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To cite this version:
Romain Wernert, Long H.B. Nguyen, Antonella Iadecola, François Weill, François Fauth, et al.. Self-discharge mechanism of high-voltage KVPO4F for K-ion batteries. ACS Applied Energy Materials, 2022, 5 (12), pp.14913-14921. 10.1021/acsaem.2c02379 . hal-03857373

HAL Id: hal-03857373
https://hal.science/hal-03857373
Submitted on 17 Nov 2022

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Self-discharge mechanism of high voltage KVPO₄F for K-ion batteries

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KEYWORDS: vanadium phosphate fluoride, potassium-ion battery, chemical deintercalation, self-discharge mechanism, side reactions.

ABSTRACT:

Current performances of Li, Na or K-ion batteries are mainly limited by the specific capacity of the positive electrode. Therefore, it is important to reach the highest capacity as possible for a given electrode material. Here we investigate the performance limitation of KVPO₄F, a prospective material for K-ion batteries but which can deliver only 80% of its theoretical capacity. We discover that the capacity limitation of KVPO₄F is related to a kinetic competition between K⁺ deinsertion and side reactions ascribed to the electrolyte degradation at high potentials. Homeotypic VPO₄F can be obtained from KVPO₄F through a chemical deintercalation process, which disproves a possible structural limitation or instability. The deintercalated compound was characterized by electron and X-ray diffraction, X-ray absorption spectroscopy and nuclear magnetic resonance spectroscopy. Despite the structural stability, a spontaneous reaction occurs between the deintercalated KₓVPO₄F (x < 0.5) and the electrolyte (0.8 M KPF₆ in ethylene carbonate : diethylene carbonate), with an electron transfer to vanadium compensated by K⁺ intercalation. This reaction leads to self-discharge until the open circuit potential is lower than 4.7 V vs K⁺/K, corresponding to the K₀.₅VPO₄F composition.
INTRODUCTION

Electrochemical energy storage systems are expected to become one of the main technologies for stationary storage of intermittent renewable energies such as photovoltaic and wind turbines. Yet, the markets of Li, Co, and Ni, which are widely used in Li-ion batteries, suffer from instability of their price, as demonstrated by the 500 % increase in the price of Li2CO3 over 2021. Such a price volatility is detrimental to the sustainability of the supply chain in the near future.1,2 Na- and K-ion batteries (KIBs) have been proposed as alternatives since Na/K-containing resources are more abundant and have a wide geographical availability. Potassium-ion batteries are attractive prospective candidates due to the low electrochemical potential of K+/K redox couple and the small Stokes radius of K+, providing fast diffusion rate in liquid electrolytes.3-5 Moreover, potassium-ion batteries can operate with graphite negative electrodes contrary to Na-ion batteries, and do not rely on expensive Co- and Ni-based positive electrodes.6,7 Prussian blue analogues K2(Fe,Mn)Fe(CN)6 and vanadium oxyfluoride phosphate KVPO4F1-yOy (0 ≤ y ≤ 1) are two of the most promising materials for positive electrode in KIBs, possessing theoretical energy densities of 500 to 600 Wh kg⁻¹.8 Such values, though inferior to state of the art Li-ion NMC622 (700 Wh kg⁻¹), are competitive to LiFePO4 (586 Wh kg⁻¹) for example.10,11

Potassium prussian blue analogues have a theoretical capacity of 155 mAh g⁻¹ with an average voltage of 3.6 V vs K+/K and 3.9 V vs K+/K for K2FeFe(CN)6 and K2MnFe(CN)6, respectively.8,12–15 Such figures yield a theoretical energy density of 550 to 600 Wh kg⁻¹. However, owing to the low density of Prussian blue analogues (c.a. 2.2 g cm⁻³), the volumetric energy density is lower than phosphate compounds. Moreover, several crystalline defects can appear during the synthesis, such as Fe(CN)6 vacancies, interstitial water molecules, K+ vacancies and oxidation of transition metals, which can considerably lower the capacity.16

