

# AVPO<sub>4</sub>F (A = Li, K): A 4 V Cathode Material for High-Power Rechargeable Batteries

Stanislav S. Fedotov,<sup>\*,†,‡</sup> Nellie R. Khasanova,<sup>†</sup> Aleksandr Sh. Samarin,<sup>†</sup> Oleg A. Drozhzhin,<sup>†</sup> Dmitry Batuk,<sup>§</sup> Olesia M. Karakulina,<sup>§</sup> Joke Hadermann,<sup>§</sup> Artem M. Abakumov,<sup>†,‡,§</sup> and Evgeny V. Antipov<sup>†</sup>

<sup>†</sup>Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russian Federation

<sup>‡</sup>Skoltech Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, 143026 Moscow, Russian Federation

<sup>§</sup>EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

Supporting Information

D ecently, fluoride-phosphate-based cathode materials for KLi-ion batteries have captured much attention because they can combine the benefits of both anionic species and demonstrate higher structural diversity. In fact, the incorporation of fluorine brought about several advantages compared to oxide materials, namely, the increase in the operating voltage due to a higher electronegativity and better kinetics arising from a lower affinity of lithium to the fluoride anion. The first fluoride-phosphate cathode, LiVPO4F, with the tavorite structure was introduced by Barker et al.<sup>1</sup> It exhibited an 0.4 V higher redox potential (4.2 V vs Li/Li<sup>+</sup>) than fluorine-free NASICON-type  $Li_3V_2(PO_4)_3$  (3.8 V vs  $Li/Li^+$ )<sup>2</sup> as well as a substantial specific capacity of 156 mAh/g. This finding boosted the examination of different families of fluoridecontaining materials such as fluoride-phosphates A2MPO4F (A = Li, Na; M = Mn, Fe, Co, Ni)<sup>3-9</sup> and fluoride-sulfates LiMSO<sub>4</sub>F (M = Mn, Fe, Zn),<sup>11-14</sup> which are also famous for their rich polymorphism. In these systems, the crystal structure strongly affects the key electrochemical properties.<sup>14,15</sup> For instance, LiFeSO<sub>4</sub>F with triplite structure displays an operating potential 0.3 V higher than tavorite,<sup>10,11,13</sup> the potential of Li<sub>2</sub>FePO<sub>4</sub>F varies depending on the crystalline form, i.e., 2.9 V in tavorite-type,7 3.3 V in layered8 and 3.4 V in stacked.9 Generally, the direct synthesis of some Li-containing polymorphs is difficult due to thermodynamic reasons. In such cases, sodium-containing counterparts with a desirable framework motif are commonly used for a subsequent chemical or electrochemical exchange of Na by Li leading to target cathode materials.<sup>8,9,16</sup> In this sense, K provides even ampler opportunities than Na for searching and stabilizing new structures due to a larger ionic radius and somewhat different crystal chemistry. With this idea in mind Tarascon's group proposed KFeSO<sub>4</sub>F cathode<sup>17</sup> with KTiOPO<sub>4</sub> (KTP) structure anticipating unique electrochemical properties. Indeed, the extraction of potassium ions resulted in a steady FeSO4F framework suitable for reversible de/intercalation of Li, Na and even K ions.

Motivated by this work we endeavored to design phosphatecontaining KTP-like compounds with higher energy density and stability. For this purpose, we screened existing KTP structures and found potassium vanadyl phosphate KVOPO<sub>4</sub> that satisfies the higher specific energy requirement.<sup>18</sup> However, a full conversion of V<sup>4+</sup> to V<sup>5+</sup> in an electrochemical cell might cause serious structural distortions induced by changing vanadium coordination from an octahedron  $(V^{4+})$  to a square-pyramid characteristic to V5+. This will inevitably introduce strain accelerating the electrode degeneration. To address these issues, we propose a replacement of V<sup>4+</sup> by V<sup>3+</sup> with a simultaneous substitution of  $O^{2-}$  by  $F^-$  to preserve the electroneutrality, which results in a KVPO<sub>4</sub>F formula. It should be noted that KTP-type KMPO<sub>4</sub>F (M = Al, Cr, Fe)<sup>19</sup> counterparts are known; however, they have never been considered as electrode materials for rechargeable batteries. Here we report on a novel vanadium-based cathode material  $AVPO_4F$  (A = Li, K) adopting a KTP-type framework for high power rechargeable batteries with enhanced specific energy and excellent rate capability. To the best of our knowledge, this is the first compound with a KTP structure containing both vanadium and fluorine.

