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Chapter 8

High-Voltage Cathodes for Na-Ion Batteries: Sodium–Vanadium Fluorophosphates

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Additional information is available at the end of the chapter

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Abstract

This chapter analyses the main advances made in the field of sodium–vanadium fluorophosphates as cathodes for Na-ion batteries and tries to clarify some discrepancies and common errors published about these compounds. The sodium–vanadium fluorophosphate family can be divided in two main members: $Na_3V_2(PO_4)_2F_3$ (V^{+3} extreme phase) and $Na_3V_2O_2(PO_4)_2F$ (V^{4+} extreme phase). $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$, where $0<x<1$ would correspond to intermediate $V^{3+/4+}$ mixed valence phases. Among them, the V^{3+} extreme has demonstrated to be difficult to isolate, whereas the V^{4+} and mixed valence phases can be more easily prepared by different synthesis methods and from different vanadium sources. In terms of electrochemical performance, mixed valent compound provides good performance, with high specific capacity at moderate/high cycling rates, and long cycle life. The future perspectives for this family of compounds are discussed in terms of raw materials availability, price, and performance relative to other cathode systems for Na-ion batteries.

Keywords: Na-ion batteries, cathodes, fluorophosphates, vanadium, High voltage

1. Introduction

Energy production is a key issue for the support of our society and way-of-life. Driven by the need to reduce the emissions of CO_2 and increase energy security, policy makers have implemented different measures in order to shift to low-carbon energy resources. One of these policies is to promote the use of renewable energy sources at the expense of the carbon-based fuels [1,2]. However, the increasing use of these clean energy sources entails other problems, such as modulating time-variable energy production from renewable resources due to their depend-

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ence on the weather to integrate them into the grid. Thus, in order to solve the problem concerning the intermittency of these resources, additional energy storage devices are needed. This way, electrochemical energy storage is a strategic research area that will help to increase the weight of renewable energy sources in the energy mix.

In this field, batteries are one of the most promising systems to act as buffer to regulate the variable energy income that can be obtained from the wind, sun and from the ocean waves. For this purpose, one of the main technologies under development is Na-ion batteries. In the last 20 years, Li-ion batteries have attracted all the attention in energy storage, but recently, Na-based compounds have made a comeback because of controversial debates regarding the size of reserves and higher cost to obtain Li [3]. The use of Na instead of Li in rocking chair batteries could mitigate the feasible shortage of lithium in an economic way for many reasons. The first one, the unlimited sodium sources, being the sodium content in the earth's crust and water of 28,400 $mg \cdot kg^{-1}$ and 11,000 $mg \cdot L^{-1}$ compared to 20 $mg \cdot kg^{-1}$ and 0.18 $mg \cdot L^{-1}$ for lithium [4]. Moreover, sodium presents lower price than lithium and it is easy to recover [5].

Although sodium (Na)-ion batteries are considered a promising alternative to lithium-ion systems, it is usually said that they possess limited electrochemical activity compared to Li due to two intrinsic reasons. First, Na has a lower ionization potential than Li (5.139eV vs. 5.392 eV) [6], leading to lower operating voltages and thus lower energy densities. Second, Na^+ ions are heavier and larger than Li^+ ions, leading to slow diffusion within a solid electrode during cycling and larger volume expansion of the electrode [7]. These two factors would induce lower gravimetric energy densities, so renewed research on these systems has been focused on their utility as buffering systems in the electrical grid, where battery volume is not so crucial due to the stationary nature of the practical use of these batteries.

However, and in spite of the great efforts devoted to the development of higher performance Li-ion batteries, if practical energy densities achieved up till now for both Li- and Na-based systems are compared, it can be seen that Na-ion batteries are catching up with the practical energy densities of Li-ion in a quite short time (**Figure 1**).

This great advance in gravimetric energy densities for Na-ion batteries is due to the extensive research that has been done in the last years to identify and optimise the best materials for these systems, so they can be soon commercially viable. As it has been said, the incorporation of this kind of systems to the electrical grid would lead to a significant increase of the proportion of renewable energies on the energy mix, with the positive environmental consequences that this fact would result in. Thus, it is a priority to continue searching for and optimising the best-performing materials to be used in the different components of a battery: cathode, electrolyte and anode.

