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Temperature dependence of structural and transport properties for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$

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Temperature dependence of structural and transport properties for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$

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Abstract

Among polyanionic-based electrode materials developed for Na-ion batteries, one of the most promising families turns out to be $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($0 \leq y \leq 2$). Here, we present the influence of the oxygen substitution for fluorine on the structural and transport properties of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$, as a function of temperature, through the comparison of the two compositions $y = 0$ and $y = 0.5$. 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 $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ the higher the electronic conductivity, in relation with the mixed valence state $\text{V}^{3+}/\text{V}^{4+}$ within the bi-octahedral units $\text{V}_2\text{O}_8\text{F}_{3-y}\text{O}_y$, and the better the electrochemical performances in Na-ion batteries.

Introduction

The increasing need for electrochemical energy storage, either for portable electronic devices or for larger-scale applications such as hybrid electric vehicles or static renewable energy storage systems, causes renewed interest in alternatives to Li-ion batteries, in order to overcome drawbacks associated to the availability and prize of lithium resources.¹ In this context, Na-ion batteries is an emerging field owing to the lower price and very large earth-abundance of sodium.² In terms of energy density, Na-ion batteries hardly compete with Li-ion ones due to the intrinsic properties of Na: a less negative standard reduction potential (-2.7 V vs SHE for the $\text{Na}^+_{\text{aq}}/\text{Na}$ against -3.04 V for the $\text{Li}^+_{\text{aq}}/\text{Li}$ one) and a higher molecular weight. Thus the Na-ion technology can be addressed for targeted applications such as domestic energy storage and load-leveling applications for the grid.

Among several polyanionic-based electrode materials,³⁻⁹ one of the most promising family of compounds turns out to be the sodium-vanadium fluorinated oxy-phosphate $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$, where y can vary from 0 to 2.¹⁰⁻¹⁹ This whole range of compositions from V^{III} -rich ($y = 0$) to V^{IV} -rich ($y = 2$) can be oxidized to an average oxidation state of V^{IV} to V^{V} respectively, by the deintercalation of two sodium ions. For instance in $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ ($y = 0$) the extraction of 2 Na^+ ions was experimentally demonstrated with two main voltage-composition plateaus at around 3.7 and 4.2 V vs. Na^+/Na for a theoretical energy density of 507 Wh/kg^{17, 20-21} (128 Ah/kg at an average potential of 3.95 V), competitive with that delivered by LiFePO_4 in Li-ion batteries. As recently depicted, a small amount of oxygen in the initial material (*i.e.* slightly oxidized) induces significant differences on the electrochemical properties although they are isostructural in the range $0 \leq y \leq 0.5$.¹⁹ In this range of compositions, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ crystallizes in the *Amam* space group at room temperature where the structure consists of a tridimensional framework of $\text{V}_2\text{O}_{8+y}\text{F}_{3-y}$ bi-octahedra which are connected by PO_4 tetrahedra. This framework provides large tunnels where Na^+ ions are mobile upon extraction/insertion reactions. Regardless the oxidation state of the initial material, the system $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ is reported to undergo an order-disorder transition at 122 °C for the V^{III} -rich ($y = 0$) composition¹⁵ and at 230 °C for the V^{IV} -rich ($y = 2$) composition.¹⁶

On the other hand, from the electrochemical point of view, the amount of oxygen in the pristine material induces significant modifications of the electrochemical behaviour, as previously reported.¹⁹ The main drawback of V^{IV} defects is the decrease of the average potential vs. Na upon Na^+ extraction. Nevertheless, higher capacity as well as lower polarization are observed for the $y = 0.5$ composition that may reveal better ionic and/or electronic conductivity. In order to obtain a deeper understanding of the transport properties of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and oxidized related phase, two samples $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$

and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ have been prepared and studied as a function of temperature via *in situ* synchrotron X-ray powder diffraction (SXRPD) and thermogravimetric analysis combined with differential scanning calorimetry (TGA-DSC). These results are confronted with temperature-controlled electrochemical impedance spectroscopy, on sintered pellets and single crystals, to evaluate the contributions of ionic and electronic conduction.

