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Mixed anion chemistry as a way to tune the electrochemical properties of vanadium oxyfluoride phosphates in alkali-ion batteries

Romain Wernert†‡Δ, Long H.B. Nguyen†Δ, Dany Carlier†Δ||, Laurence Croguennec†Δ||*

AUTHOR ADDRESS
† Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France
‡ ICGM, Université de Montpellier, CNRS, ENSCM, 34095 Montpellier, France
Δ RS2E, Réseau Français sur le Stockage Electrochimique de l’Energie, FR CNRS #3459, Amiens F-80039 Cedex 1, France
|| ALISTORE-ERI European Research Institute, FR CNRS 3104, F-80039 Amiens Cedex 1, France
* corresponding authors

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ABSTRACT
Alkali vanadium fluoride phosphates such as Tavorite LiVPO₄F, Na₃V₂(PO₄)₂F₃ and KTP-type KVPO₄F are attractive materials for positive electrodes in rechargeable alkali-ion batteries. In such compounds, the presence of fluoride ions further increases the electrode’s electrochemical potential compared to their phosphate counterparts such as Na₃V₂(PO₄)₃. Furthermore, the fluoride anions in these structures can be fully or partially substituted by oxide anions, leading to the formation of V⁴⁺=O vanadyl centres and a great number of mixed valence and mixed anion compositions. The oxygen substitution for fluorine has a considerable impact on the structural, electronic, and electrochemical properties of the resulting compounds. In this review, the similarities and peculiarities in the crystal structures, electronic structures, and electrochemical properties of the three analogous LiVPO₄F–LiVPO₄O, Na₃V₂(PO₄)₂F₃–Na₃V₂(PO₄)₂O₂, and KVPO₄F–KVPO₄O material families will be compared in detail. Such a comparison is expected to provide an insightful understanding on the factors governing the structure and properties of vanadium oxyfluoride phosphates.
INTRODUCTION

Vanadium phosphates are well known for their extensive crystal chemistry, owing to the variety of oxidation states and coordination polyhedra that vanadium can adopt. Among these compounds, $V^{3+}$ and $V^{4+}$ containing phosphates are of particular interest to be used as materials for positive electrode in rechargeable alkali-ion batteries. Despite the density and weight penalty of “large and heavy” PO$_4$ groups, phosphates remain attractive materials due to the stability of their frameworks (for long range cycling and safety issues) and the increased potential of a given $M^{n+}/M^{(n+1)+}$ redox couple compared to their oxide counterparts. The first vanadium phosphate possessing great electrochemical interests, Na$_3$V$_2$(PO$_4$)$_3$, was reported in 1978. This compound belongs to a structural family that is widely known as NASICON (Na Super Ionic CONductor). Following the booming of material research from the late 1990s, several vanadium fluoride phosphates, including LiVPO$_4$F, NaVPO$_4$F, Na$_3$V$_2$(PO$_4$)$_2$F$_3$, and KVPO$_4$F were discovered; however, their applications as electrode materials for rechargeable alkali-ion batteries have just been reported in recent years. Comparing to their phosphate counterparts, the fluoride phosphate materials can offer a higher redox potential, which is beyond other different frameworks, mainly assigned to the inductive effective of F-. For instance, a redox potential difference up to 0.5 V is observed in the case of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ vs. Na$_3$V$_2$(PO$_4$)$_3$ (Figure 1b) which improves the energy density of the former by 26% compared to the latter. Such an increase in the redox potential can partially compensate for the capacity loss due to weight penalty of polyanion materials and hence allow vanadium phosphates to compete with layered oxide in terms of energy density.

In parallel to these trivalent vanadium fluoride phosphates, there exist homeotypic oxide phosphate compositions, i.e. LiVPO$_4$O, Na$_3$V$_2$(PO$_4$)$_2$FO$_2$, and KVPO$_4$O, which can also be used as positive electrode materials in batteries. In these oxide phosphates, F$^-$ is replaced by O$_2^-$, and all the vanadium ions present in the structure thus exist as $V^{4+}$ to maintain the charge neutrality. Besides these fluoride and oxide phosphate end members, partially substituted oxyfluoride phosphates, such as LiVPO$_4$F$_{0.45}$O$_{0.55}$, were also reported in the literature. Such a substitution can occur on all labile fluorine sites in the structure leading to an infinite number of compositions that differ in F/O content; nonetheless, well-controlled anionic stoichiometries can only be obtained from syntheses carried out under inert atmosphere. Even though the F/O substitution occurs only on the anionic framework, a significant impact might be observed on the atomic and electronic structure, alkali ion distribution, and thus structural, redox and diffusion mechanisms involved upon cycling, and more generally on the electrochemical properties in batteries. Throughout this review, three prominent vanadium fluoride phosphates, i.e. LiVPO$_4$F, Na$_3$V$_2$(PO$_4$)$_2$F$_3$, and KVPO$_4$F, will be discussed in detail to highlight the
impact of oxygen substitution for fluorine in each case and how it can be used to control the electrochemistry of vanadium fluoride phosphates. The Tavorite type NaVPO₄F derived materials obtained by a high temperature solid state synthesis were shown earlier to provide limited interest as positive electrode materials due to the low mobility of Na⁺ ions and will hence be excluded from this work.¹⁴