In the case of the cathode, a good performing material should provide high energy density to the battery, that is, it should be able to charge and discharge the highest possible specific capacities with also high operating voltage and for many cycles (long cycle life). In this sense, sodium–vanadium fluorophosphates have demonstrated to fulfil all of these characteristics.

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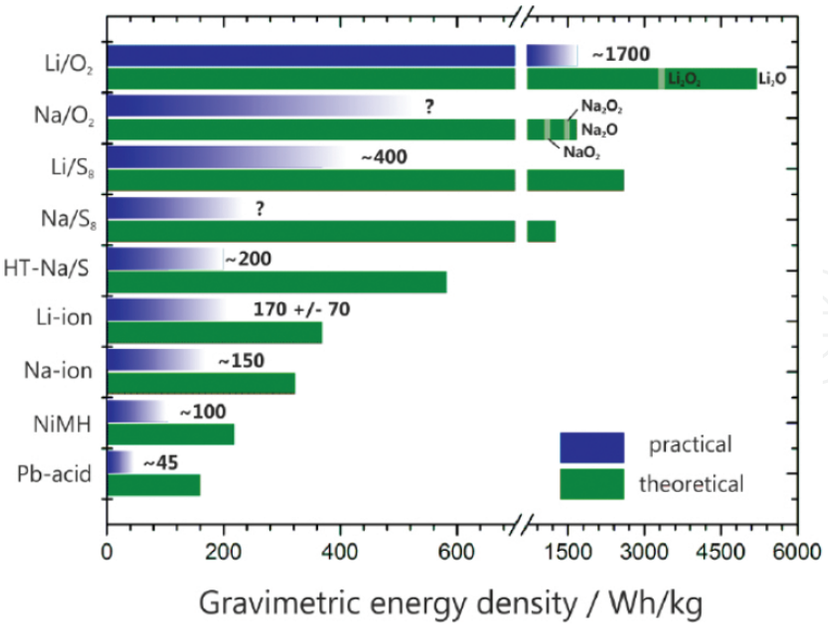


Figure 1. Theoretical and (estimated) practical energy densities of different rechargeable batteries: Pb–acid (lead acid), NiMH (nickel metal hydride), Na-ion (estimate derived from data for Li-ion assuming a slightly lower cell voltage), Li-ion (average over different types), HT-Na/S_8 (high temperature sodium–sulphur battery), Li/S_8 and Na/S_8 (lithium–sulphur and sodium–sulphur battery assuming Li_2S and Na_2S as discharge products), Li/O_2 and Na/O_2 (lithium–oxygen battery, where theoretical values include the weight of oxygen and depend on the stoichiometry of the assumed discharge product, i.e., oxide, peroxide or superoxide). Reproduced from reference [8].

2. High-voltage cathode materials for Na-ion batteries

In the last decade, three dimensional frameworks built on transition metals (M) and polyanions $(XO_4)^{n-}$ have become a hot topic in the research field of electroactive materials for lithium and Na-ion batteries. The smaller theoretical gravimetric capacity achieved due to the presence of polyanion groups is compensated by the positive features presented by these compounds, such as very stable frameworks and high inductive effect [9]. The "inductive effect" is a concept proposed by Goodenough *et al.* consisting on the tune of the redox potential of the 3d metal centre (M) depending on the electronegativity of the X-O bonding [10].

On one hand, sulphate-based cathodes offer a good combination of sustainable syntheses and high energy density owing to their high-voltage operation due to electronegative SO_4^{2-} units [11]. $Na_2Fe_2(SO_4)_3$ has demonstrated to be the most promising compound being operable at 3.8 V *versus* sodium and offering a reversible capacity of over 100 $mAhg^{-1}$ with a 50% capacity retention at high rates (20C) [12]. However, the main issues concerning sulphur-containing cathodes are the low utilisation of active material, volume expansion during extraction/insertion of Na ions and the dissolution of polysulphide into the electrolyte [13].