KVPO<sub>4</sub>F was synthesized via freeze-drying assisted solid-state route in two steps. First, vanadium phosphate VPO<sub>4</sub> was obtained. For this, NH<sub>4</sub>VO<sub>3</sub> (99.9%) and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (99.99%) were dissolved in distilled H<sub>2</sub>O under stirring at 70 °C with a dropwise addition of an ascorbic acid solution as a carbon source and reducing agent. The resulting clear blue-colored solution was dispersed into liquid nitrogen and the water was sublimated at low pressure (10<sup>-2</sup> bar) within 72 h. The obtained cryogranulated powder was annealed at 800 °C for 7 h. The residual carbon content in VPO<sub>4</sub> was estimated by thermogravimetric analysis to be ~3 wt %. Then the product was mixed with the equimolar amount of KHF<sub>2</sub> (99.9%), grinded and fired in an Ar flow at 600 °C for 1 h followed by quenching to room temperature.

According to the powder XRD analysis, this synthetic procedure resulted in a phase-pure  $KVPO_4F$  sample. The material consists of elongated rounded particles of 200–400 nm in the long direction, as determined by SEM (Figure S1 of the Supporting Information (SI)). The bulk K:V:P ratio measured by ICP-AES, 0.31(2):0.34(2):0.35(2), is consistent with TEM-EDX data, 0.33(1):0.32(1):0.35(2), acquired on

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Figure 1. Crystal structures of KVPO4F, K0.17VPO4F, Li0.70K0.12VPO4F shown along [100] and [010] directions.

individual particles. Also, TEM-EDX undeniably demonstrates the presence of fluorine in KVPO<sub>4</sub>F (Figure S2 of the SI). To analyze a possible  $F^-/OH^-$  mixing in KVPO<sub>4</sub>F, FTIR spectroscopy analysis was performed. No characteristic bands in the 1500–4000 cm<sup>-1</sup> region were identified (Figure S3 of the SI), which clearly confirms the absence of either –OH groups or adsorbed water.

The structure of KVPO<sub>4</sub>F was refined from powder XRD data (Figure S4 of the SI) using the Rietveld method with the JANA2006 program.<sup>22</sup> The KFeSO<sub>4</sub>F structure was used as a starting model.<sup>17</sup> The powder diffraction pattern was fully indexed on an orthorhombic lattice (S.G. No. 33 *Pna2*<sub>1</sub>) with a = 12.8200(3) Å, b = 6.3952(1) Å, c = 10.6115(2) Å. No additional ordering or superstructure was detected with electron diffraction (Figure S5 of the SI). The main crystallographic parameters, atomic positions, atomic displacement parameters and main interatomic distances are given in Tables S1–S3 of the SI. The refined structure was confirmed using aberration-corrected high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images taken along the [100] and [010] directions (Figure S6 of the SI).

KVPO<sub>4</sub>F is built up of helical chains of VO<sub>4</sub>F<sub>2</sub> octahedra and PO<sub>4</sub> tetrahedra forming a rigid framework, which accommodate potassium ions in a 3D system of continuous spatial cavities (Figure 1A). Alternating  $VO_4F_2$  octahedra are corner-shared with fluorine atoms located in two equatorial (*cis*) positions for V1 and two axial (trans) positions for V2 and the other four oxygen corners shared with PO<sub>4</sub> tetrahedra. The average V-X (X = O, F) interatomic distances for both metal sites are 1.98 Å characteristic to a V<sup>3+</sup> environment. The bond valence sum for V1 and V2 is 3.15(6) validating +3 oxidation state of vanadium. The other confirmation comes from the EELS spectrum (Figure S7 of the SI) showing the V  $L_{2,3}$  edge typical for V<sup>3+</sup> in the octahedral coordination. Potassium in the structure occupies two 9-coordinated positions, K1 and K2, located in the open tunnels along the *a* and *b* axes, respectively (Figure 1A).

For the electrochemical evaluation the initial  $KVPO_4F$ material was oxidized by charging up to 4.8 V vs Li/Li<sup>+</sup> at C/20 rate and holding at this potential for 5 h (Figure S8 of the SI). The charged electrode was recovered, washed twice with dimethyl carbonate (DMC) and put into a fresh cell with a new portion of electrolyte and Li-foil anode for further testing. According to the EDX data, potassium is not completely removed and about 15% remains in the structure. Therefore, we ascribe the  $K_{0.15}$ VPO<sub>4</sub>F composition to the oxidized material. Such a possibility to produce vanadium phosphate frameworks by electrochemical oxidation was first shown by Song et al,<sup>23</sup> who formed a new  $\varepsilon$ -VOPO<sub>4</sub> polymorph from a H<sub>2</sub>VOPO<sub>4</sub> precursor.

