



	Experiment title: Understanding the charge mechanisms process occurring in $KV_{1-y}(VO)_y(PO_4)F_{1-y}$ positive electrodes for K-ion batteries by XRS and VtC XES	Experiment number: CH-6327
Beamline: ID20	Date of experiment: from: 14 June 2022 to: 20 June 2022	Date of report: 03 February 2023
Shifts: 15	Local contact(s): Alessandro Longo	<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. $KV^{+3}PO_4F$ and $KV^{+4}OPO_4$ showing $KTiOPO_4$ -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 $KVPO_4F_{1-x}O_x$ exhibits a three-dimensional framework (orthorhombic Pna21 space group) containing distorted chains of corner-sharing octahedra $[X \cdots VO_4 \cdots X \cdots VO_4 \cdots X]$ connected through PO_4 tetrahedra and forming tunnels for the diffusion of K^+ ions. The V oxidation state and its local environment in $KVPO_4F_{1-x}O_x$ ($x = 0, 0.25, 0.5, 0.75, 1$) 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 V^{2+} 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 $KV^{+3}PO_4F$, $KV^{+3.5}PO_4F_{0.5}O_{0.5}$ and $KV^{+4}OPO_4$; 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) and valence-to-core (VtC) X-ray emission spectroscopy (XES) at the $K\beta$ emission lines to retrieve bulk information on the V oxidation state and the V-X contributions in the pristine electrodes.

Results and findings:

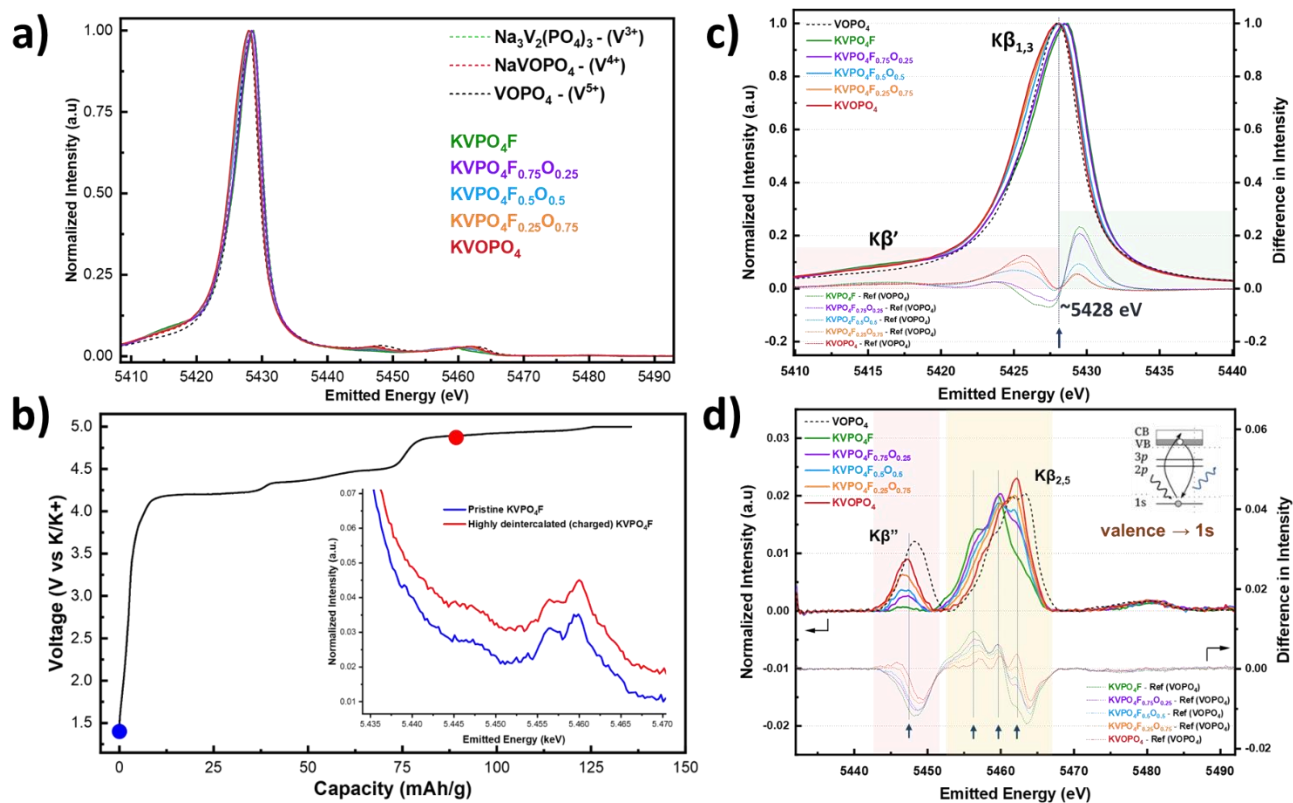


Figure 1. Normalized Vanadium X-ray emission spectra (solid lines) at the K β emission line for KV_{1-y}(VO)_y(PO₄)F_{1-y} (y = 0, 0.25, 0.50, 0.75, 1) with other reference materials for comparison, b) the electrochemical curve of KVPO₄F during operando measurements with VtC-K β emission lines shown at the inset c) CtC-K β and d) VtC-K β emission lines are also shown

We present the results of measurements performed at ID20 on KV_{1-y}(VO)_y(PO₄)F_{1-y} (y = 0, 0.25, 0.5, 0.75, 1) pristine materials. We measured the emission spectra at the CtC- and VtC-K β emission lines.

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. 1b**). 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 valence-to-core (VtC) region is a useful tool for determining the identity, ionization potential, and protonation state of a ligand. This is because it is highly unlikely for a valence electron to fill the 1s core hole, leading to the observation of K β _{2,5} (ligand np to metal 1s) and K β ' (ligand ns to metal 1s) transitions. During the experiment, the VtC-K β region was studied with high precision using the three detectors available in ID20. Distinct spectral signatures of different materials were observed and intriguing results were obtained.

The K β ' feature is related to the “cross-over” transition from a molecular orbital with primarily ligand character (ligand 2s to metal 1s). An increase in the intensity of the K β ' is expected with changes in the V=O bond

distances. A stronger signal is linked to a more distorted local octahedral geometry, which is attributed to the presence of V=O vanadyl bonding. On the other hand, the position of the $K\beta_{2,5}$ is highly sensitive to changes in oxidation state, with more oxidized V found at higher emission energies.

In all the vanadyl phosphates, a triple-peak structure is observed in the main bonding-derived VtC feature. An increase in the intensity of the $K\beta''$ with increasing oxidation state is likely due to the effect of V=O. Similarly, a shift in the $K\beta_{2,5}$ triple peak to higher emission energy is also attributed to the influence of V=O.

We are still working to understand the splitting seen in the reference material $VOPO_4$ and to determine the impact of the presence of *cis*- and *trans*- configurations of F and O in the octahedra. To do this, we plan to use advanced computational methods such as ab initio and first-principle calculations to separate the effects of these various parameters.

Challenges during the experiment:

Several challenges were encountered during the experiment, including difficulties in measuring the valence-to-core (VtC) $K\beta$ emission lines of *ex situ* $KVPO_4F$ materials, hindering the planned investigation into the charge compensation mechanism in *ex situ* $KVPO_4F$ at different states of charge. The emission spectra did not show significant changes, as a self-discharge phenomenon was observed during the cell disassembling^[8]. 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 $KVPO_4F$, but it was discovered that local beam damage to the materials was encountered, leading to indifferent measured spectra. Despite yielding good electrochemical measurements (**Fig. 1b**) during the *operando* measurements, the emission spectra were not changing. To address these challenges for future experiments, we plan to modify our measurement strategy by focusing on the handling of *ex situ* samples. The samples will be prepared directly in *operando* cells, and will charge or discharge without disassembly and directly subjected to measurements.

References:

1. R. Wernert et al., Chem Mater, 2022, 34, 4523-4535
2. K. Kubota et al, Chem. Rec., 2018, 18, 1–22
3. K. Chihara et al, Chem. Commun., 2017, 53, 5208-5211
4. L. Caracciolo et al, Journal of the Electrochemical Society, 2020, 167, 130527.
5. L.H.B. Nguyen et al, Energy Storage Materials, 2019, 20, 324-334
6. L.H.B. Nguyen et al, Journal of Physical Chemistry C, 2020, 124 (43), 23511.
7. E. Boivin et al, Chem. Mater., 2019, 31 (18), 7367.
8. R. Wernert et al., ACS Appl. Energy Mater, 2022, 5 (12), 14913-14921