On the other hand, framework materials based on the phosphate polyanion have also been identified as promising electro-active materials for sodium metal and Na-ion battery applications. It is the strong inductive effect of the PO_4^{3-} polyanion that moderates the energetic of the

transition metal redox couple to generate relatively high operating potentials for these compounds [14]. $NaMnPO_4$ is one of the most studied compounds in this field due to the high operating voltage provided by its lithium analogue: $LiMnPO_4$ which works at 4.1 V *versus* lithium [15]. However, contrary to $LiMnPO_4$, $NaMnPO_4$ possesses two structure modifications: marycite-type and olivine-type structures being this latter one the electroactive one. Boyadzhieva *et al.* have recently reported, for the first time, the reversible lithium and Na ion intercalation into the olivine $NaMnPO_4$ phase when testing it *versus* lithium. However, the electrochemical performance of this material is not yet competitive compared to the well-known $LiMnPO_4$ analogue so that further optimisation is needed [16].

$Na_4Co_3(PO_4)_2P_2O_7$ pyrophosphate is another promising candidate due to its high working potential region (between 4.1 and 4.7 V *versus* sodium). In the work presented by Nose *et al.* [17], this compound offers 95 $mAhg^{-1}$ reversible capacity with negligible fading after 100 cycles and 84% of capacity retention at rates of 25C. Moreover, the battery presented may be capable of running at even higher potentials (~5.1 V) in order to utilise the $Co^{3+}/^{4+}$ redox couple leading to the extraction of 4 Na ions from the $Na_4Co_3(PO_4)_2P_2O_7$ phase. Something similar is proposed by Xu *et al.* in the case of $Na_3V_2O_2(PO_4)_2F$ sodium–vanadium fluorophosphate. Due to the difficulty to access the third sodium in the formula unit some theoretical calculations suggested the substitution of oxygen with chlorine to form $Na_3V_2Cl_2(PO_4)_2F$ which would increase the energy density from 520 to 758 $Whkg^{-1}$[18]. However, a suitable electrolyte would be needed in both cases in order to work in such high-voltage conditions.

Among the framework materials fluorophosphates possess even higher operating voltages than phosphates, because the inductive effect of fluorine is added to the effect of phosphate. This latter feature makes them a key to solve the energy density issue of sodium-based batteries. Fe, Mn, and V have been the most investigated transition metals but the three of them present different structures: Whereas the sodium–iron fluorophosphate possesses a two-dimensional layered structure [19], the sodium–manganese fluorophosphate presents a three-dimensional tunnel structure [20]. However, manganese compound has demonstrated to be poorly electrochemically active so that more studies have been performed for the iron-based compound. For the moment, one of the best results achieved has been for carbon coated porous hollow spheres of Na_2FePO_4F phase. This nanostructured material contained about 6–8 *wt.*% of carbon and presented a specific surface area of 8.7 m^2g^{-1} which led to a specific capacity of 90 $mAhg^{-1}$ at C/10 and a good cycling stability for 100 cycles [21].

Regarding sodium–vanadium fluorophosphates, three phases have been described in the literature: $NaVPO_4F$, $Na_3V_2O_2(PO_4)_2F$ and $Na_3V_2(PO_4)_2F_3$ with theoretical specific capacity values of 143, 130 and 128 $mAh{\cdot}g^{-1}$, respectively. Barker *et al.* first proposed $NaVPO_4F$ as a tetragonal structure with *I4/mmm* space group [22]. On the other hand, several groups reported also the existence of a $NaVPO_4F$ polymorph which they indexed with *C2/c* space group [23–26]. The $Na_3V_2O_2(PO_4)_2F$ phase has been described as a tetragonal symmetry compound with *I4/mmm* space group by Sauvage *et al.* [27] and Massa *et al.* [28] but, more recently, Tsirlin *et al.* [29] proposed the $P4_2/mnm$ space group for the room temperature phase among the diverse polymorphs of this material at different temperatures. The third of the sodium–vanadium fluorophosphates mentioned in the literature, $Na_3V_2(PO_4)_2F_3$, is also described as a tetragonal

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symmetry with $P4_2/mnm$ space group [30–32] but more recently some authors have proposed a different space group for this compound: *Amam* [33,34].

