STRUCTURE AND ELECTROCHEMISTRY OF $Na_{1+y}VPO_4F_{1+y}$ ($0 \leq y \leq 0.5$) FOR Na- AND Li-ION BATTERIES

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$NaVPO_4F$ and $Na_3V_2(PO_4)_2F_3$ are interested for both sodium- and lithium-ion batteries application due to their ability to reversibly intercalate Na^+ and Li^+ ions in their structure [1-4]. $NaVPO_4F$, first proposed by Barker *et al.* [1], crystallizes in the tetragonal symmetry with the *I*4/*mmm* S.G. Meins *et al.* reported that $Na_3V_2(PO_4)_2F_3$ also exhibits the tetragonal symmetry with the $P4_2/mnm$ S.G. [2]. Barker *et al.* investigated its electrochemical properties [3]. Recently, Bianchini *el al.* using synchrotron radiation have identified $Na_3V_2(PO_4)_2F_3$ in another, orthorhombic structure with the *Amam* S.G. [4]. The structural and electrochemical behavior similarity of these two compounds allows one to assume that they belong to one and the same phase with some deviation from the stoichiometry.

In this study, a series of $Na_{1+y}VPO_4F_{1+y}$ ($0 \leq y \leq 0.5$) compositions was investigated in detail to establish structural similarity and distinctive features between $NaVPO_4F$ and $Na_3V_2(PO_4)_2F_3$ (or $Na_{1.5}VPO_4F_{1.5}$). $Na_{1+y}VPO_4F_{1+y}$ were prepared by mechanochemically assisted solid state synthesis. Composition, structure, morphology and electrochemistry of the materials were analyzed by XRD, SEM, EDX, FTIR, ^{23}Na and ^{31}P NMR spectroscopy, and galvanostatic cycling in Na^+ and Li^+ cells.

XRD analysis showed that the as-prepared products are well-crystallized single-phase materials. The Rietveld refinement using TOPAS software and two models $P4_2/mnm$ and *Amam* revealed that the experimental data are better described with the orthorhombic *Amam* S.G. ^{23}Na and ^{31}P NMR spectra of $Na_{1+y}VPO_4F_{1+y}$ are very similar to each other. The ^{23}Na NMR spectra exhibit resonance at 170-180 ppm, while ^{31}P spectra exhibit two intense resonances at ~6700 and 5000 ppm in addition to a series of weaker resonances at lower frequencies. The presence of antisite defects has been proposed in $Na_{1+y}VPO_4F_{1+y}$. The smallest structural disorder and the best electrochemical performance was observed for the sample with y=0.25 both in Na^+ and Li^+ cells. Voltage profile of charge-discharge curves was similar for all the samples. *Ex situ* XRD and EDX studies were carried out to control the phase transformations and Na^+/Li^+ ion exchange upon cycling of $Na_{1+y}VPO_4F_{1+y}$ in Li cells.

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