**CRYSTAL STRUCTURES**

LiVPO₄F, Na₃V₂(PO₄)₂F₃ and KVPO₄F are undoubtedly the most well-studied vanadium fluoride phosphates. These compounds can be obtained by a direct synthesis between the alkali fluoride AF (A = Li, Na, K) and vanadium phosphate, VPO₄, in the right stoichiometry under inert atmosphere. These compounds crystallise in three different structural types as shown in **Figure 2**. Despite the difference in their long-range structures, they are constructed based on the same structural building units, *i.e.* VO₄F₂ octahedra and PO₄ tetrahedra. The stoichiometry (AVPO₄F or A₁.₅VPO₄F₁.₅) and the radius of the alkali ion (0.76, 1.02 and 1.38 Å for Li⁺, Na⁺ and K⁺ respectively) are indeed the key factors determining the thermodynamic stability of the phase formed during the synthesis.

LiVPO₄F belongs to the triclinic (*P̅1*) Tavorite structural type and shows a zigzag quasi-1D diffusion pathway for Li⁺ ions.⁵,⁶ The fluorine atoms in the VO₄F₂ unit are localized in the apical positions and these *trans*-VO₄F₂ units are connected via F-corner sharing to form infinite chains of [F–VO₄F–F]ₙ running parallel to each other and connected by PO₄ tetrahedra (**Figure 2**). The crystal structure of Na₃V₂(PO₄)₂F₃ is often falsely claimed as being NASICON, although they share no crystal features in common: the lantern unit typical of NASICON structure (VO₆)₂(PO₄)₃ are not observed in Na₃V₂(PO₄)₂F₃.¹⁵–¹⁷ The crystal structure of Na₃V₂(PO₄)₂F₃ (*Amam*) is also built up from *trans*-VO₄F₂ units; however, the vanadium unit extension is only limited to FO₄V–F−VO₄F₂ biocahedra aligned along the c direction and maintained together by PO₄ groups in the (*a*, *b*) plane (**Figure 2**). Na₃V₂(PO₄)₂F₃ shows a quasi-2D diffusion pathway for Na⁺ ions.⁷,¹⁸ Finally, KVPO₄F crystallises in the non-centrosymmetric KTiOPO₄ (KTP) type structure (*Pna₂*) and shows a quasi-1D diffusion pathway for diffusion of K⁺ ions.⁸,⁹ Although the stoichiometry is analogous to Tavorite type LiVPO₄F, the structure is very different and should not be confused. The KTP structure features also chains of F-corner sharing VO₄F₂ octahedra; however, the fluorine positions on two adjacent VO₄F₂ units are alternating between *cis* and *trans* configurations, and the connection between these [VO₄F₂]ₙ chains is also ensured by PO₄ groups (**Figure 2**). Despite differences in the three crystalline structures, the V³⁺ local environment is in all cases quasi-symmetric with all the V³⁺–X bonds length (X = F or O) almost identical (~ 1.98 Å) regardless the nature of the ligand.
Figure 2: Comparison of the crystal structures of Tavorite-type LiVPO₄(F,O), Na₃V₂(PO₄)₂F(F,O)₂ and KTP-type KVPO₄(F,O). The topology and the connectivity of the vanadium polyhedra are shown below each crystal structure.

The corresponding vanadium oxide phosphates LiVPO₄O, Na₃V₂(PO₄)₂FO₂, and KVPO₄O can be obtained from the syntheses using V³⁺-containing precursor together with a stoichiometric amount of oxidant, e.g. VOPO₄, or combining V⁵⁺-containing precursor with an appropriate reduction. The structures of these V⁴⁺ oxide phosphates are closely related to their fluoride phosphate counterparts with all (or some) of the fluorine positions now occupied by oxygen. LiVPO₄O also crystallises in the Tavorite structure; however, along the [O−VO₄−O]∞ chains the V−O distances alternate between a short (~ 1.67(3) Å) and a long (~ 2.19(2) Å) one. Similarly, in KVPO₄F all the fluorine sites (with cis and trans configurations) can be replaced by oxygen to obtain KVPO₄O. An alternating between short (~ 1.66 Å) and long (~ 2.11 Å) V−O bonds is only observed on the trans sites. On the cis sites, a shortened V−O bond (~ 1.66 Å) is evident, but no elongation is detected (Figure 2): all the other five V−O distances are similar (~ 2.01 Å). In Na₃V₂(PO₄)₂F₃, there exist two different fluorine sites in the FO₄V−F−VO₄ biooctahedron; however, only the one corresponding to the outer apical site can be replaced by oxygen to generate the homologue Na₃V₂(PO₄)₂FO₂. In the O−VO₄−F unit the V−O bond is shortened to ~ 1.62 Å while the opposite V−F bond is elongated to ~ 2.11 Å, in comparison to ~ 1.98 Å in Na₃V₂(PO₄)₂F₃.

