



	Experiment title: Exploring the charge compensation mechanism in KVPO ₄ F _{1-x} O _x positive electrodes for K-ion batteries using <i>operando</i> and <i>ex situ</i> XES	Experiment number: CH-6103
Beamline: BM16	Date of experiment: from: 28 October 2021 to: 02 November 2021	Date of report: 03 February 2023
Shifts: 15	Local contact(s): Mauro Rovezzi	<i>Received at ESRF:</i>
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Report:

Background:

Among the positive electrode materials developed up to now for K-ion batteries (KIB), layered oxides have been proposed as active materials due to their ability of reversibly inserting alkali ions.^[1] Nevertheless, strong limitations and irreversibility in the charged state of the battery (K⁺ deintercalated state of the electrode materials) were reported. KV⁺³PO₄F and KV⁺⁴OPO₄ showing KTiOPO₄-type structure were the first materials able to deliver a reversible capacity exceeding 100 mAh/g above 4 V vs. K⁺/K.^[1-2] The family of compounds KVPO₄F_{1-x}O_x exhibits a three-dimensional framework (orthorhombic Pna21 space group) containing distorted chains of corner-sharing octahedra [X···VO₄···X···VO₄···X] connected through PO₄ tetrahedra and forming tunnels for the diffusion of K⁺ ions. The V oxidation state and its local environment in KVPO₄F_{1-x}O_x (x= 0, 0.25, 0.5, 0.75, 1) have been recently investigated by *ex situ* and *operando* X-ray absorption spectroscopy. While the V mean oxidation state of the pristine compounds agrees with those obtained by XPS, the presence of V²⁺ was not detected by XAS.^[3] Such discrepancy probably relies on the different probing depth of XAS and XPS, indicating different V oxidation states at the surface and in the bulk of the material. During the *operando* XAS experiment, only one electron is exchanged upon K extraction for KV⁺³PO₄F, KV^{+3.5}PO₄F_{0.5}O_{0.5} and KV⁺⁴OPO₄; the observed shift of the edge position, however, exceeds that expected only from the V redox activity (the electrolyte reactivity is responsible for extra-capacity in charge), indicating that the edge position is not adapted to describe the redox mechanism when the ligands have a different covalent nature. As reported in our previous study, the pre-peak features could provide important information on the V-F, V-O and V=O bonds involved in the charge compensation.^[4-7] However, a quantitative deconvolution of the V-X pre-peak contributions is not straightforward due to the lack of selectivity of X anions and a sub-optimal energy resolution of XAS experiment. To address these issues, we performed to core-to-core (CtC) X-ray emission spectroscopy (XES) at the K α and K β emission lines to retrieve bulk information on the V oxidation state and the V-X contributions in the pristine electrodes.

Results and findings:

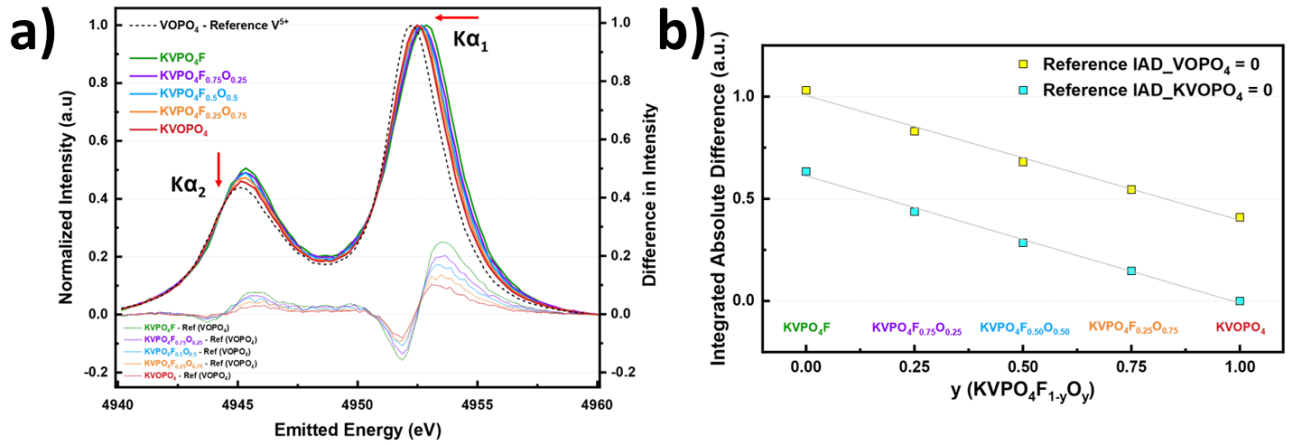


Figure 1. a) Normalized Vanadium CtC-K α X-ray emission spectra (solid lines) at for KVPO₄F_{1-x}O_x ($x = 0, 0.25, 0.50, 0.75, 1$). b.) The calculated integrated absolute difference (IAD) of CtC-K α are also shown.

We present the results of measurements performed at BM16 on KVPO₄F_{1-x}O_x ($x = 0, 0.25, 0.5, 0.75, 1$) pristine materials. We measured the emission spectra at the CtC-K α and CtC-K β emission lines (**Fig. 1 and 2**).