KVPO4F crystallizes in the KTiOPO4 type (KTP) structure (Pna2₁) which can be described as a framework made of VO4F2 chains connected by PO4 tetrahedra. The F site in KVPO4F structure can be partially or totally substituted by O to form KVPO4F1-yOy (0 ≤ y ≤ 1) where each composition crystallizes in Pna2₁ as well and forms an anion disordered solid solution. The KTP structure has been highlighted for the high operating voltage of the V⁴⁺/³⁺ (4.3 V vs K+/K), Ti⁴⁺/³⁺ (3.2 V vs K+/K) and even {V⁵⁺/⁴⁺=O} (4.3 V vs K+/K) redox couples.17-20 Moreover, the density of KVPO4F is 3.1 g cm⁻³ (40% more than Prussian blue analogues) which is highly desirable for improving the volumetric energy density of K-ion batteries. Despite its attractive theoretical capacity of 131 mAh g⁻¹, full electrochemical depotassiation has never been achieved for KVPO4F.21,22 A typical charge-discharge galvanostatic curve of KVPO4F shows that only 0.8 K+ ion per formula unit can be exchanged during the first charge of the battery (Figure 1). As a consequence, the actual energy density at the material scale is limited to 450 Wh kg⁻¹ whereas the utilization of one full K+ would provide more than 560 Wh kg⁻¹. However, it is unclear whether the impossibility to reach full deintercalation in KVPO4F is due to structural constraints or kinetic limitations.

**Figure 1:** Electrochemical curve of KVPO4F vs. K metal at C/20. The red hatched area corresponds to the capacity (26 mAh g⁻¹) that is not accessible in the 3.5 – 5.0 V vs K+/K voltage window.

Indeed, Caracciolo et al. and Kim et al. have already demonstrated the effect of side reactions between KxVPO4F (x < 1) with the 0.8 M KPF6 in ethylene carbonate : diethylene carbonate electrolyte, leading to a capacity loss upon cycling, especially in the high voltage region (> 4.5 V vs. K+/K).21,23 The kinetics of these reactions might prevent KxVPO4F from reaching the fully charged state. In fact, if the alkali deinsertion and parasitic reaction rates are of the same order of magnitude, one can expect a competition between the two phenomena, leading to a lower experimental deinsertion rate than the theoretical one. Such a competition mechanism was proposed by Brutti et al. to explain the self-discharge and surface reactivity of LiCoPO4, another high-potential electrode material (4.8 V vs Li⁺/Li).24-26 In this study, several
depotassiated \( K_x VPO_y F \) samples have been prepared via chemical or electrochemical approach. The structure and electrochemical properties of the depotassiated samples were compared to obtain an insight on the mechanism behind the impossibility of \( KVPO_{x+y/2} \) \((0 \leq y \leq 0.5)\) electrode materials to achieve their full theoretical capacity in cycling. Such information is required to establish the interplay between thermodynamic and kinetic factors that control the reactivity of high-voltage electrodes in rechargeable batteries, in such highly reactive \( K \) systems.

### METHODS AND EXPERIMENTS

**Material synthesis.** \( KVPO_4F \) was obtained by mixing \( KF \) (Alfa Aesar) with \( VPO_4 \), the latter being synthesized by heating \( V_2O_3 \) (99.6%, Sigma-Aldrich) and \( NH_4H_2PO_4 \) 98% (Sigma-Aldrich) to 850°C for 10 hours under \( Ar/H_2 \) atmosphere. The pelletized mixture was then calcined in a argon sealed gold tube at 650°C for 6 hours. The chemical deintercalation of \( KVPO_4F \) was conducted under \( Ar \) atmosphere according to **Reaction 1**. A solution of 1.3 g (2 equiv.) of \( NO_2BF_4 \) (Sigma-Aldrich, > 95%) dissolved in 200 mL anhydrous acetonitrile (Sigma Aldrich, anhydrous, 99%), was added dropwise into a suspension of 1 g (1 equiv.) of \( KVPO_4F \) in 150 mL of acetonitrile. The reaction was carried out for 48 hours at room temperature with a constant magnetic stirring. The product was then rinsed with acetonitrile, vacuum filtered and further dried by evaporating the residual solvent under vacuum.

\[
KVPO_4F (s) + NO_2BF_4 (sol) \rightarrow K_0VPO_4F (s) + KBF_4 (s) + NO_2(g) \quad \text{Reaction 1}
\]