When moving from fluoride phosphates to oxide phosphates, all V³⁺ in the structure are oxidised into V⁴⁺ to maintain the charge neutrality. Furthermore, the V⁴⁺ is shifted out of the centre of the VO₆ octahedron that lowers the local symmetry of the vanadium site from “quasi”-O₈ to C₄v.¹⁹ This local structural distortion leads to two important consequences: (i) the t₂g (dₓz, dᵧz, and dₓz) levels of V⁴⁺ are split into two groups ε (dₓz, dᵧz) and b₂ (dₓz), and (ii) the π-bonding interaction that stabilises the occupied nonbonding O 2p states is enhanced due to the shorter distance between the vanadium center and the apical oxygen. The distorted V⁴⁺O₆ octahedron is more energetically favourable than the non-distorted one thanks to the energetic stabilisation of (i) occupied dₓz states of V⁴⁺ and (ii) occupied nonbonding O 2p states. The short V−O bond (~ 1.66 Å) detected in all vanadium oxide phosphates involves a strong σ and a strong π interaction. This chemical bond is widely known as
“vanadyl” bond or V=O. As the vanadyl bond becomes highly covalent, the V−O bond opposite to it becomes highly ionic with an elongated distance up to ~2.19(2) Å. This antagonist behaviour is observed in LiVPO₄O, Na₃V₃(PO₄)₂FO and for the trans-VO₆ site in KVPO₄O. For the cis-VO₆ site in KVPO₄O, the O ions of the V−O bond opposite to V=O is engaged in a P-O bond, which prevents a full elongation.

A particular feature of these vanadium fluoride/oxide phosphates is the existence of the mixed oxyfluoride phosphate compositions, i.e. LiVPO₄F₁₋ₓOₓ (0 < x < 1), Na₃V₃(PO₄)₂FₓO₁₋ₓ (0 < x < 2) and KVPO₄F₁₋ₓOₓ (0 < x < 1). Depending on the oxidation state of vanadium in the precursors, these compositions can be obtained by introducing a certain amount of oxidant or reductant during the synthesis process. Nonetheless, the main challenge in the synthesis of these compounds is the accurate control of the F/O content, which greatly depends on the nature of the precursors and the reaction conditions. Using diffraction techniques, Na₃V₃(PO₄)₂FₓO₁₋ₓ (0 ≤ x ≤ 2) and KVPO₄F₁₋ₓOₓ (0 ≤ x ≤ 1) are determined to form a complete solid solution with a linear evolution in the cell parameters (a, b, and c) over the full range of F/O content, implying that F and O are randomly distributed on the mixed anionic sites. On the other hand, the cell parameters of Tavorite LiVPO₄F₁₋ₓOₓ (0 ≤ x ≤ 1) deviate significantly from the Vegard’s law (Figure 3a). The reason behind this deviation is the segregation of VO₆ units upon oxygenation, which could be detected using X-ray diffraction but fully explained by solid state nuclear magnetic resonance (ss-NMR) spectroscopy as illustrated in Figure 3b.