The obtained  $K_{0.15}VPO_4F$  material was cycled in a galvanostatic regime within the 2.0–4.7 V vs Li/Li<sup>+</sup> potential range at different rates from C/5 to 40C showing an uptake of 0.7 Li per formula unit at the average voltage of ~4 V.  $K_{0.15}VPO_4F$  exhibits a sloping voltage profile indicating a solid-solution-like de/intercalation mechanism, which is favorable to high-power applications (Figure 2).



**Figure 2.** A typical charge–discharge curve of  $\text{Li}_{*}K_{0.15}\text{VPO}_4\text{F}$  at C/5. The inset demonstrates the capacity retention and Coulomb efficiency in the cycling ability test at 1C rate.

To get insight into structural and compositional changes taking place in the electrochemical cell, an ex situ investigation was performed on recovered electrode materials. The detailed information on the preparation of the oxidized and lithiated electrode materials is given in the SI section. The XRD patterns of the recovered electrodes displayed a close resemblance with those of the initial material confirming that the KTP-type structure is preserved (Figure S9 of the SI). Because of insufficient quality of *ex situ* XRD patterns, selected area electron diffraction (SAED) and electron diffraction tomography (EDT) were applied to examine the crystal structure of the recovered electrode materials. The electron diffraction study revealed that in contrast to the noncentrosymmetric parent KVPO<sub>4</sub>F phase (*Pna2*<sub>1</sub>) the crystal structures of both oxidized and lithiated electrode materials possess a centrosymmetric space group (*Pnan*) (Figure S10 of the SI). The cell parameters refined from *ex situ* XRD with the determined space group were taken for the refinement of atomic positions and occupancies using EDT data. All details of the refinement are described in the SI.

The structure refinement of the oxidized electrode indicated that the K1 site is empty and all residual K is located in the K2 position, in the voids along the [010] direction (Figure 1B). The refined amount of residual K (~17%) gave the  $K_{0.17}$ VPO<sub>4</sub>F formula consistent with the bulk EDX measurements (~15%). A complete removal of K is likely to occur at potentials over 5 V that may be accompanied by severe electrolyte decomposition or degradation of the material itself. At the same time, the residual K in the oxidized material might stabilize the "VPO<sub>4</sub>F" framework by "pillaring" the tunnels.

The crystal structure refinement of the discharged material revealed that the intercalation of lithium takes place in the channels along [010] leaving the channels along [100] unoccupied. The inserted Li shares the K2 site with the residual potassium and creates a new Li3 position, which was localized using a difference Fourier map (Figure S12 of the SI). The refined occupancy for K turned out to be 0.12 and the amount of the inserted Li+ ions was calculated from the electrochemical measurements as 0.7. The latter was taken as a constraint during the refinement which resulted in the  $Li_{0.70}K_{0.12}VPO_4F$  composition. The Li3 has a [4 + 2] coordination with four short 1.99-2.14 Å Li3-O bonds. It resides in the channels along the b axis forming an alternating row with Li2 atoms (Figure 1C). The main crystallographic parameters, structure information and interatomic distances of the oxidized and lithiated materials are given in Tables S4-S8.

According to the structure refinement, the electrochemically cycled material preserves the KTP framework, but the accommodation of Li does not completely follow the initial crystallographic positions of K. The difference in the unit cell volume of all three phases is small and does not exceed 2.2% (Table S1 and S4 of the S1) in contrast to tavorite-type LiVPO<sub>4</sub>F, which exhibits an 8.5% volume change between charged and discharged forms.<sup>24</sup> The slight decrease in the cell parameters of the lithiated material can be explained in terms of Coulomb interactions between the oxygen framework and the new Li3 ions inserted in the channels along the *b*-axis. It reduces the *a* and *c* parameters while the *b* parameter remains almost the same.

To analyze diffusion paths in the crystal structure, the bond valence sum mapping (BVSM)<sup>25</sup> method was utilized. In the initial KVPO<sub>4</sub>F structure, K<sup>+</sup> ions follow a curved pathway along the *c* axis (Figure S14a of the SI). This is in good agreement with ionic conductivity measurements on the isostructural KTP materials, which revealed the highest conductivity values along the *c*-direction  $(10^{-4}-10^{-6} \text{ S/cm} \text{ along } c \text{ vs } 10^{-7}-10^{-10} \text{ S/cm} \text{ along } a \text{ and } b, 400 \text{ K}).^{26,27}$  In the oxidized material, the Li<sup>+</sup> diffusion map becomes three-dimensional (Figure S14b of the SI). In this case, we cannot observe a distinct "pathway" for the Li<sup>+</sup> ions because of their tiny radius compared to the radius of the channels. The

obtained stretched diffusion map implies a high mobility for the Li<sup>+</sup> ions that was confirmed by the electrochemical testing.

