TEMPERATURE-DRIVEN ORDER-DISORDER TRANSITIONS IN $Na_3V_2(PO_4)_2F_3$ AND $Na_3V_2(PO_4)_3$ POSITIVE ELECTRODES

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Both $Na_3V_2(PO_4)_3$ and $Na_3V_2(PO_4)_2F_3$ compositions represent very attractive positive electrode materials for Na-based high power-density applications. Although being close in chemical formulas, their crystal structures have nothing in common, besides being phosphate-based frameworks within which Na^+ ions are distributed in a more or less ordered fashion. Given the critical impact of Na^+ distribution schemes on ion transport properties and on response to high charge-discharge currents, we undertook precise temperature-controlled structural studies

Until very recently the crystal structure of $Na_3V_2(PO_4)_2F_3$ was described in the tetragonal space group *P4₂/mnm*. We revealed, thanks to very high angular resolution synchrotron radiation diffraction, that a small orthorhombic distortion exists [1], described in the *Amam* space group: the structural framework is preserved but a different arrangement of the sodium ions was evidenced. Upon increasing slightly the temperature to ~130°C, Na^+ are fully disordered and give rise to a more symmetrical structural form (space group *I4/mmm*).

The crystal structure of the NASICON $Na_3V_2(PO_4)_3$ phase (NVP) has been investigated as a function of T, combining laboratory and synchrotron X-ray powder diffraction as well as single crystal X-ray diffraction. The existence of four polymorphs from -30°C to 225°C was demonstrated. While the high temperature γ-NVP crystallizes in the classical rhombohedral cell (*R-3c*, 200°C), the low temperature α-NVP undergoes a monoclinic distortion (S.G. *C2/c*, -10°C) together with a complete ordering of the Na^+ ions [2]. Additionally, partial substitution of Al for V results in a significant increase of the energy density of this electrode by activating the V^{4+}/V^{5+} couple at 3.95 V vs. Na^+/Na [3]. $Na_3V_2(PO_4)_3$ was used to build all solid state symmetrical cells operating at 200°C together with NASICON $Na_3Zr_2Si_2PO_{12}$ as the Na^+ solid electrolyte. The battery operates at 1.8 V with 85 % of the theoretical capacity attained at C/10 with satisfactory capacity retention [4].

References

[1] M. Bianchini et al., *Chem. Mater.*, 26(14), 4238-4247 (2014)
[2] J.N. Chotard et al., *Chem Mater.*, 27(17), 5982-5987 (2015)
[3] F. Lalère et al., *J. Mater. Chem. A*, 3, 16198-16205 (2015)
[4] F. Lalère et al., *J. Power Sources*, 247(1), 975-980 (2014)