MS40 Operando and in situ crystallographic studies

MS40-01

Operando X-ray diffraction studies of NASICON-type positive electrodes for Na-ion batteries

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Abstract

Polyanionic materials (phosphates in particular) are of special interest as positive electrodes for Li-Ion or Na-ion batteries since they offer competitive electro-chemical performances compared to sodiated or lithiated transition metal oxides [1,2]. They are based upon stable 3D frameworks, which provide long-term structural stability and demonstrate a unique variety of atomic arrangements in their crystal structures. Recent electrochemical and structural investigations of vanadium-based phosphate compounds ($LiVPO_4O$-$LiVPO_4F$, $Na_3V_2(PO_4)_2F_3$, $Na_3V_2(PO_4)_3$ …..) revealed promising perspectives [3-5].

The NASICON structural family with its large panel of compositions, $Na_xMM'(PO_4)_3$ ($0 \leq x \leq 4$; M,M' = Ti, Fe, V, Cr, Mn) is among the most widely investigated due to its specific three-dimensional framework structure, stable long-term cycling ability and high Na+ mobility [1-2, 5-6]. Among them, the vanadium phosphate $Na_3V_2(PO_4)_3$ [7] is of particular interest. We will present several new structures that we determined, from pristine powders or for intermediate compositions spotted by operando X-Ray diffraction.

Recently, we succeeded in synthesizing Fe-substituted $Na_4FeV(PO_4)_3$ that allows the reversible extraction of close to 3 Na^+ (for two transition metals) and we will report on its crystal structure and on that of $Na_3FeV(PO_4)_3$ for which new Na^+ order-disorder phenomena have been spotted [8, 9]. Even more recently, we reported on the existence of an intriguing definite phase of composition $Na_2V_2(PO_4)_3$ through computational methods [10] and operando X-ray diffraction and X-ray absorption spectroscopy during battery operation [11].

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