The deintercalated material was then exposed to a solvent mixture or electrolyte by mixing 100 mg of powder in 0.8 mL of ethylene carbonate : diethyl carbonate (EC:DEC 1:1 by vol.%). EC, Sigma-Aldrich, anhydrous, 99%; DEC, Sigma-Aldrich, anhydrous, >99%, without or with 0.8 M KPF_6 (Sigma-Aldrich, >99%), respectively. Such conditions ensure a stoichiometric excess of 2 \( K_+ \) ions in the electrolyte per \( VPO_4F \) formula unit. The powder was subsequently rinsed with dimethyl carbonate. All the samples were stored in an Ar-filled glovebox. \( KVPO_{0.5}O_{0.5} \) was prepared according to our previous work and its chemically deintercalated and electrolyte exposed counterparts were prepared with the same protocol as described just above.\(^{20}\)

**Transmission Electron Microscopy (TEM)** experiments were performed either with a JEOL 2100 TEM, equipped with a GATAN Orius 200D camera, or with a selected JEOL Electron Diffraction (SAED) was performed, or with a JEOL 2200FS TEM equipped with a Si(Li) JEOL EDX detector for obtaining EDX mapping. Both microscopes operated at 200kV. A suspension of the specimen was prepared in dimethyl carbonate and a drop of the suspension was deposited on a holey carbon coated copper grid. An air-tight sample holder was used to transfer the sample from the glovebox to the TEM.

**X-ray diffraction (XRD)** experiments were carried out with a laboratory X'Pert3 diffractometer equipped with a capillary spinner and a Cu Kα,2 X-ray source. The powder was packed in a 0.5 mm diameter glass capillary and measured with steps of 0.016°. Structural determination of \( K_x VPO_y F \) was performed with data measured at ALBA synchrotron (Barcelona, Spain) on BL04-MSPD beamline. The data was collected at \( \lambda = 0.61908 \) Å, in Debye-Scherrer geometry with the position sensitive MYTHEN detector with a 0.006° effective bin step. The refinement of powder diffraction patterns was carried out with JANA2006 software.\(^{27}\) The atomic displacement parameters were refined together for all P atoms as well as for all O atoms. A semi-rigid body restraint was applied to the very covalent phosphate groups, allowing the P-O distances to vary between 1.535 ± 0.015 Å.\(^{28}\) The Bérar-Lelann correction was applied to standard uncertainties.\(^{29}\) VESTA software was used to visualize the crystal structures.\(^{30}\)

**X-ray absorption spectroscopy (XAS)** was performed at synchrotron SOLEIL (Saint-Aubin, France) at ROCK beamline. The samples were measured at V K-edge in transmission geometry with a V foil used as a reference for energy calibration. The oscillating frequency of the Si (111) quick-EXAFS monochromator was set at 2 Hz. The samples were diluted in cellulose to form a 13 mm diameter disk with a mass loading of 4.5 mg cm\(^{-2}\). 600 spectra were averaged for each sample. The energy calibration, spectrum normalization and linear combination fitting were all carried out with DEMETER software.\(^{31}\)

\(^{31}P\) solid-state nuclear magnetic resonance (NMR) spectroscopy was performed with a Bruker Avance III 100 MHz spectrometer, equipped with a 2.4 T wide-bore magnet, leading to a Larmor frequency of 40.6 MHz for \(^{31}P\). The 2.5 mm rotors were filled with around 15 mg of powder and the magic angle spinning (MAS) frequency was set at 30 kHz. The sequence consisted in a Hahn echo with a 1.7 µs 90° pulse duration and a recycle time of 0.2 s. An aqueous 85 wt. % \( H_3PO_4 \) (Sigma-Aldrich) solution was used to reference the chemical shift of \(^{31}P\) at 0 ppm.