As the oxygen substitution for fluorine can occur on the full range of compositions, an accurate determination of the F/O content is essential to establish the relationship between the composition and the physicochemical properties of the materials, as well as to be able to propose a synthesis process with the ability to finely tune the composition. Due to similarity in their X-ray and neutrons scattering factors, a direct probing of F⁻ and O²⁻ by diffraction techniques is not possible. As the Vegard’s law is observed for Na₃V₃(PO₄)₂FₓO₁₋ₓ (0 ≤ x ≤ 2) and KVPO₄F₁₋ₓOₓ (0 ≤ x ≤ 1), the cell parameters of references, such as the end members, can be used to establish calibration curves and determine the x value in a new composition. Energy dispersive X-ray spectroscopy (EDX) can also be used to obtain an approximative value of the F/O content; however, it should be kept in mind that this technique is not accurately quantitative for light elements and a suitable reference is usually required. Electrochemical methods such as F⁻ ion-selective electrode can also be used provided a considerable amount of powder is available.
As discussed above, oxygen substitution for fluorine in these structures induces the formation of vanadyl bonds (\(V^{3+}=O\)). The stretching modes of these vanadyl bonds are active on both infrared (IR) and Raman spectroscopies, with an intense signal usually observed at \(-900\ \text{cm}^{-1}\).\(^{26}\) In IR spectroscopy, this vibrational band slightly overlaps with the bands of P−O stretching modes in PO\(_4\) group; however, the activity of P−O stretching bands is greatly reduced in Raman spectroscopy, and thus the visibility of V=O band is enhanced significantly.\(^{27}\) Either IR or Raman spectroscopy is employed, the intensity of V=O stretching band increases gradually with the O-substitution rate in all LiVPO\(_4\)F\(_1\).\(_y\)O\(_y\), Na\(_3\)V\(_2\)PO\(_4\)F\(_{3.5}\)O\(_{0.5}\), and KVPO\(_4\)F\(_1\).\(_y\)O\(_y\) (as highlighted in Figure 4a for Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\).\(_y\)O\(_y\)), which is an effective and rapid probe for the existence of O-substitution in the structure.

When O-substitution occurs, V\(^{3+}\) is simultaneously oxidised into V\(^{4+}\) for charge compensation. The extent of the F/O substitution can thus be deduced from the V\(^{3+}/V^{4+}\) ratio. Vanadium K-edge X-ray absorption spectroscopy (XAS) is a technique that can directly access the local environment and oxidation state of vanadium species in the structure. Every X-ray absorption near edge structure (XANES) spectrum can be divided into the pre-edge and edge regions. The signal in the pre-edge region is generated from the transitions of vanadium 1s core states to its empty 3d states, which are only allowed in non-centrosymmetric environments, \(i.e.\) V\(^{4+}\) involved in the vanadyl bond. The intensity of this signal is directly proportional to the amount of substituted O in the structure (as highlighted in Figure 4b for KVPO\(_4\)F\(_1\).\(_y\)O\(_y\) as well as in Figure 4c where each oxygen rich end-member displays a very intense pre-edge), which can be used as qualitative probe for the presence of vanadyl bonds, as in the case of IR or Raman spectroscopy. The edge signal originates from the allowed 1s → 4p transitions, and its position is closely related to the oxidation state of the vanadium species. The edge position will shift to higher energies in higher oxidation states, which will help to determine the average oxidation state of vanadium, and thus the V\(^{3+}/V^{4+}\) and F/O ratios for a given composition. Nonetheless, the edge energy is also dependent on the vanadium’s surrounding environment, and in the best scenario, some standards of similar crystal structure are required to establish a calibration curve (Figure 4b). This technique can be precise to c.a. 5% but is not relevant for very small substitution rates.

These material families contain several easily accessible NMR active nuclei (\(^{6}Li\), \(^{19}F\), \(^{23}Na\), \(^{31}P\), and \(^{51}V\)), which can be investigated to provide insightful information on the local environments in the structure.\(^{13,21,24,28-31}\) Among them, \(^{31}P\) ss-NMR is widely studied and can reveal similarities and differences between these crystal structures at the atomic scale. The phosphorus atoms in these structures are tetrahedrally coordinated with four neighbouring vanadium octahedra giving rise to the P(OV)\(_4\) sub-units. As all the compounds in these three material families contain paramagnetic ions, \(i.e.\) V\(^{3+}\) and/or V\(^{4+}\), the Fermi contact would be the dominant interaction leading to highly shifted \(^{31}P\) NMR resonances. Experimental work coupled with theoretical modelling have shown that the magnitude of \(^{31}P\) NMR shifts in these three systems depends significantly on the distribution of V\(^{3+}/V^{4+}\) in the P(OV)\(_4\) sub-unit, and the spin transfer pathway between vanadium ions and the phosphorus nucleus. Other parameters, such as torsion angle, V−P distance, V/P−O bond length, thus also play a role as they directly impact the spin transfer pathway. In LiVPO\(_4\)F\(_1\).\(_y\)O\(_y\) and KVPO\(_4\)F\(_1\).\(_y\)O\(_y\), well-defined \(^{31}P\) ss-NMR resonances corresponding to P(OV\(_3\))\(_4\) and P(OV\(_4\))\(_4\) are observed for V\(^{3+}\) and V\(^{4+}\)-containing end members. The \(^{31}P\) resonances in LiVPO\(_4\)F and KVPO\(_4\)F are greatly shifted compared to their oxide phosphate counterparts as V\(^{3+}\) possesses two unpaired electrons versus only one for V\(^{4+}\) and thus the Fermi contact in P(OV\(_3\))\(_4\) is stronger than P(OV\(_4\))\(_4\), as quantified in Table 1.\(^{13,21}\) When the O-substitution occurs, new resonances corresponding to P(OV\(_3\))\(_3\)(OV\(_4\)), P(OV\(_3\))\(_2\)(OV\(_4\))\(_2\), and P(OV\(_3\))(OV\(_4\))\(_3\) local environments emerge. Nevertheless, these new resonances are rather broad leading to significant overlapping and preventing a clear deconvolution of the signals. The same scenario is observed for Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\).\(_y\)O\(_y\); however, all the \(^{23}Na\) and \(^{31}P\) NMR resonances in this system are well separated, and thus the relative ratio between all local environments can be deduced when the acquisition is performed in quantitative conditions.\(^{21}\) Despite still difficult sometimes to be interpreted, \(^{19}F\) ss-NMR is interesting to be studied.\(^{21,32}\) In Tavorite structure, fluorine nuclei are surrounded by two vanadium ions in the [F−VO\(_x\)−F\(_x\)] chains. Theoretically, when substituted by oxygen for fluorine, a statistical distribution of O/F in oxyfluoride LiVPO\(_4\)F\(_1\).\(_y\)O\(_y\) (0 < y < 1) should lead to two different fluorine local environments, \(i.e.\) V\(^{3+}\)−F−V\(^{3+}\) and V\(^{3+}\)−F−V\(^{4+}\); in fact, only the V\(^{3+}\)−F−V\(^{3+}\) environment
is experimentally detected showing that substituted oxygens in Tavorite structure are not randomly distributed, but segregated into O-rich domains next to F-rich domains.\textsuperscript{21,33}