The CtC-K α lines, which arise from fluorescence after a 2p electron fills a 1s core hole, are the lowest energy emission lines. The 2p spin-orbit coupling causes the K α line to split into two components: K α 1 (K-L₃, 2p_{3/2} → 1s) and K α 2 (K-L₂, 2p_{1/2} → 1s). CtC-K α emission lines showed a shift to lower emission energy as the oxidation state increased as a function of the O content of the pristine materials. This was observed at the K α 1 line of the CtC-K α emission, and the intensity of the K α 2 line decreased with increasing oxidation (**Fig. 1a**). A linear shift was observed for the CtC-K α emission as the vanadium oxidation state increased. This finding confirms our previous X-ray absorption spectroscopy results.

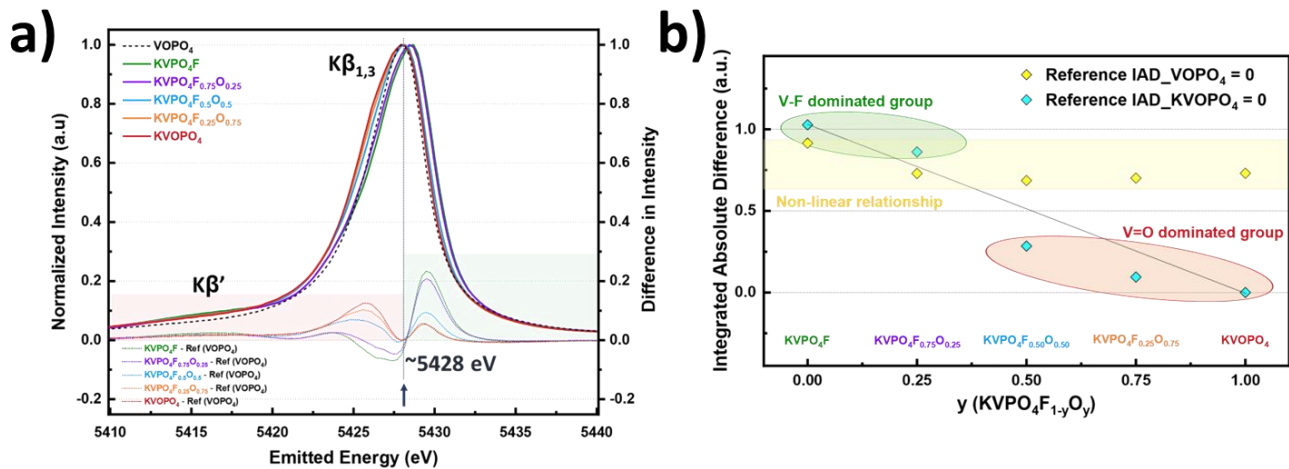


Figure 2. a) Normalized Vanadium CtC-K β X-ray emission spectra (solid lines) at for KVPO₄F_{1-x}O_x ($x = 0, 0.25, 0.50, 0.75, 1$). b.) The calculated integrated absolute difference (IAD) of CtC-K β are also shown.

The CtC-K β lines result from fluorescence that happens when 3p (or higher) electrons fill the 1s core hole. The 3p-3d exchange interactions cause the main K β line to separate into K β 1,3 and K β ' features. Basically, the more unpaired electrons there are, the larger the splitting of K β 1,3 and K β ', making this spectral region a useful indicator of the spin state. Result of the analysis at the CtC-K β emission lines showed a different trend compared to the CtC-K α results (**Fig. 2a**). Although a shift to lower emission energy was observed as the V oxidation state increased, the trend was not linear. The spectra differences between KVPO₄F_{1-x}O_x and the reference material VOPO₄ showed segregation into two groups at an emission energy of ~5427.9 eV, the peak position of VOPO₄. This indicates that the peak position in the emission spectrum of VOPO₄ is a point of disparity among the materials. The segregation can be divided into a V-F dominated group (KVPO₄F_{1-x}O_x with $x = 0, 0.25$) and a V=O dominated group (KVPO₄F_{1-x}O_x with $x = 0.5, 0.75, 1$). Structural analysis from our XRD results support the presence of a V=O bond as O content increases. The peak position of KVPO₄F_{1-x}O_x ($x = 0.5, 0.75, 1$) does

not change much and remains at the peak position of the reference material VOPO₄ with a higher oxidation state (V⁵⁺). The only difference observed was a broadening of the K β _{1,3} peak, which we suspect is due to the presence of the V=O bond causing more distortion in the local geometry.

The results of the CtC-K α and CtC-K β emission lines show different sensitivities. The CtC-K α emission line appears to be sensitive to the local structure of the material, similar to conventional XAS measurements. Meanwhile, the CtC-K β results suggest sensitivity to both the local geometry and may be used to distinguish the differences in ligands, due to 3p-3d electron exchange interactions.

We aim to perform further analysis through *ab initio* and first principle calculations to understand the emission spectra obtained. We ultimately aim to disentangle the different factors affecting the spectral signatures and to relate these factors to the electronic properties, which affects the electrochemical properties of these materials.

Challenges during the experiment:

Several challenges were encountered during the experiment, including difficulties in measuring the valence-to-core (VtC) K β emission lines due to a low signal-to-noise ratio. Despite this setback, the collected data will still be used for alternative analysis. Another issue encountered was the measurement of *ex situ* materials, which were susceptible to oxidation, hindering the planned investigation into the charge compensation mechanism of KVPO₄F at different states of charge. The emission spectra did not show significant changes. To overcome these issues in future experiments, it is recommended to adopt better material handling techniques to avoid oxidation and damage to delicate samples. Additionally, an attempt was made to perform *operando* measurements for KVPO₄F, however, frequent beam dumps during battery operation forced the measurements to be stopped.

References:

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