**Density Functional Theory calculations** were performed using the projector-augmented wave (PAW) method with the Vienna Ab initio simulation package (VASP) code.\(^{32–37}\) The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used for all calculations.\(^{38}\) A Hubbard correction (\( U_{\text{eff}} = U-J = 3 \) or 5 eV) was used to take into account the self-interaction error of strongly correlated 3d electrons.\(^{39}\) All calculations were spin-polarized considering a ferromagnetic ordering as required to model NMR Fermi contact shifts.\(^{40}\) The planewave
cutoff energy was set to 600 eV and a $4 \times 4 \times 4 k$-mesh was used. The $K_0VPO_4F$ input model was generated by removing all K from the parental $KVPO_4F$ structure. The isotropic hyperfine coupling parameters were computed from the relaxed structure and further used for the calculation of Fermi contact shifts, as described in earlier work of our group. \textsuperscript{41–43} Briefly, the theoretical molar magnetic susceptibility of V$^{4+}$ ($\mu_{eff} = 1.76 \mu_B$) was considered and the Curie-Weiss temperature was hypothesized to be 0 K. The temperature at which the Fermi contact shifts were computed was chosen to be 320 K.

**Electrochemical characterisations** consisted in cycling self-standing electrodes vs K metal (Alfa Aesar, 99.95%) in CR2032 coin cells. The electrodes were made by mixing active material (impurities included), carbon black (Super P) and PTFE (Sigma Aldrich) in the 80:15:5 ratio (by wt.%). 50 µL of 0.8 M KPF$_6$ dissolved in a 1:1 volumetric mixture of EC:DEC was used as electrolyte and two polymer fiber mat disks (Viledon, Freudenberg) were used as separators. Electrochemical cycling was performed at C/20 current rate (exchange of 1 K$^+$ per formula unit in 20 hours) between 3.5 and 5 V vs K$^+/\text{K}$.

**RESULTS**

**Structural characterization.** The fully depotassiated, $K_0VPO_4F$ sample, was prepared via a chemical deintercalation with NO$_2$BF$_4$ dissolved in acetonitrile media under argon atmosphere. The standard potential of NO$_2^+$/NO$_2$ lies at 2.1 V vs NHE, \textit{i.e.} 5.1 V vs K$^+/\text{K}$.$^{44}$ The crystal structure of this material was investigated with XRD. The diffractograms of $KVPO_4F$ before and after K desintercalation are compared in Figure 2a which shows that the characteristic peaks of $KVPO_4F$ are conserved after chemical deintercalation suggesting that the KTP-type framework is maintained (Figure 2a). The Bragg reflections shifted towards higher angles indicating a decrease of the cell parameters upon the K$^+$ removal process. The splitting of the 201 and 011 peaks highlights a larger decrease of the $b$ cell parameter compared to $a$. According to Reaction 1, KBF$_4$ was generated as a by-product during the de-potassiation with NO$_2$BF$_4$, which could not be dissolved in any glovebox-compatible solvents (carbonates, acetonitrile…). Besides, TEM-EDX maps (Figure S1) clearly show the presence of two different phases, one being V and P rich (spot 1) and the other being K and F rich (spot 2). Thus, KBF$_4$ stayed as an impurity in all the following investigations.

**Figure 2:** a) X-ray diffraction pattern of the first four Bragg peaks for $KVPO_4F$ and $K_0VPO_4F$ obtained from chemical deintercalation of $KVPO_4F$. b) Representative selected area diffraction patterns of $K_0VPO_4F$, the three patterns were obtained from the same primary particle. c) Rietveld refinement of the synchrotron XRD pattern collected after the chemical deintercalation of $KVPO_4F$, considering $K_0VPO_4F$ with KBF$_4$ as by-product.

Fedotov \textit{et al.} have already reported the crystal structure of quasi deintercalated $K_{0.17}VPO_4F$, however its cell parameters are different compared to those of our chemically deintercalated sample.$^{17}$ Thus, the crystal structure of highly deintercalated $K_0VPO_4F$ was reinvestigated using selective area electron diffraction combined with synchrotron X-ray diffraction. Figure 2b shows the electron diffraction patterns of $K_0VPO_4F$ along the three characteristic zone axes [100], [010] and [001], with the observed reflection conditions $k+l = 2n$, $h = 2n$ and $h+k = 2n$, respectively. It indicates that $K_0VPO_4F$ crystallizes in the $P\text{nan}$ space group. Due to the presence of KBF$_4$ impurity, a two-phases Rietveld refinement was performed on SXRD pattern collected for the chemically deintercalated sample (Figure 2c). The refinement shows that $K_0VPO_4F$ has the cell parameters of $a = 12.504(1)$ Å, $b = 6.0875(4)$ Å and $c = 10.462(1)$ Å, corresponding to a 9.2% cell volume decrease compared to $KVPO_4F$. The full K$^+$ deintercalation is supported by i) no major residual electron
density in the structural tunnels is observed on the Fourier difference maps (Figure S2), ii) the occupancy of K(1) and K(2) site converging to 0 and iii) the quantification of KBF₄ phase fraction (39 wt. %) very close to the 43 wt.% as expected from Reaction 1. The detailed crystallographic description of K₀VPO₄F is given in Table S1. From these structural characterisations, it can be concluded that KTP-type framework is stable at the fully de-intercalated state as no significant structural rearrangement occurs even with fully empty alkali sites.