1. Experimental

The two $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ powder samples were synthesized according to the method already described in details elsewhere.¹⁹ NaF , Na_2CO_3 , $\text{V}^{\text{III}}\text{PO}_4$ and $\text{V}^{\text{V}}\text{OPO}_4$ precursors were mixed in stoichiometric proportions by ball milling and the resulting mixtures were heated at 750°C under Argon for 2 hours. The O content in our materials was extrapolated from XRD, XAS, and NMR data, as described in details in¹⁹. As expected, the $y = 0$ compound $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ has similar cell parameters to those already reported by Bianchini et al.¹⁵ ($a = 9.0285(1)$ Å, $b = 9.0444(1)$ Å, and $c = 10.7467(1)$ Å), and once again the orthorhombic distortion with a b/a ratio of 1.002 is confirmed. Here the oxidized composition $y = 0.5$ is near to be tetragonal as the b/a ratio is as low as 1.0003 ($a = 9.0323(1)$ Å, $b = 9.0352(1)$ Å, $c = 10.6847(1)$ Å) in line with the values reported in¹⁹.

Electrochemical tests were performed in CR2032-type coin cells. The positive electrodes were prepared from a slurry made of 80 wt% $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($0 \leq y \leq 0.5$), 10 wt% carbon black, and 10 wt% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidone (NMP), casted on an Al foil and dried at 80°C overnight. The loading of the active material on the electrodes was around 2.5 mg/cm². The negative electrode was sodium metal, whereas the electrolyte was home-made from a 1 M solution of NaPF_6 (Strem Chemical; 99%) in ethylene carbonate and dimethyl carbonate (EC:DMC = 1:1) with 3 wt% of fluoroethylene carbonate (FEC) as additive. The electrochemical cells were charged and discharged in galvanostatic mode, at a C/20 between 2.5 and 4.3 V vs Na^+/Na corresponding to the exchange of 0.1 mol of sodium ions/electrons per hour. Galvanostatic intermittent titration technique (GITT) measurements have been performed at the beginning of the charge (*i.e.* near the as prepared compositions) and such as 10 minutes of C/25 galvanostatic charge were followed by a relaxation up to 1 mV/h.

High angular resolution SXRPD data as a function of temperature from room temperature (RT) to 180°C were collected using the MSPD diffractometer at ALBA (Barcelona, Spain). The powders were placed in a 0.5 mm diameter capillary and data recorded in Debye-Scherrer geometry with a wavelength of 0.9530 Å in the 2θ angular range of $1 - 52^\circ$ with a 0.006° step and an accumulation

time of 5 minutes. As already reported by Bianchini et al.¹⁵ for the structural determination of $\text{Na}_3\text{V}^{\text{III}}_2(\text{PO}_4)_2\text{F}_3$ ($y=0$), the use of very high angular resolution techniques is essential as a very small orthorhombic distortion exists. Their detection is important to reveal significant changes in the distribution of sodium ions within the 3D framework and thus in the interpretation of electrochemical processes.

TGA-DSC has been performed in inert atmosphere with heating/cooling ramps of 10 °C/min under argon. A first heating/cooling cycle between RT and 150 °C has been carried out to remove possible adsorbed water that might influence TGA-DSC curves then a cycle from RT to 500 °C is performed to highlight temperature dependent structural transitions. No significant weight loss or gain was detected by TGA (<0.5%) that I hence not shown.

The growth of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ single crystals was performed by the flux method from a $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ solute and a NaF solvent acting as a self-flux. As previously reported,¹⁵ the pristine powder of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ was obtained by planetary milling between NaF and VPO_4 . Here, an excess of NaF was added in order to obtain a 75 % mol of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and 25 % mol of NaF mixture for the pellet which was sintered at 800 °C during 1 hour under 95%/5% Ar/H₂. This sintered pellet was placed into a platinum assembly sealed under primary vacuum²². The platinum assembly was first heated for 24 h at 1050 °C in a vertical resistive furnace, then cooled down to 950 °C at 0.5 °C.h⁻¹ within a longitudinal thermal gradient about 0.5 °C.cm⁻¹ and finally cooled down to room temperature at 120 °C.h⁻¹. The as-grown piece was cut into a single crystal (2.4 x 3.1 x 1.4 mm³) oriented along 3 crystallographic directions [100], [010] and [001] checked by Laue X-rays backscattering.