Table 1: \textsuperscript{31}P MAS NMR Fermi contact shifts for end member compounds of the LiVPO$_4$F$_{1-y}$O$_y$, Na$_3$V$_2$(PO$_4$)$_2$F$_3$-$y$O$_y$ and KVPO$_4$F$_{1-y}$O$_y$ compounds.

<table>
<thead>
<tr>
<th>Site</th>
<th>LiVPO$<em>4$F$</em>{1-y}$O$_y$</th>
<th>Na$_3$V$_2$(PO$_4$)$_2$F$_3$-$y$O$_y$</th>
<th>KVPO$<em>4$F$</em>{1-y}$O$_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$^{3+}$-F</td>
<td>P(1) 4000</td>
<td>P(1) 6000</td>
<td>P(1) 5800</td>
</tr>
<tr>
<td>V$^{4+}$-O</td>
<td>1600</td>
<td>0</td>
<td>2000</td>
</tr>
</tbody>
</table>

Figure 4: a) FTIR spectra of Na$_3$V$_2$(PO$_4$)$_2$F$_3$-$y$O$_y$ b) V K-edge XAS of KVPO$_4$F$_{1-y}$O$_y$ adapted with permission from ref\textsuperscript{13} Copyright 2022 American Chemical Society, and c) V K-edge XAS of oxygen-rich and fluorine-rich end-members in LiVPO$_4$F$_{1-y}$O$_y$, Na$_3$V$_2$(PO$_4$)$_2$F$_3$-$y$O$_y$ and KVPO$_4$F$_{1-y}$O$_y$.

A detailed comparison of these three systems has shown that the O-substitution has a great impact on the average and local structures of the materials. Regardless of the nature of the system, the O-substitution leads to the formation of distorted vanadium sites and highly covalent vanadyl bonds. The presence of these vanadyl bonds can be easily evaluated using vibrational spectroscopy or the pre-edge signature on the V K-edge XANES spectra. Despite these similarities, those systems exhibit subtle differences in the F/O distribution and the local environments of other atoms. In LiVPO$_4$F$_{1-y}$O$_y$, the O/F atoms are not randomly distributed along the chains, but segregated at the local scale. This behavior results in a deviation from the Vegard’s law when examining the cell parameters, and thus V K-edge XAS is more informative to determine the F/O content in the structure. For Na$_3$V$_2$(PO$_4$)$_2$F$_3$-$y$O$_y$ and KVPO$_4$F$_{1-y}$O$_y$, the Vegard’s law is obeyed, and thus the use of diffraction techniques together with some standard samples would suffice to obtain reliable F/O content. Finally, each member in the Na$_3$V$_2$(PO$_4$)$_2$F$_3$-$y$O$_y$ family gives rise to distinct and well-defined signatures on $^{23}$Na and $^{31}$P ss-NMR that can be easily deconvoluted and used in the compositional determination. With the accurate determination of the chemical formula, those materials can now be tested in different applications to understand the impact of O-substitution on the properties of the materials. In the context of this review, only the electrochemical properties will be further discussed.
ELECTROCHEMICAL PROPERTIES

All the compositions in the three systems are electroactive and can be used as positive electrode materials for alkali ion rechargeable batteries. Even though the host structures are quite versatile and one material might be used in different battery technologies, the following discussions will be limited in the case where the mobile ion is the same as in the host structure.