A deep study of the bibliographic data related to these three sodium fluorophosphates leads to doubt about the real existence of these three different compounds. It is worth noting that the existence of the $NaVPO_4F$ phase has already been questioned by authors such as Sauvage *et al.* [27]. Furthermore, there are no structural data about the suggested monoclinic polymorph of $NaVPO_4F$ [23–26]. Besides, the diffractogram shown in their works as well as the electrochemical curves obtained match with the one of $Na_3V_2(PO_4)_3$ NASICON compound. In this case, the formation of a NASICON type phase instead of $NaVPO_4F$ could be possible because the samples were prepared by the ceramic method and sublimation of VF_3 could occur, as it has been described for other lithium–vanadium fluorophosphates [35]. Thus, structural data of only two compounds are found in the literature: $Na_3V_2O_2(PO_4)_2F$ [29] and $Na_3V_2(PO_4)_2F_3$ [30]. The diffractograms of both phases are quite similar that it is possible to establish a relationship between them.

Electrochemical studies on the three mentioned tetragonal structure compounds have been performed under different conditions *versus* lithium or sodium [22–24,27,36–39] and in all cases the charge–discharge curves display two voltage *plateaux* of similar length at the same voltages with little differences depending on the anode material used (*ca.* 3.6 and 4.1 V *versus* Na/Na^+).

3. Sodium–vanadium fluorophosphates as cathode materials for Na-ion batteries

The study of sodium–vanadium fluorophosphates is especially relevant because of the high operating voltages offered by these compounds that could lead the way to high energy Na-ion batteries.

The similarity of the X-ray diffraction patterns as well as the almost identical electrochemical data for $Na_3V_2O_2(PO_4)_2F$ and $Na_3V_2(PO_4)_2F_3$ suggested that both materials could belong to the same family of compounds, where the fluorine content is modulated by the presence of V^{3+} and VO^{2+} (V^{4+}) leading to the following general formula $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ which was proposed by our group for the first time [40]. The extreme members (x = 0 and x = 1) would correspond to the mentioned phases, $Na_3V_2(PO_4)_2F_3$ for x = 0 (**Figure 2a**) and $Na_3V_2O_2(PO_4)_2F$ for x = 1 (**Figure 2b**), whereas intermediate compounds ($0 < x < 1$) would be V^{3+}/V^{4+} mixed valence phases (**Figure 3**). The existence of a mixed valence family of compounds between $Na_3V_2(PO_4)_2F_3$ and $Na_3V_2O_2(PO_4)_2F$ phases was also reported by Park *et al.* [41] and more recently, by Qi *et al.* [42].

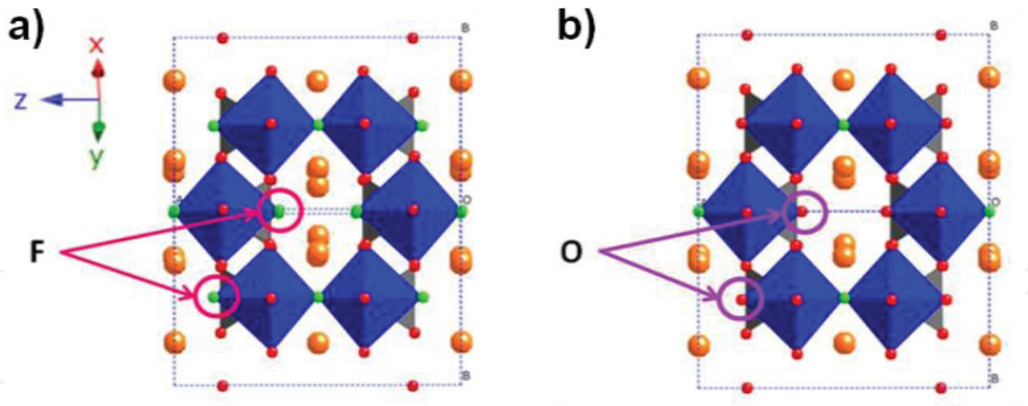


Figure 2. Crystallographic structure of a) $Na_3V_2(PO_4)_2F_3$ and b) $Na_3V_2O_2(PO_4)_2F$. Oxygen in red and fluorine in green. Vanadium octahedron is represented in blue and phosphate tetrahedron in grey.