For electrochemical impedance spectroscopy of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$, the powders were pressed into pellets of 10 mm diameter by means of a uniaxial press (700 MPa). The pellets were sintered at 650 °C for 1 hour under argon (to reach 82 % compactness), polished and then metalized on each face by gold sputtering used as ion-blocking electrodes. After being dried at 120 °C under vacuum during one night, the pellets were transferred into a dry glove-box to be introduced into an air tight high temperature sample holder (HTSH) to perform AC impedance measurements under argon. The samples were thus maintained out of contact with oxygen and/or moisture during the AC impedance measurements which were performed, at various stabilized temperatures ranging from RT to 250 °C (upon heating and cooling in steps of 15 °C), outside the glove-box, by means of a MTZ-35 frequency response analyser and the specific high temperature furnace HTF-1100 developed by BioLogic. A frequency range of 30 MHz to 10 mHz (20 points per decade and 10 measures per points) and an excitation voltage of 0.1 V were applied during the measurements. From the Nyquist and Phase-Bode plots of the complex impedance, the total grains and grain boundaries conductivities (ionic and electronic) were obtained as well as the activation energy. The Hebb-Wagner method was

used to extract the grain electronic conductivities by DC measurement at different potentials: 0.1, 0.2, 0.3, 0.4, 0.5 V with 7 h of current stabilisation wait for each potential. The same types of experiments were performed on the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3.0}$ single crystal along the $[001]_{\text{Amam}}$ direction: gold contacts were sputtered on opposite faces along this direction and the single crystal was placed in the air tight high temperature sample holder (HTSH) to perform AC/DC measurements in temperature with the same method that described previously for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ pellets.

2. Results and discussion

a. Electrochemical Properties

As previously reported¹⁹ the amount of oxygen in the pristine material $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($0 \leq y \leq 0.5$) induces significant changes in the electrochemical performances. Figure 1 shows the voltage composition data obtained for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($y = 0$ or 0.5) during their second cycle in Na batteries at the rate of C/20. These electrochemical data are similar to each other with two main voltage domains at around 3.65 and 4.15 V versus Na^+/Na and a voltage jump around $x = 2$. In fact, in agreement with our previous study,¹⁹ the average potential of the cell decreases as y increases : from 3.89 V for $y = 0$ to 3.83 V for $y = 0.5$. This effect was ascribed to the formation of highly covalent vanadyl-type bonds $(\text{V}=\text{O})^{2+}$ at the apex of the bi-octahedra $\text{V}_2\text{O}_8\text{F}_{3-y}\text{O}_y$ that “continuously” replace the more ionic V-F bonds as y increases. A more covalent environment around the transition metal ion raises the energy of its antibonding levels closer to the Fermi energy of sodium and thus induces a decrease in voltage for the involved redox couple versus Na^+/Na . Thus the electrochemical voltage-composition data differs significantly in their shape depending on the oxygen content: the more oxidized the compound, the “smoother” their cycling profiles. A small change in the initial oxygen content composition of the material and thus in their vanadium average oxidation states has a major impact on the phase diagram stabilized upon cycling. It evolves from a complex series of biphasic domains and solid solutions for $y = 0$, as determined for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ by Bianchini et al.¹⁵ to an “extended solid solution” for $y = 0.5$.

In addition, another noteworthy feature of the electrochemical performances is the decrease of the hysteresis between charge and discharge as y increases. To verify this, galvanostatic intermittent titration technic (GITT) was used to observe the evolution of the ohmic drop as a function of oxygen amount in the pristine material at the beginning of the charge (i.e. near the as prepared compositions). As presented in Figure 1, the lower polarization resistance for the oxidized compound is also confirmed by a lower iR drop in similar conditions. Besides, the lower relaxation time for the oxygen-rich composition reveals a faster return to equilibrium. At a first glance the smaller relaxation time for

the $y = 0.5$ composition might be ascribed to better transport properties (ionic and/or electronic conductivity) which also may be responsible for higher capacity and lower polarization. Thus the amount of oxygen in the pristine material that induces a mixed valence V^{III}/V^{IV} improves electrochemical properties despite the lower voltage.¹⁹

b. Temperature dependence of the crystal structure

The DSC data collected on $Na_3V_2(PO_4)_2F_3$ and $Na_3V_2(PO_4)_2F_{2.5}O_{0.5}$ when heated under argon are presented in Figure 2. They clearly show endothermic peaks for both compositions without any mass change which corresponds to a temperature dependent structural transition around 130 °C. More precisely, the transition temperature varies from 125 °C to 135 °C for $Na_3V_2(PO_4)_2F_3$ to $Na_3V_2(PO_4)_2F_{2.5}O_{0.5}$ respectively. Previous works on the $y = 0$ ¹⁵ and $y = 2$ ¹⁶ compositions reported transition temperatures of 122 °C and 230 °C respectively which is in good agreement with our observations, i.e. an increase of the transition temperature with the oxygen content.