Figure 5: a-c) Comparison of the galvanostatic electrochemical curves of LiVPO₄,F(O), Na₃V₂(PO₄)₂(F,O)₂ and KVPO₄(F,O) cycled versus their respective alkali metal counter electrode at a C/20 current rate. d) Comparison of the electrochemical curves of KVPO₄F vs. K metal, NaVPO₄F obtained by ion exchange from KTP type NH₄VPO₄F vs Na metal, and Na₃V₂(PO₄)₂F₃ vs Na metal reference vs NHE.

All members in the LiVPO₄,F₁−yOₙ series can allow the reversible extraction and re-insertion of one Li⁺ per formula unit in the voltage range of 3.0 − 4.5 V vs Li⁺/Li (Figure 5a). The presence of the flat voltage plateau implies that the delithiation process would occur through biphasic reaction for all compositions. However, meticulous operando diffraction measurements disclosed complicated electrode reaction mechanisms: (i) two successive biphasic reactions together with the formation of Li₂/₃VPO₄F as intermediate phase is detected in charge for LiVPO₄F and an asymmetric reaction in discharge with a single biphasic reaction,35 (ii) a single reversible biphasic reaction is observed for LiVPO₄O, and (iii) successively and reversibly, one monophasic and two biphasic reactions for all partially O-substituted LiVPO₄,F₁−yOₙ. The complexity in the reaction mechanism of partially substituted phases is the existence of the different F- and O-rich domains, inducing local inhomogeneous delithiation at the atomic scale. In LiVPO₄F, all the redox centres are V³⁺−F and they are oxidised into V⁴⁺−F during delithiation. When O-substitution occurs, V⁴⁺=O centres are generated, which are
further oxidised into \( V^{4+} = O \) upon delithiation. In \( \text{LiVPO}_4 \text{F}_1 \text{yO}_y \), \( V^{4+} = O \) is oxidised at a lower potential than \( V^{3+} = F \), which can be explained by the "reverse inductive effect" due to the difference in the covalent \( V^{4+} = O \) bonds compared to ionic \( V^{3+} = F \). Consequently, the redox potential of the material will shift to lower value when the O-content increases, ultimately reaching a difference of -0.3 V for \( \text{LiVPO}_4 \text{O} \) compared to \( \text{LiVPO}_4 \text{F} \).

A similar situation is also observed for \( \text{Na}_3 \text{V}_2(\text{PO}_4)_2 \text{F}_3 \text{yO}_y \) (Figure 5b) with the exchange of one electron per vanadium redox centre upon charge and discharge of the battery. For the two end members, the presence of two main plateaus indicates biphase reactions upon charge and discharge. Operando diffraction/spectroscopy measurements coupled with theoretical calculations reveal that the voltage jump at \( \text{Na}_3 \text{V}_2(\text{PO}_4)_2 \text{F}_3 \) and \( \text{Na}_3 \text{V}_2(\text{PO}_4)_2 \text{F}_2 \text{O}_2 \) corresponds to the \( V^{3+}/V^{4+} \) charge ordering on the bioctahedral units in the structure while several \( \text{Na}^- \) vacancy orderings are detected for other key compositions, but with much smaller voltage jumps. The voltage jump due to charge ordering on the octahedra is still obvious in partially O-substituted phases.\(^{18,16,24,26} \) Furthermore, the \( V^{4+} = O \) redox centres in \( \text{Na}_3 \text{V}_2(\text{PO}_4)_2 \text{F}_3 \text{yO}_y \) are oxidised at a potential that is slightly lower than that of \( V^{3+} = F \) (down by 0.1 V for the fully oxygenated end-member). Increasing the substitution rate will lower the redox potential, but it is not as important as in \( \text{LiVPO}_4 \text{F}_1 \text{yO}_y \). Due to a small difference in their activation potential, \( V^{4+} = O \) and \( V^{3+} = F \) are oxidised simultaneously in partially O-substituted compositions.