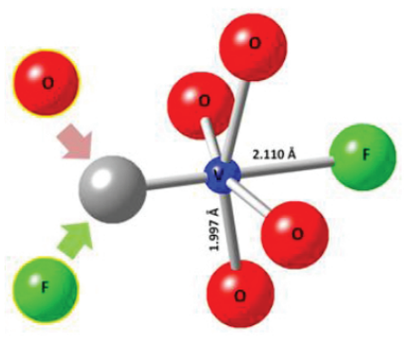


Figure 3. Vanadium octahedron for mixed valent $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ ($0 < x < 1$) compounds. Vanadium is represented in blue, oxygen in red and fluorine in green.

In order to understand the structure and properties of this family of compounds, a series of sodium–vanadium fluorophosphate samples were hydrothermally prepared, varying the type and amount of carbon used as reductive agent during the synthesis [40]. This way, the possible influence of that carbon on both the final properties of the sample and the attainment of different compositions in the family of general formula $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ ($0 < x < 1$) was analysed. Intermediate amounts of carbon present in the $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ final product (1 – 50 *wt.*% C) led to V^{3+}/V^{4+} mixed valence phases ($0 < x < 1$) while a sample containing almost only V^{4+} was obtained in a composite with less than 1 *wt.*% of carbon. The electrochemical study of these samples showed the presence of two reaction voltages at 3.6 and 4.1 V *versus* Na/Na^+ and good specific capacity values up to 100 $mAhg^{-1}$ at 1C when an electrochemical grade carbon was employed. The material containing a moderate amount of this type of carbon (~6 *wt.*%) showed the best electrochemical results. A deeper analysis of this sample with an average oxidation state of +3.8 for the vanadium, showed excellent specific capacity values from 100 to 75 $mAhg^{-1}$ for charging rates of C/20 and 5C, respectively. It is worth mentioning the high capacity retention up to 95% after 200 cycles at 1C [43]. A combined experimental and theoretical study on this family of compounds was also carried out by Park *et al*. [44,45].

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Different samples with compositions x = 0, 0.2, 0.5, 0.8 and 1 were synthesised by solid state reactions. The obtained compounds were characterised by the use of different techniques such as X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Nuclear Magnetic Resonance (NMR), etc. The electrochemical study showed specific capacity values of approximately 100 $mAhg^{-1}$ only in the case of the V^{4+} composition. The specific capacity value was maintained for all the compounds during 150 cycles at C/2. Recently and in order to achieve different compositions of the family of sodium–vanadium fluorophosphates a new synthesis based on the solvothermal method at low-temperature (60-120°C) has been employed [42]. The size of the particles obtained with this method was in the range of 20–50 nanometers. The electrochemical analysis of these compounds showed a rate capability of 73 $mAhg^{-1}$ at 10C rate and long cycle stability over 1200 cycles at 2C.

Regarding the V^{4+} phase, $Na_3V_2O_2(PO_4)_2F$, the first electrochemical results were presented by Sauvage *et al.* getting a capacity of 87 $mAhg^{-1}$ at C/100 through a two voltage-step behaviour at 3.6 and 4.0 V vs. Na/Na^+. They found that the obtained electrochemical curve was almost identical to the ones reported for $Na_3V_2(PO_4)_2F_3$ and $NaVPO_4F$ phases giving rise to doubt about the real existence of this latter one in light of lack reliable information about its structure [27]. Some years after, a novel single-step hydrothermal treatment was discovered to obtain the $Na_3V_2O_2(PO_4)_2F$ phase [46]. The absence of *in-situ* carbon in the synthesised product made it necessary to employ an *ex-situ* carbon coating in order to improve the conductivity of the material and hence its electrochemical performance. However, control of the thermal treatment process resulted determinant to avoid the degradation of the material and the appearance of secondary phases such as NASICON $Na_3V_2(PO_4)_3$. The carbon coated material prepared by impregnation and a flash thermal treatment, exhibited good rate capabilities between 100 and 65 $mAhg^{-1}$ for rates of C/20 and 1C respectively and good cycling stability (**Figure 4**).