 $Li_x K_{0.15} VPO_4 F$  shows remarkable capacity retention at 40C maintaining more than 50% of theoretical (156 mAh/g) or 75% of initial specific capacity (111 mAh/g at C/5) (Figure 3). Extended cycling was carried out at a rate of 1C. After 100 cycles, a moderate capacity fading of 27% with a Coulomb efficiency over 99% was observed (inset in Figure 2).



**Figure 3.** C-rates capability upon cycling and corresponding discharge curves of  $\text{Li}_x \text{K}_{0.15} \text{VPO}_4 \text{F}$ . Before each discharge, the cells were charged up to 4.7 V at C/5 for the first three cycles and then at C/2 rate starting from the fourth cycle.

The observed extremely low polarization (Figure S13 of the SI) is likely caused by comparably high ionic and electronic conductivities of this material. Apparently, Li ion diffusion in  $\text{Li}_x \text{K}_{0.15} \text{VPO}_4 \text{F}$  is not hindered by "pinning" interactions with the lattice as it occurs in case of FeSO<sub>4</sub>F.<sup>19</sup> Presumably, it is due to the smaller but much more suitable channels in the "VPO<sub>4</sub>F" framework (ionic radius of V<sup>3+</sup>, 0.64 Å comparing to that of Fe<sup>2+</sup>, 0.78 Å). Rapid kinetics of the Li de/intercalation is also evidenced by rate capability measurements (Figure 3).

It should be noted that this material also exhibits reversible capacity at potentials around 2 V (Figure S15 of the SI) indicating a multiredox process similar to  $\text{LiVPO}_4\text{F}$  tavorite.<sup>1,24</sup> This electrochemical activity in a low-voltage domain needs further investigation.

The obtained cathode material reveals remarkable electrochemical properties in a Li-anode cell. After optimization it can compete with many renowned materials in terms of energy density or rate capability. The theoretical 624 Wh/kg specific energy of  $\text{Li}_x \text{K}_{0.15} \text{VPO}_4 \text{F}$  exceeds that of LiFePO<sub>4</sub> (583 Wh/kg) and is comparable to that of tavorite LiVPO<sub>4</sub>F (655 Wh/kg). A significant advantage of the discovered material is its much smaller volume variation upon cycling in comparison with the latter ones.

The possibility to operate at 40C preserving a substantial capacity level and retention makes it a serious contender to existing high-power cathodes such as NASICON-type  $Li_3V_2(PO_4)_3$ . Because of the presence of spatial voids and channels,  $Li_xK_{0.15}VPO_4F$  has a slightly lower volumetric energy density (~2000 Wh/l) compared to LiFePO<sub>4</sub> (2135 Wh/l) or tavorite-LiVPO<sub>4</sub>F (2140 Wh/l), which is still attractive for high-power or large-scale applications.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.5b04065.

Experimental details, SEM and TEM images, typical EDX spectrum for KVPO<sub>4</sub>F, ED patterns for KVPO<sub>4</sub>F,  $K_{0.17}$ VPO<sub>4</sub>F and  $Li_{0.70}K_{0.12}$ VPO<sub>4</sub>F, FTIR and EELS spectra, results of Rietveld refinement of KVPO<sub>4</sub>F, details of structure solution for  $K_{0.17}$ VPO<sub>4</sub>F and  $Li_{0.70}K_{0.12}$ VPO<sub>4</sub>F using EDT, crystallographic parameters for the refined structures, BVS maps, electrochemical data (PDF).

Crystallographic parameters of KVPO<sub>4</sub>F (CIF). Crystallographic parameters of  $K_{0.17}$ VPO<sub>4</sub>F (CIF). Crystallographic parameters of Li<sub>0.70</sub>K<sub>0.12</sub>VPO<sub>4</sub>F (CIF).

#### AUTHOR INFORMATION

#### Corresponding Author

\*S. S. Fedotov. E-mail: fedotov.msu@gmail.com.

#### Author Contributions

The paper was written through contributions of all authors. **Notes** 

The authors declare no competing financial interest.

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