Vanadium-containing phosphates and fluorophosphates for Na batteries

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Among polyanionic-based electrode materials developed for Na-ion batteries, one of the most promising families turns out to be $Na_3V_2(PO_4)_2F_{3-y}O_y$ ($0 \leq y \leq 2$). We will present the influence of the oxygen substitution for fluorine on the structural and transport properties of $Na_3V_2(PO_4)_2F_{3-y}O_y$, as a function of temperature. An order-disorder phase transition is observed whatever the content in oxygen, in relation with changes in the ionic conductivity and thus with the mobility of the Na^+ ions within the tunnels of the tridimensional structure. The richer the content in oxygen in $Na_3V_2(PO_4)_2F_{3-y}O_y$, the higher the electronic conductivity is, in relation with the mixed valence state V^{3+}/V^{4+} within the bi-octahedral units $V_2O_8F_{3-y}O_y$. The electrochemical performance of $Na_3V_2(PO_4)_2F_{3-y}O_y$ in Na-ion batteries will be also discussed in details.

We also investigated the substitution of a part of vanadium by aluminum, iron or manganese in several alternative crystal structures. As a result of our work, we discovered and electrochemically characterized a novel mixed-valence $Na_{11}V^{3+}(V^{4+}O)(P_2O_7)_4$ compound, a new cmposition $Na_3V^{III}(PO_4)_2$ and two groups of new M^{3+}-substituted phases, namely, $Na_7V_{4-x}Al_x(P_2O_7)_4(PO_4)$ (x = 2 and 1) and NASICON-type $Na_{3\pm y}V_{2-x}M_x(PO_4)_3$ (M = Al, Ti, Mn, Fe) compositions.

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