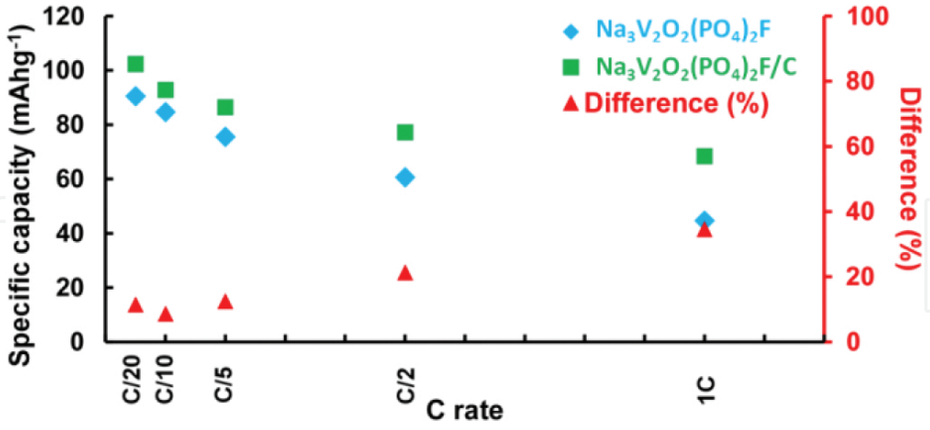


Figure 4. Comparison of discharge specific capacity values between raw $Na_3V_2O_2(PO_4)_2F$ and carbon coated flash thermally treated $Na_3V_2O_2(PO_4)_2F/C$ samples.

Additional works showed that the reversible capacity of $Na_3V_2O_2(PO_4)_2F$/graphene electrodes exceed 100 $mAhg^{-1}$ after 200 cycles at a C/20 current rate [37]. Apart from that, a theoretical and experimental study on a solvothermally obtained $Na_3V_2O_2(PO_4)_2F$ phase was presented were structural and electrochemical characterisation of this material was carried out [18].

Moreover, computational studies revealed the possibility of extracting the third sodium of the mentioned phase at 5.3 V *versus* sodium. However, this would be experimentally complicated due to the overcoming of the stability window of the electrolyte (4.8 V). However, a hypothetical new vanadium fluorophosphate phase, $Na_3V_2Cl_2(PO_4)_2F$, where the oxygen is substituted by chlorine , was proposed from the theoretical study. This latter compound would provide 188 $mAh{\cdot}g^{-1}$ theoretical specific capacity and 758 $Wh{\cdot}kg^{-1}$ energy density. Finally, electrochemical results of RuO_2-coated $Na_3V_2O_2(PO_4)_2F$ nanowires were presented were a reversible capacity of 120 $mAh{\cdot}g^{-1}$ was achieved at 1C rate during more than 1000 cycles [47].

Concerning the V^{+3} phase, $Na_3V_2(PO_4)_2F_3$, the electrochemical mechanism of the reversible Na extraction was described by Chihara *et al.* [48] and Shakoor *et al.* [38]. Both groups reported that the electrochemical reaction occurs through a single-phase reaction with negligible volume variation (~2%). More recently, the ion migration mechanism and diffusion capability of the $Na_3V_2(PO_4)_2F_3$ phase have been explored [49,50]. However, the presented results could correspond to any of the sodium–vanadium fluorophosphates included in the general formula $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$. Moreover, one of the three discharge *plateaux* that they achieve in the phase (the one at 3.4 V) could correspond to the non fluorinated NASICON $Na_3V_2(PO_4)_3$ phase as recently reported[46]. On the other hand, an *ex situ* high resolution ^{23}Na and ^{31}P solid state NMR study on this $Na_3V_2(PO_4)_2F_3$ phase was reported [51]. It is mentioned that ^{23}Na NMR spectrum of pristine $Na_3V_2(PO_4)_2F_3$ phase exhibits two major resonances at 92 and 146 ppm, which are assigned to partially filled Na(2) site and fully occupied Na(1) site, respectively. However, in recent works concerning ssNMR of the mixed valent sodium–vanadium fluorophosphate phase the peaks found in the spectra were assigned to the presence of different vanadium environments instead of the occupancy of the Na cations [44,52]. Similar results were found in the case of the $Na_3V_2O_2(PO_4)_2F$ phase containing only V^{4+} . The results of the ^{23}Na ssNMR spectrum obtained in this phase show the presence of a unique peak with an occupancy factor of the two Na cations of 1 for Na(1) site and ½ for Na(2) site (see **Figure 5**) [53].