In \( \text{KVPO}_4 \text{F}_1 \text{yO}_y \) (Figure 5c), the number of exchanged electrons is slightly less than one per vanadium ion in batteries versus K metal. However, the redox potential in those materials is so high that an upper cut-off voltage of 5.0 V vs K+/K is required, and the limited number of electrons exchanged is a limitation of the employed electrolyte.\(^{37} \) The voltage--composition curve of \( \text{KVPO}_4 \text{F} \) is dominated by four different K\(^+\)--vacancy orderings.\(^{23} \) Furthermore, the voltage jump at \( \text{K}_{0.3} \text{VPO}_4 \text{F} \) is assigned to the change in the vanadium site that participates in the redox reactions: whereas \( \text{LiVPO}_4 \text{F} \) and \( \text{Na}_3 \text{V}_2(\text{PO}_4)_2 \text{F}_3 \text{O}_y \) only possess \( \text{trans} \) VO\(_4\)F\(_2\) sites, the KTP structure features a \( \text{cis} \) and a \( \text{trans} \) VO\(_4\)F\(_2\) site and it was demonstrated that the \( \text{cis}-\text{VO}_4\)F\(_2\) sites are preferentially oxidised when K\(^+\) is deintercalated up to the composition \( \text{K}_{0.3} \text{VPO}_4 \text{F} \), and that further K\(^+\) removal leads to the oxidation of \( \text{trans}-\text{VO}_4\)F\(_2\).\(^{38} \) Contrary to previous observations made for the two other systems, the \( V^{4+} = O \) redox centres in partially O-substituted \( \text{KVPO}_4 \text{F}_1 \text{yO}_y \) are oxidised after \( V^{3+} = F \). Furthermore, the redox potential of \( \text{KVPO}_4 \text{O} \) is even higher than that of \( \text{KVPO}_4 \text{F} \).

In all three systems, the substitution of O for fluorine has a great impact on the redox mechanism involved upon cycling. In \( \text{LiVPO}_4 \text{F}_1 \text{yO}_y \) and \( \text{Na}_3 \text{V}_2(\text{PO}_4)_2 \text{F}_3 \text{yO}_y \), O-substitution results in the formation of \( V^{4+} = O \) redox centres which oxidised at (slightly) lower potentials, shifting down the whole redox potential of the material; however, reverse behaviour is observed for \( \text{KVPO}_4 \text{F}_1 \text{yO}_y \). Furthermore, in a recent study, \( \text{NaVPO}_4 \text{F} \), synthesised through an ion exchange from KTP type \( \text{NH}_4 \text{VPO}_4 \text{F} \), has revealed an electrochemical signature (\( i.e. \) number of exchanged electrons per vanadium and voltage-composition curve) completely different from \( \text{KVPO}_4 \text{F} \) (Figure 5d).\(^{34} \) Indeed, depending on the ionic radii of the alkali ion, different alkali-vacancies orderings are stabilized during the alkali deintercalation in order to mitigate the electrostatic repulsions between them: it appears that the bigger the alkali ion is, the more phase transitions are observed upon charge and discharge, as also demonstrated for \( \text{A}_x \text{MO}_2 \) layered oxides. Furthermore, it can be seen on Figure 6 that the average electrochemical potential of all the fluoride rich composition is nearly identical (1.4 V vs NHE) whereas there is a large variation for the three vanadyl phosphates. It is yet unclear whether this is really due to a size effect of the \( \text{A}^+ \) cations, but a sensible explanation would be that the topology of the shortened V=O and elongated V—O bonds matters a lot (Figure 2) as it has a huge influence on the V−V distances and the Coulombic interaction that results.

Playing with the anionic chemistry is one of the routes explored to develop high voltage electrode materials for high energy density alkali ion batteries. As discussed here, this substitution leads to the formation of highly covalent vanadyl type V=O bonds and it appears that the electrode reactions are highly reversible if \( V^{3+} \) ions (when formed) are localized in these sites that can be distorted thanks to the presence of vanadyl type V=O bonds. All the polyanionic materials mentioned here are thus promising as alternative high energy density materials for Li, Na and K-ion batteries, \( i.e. \) with \( \text{LiVPO}_4(\text{F,O}) \), \( \text{Na}_3 \text{V}_2(\text{PO}_4)_2(\text{F,O})_2 \) and \( \text{KVPO}_4(\text{F,O})_2 \) respectively. It is interesting to mention that cationic substitution has also been widely explored in the last few years in order to increase the energy density delivered for instance by the NASICON type material \( \text{Na}_3 \text{V}_2(\text{PO}_4)_3 \).
Iron and manganese substitutions allowed the formation of sodium rich compositions, i.e. Na$_2$FeV(PO$_4$)$_3$ and Na$_2$MnV(PO$_4$)$_3$. The exchange of more than one electron per transition metal ions was demonstrated, but strong irreversibility was observed as soon as the oxidation of V$^{3+}$ to V$^{5+}$ was activated. Indeed, in these cases, all oxygen atoms in VO$_6$ units are covalently bonded to PO$_4$ groups, and thus VO$_6$ cannot be distorted to accommodate V$^{5+}$ formation, leading to the migration of vanadium to reduce the energy of the system.