Concerning $Na_3V_2(PO_4)_2F_3$, the thermal effect observed by DSC can be attributed to the order-disorder transition from the RT *Amam* orthorhombic space group to the high temperature *I4/mmm* tetragonal space group already mentioned by Bianchini et al.¹⁵ $Na_3V_2(PO_4)_2F_{3-y}O_y$, $0 \leq y \leq 0.5$ compositions are isostructural at RT and crystallize in the orthorhombic space group *Amam* with the distribution of the Na^+ ions among a larger number of crystallographic sites, suggesting also an increased ionic mobility within the tunnels of the three-dimensional structure-

Figure 3 displays the temperature-controlled SXRPD data for $Na_3V_2(PO_4)_2F_{2.5}O_{0.5}$, from 40 °C to above the transition temperature (137 °C). A progressive decrease of several peak intensities is observed. The (011), (211) and (031) reflections (among others not displayed here) satisfying the condition $k + l = 2n$ allowed in a *A*-centered symmetry progressively vanish to account for the transition from the *Amam* to the *I4/mmm* space group, similarly to $Na_3V_2(PO_4)_2F_3$ but at higher temperature, in accordance with the DSC data described previously.

As expected, the present $y = 0$ compound $Na_3V_2(PO_4)_2F_3$ has similar cell parameters to those already reported by Bianchini et al.¹⁵ ($a = 9.0285(1)$ Å, $b = 9.0444(1)$ Å, and $c = 10.7467(1)$ Å), and once again the orthorhombic distortion with a b/a ratio of 1.002 is confirmed. Here the oxidized composition

$y = 0.5$ is near to be tetragonal as the b/a ratio is as low as 1.0003 ($a = 9.0323(1)$ Å, $b = 9.0352(1)$ Å, $c = 10.6847(1)$ Å) in line with the values reported in¹⁹. In both cases, as shown in Figure 4, a and b cell parameters are progressively merging as the temperature is increased. Furthermore the smaller orthorhombic distortion and the higher disordered sodium distribution observed for the oxygen-rich

composition may explain the lower enthalpy of the order-disorder phase transition as displayed in Figure 2. On the other hand the temperature dependence of the c parameter is straightforward as it linearly increases with temperature (thermal expansion).

As presented in Figure 5, the structure of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($0 \leq y \leq 0.5$) consists of a tridimensional framework of $\text{V}_2\text{O}_8\text{F}_{3-y}\text{O}_y$ bi-octahedra, which are connected by PO_4 tetrahedra. For $y > 0$, the substitution of oxygen for fluorine occurs at the apex of the $\text{V}_2\text{O}_8\text{F}_{3-y}\text{O}_y$ bi-octahedra, which induces the formation of shorter covalent vanadyl-type bonds as terminal bonds and thus the contraction of the bi-octahedra. Regardless the F/O ratio, the framework of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ is characterized by large tunnels where the Na^+ ions are mobile upon the intercalation and deintercalation reactions. Compared to $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, an additional sodium site Na(4) is necessary to describe the structure of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$.¹⁹ At room temperature, Na(1) is localized at the center of a pyramid with an occupancy around 85% (figs. 5 and 6) whereas the remaining Na^+ ions reside in pyramidal (Na(2) and Na(4)) or capped prismatic (Na(3)) sites, but not at their center. Because of their vicinity, and to minimize the electrostatic repulsions, neighboring Na(2), Na(3), and Na(4) positions cannot be occupied simultaneously. For the same reason, the more distant a Na site is from its equivalent position, the more occupied appears this site. In fact, the sodium ions are located within the whole torus provided by the polyanionic framework similarly to what has been reported before for the high temperature structure of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$.¹⁵ Rietveld refinements of temperature-controlled SXRPD of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ give new insights on how the transition proceeds. First the framework do not undergoes major structural modifications. As highlighted in **Figure 6**, from RT to 40 °C, no major change is observed in Na site occupancies. From 40 °C to the transition temperature (137 °C) the Na(4) site occupancy increases concomitantly with the decrease of the Na(1) site. This progressive smooth phase transition involving no major structural rearrangement is of the second-order (order-disorder) type.