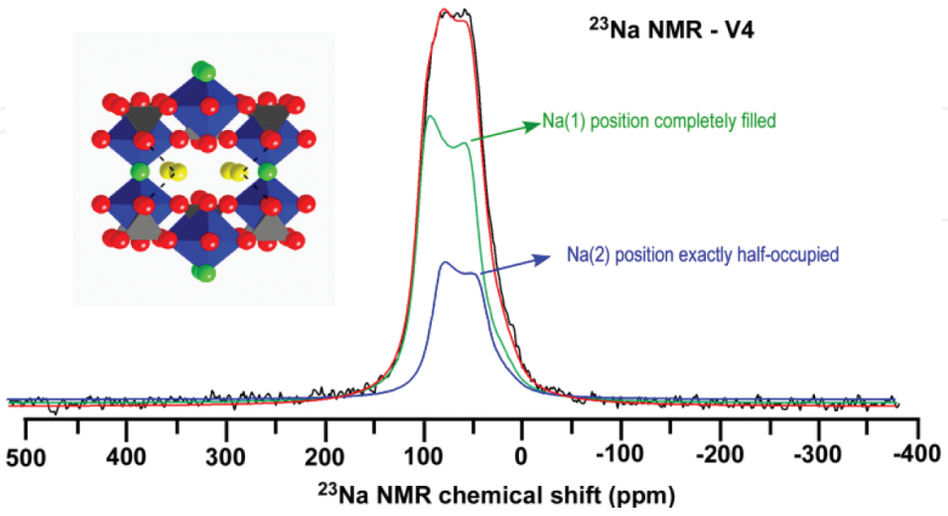


Figure 5. ^{23}Na ssNMR spectrum of $Na_3V_2O_2(PO_4)_2F$ sample (black line). Fittings for Na(1) and Na(2) are shown in green and blue, respectively.

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The crystal structure of the $Na_3V_2(PO_4)_2F_3$ phase at high temperature (400 K) obtained from high resolution synchrotron radiation measurements in *operando* revealed the existence of a combined solid solution region and four intermediate phases during the charge process [33,34]. In addition, a new space group (*Amam)* was achieved for the $Na_3V_2(PO_4)_2F_3$ phase . On the other hand, the electrochemical results obtained in a full cell using $Na_3V_2(PO_4)_2F_3$ as cathode, *hard carbon* as anode and an optimised electrolyte showed a capacity of 97 $mAh{\cdot}g^{-1}$ after more than 120 cycles at C/5 and 70 $mAh{\cdot}g^{-1}$ at 5C rate. [39].

Concerning *ex-situ* structural study of the aforementioned phases, a detailed study was recently presented [44,45] to determine the sodium extraction/insertion mechanism of the mixed valent fluorophosphate materials. Examination of the *ex-situ* XRD patterns of $V^{3.8+}$ $Na_3V_2O_{1.6}(PO_4)_2F_{1.4}$ compound revealed the coexistence of a two-phase region in the first half of the charge indicating the presence of a stable intermediate phase between the two *plateaux* at 3.6 and 4.1 V *versus* Na/Na^+. It was also reported that the V^{3+} present in the $V^{3.8+}$ $Na_3V_2O_{1.6}(PO_4)_2F_{1.4}$ phase creates a local environment similar to the one presented by $Na_3V_2(PO_4)_2F_3$ phase [38] leading to a high-voltage V^{3+}/V^{4+} redox reaction. It is assumed that 2.4 electrons are supplied from the $V^{3.8+}$ / V^{5+} redox couple leading to a theoretical specific capacity of 155.6 $mAhg^{-1}$. On the other hand, X-Ray Absorption Near Edge Spectroscopy (XANES) studies revealed that an oxidation process happens while charging and that the reverse process occurs when discharging but no evolution of the value of the vanadium oxidation state was determined.

