrees well with the observation in ex situ XRD, which strongly suggests that the first Na occupies the same crystallographic positions emptied by the extracted K. For  $K_{0.36}$ VOPO<sub>4</sub> and the fully charged sample, the spectra exhibits similar outlines but differ in some details (Figure 6d). The two products have slightly different ratio in the intermediate phase. Therefore, the difference in the spectra may result from some change in phase proportion or certain sodium residue after the second charge. The fully discharged sample (i.e., Dis. 1.3) exhibits major structure changes comparing to the pristine and Dis. 2.7 sample.

For more detailed study on the structure evolution upon Na cycling, we focused on the infinite VO<sub>3</sub> chain which is a representative structure unit in vanadyl phosphate. Based on the capacity of the cycling data (i.e., 1.5 Na<sup>+</sup> per formula unit), we simulated a series of  $K_{0.5}Na_xVOPO_4$  (x = 0, 0.5, 1, 1.5) phases with lowest energy by DFT, to investigate the structure change upon the multielectron Na intercalation. The VO<sub>3</sub> chains of the computational phases are shown in Figure S8 of the Supporting Information. Overall the VO<sub>3</sub> chain in the VOPO<sub>4</sub> framework is very stable in shape. With Na intercalated, the asymmetric coordination environment of the V has largely reduced, as the transition from long and short alternated V-O bond length became increasingly homogeneous. It is expected because the conversion from  $V^{5+}/V^{4+}$  to  $V^{3+}$  leads to the diminishing of the vanadyl bonds. As shown in Figure S9 of the Supporting Information, the V–O–V angles decreased from  ${\approx}136^{\circ}{-}142^{\circ}$  for  $K_{0.5}$  to  $\approx 122^{\circ}-125^{\circ}$  for  $K_{0.5}Na_{1.5}$ , indicating that the VO<sub>3</sub> chain



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Figure 7. a) Rate performance of  $K_{0.36}$ VOPO<sub>4</sub> in a sodium cell (C rate = 0.54 mA cm<sup>-2</sup>), and b) voltage profiles of  $K_{0.36}$ VOPO<sub>4</sub> at various rates.

became even more distorted after the multiple sodium ions intercalation. The average V–O bond lengthens slowly between  $K_{0.5}$  and  $K_{0.5}Na_{1.0}$  (1.871–1.901 Å), with rapid changes again between  $K_{0.5}Na_{1.0}$  and  $K_{0.5}Na_{1.5}$  (1.901–1.977 Å). The increase in V–O bond length upon discharge was also observed in other lithium vanadyl phosphate as multiple lithium ions have intercalated into the structure.<sup>[19,35]</sup> The elongated V–O bonds agree with the enlarged dimension of the  $K_{0.5}Na_xVOPO_4$  unit cell upon sodiation.

#### 2.4. Kinetics of Sodium Intercalation

The rate capability of the  $K_{0.36}$ VOPO<sub>4</sub> electrode in a sodium cell is shown in **Figure 7**a. The electrode maintains ~65% of the reversible capacity as the current density increases from C/20 to 1 C rate. Figure 7b displays the voltage profiles of the electrode at various rates. It can be clearly seen that the high voltage (i.e., 2.7–4.5 V) capacity decays more slowly than the low voltage (i.e., 1.3–2.7 V) capacity, suggesting slower kinetics for the 2nd Na intercalation. The diffusion coefficients were determined by performing CV scans at different rates (shown in Figure S10, Supporting Information). The values were calculated to be  $9.6 \times 10^{-12}$  cm<sup>2</sup> s<sup>-1</sup> for the 1st Na and  $4.7 \times 10^{-12}$  cm<sup>2</sup> s<sup>-1</sup> for the 2nd Na, which again indicated the more sluggish diffusion for the 2nd Na ion.

The kinetics of sodium diffusion in the KVOPO<sub>4</sub> structure was calculated using climbing-image nudged elastic band (CI-NEB) method for a single Na<sup>+</sup> ion in a potassium-free host lattice. **Figure 8**a shows the three percolating 1D Na<sup>+</sup> migration paths, which are labeled 1)  $F \rightarrow D \rightarrow A \rightarrow B \rightarrow G$  along *c* direction ( $F \rightarrow D$  is equivalent to  $A \rightarrow B$ ;  $B \rightarrow G$  is equivalent to  $D \rightarrow A$ ), 2)  $C \rightarrow A \rightarrow B$  along *a* direction, and 3)  $E \rightarrow A \rightarrow D$  along *b* direction. The corresponding Na<sup>+</sup> migration barriers are 204, 364, and 451 meV, respectively, as shown in Figure 8b–d. Based on these results we conclude that the lowest barriers of 1D, 2D,



**Figure 8.** a) Investigated distinct single  $Na^+$  migration paths in fully depotassiated VOPO<sub>4</sub>, where the green and yellow spheres denote symmetrically distinct K sites in KVOPO<sub>4</sub>. b–d) Single  $Na^+$  migration barriers of the three distinct percolating paths in fully depotassiated VOPO<sub>4</sub>.