The deintercalated compound K₀VPO₄F was further characterised by X-ray absorption spectroscopy in order to assess the vanadium oxidation state. The X-ray absorption near edge structure (XANES) spectra, featuring the 1s → 4p dipole allowed transitions, of some selected references, such as KV³⁺PO₄F, KV⁴⁺OPO₄ and V⁵⁺OPO₄, are presented together with the spectrum of K₀VPO₄F (Figure 3a). For the latter compound, the position of the main edge superposes that of KVPO₄ reference indicating the +4 oxidation state in accordance with a full depotassiation of KVPO₄F. The pre-edge region of K₀VPO₄F shows more intense features compared to the pristine compound, indicating a breaking in the centrosymmetry of VO₄F₂ octahedra. Indeed, site distortion evolved from 2.5·10⁻⁴ and 3.3·10⁻⁴ for V(1) cis and V(2) trans respectively in KVPO₄F to 17.2·10⁻⁴ and 4.4·10⁻⁴ in K₀VPO₄F (Table S1). In KVPO₄, the site distortion is 37.2·10⁻⁴ and 68.4·10⁻⁴ which is consistent with the even more intense pre-edge, as such distorted octahedral environments induce mixing of V 3d→4p orbitals and hence allows the 1s → 3d transitions to occur.

![Figure 3](image-url)

**Figure 3:** a) V K-edge XANES spectrum of K₀VPO₄F at the V K-edge along with V³⁺/⁴⁺/⁵⁺ phosphate references. b) ³¹P MAS-NMR spectra of K₀VPO₄F and KVPO₄F recorded at B₀ = 2.4 T. The spinning sidebands are indicated by asterisks.

³¹P MAS-NMR spectrum of KVPO₄F (Figure 3b) shows two intense resonances that were previously attributed to P(1) and P(2) crystallographic sites being surrounded by four V³⁺. The large ³¹P NMR shifts (5800 and 4500 ppm) result from the Fermi contact interaction between vanadium’s unpaired electrons (3d electronic configuration) and phosphorus nuclei. In a similar way, the NMR spectra of K₀VPO₄F displays two main peaks at 4120 ppm and 865 ppm (Figure 3b). In K₀VPO₄F, V exhibits the +4 oxidation state with the 3d⁰ electronic configuration and thus the magnitude of the Fermi contact interaction is much weaker and lower ³¹P NMR shift values are expected as compared to KVPO₄F. Nonetheless, the resonance at 4120 ppm indicates that a strong Fermi contact interaction remains between V³⁺ ions and the P1 sites. DFT calculations were carried out to understand the spin transfer mechanism in the K₀VPO₄F structure. The input model for K₀VPO₄F was generated by removing all K from the parental KVPO₄F structure and relaxed using the GGA+U
approach with \( U_{\text{eff}} = 3 \) or \( 5 \) eV. The cell parameters and bond lengths of the relaxed structure agreed with those observed by TEM and SXRD refinements (Table S2). The bond distances range from 1.89 Å to 1.96 Å for V-O and 1.94 Å to 2.02 Å for V-F indicating as expected more ionic bonding towards fluorine than oxygen.

