

NEW INSIGHTS INTO VANADIUM FLUOROPHOSPHATES OF FIRST INTEREST DEVELOPED FOR Li AND Na-ION BATTERIES

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LiVPO₄F and Na₃V₂(PO₄)₂F₃ are respectively positive electrode materials for Li-ion and Na-ion batteries, which are attracting strong interest due to their high capacity, rate capability and long-term cycling stability.^{1,2}

We will show how challenging is the control of oxygen over fluorine stoichiometry in these fluorophosphates. Existence of characteristic lithium defect environments has been for instance recently revealed using solid-state ⁷Li nuclear magnetic resonance in well-crystallized Tavorite LiVPO₄F,³ despite they were not seen by high resolution X-ray and neutron diffraction as well as scanning transmission electron microscopy. The nature of these defects will be discussed, considering different possible sources of aging of LiVPO₄F.

We already showed a complex phase diagram as a function of the charge state for Na₃V₂(PO₄)₂F₃, on the contrary to the straightforward solid solution described in the literature.⁴ From structural determination based on high resolution X-ray powder synchrotron data and bond valence sum analysis we proposed for instance in NaV₂(PO₄)₂F₃ two vanadium environments, V³⁺ and V⁵⁺, instead of a single one (i.e. V⁴⁺). We will report on the *operando* investigation of the redox processes involved during sodium deintercalation and on the charge compensation mechanism on the V site, considering X-ray absorption near edge structure measurements collected at the V k-edge.

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