![Figure 6](image)

**Figure 6:** Average redox potential of the different LiVPO$_4$(F,O), Na$_3$V$_2$(PO$_4$)$_3$F(F,O)$_2$ and KVPO$_4$(F,O) compounds. Green rectangles correspond to vanadium fluoride phosphates, blue rectangles correspond to partially substituted compounds and red rectangles correspond to vanadyl phosphates. For KVOPO$_4$, the capacity limitation prevents the determination of the V$^{5+/4+}$O redox potential such that a slightly different method was used. The average redox potential was extrapolated from the trend observed in the K$_{1-0.5}$VOPO$_4$ composition domain compared to that of K$_{1-0.5}$VOPO$_4$F.

**CONCLUSIONS**

Vanadium fluoride phosphates are promising electrode materials for high energy rechargeable alkali-ion batteries thanks to their high redox potentials and their capability to support long-term cycling. Alongside their potential application, they also exhibit a great diversity of crystal structures. Despite their closely related chemical formula (A$_{1-x}$VPO$_4$F$_{1-x}$ (x = 0, ½)), the structural framework depends strongly on the nature of the alkali ion and stoichiometry, as shown by the formation of Tavorite LiVPO$_4$F, Tavorite NaVPO$_4$F and Na$_3$V$_2$(PO$_4$)$_2$F$_3$, as well as KTP-type KVPO$_4$F. In these materials, fluoride anions can be partly or fully substituted, leading to the formation of vanadium oxyfluoride phosphates or oxide phosphates, respectively. Structural peculiarities lead to different behaviours at the local scale: the substituted oxygens tend to segregate in LiVPO$_4$F due to cooperative vanadyl distortions, but distribute randomly in Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and KVPO$_4$F. The replacement of ionic V$^{3+}$F by highly covalent V$^{4+}$=O bonds in the mixed O/F compounds results in significant changes in the physicochemical properties, redox mechanisms, and electrode potentials. During alkali ion de-insertion, end-member compounds undergo biphasic reactions due to alkali – vacancy orderings while partially substituted compounds tend to behave as solid solutions owing to anion disorder which breaks local periodicity. The redox potential of these compounds is affected by up to 350 mV difference between the F- and O$_2^-$ compounds and up to 0.5 V compared to non-mixed anion phosphates such as Na$_3$V$_2$(PO$_4$)$_3$. Mixed
anion chemistry is therefore one of the most promising routes that can be used to tune the electrochemical behaviour of these polyanionic systems.
AUTHOR INFORMATION

Corresponding authors

Laurence Croguennec – Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France; RS2E, Réseau sur le Stockage Electrochimique de l’Energie, FR CNRS 3459, Amiens F-80039 Cedex 1, France; ALISTORE-ERI European Research Institute, FR CNRS 3104, F-80039 Amiens Cedex 1, France; orcid.org/0000-0002-3018-0992; Email: Laurence.Croguennec@icmcb.cnrs.fr

Romain Wernert – Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France; ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France; RS2E, Réseau sur le Stockage Electrochimique de l’Energie, FR CNRS 3459, Amiens F-80039 Cedex 1, France; orcid.org/0000-0002-5073-4008; Email: Romain.Wernert@chem.ox.ac.uk

Present address: Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, UK

Authors

Dany Carlier – Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France; RS2E, Réseau sur le Stockage Electrochimique de l’Energie, FR CNRS 3459, Amiens F-80039 Cedex 1, France; ALISTORE-ERI European Research Institute, FR CNRS 3104, F-80039 Amiens Cedex 1, France; orcid.org/0000-0002-5086-4363

Long H.B. Nguyen – ICGM, Université de Montpellier, CNRS, ENSCM, 34095 Montpellier, France; RS2E, Réseau Français sur le Stockage Electrochimique de l’Energie, FR CNRS #3459, Amiens F-80039 Cedex 1, France; https://orcid.org/0000-0001-7823-1595

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\begin{align*}
\text{LiVPO}_4F_{1-y}O_y & \quad \text{Na}_3V_2(PO_4)_2F_{3-2y}O_{2y} & \quad \text{KVPO}_4F_{1-y}O_y \\
\text{Li}_{1-x}V^{4+/3+}PO_4F & \quad \text{Na}_{3-x}V^{4+/3+}_{2}(PO_4)_2F_3 & \quad \text{K}_{1-x}V^{5+/4+}PO_4O \\
-200 \text{ mV} & \quad -100 \text{ mV} & \quad +100 \text{ mV} \\
\text{Li}_{1-x}V^{5+/4+}PO_4O & \quad \text{Na}_{3-x}V^{5+/4+}_{2}(PO_4)_2FO_2 & \quad \text{K}_{1-x}V^{4+/3+}PO_4F
\end{align*}
\]