Spin density maps around the P(1) and P(2) crystallographic sites (Figure 4) show the spatial distribution of “spin up” electrons. For both vanadium sites, a single \( t_{2g} \) orbital is occupied, indicating a lift of \( (d_{xy}, d_{yz}, d_{xz}) \) degeneracy. All the orbitals containing vanadium’s electron spin pointed their lobes towards P(1) site (Figure 4 and Figure S3) for a proper \( d(V^{IV})-p_{d}(O)-sp^{3}(P) \) interaction\(^{20}\), the P(1) site thus receives the electron spin from the four surrounding vanadium atoms with a strong Fermi contact. On the contrary, around P(2) each of the spin containing orbital plane of \( V^{4+} \) are quasi perpendicular to the \( \text{V–O–P} \) bond path, thus geometrically limiting the strength of the interaction (Figure 4) due to the absence of \( \text{V–O} \pi \) overlap. This is further supported by the presence of spin density around P(1) (Figure S3), forming two crescents, whereas no spin density is observed around P(2) at \( 10^{-3} \) spin Å\(^{-3}\). Finally, The theoretical Fermi contact shifts of P(1) and P(2) in \( K_{0}VPO_{4}F \) calculated using GGA+U method are given in Table 1. Whatever the \( U_{\text{eff}} \) value is, the predicted shift for P(1) is approximately five times higher than for P(2), which is consistent with experimental observations.

**Figure 4**: Spin density maps of the P(1) and P(2) local environments showing the majority spin in yellow with isosurface of \( 5\cdot10^{-3} \) spin Å\(^{-3}\) for the calculation performed with \( U_{\text{eff}} = 5 \) eV. Only the “spin-up” density is shown for clarity.

**K\(_{0}\)VPO\(_{4}\)F stability in electrochemical reactions.** The results obtained so far have shown that \( K_{0}VPO_{4}F \) can be chemically isolated as a stable phase; nonetheless, full capacity could not be achieved from \( KVPO_{4}F \) during electrochemical reactions. The chemical stability of \( K_{0}VPO_{4}F \) was thus explored by exposing the powder to either the EC:DEC mixture solvent (1:1 by volume) or the electrolyte, consisting in 0.8 M KPF\(_{6}\) dissolved in the previous solvent mixture. The unchanged diffractograms before and after exposure to the solvent demonstrate that this treatment does not affect the crystal structure (Figure S4). However, a radical change of the long-range structure was detected when the deintercalated compound was exposed to the electrolyte.

**Table 1**: Experimental and computed \(^{31}\)P NMR shifts for \( K_{0}VPO_{4}F \)

<table>
<thead>
<tr>
<th></th>
<th>Experimental shift (ppm)</th>
<th>GGA + 3 eV (ppm)</th>
<th>GGA + 5 eV (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)</td>
<td>4120</td>
<td>6169</td>
<td>5271</td>
</tr>
<tr>
<td>P(2)</td>
<td>865</td>
<td>1360</td>
<td>986</td>
</tr>
</tbody>
</table>
Table 2: Cell parameters retrieved by XRD refinement for KVPO₄F, K₀VPO₄F and KₓVPO₄F.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V/Z (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KVPO₄F</td>
<td>12.8223(1)</td>
<td>6.39721(3)</td>
<td>10.6203(1)</td>
<td>108.90</td>
</tr>
<tr>
<td>K₀VPO₄F</td>
<td>12.504(1)</td>
<td>6.0875(5)</td>
<td>10.462(1)</td>
<td>99.54</td>
</tr>
<tr>
<td>KₓVPO₄F</td>
<td>12.632(3)</td>
<td>6.142(1)</td>
<td>10.545(3)</td>
<td>102.28</td>
</tr>
</tbody>
</table>

The comparison of XRD patterns in Figure 5a shows that after an immersion in the electrolyte, the diffraction peaks became broader and shifted to intermediate positions located between those of KVPO₄F and K₀VPO₄F. The obtained XRD pattern was refined using the Pna₂ space group (Figure S5) and cell parameters of the phase were compared to those of KVPO₄F and K₀VPO₄F (Table 2). A clear expansion of 2.7% of the unit cell volume is observed after the electrolyte exposure, which could be due to a spontaneous K⁺ insertion in the empty framework. Consequently, this sample will be referred to “KₓVPO₄F” in the rest of the text. The reduction of vanadium should occur concomitantly to compensate the charge, which was fully supported by V K-edge XAS (Figure 5b). The edge position of KₓVPO₄F is located between those of KVPO₄F and K₀VPO₄F. Linear combination fitting performed between 5474 and 5510 eV (Figure S6), using KVPO₄F and K₀VPO₄F as standards. It suggested that the recovered sample has a V³.₅⁺ average oxidation state. Given that the crystal framework is maintained and half of V ions were reduced to V³⁺, one can expect that the composition of “KₓVPO₄F” is actually K₀.₅VPO₄F. Unfortunately, the direct chemical titration of K⁺ content was not possible since the chemically deintercalated powder contained KBF₄ as impurities.