c. Temperature dependence of electronic and ionic transport properties

The characteristic complex impedance spectra obtained at various temperatures for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ are given in Figure 7a in Nyquist coordinates. An asymmetric semicircle is observed classically at high frequencies, ascribed to the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ ceramic resistance. At low frequencies, a straight line with an angle of 45° vs. the horizontal real axis is observed, as a clear signature of a mixed ionic/electronic conductor²³. A fast reduction of the asymmetric semicircle diameter upon heating reveals the enhancement of the total conductivity as the temperature increases. This asymmetric semicircle indicates the presence of two separated phenomena. Hence, the spectra were fitted by an equivalent circuit (Figure 7b) composed by an initial resistor R_0 (for the device and current collectors resistance), in series with i) a system constituted by one resistor R_1 in parallel with a constant phase element CPE1 for the non-ideal capacitance, ii) a second $R_2 / \text{CPE2}$ system (attribution will be discussed later) and

iii) a Warburg element for the diffusion. An example of fit of the data with this equivalent circuit is presented in Figure 7b. The value of the n factor for the pseudo-capacitor CPE1 is around 0.9 for all temperatures. The final capacitance extracted value for the corresponding capacitor is temperature independent and around $2.5 \cdot 10^{-10} \text{ F.cm}^{-2}$. The first semicircle at higher frequency is thus attributed to the bulk conductivity of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$. The n factor of the second CPE in parallel with the third resistor R_2 is around 0.7 with a CPE value around $5 \cdot 10^{-9} \text{ F.s}^{n-1}$, characteristic of material grain boundaries.

The total, grains and grain boundaries conductivities were calculated from $\sigma = \frac{1}{R_x} \frac{d}{A}$ where d is the pellet thickness, A the pellet surface area and R_x the respective resistances deduced from the Nyquist and Phase Bode plots. The evolution of these different conductivities as a function of temperature is shown in Figure 8. The bulk (grains) conductivity (electronic and ionic) is very close to the value of the total conductivity. The grain boundaries appear thus not detrimental to these measurements. The determination of the electronic conductivity of our bulk material, on the same pellet, allowed the extraction of the ionic conductivity, from the difference between grains conductivity and grains electronic conductivity.

The Hebb-Wagner method was used to determine the bulk electronic conductivity of our material. As shown in Figure 9a, a DC electric potential was applied across the sample sandwiched between two blocking electrodes (gold electrodes in the present study) and the current was monitored as a function of time. During the first instants of polarization at fixed potential, the peak current obtained initially decreased rapidly with time. For each potential polarization, the current reached a constant value after a certain time (~ 7 hours), as the signature of a partial electronic conductivity and in line with the straight line observed in the Nyquist diagrams (Figure 7a). The ohmic-law was verified through varying potentials (in our case 0.1, 0.2, 0.3, 0.4 and 0.5 V) and temperatures. The stabilized currents are plotted as a function of polarization potential and temperature in Figure 9b. As expected, a linear relationship between stabilized current and applied potential is obtained for each temperature. The ohmic-law was confirmed and for each temperature the electronic resistance was extracted.

The conductivities (total grains from AC impedance and electronic from DC measurements) follow a linear Arrhenius behavior when $\log(\sigma.T)$ is plotted as a function of $1/T$ as represented in Figure 10a for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$. From the slopes of the linear fittings, the values of the activation energies are 1.05 eV before 125 °C and 0.77 eV after for the total grains conductivity, whereas they are 0.79 eV and 0.68 eV respectively for the electronic part. A break of slope is observed for total grains and electronic conductivities at around 125 °C, which corresponds exactly to the temperature of the disappearance of

the orthorhombic form of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$.¹⁵ The ionic and electronic conductivity values obtained at various temperatures, as well as the corresponding activation energies, are summarized in Table 1.