and 3D Na diffusion are, respectively, 204, 364, and 451 meV. This suggests that the VOPO<sub>4</sub> is an anisotropic 3D Na<sup>+</sup> conductor; i.e., the Na<sup>+</sup> ions migrate most easily down the hexagonal tunnels. We have also estimated the bottleneck size, which is defined as the radius of the largest free sphere that can pass through each diffusion pathway using the open source Zeo++ software.<sup>[46,47]</sup> The associated bottleneck sizes for paths  $F \rightarrow D \rightarrow A \rightarrow B \rightarrow G$ ,  $C \rightarrow A \rightarrow B$  and  $E \rightarrow A \rightarrow D$  are estimated to be 1.98, 1.75, and 1.55 Å, respectively, which are negatively correlated to the computed barriers. These bottleneck sizes are comparable to that in the layered  $\alpha_{I}$ -NaVOPO<sub>4</sub>, which similarly shows more facile Na<sup>+</sup> diffusion compared to the  $\varepsilon$  and  $\beta$  polymorphs.<sup>[48]</sup> In addition, the energy barrier of the lowest 1D percolating path is very close to that in the Na-ion conductor  $\beta$ -Al<sub>2</sub>O<sub>3</sub> and layered Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> ( $\approx$ 0.19 eV), and the Li-ion diffusion barrier of  $\approx 0.1 - 0.3$  eV in the 1D-conductor Li<sub>x</sub>MPO<sub>4</sub>.<sup>[49-51]</sup>

#### 2.5. Multielectron Storage Capability in Other Alkali-Ion Batteries

As described above, the KVOPO<sub>4</sub> structure can intercalate Na<sup>+</sup> ions to a capacity equal to two alkali ions per vanadium ion. One would expect this structure to be also capable of intercalating a number of other cations, including lithium and potassium and perhaps even ammonium. We do not expect it to readily intercalated divalent cations, such as magnesium and calcium because of the anticipated very low diffusion coefficients of these ions and their tendency to react by a conversion mechanism. CV curves (Figure S11, Supporting Information) indicate that both vanadium redox couples are active, suggesting that both lithium and potassium can be intercalated in excess of one cation into K<sub>0.36</sub>VOPO<sub>4</sub>. For Li ions, the low featured CV and low capacity of 200 mA g<sup>-1</sup> suggest that the tunnels in this structure are too large; the smaller volume  $\varepsilon$ - and related VOPO<sub>4</sub> lattices are a better structural fit. The KVOPO<sub>4</sub>based cathode can store 1.50 Li<sup>+</sup> or 1.54 K<sup>+</sup> per formula unit within a full voltage window. Paralleling with our study, Chihara et al.<sup>[25]</sup> also tested the potassium storage behavior of KVOPO<sub>4</sub> in a potassium cell, but only for the one-electron potassium storage. The result shows that  $\approx 0.55$  K<sup>+</sup> per formula unit can be achieved, which agrees well with our capacity value in a similar voltage region (2-4.6 V vs K/K<sup>+</sup>). Whereas our data prove the KVOPO<sub>4</sub> lattice is accessible for the accommodation of the second K<sup>+</sup>. Therefore, the KVOPO<sub>4</sub> compound can be a universal multielectron cathode for insertion and release alkali metal (e.g., Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) ions.

# 3. Conclusion

In summary, we prepared a novel KVOPO<sub>4</sub> cathode that delivers a very promising multielectron charge storage in a sodium ion battery. The V<sup>3+</sup>  $\leftrightarrow$  V<sup>5+</sup> redox couple in the vanadyl phosphates was for the first time activated, intercalating 1.66 sodium ions per formula unit intercalation reaction. Structural characterization including X-ray absorption spectroscopy, ex situ XRD revealed the highly reversible evolution of the polyhedron framework with a small volume change upon multiple sodium intercalation/extraction. The multielectron reaction and the small volume change enabled the discharge capacity of over 200 mAh  $g^{-1}$  for this phosphate-based compound with excellent capacity retention upon extended cycling. This capacity combined with an average voltage of 2.56 V delivers an energy density of over 600 Wh kg<sup>-1</sup>, which exceeds that of the current sodium ion battery intercalation cathodes. Moreover, both rate capabilities and DFT calculations indicate that the sodium diffusion kinetics within the unique wide-open vanadyl phosphate framework are quite facile, which could yield a high power cathode.

## 4. Experimental Section

The KVOPO<sub>4</sub> compound was synthesized via a one pot solid state reaction. The precursor was prepared by planetary ball milling stoichiometric amounts of K<sub>2</sub>CO<sub>3</sub> (Sigma-Aldrich, ≥99%), NH<sub>4</sub>VO<sub>3</sub> (Sigma-Aldrich, ≥99%), and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (Sigma-Aldrich, ≥99.99%) for 4 h. The obtained fine powder was pressed into pellets with ≈50 mg for each. The solid state reaction was conducted at 700 °C for 10 h in helium atmosphere. The heating rate was 4 °C min<sup>-1</sup>. Before the electrochemistry test, the pristine KVOPO<sub>4</sub> powder was further high energy ball milled together with graphene nanoplatelets (Sigma-Aldrich, Grade C) in a mass ratio of 7:2 for 6 min. The obtained KVOPO<sub>4</sub>/carbon composite was used as active cathode material for the electrochemical tests.

Details of electrochemical measurements, characterization, and computational methods are included in the Supporting Information.

# **Supporting Information**

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

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## **Conflict of Interest**

The authors declare no conflict of interest.

### Keywords

high capacity, high energy, multielectron, sodium ion batteries, vanadyl phosphate

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