The electrochemical properties of the chemically depotassiated powder, “K₀VPO₄F”, were evaluated in a coin cell with metallic K as a negative electrode. The starting point of the electrochemical curve (Figure 6a) was set at 0.5 K⁺ per VPO₄F unit, consistently with the oxidation state determined from XAS measurements and with the open circuit voltage of the cell measured at 4.7 V vs K⁺/K as depicted in Figure 1. Moreover, the discharge curve suggests a fully potassiatised compound after only 0.5 K⁺ inserted into the structure, suggesting that K₀VPO₄F was immediately converted to K₀.₅VPO₄F when it was in contact with the electrolyte. In the next cycle, the shape of the electrochemical curve in the low potential region (< 4.6 V) was similar to the one of pristine KVPO₄F reported in Figure 1, thus indicating that a full potassiation could be achieved starting from K₀VPO₄F. Further charge above 4.5 V was strongly affected by side reactions, leading to a very low coulombic efficiency. Nevertheless, the derivative curve of second discharge (Figure S7) overlaps the first one. Overall, the electrochemical tests indicated that the total insertion of 1 mol of K⁺ in K₀VPO₄F is possible and reversible.

![Image](image-url)

Figure 5: a) X-ray diffraction patterns and b) V K-edge XANES spectra of pristine KVPO₄F, chemically deintercalated K₀VPO₄F and electrolyte exposed KₓVPO₄F.

**Self-discharge**

Hence it seems that the limited capacity originates from an internal mechanism that can be attributed to self-discharge. In order to confirm this hypothesis, a KVPO₄F/K coin cell was assembled and charged up to 5 V vs. K⁺/K, resulting in ≈100 mAh·g⁻¹ reversible capacity. After the second charge to 5 V, the battery was kept in open-circuit conditions at room temperature for 10 days. The open circuit voltage was recorded (Figure S8) and the rest potential decreased gradually.
from 5 V to 4.75 V during the rest period. Only 65 mAh·g⁻¹ (i.e., 0.5 K⁺ exchanged) was observed in the consequent discharge (Figure 6b). The capacity at the high-voltage plateau completely disappeared after the resting period, indicating that the material suffered from a self-discharge at high depottassiated states. Nevertheless, the voltage curve at low potential region (< 4.5 V) was clearly reversible, implying that K₀.₅VPO₄F was the thermodynamic limit of KVPO₄F system in the current electrolyte.

Figure 6: a) Galvanostatic curve obtained for K₀VPO₄F versus K metal at C/20. The initial K⁺-content was set at 0.5 corresponding to composition formed when K₀VPO₄F was in direct contact with the electrolyte. b) Comparison of discharge curves obtained for KVPO₄F versus K metal after a first charge without relaxation and a second charge with 10 days relaxation.

GENERAL DISCUSSION

The results previously discussed evidenced, firstly, that K₀VPO₄F composition can be reached and that the structure is stable, secondly, that when exposed to the electrolyte, the compound undergoes spontaneous K uptake and V reduction. Based on these results, we propose the following reaction mechanism: the highly oxidizing power of the material in its highly deintercalated state leads to the decomposition of the electrolyte and involves an electron transfer from decomposing molecules to the vanadium phosphate fluoride. Some V ions are then reduced to V³⁺ and a K⁺ ion is spontaneously inserted from the electrolyte to the crystal framework in order to ensure the charge neutrality. Such a mechanism was also proposed by Manzi et al. in their earlier work on LiCoPO₄. The self-discharge mechanism is thermodynamically driven as soon as the electrochemical potential of the active material is higher than that of the electrolyte stability. It involves that this process does not occur only at rest, after a full charge, but that it is a dynamical process which starts during the charge and competes with the K⁺ extraction. Indeed, the galvanostatic current applied to charge the battery is a driving force for ion deintercalation whereas the oxidation of the electrolyte reduces the active material and is therefore a competitive driving force for ion re-intercalation. At the end of charge, the two phenomena have similar kinetics that limit the reversible capacity of KVPO₄F at about 80% of the theoretical one.