$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ is a mixed-conductor electrode material with the same order of electronic ($1.2 \cdot 10^{-10} \text{ S.cm}^{-1}$ at 95°C) and ionic ($5 \cdot 10^{-10} \text{ S.cm}^{-1}$ at 95°C) conductivities below the order-disorder transition. Above this order-disorder transition a difference of around one decade is observed in favor of the ionic conductivity ($2.2 \cdot 10^{-7} \text{ S.cm}^{-1}$ compared to $1.4 \cdot 10^{-8} \text{ S.cm}^{-1}$ for the electronic conductivity at 200°C). In parallel, the activation energy decreases more drastically for the ionic part (from 1.10 eV to 0.79 eV) than for the electronic one (0.79 eV to 0.68 eV) before and after the order-disorder transition respectively. This may be correlated with the strong anisotropic variation of a and b lattice parameters with T , as ionic motion essentially occurs in (001) planes. The lower variation of electronic transport properties from below to above the transition temperature could be correlated with the weaker variation of the c cell parameter as a function of temperature.

Same types of measurements were performed for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$: the obtained conductivity values are gathered in Figure 10b and in Table 1. Contrary to $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, the activation energy of electron transport within $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ is not affected by the order-disorder structural transition, with a constant activation energy value around 0.58 eV. This can be related by the linear evolution of the c cell parameter presented in Figure 4, contrary to that of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$. It worth noticing that this activation energy (0.58 eV) is lower than those of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$. The electronic conductivity is higher ($3.8 \cdot 10^{-10} \text{ S.cm}^{-1}$ compared to $1.2 \cdot 10^{-10} \text{ S.cm}^{-1}$ at 95°C) when NVPF is partially oxidized, which is attributed to the mixed valence $\text{V}^{\text{III}}/\text{V}^{\text{IV}}$ in $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ with $y > 0$. Indeed, it induces the contraction of the c cell parameter along the bi-octahedra $\text{V}_2\text{O}_{8+y}\text{F}_{3-y}\text{O}_y$ and could promote electron conduction. However, a break of slope is observed in the Arrhenius plot of total grains conductivities at around 135°C . This temperature corresponds to the structural transition temperature highlighted by DSC and XRD. The activation energy for the ionic conductivity evolves from 0.97 eV to 0.72 eV below and above the order-disorder transition. This variation is lower than that of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ as is the variation of a and b lattice parameters. The slightly higher ionic conductivity in $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.0}\text{O}_{0.5}$ compared to that of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ is to be related with the smaller degree of orthorhombicity (hence higher disorder) at a given T .

To link the ionic and electronic conduction properties with the crystallographic directions of NVPF, same types of measurements were performed on a single crystal of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, along the [001] direction with coupled studies in AC and DC (Figure 11). Due to the shape of the single crystal, we were able to obtain data only above 185°C . The overall data overlapped those obtained for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ pellets by DC measurements showing thus that the electronic conduction occurs only

along the [001] direction, which is expected from the structure itself, made of isolated vanadium bi-octahedra connected through PO_4 groups. As a consequence, the ionic conductivity is essentially 2D, perpendicular to [001]. The increasing content in oxygen in $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ induces an increase of the structural order-disorder transition temperature combined with an increase of the electronic conduction with a lower activation energy, that latter being not affected by the structural transition which is essentially linked with the ionic mobility.

Conclusion

$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($0 \leq y \leq 0.5$) compositions are isostructural and crystallize in the orthorhombic space group *Amam*, with an increasing disorder in the Na^+ ions distribution and a continuous oxidation of vanadium resulting in the formation of vanadyl-type bonds. The electrochemical signature obtained for the sodium cells $\text{Na}/\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ evolves from a complex phase diagram with two voltage plateaus for $y = 0$, to solid solution type reactions with a “S-shape” for the two voltage domains for $y = 0.5$. The influence of the oxygen substitution for fluorine on the structural and transport properties of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ ($0 \leq y \leq 0.5$) has been investigated as a function of temperature. Changes in the crystal structure have been identified using high resolution Synchrotron powder X-ray diffraction, whereas the electronic and ionic conductivities have been determined for powders and single crystals and separated using Electrochemical Impedance Spectroscopy in AC-DC configuration. The order-disorder transition occurs at 125°C for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, with the formation of a more symmetrical tetragonal structure (space group *I4/mmm*) and a full disorder on the Na^+ sites. The temperature of this transition increases slightly with the content in oxygen. This transition affects only the ionic transport properties, with a significant decrease of the activation energy associated with a break of slope in the evolution of *a* and *b* cell parameters with the temperature. The oxygen substitution allows improving the electronic transport properties (higher electronic conductivity and smaller activation energy), which can explain the better electrochemical performances of the mixed valence $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ materials (with $y > 0$).

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