The same experiments were conducted on the closely related KVPO₄F₀.₅O₀.₅ compound. Its chemically deintercalated counterpart gives a very similar XRD pattern to that observed for K₀VPO₄F (Figures S9 and S10). It can be refined with close cell parameters: \(a = 12.481(1) \text{ Å}, b = 6.092(1) \text{ Å} \) and \(c = 10.546(1) \text{ Å}\) (Figures S9 and S10). The V K-edge XANES spectrum of K₀VPO₄F₀.₅O₀.₅ lies between those of KV⁴⁺OPO₄ and V⁵⁺OPO₄ (Figure 7a), which was in line with the expected oxidation state of V⁴.₅⁺. After being exposed to the K⁺-containing electrolyte, the edge shifted to lower energy and superposed to that of V⁴⁺ reference. This observation suggests that K₀VPO₄F₀.₅O₀.₅ was reduced together with a K⁺ insertion for charge compensation. A similar behaviour to that discussed just before for KVPO₄F was thus expected when testing the material in an electrochemical cell. Similarly, we hypothesized the composition K₀.₅VPO₄F₀.₅O₀.₅ and started the electrochemical cell in discharge (Figure 7b). Here again, the discharge was completed after the reinsertion of 0.5 K⁺ and the consecutive charge gives the expected voltage-composition curve for KVPO₄F₀.₅O₀.₅ versus K metal.
Figure 7: a) XANES spectra at the V K-edge of KVPO$_4$F$_{0.5}$O$_{0.5}$ together with its chemically deintercalated and then electrolyte exposed counterparts. KVOPO$_4$ and β-VOPO$_4$ are used as V$^{4+}$ and V$^{5+}$ references, respectively. b) Electrochemical curve of first discharge and successive cycle for K$_x$VPO$_4$F$_{0.5}$O$_{0.5}$ assembled in a half-cell vs K metal.

CONCLUSION

In this work, we demonstrated that the impossibility to electrochemically deintercalate more than 0.8 K$^+$ ions from KVPO$_4$F positive electrode was due to a competition between two opposite phenomena. On one hand, the galvanostatic charge drives K$^+$ deintercalation with simultaneous oxidation of V whereas, on the other hand, the instability of the electrolyte at high potential results in redox degradation reactions, leading to reduction of V concomitantly with insertion of K$^+$ into the structure. As a consequence, the practical capacity of KVPO$_4$F is limited to 65 mAhr$^{-1}$, that is to say half the theoretical capacity. The study is extended to the KVPO$_4$F$_{0.5}$O$_{0.5}$ composition and the same conclusions were drawn. Moreover, this study leads to the discovery, for the first time to our knowledge, of a fully deintercalated KTP-type phosphate with empty tunnels, whose structure was characterized by SXRD, electron diffraction, $^{31}$P solid-state NMR coupled with DFT calculations. Finally, our study highlights the interest of combining chemical and electrochemical K insertion/de-insertion to investigate the structure, stability and reactivity of electrode materials.

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SUPPORTING INFORMATION

Supporting information includes EDX maps, detailed crystal structure solving and crystallographic data, complementary spin density maps and spin transfer mechanism drawings, XANES linear combination fitting, complementary electrochemical characterisations, full pattern matching refinements of K$_x$VPO$_4$F and K$_a$VPO$_4$F$_{0.5}$O$_{0.5}$.

ACKNOWLEDGEMENTS

This work was part of the TROPIC project supported by Agence Nationale de la Recherche (ANR) under the grant ANR-19-CE05-0026. ANR is also acknowledged for funding the RS2E network through the STORE-EX Labex Project ANR-10-LABX-76-01. Synchrotron Soleil (France) is acknowledged for providing beamtime at the beamline ROCK which also benefits from ANR grant as part of the “Investissements d’Avenir” program ANR-10-EQPX-45. The Mésocentre de Calcul Intensif Aquitain (MCIA) and the modeling center of ISM are acknowledged for computing facilities. We thank Marion Gayot (PLACAMAT UMS CNRS 3626) for operating the TEM-EDX measurements, Cathy Denage, Jérôme Kalisky and Emmanuel Petit (ICMCB) for their technical support.

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