Concerning $Na_3V_2O_2(PO_4)_2F$ phase, different space group symmetries have been described in the literature to define it [28,29]. In terms of sodium insertion/extraction, the *I4/mmm* is shown to reversibly cycle 1.12 Na ions per formula unit ($Na_3V_2O_2(PO_4)_2F$) [27] while the $P4_2/nmn$ polymorph with a carbon-coated synthetic procedure, reversibly cycles 1.56 Na ions per formula unit [46].

Finally, different time-resolved *in-situ* synchrotron X-ray powder diffraction studies have been carried out in order to analyse reaction mechanism evolution, lattice parameters ,and sodium extraction of $V^{3.8+}$($Na_3V_2O_{1.6}(PO_4)_2F_{1.4}$), V^{4+} $Na_3V_2O_2(PO_4)_2F$ and V^{+3} $Na_3V_2(PO_4)_2F_3$ materials [34,54,55].

The electrochemical behaviour of the two electrode materials studied *versus* Na/Na^+ showed similar electrochemical reaction mechanism evolution where a simultaneous solid solution and two-phase region were observed. However, the maximum sodium amount that can be extracted when a potentiostatic step is applied (2 hours at 4.3 V) is higher for $V^{3.8+}$ ($Na_3V_2O_{1.6}(PO_4)_2F_{1.4}$) sample than for the V^{4+} $Na_3V_2O_2(PO_4)_2F$ one, 2.23 *versus* 1.75, respectively. This fact can be due to several reasons, such as better intrinsic conductivity, the presence of *in-situ* carbon in the mixed valent sample or to the more rigid structure of the only V^{4+} containing sample. Nevertheless, both materials present high reversibility and flexibility during charge/discharge process. The effects of overcharging up to 4.8 V and cycling-related degradation of the same two compounds, $V^{3.8+}$($Na_3V_2O_{1.6}(PO_4)_2F_{1.4}$) and V^{4+} $Na_3V_2O_2(PO_4)_2F$ [56] have been recently reported. The $V^{3.8+}$($Na_3V_2O_{1.6}(PO_4)_2F_{1.4}$) phase presents less stress than V^{4+} phase due to the more disordered structure and the presence of *in situ* carbon. Thus, this

phase is able to reach the maximum theoretical Na^+ extraction limit when charging up to 4.8 V while in the case of V^{4+} $Na_3V_2O_2(PO_4)_2F$ phase this limit is established at the usual 4.3 V cut-off voltage. Moreover, mid-term cycling shows the formation of secondary products due to the degradation of the materials in both cases.

To finish with, the structural evolution of V^{3+} $Na_3V_2(PO_4)_2F_3$ phase has recently been analysed by using high angular and intensity resolution synchrotron radiation [34]. The two voltage domains (at 3.7 and 4.2 V *versus* Na/Na^+) have been studied separately. In the case of the low voltage *plateau* (3.7 V) three biphasic reactions have been observed while in the higher voltage region (4.2 V) a small solid solution zone together with a biphasic zone is shown (**Figure 6**). Unexpectedly, the structure of the $NaV_2(PO_4)_2F_3$ end member is different from the previous ones revealing a different space group ($Cmc2_1$) and two different vanadium environments (V^{3+} and V^{5+}).

4. Conclusions

Polyanions $(XO_4)^{n-}$ based on transition metals (M) are one of the most promising candidates for high-voltage Na-ion batteries. Among them, sulphate and phosphate based framework materials stand out. Regarding phosphate-based materials, and as it has been previously shown in this chapter, there has been some controversy about the structural and electrochemical features of sodium–vanadium fluorophosphates. This family of materials show very high

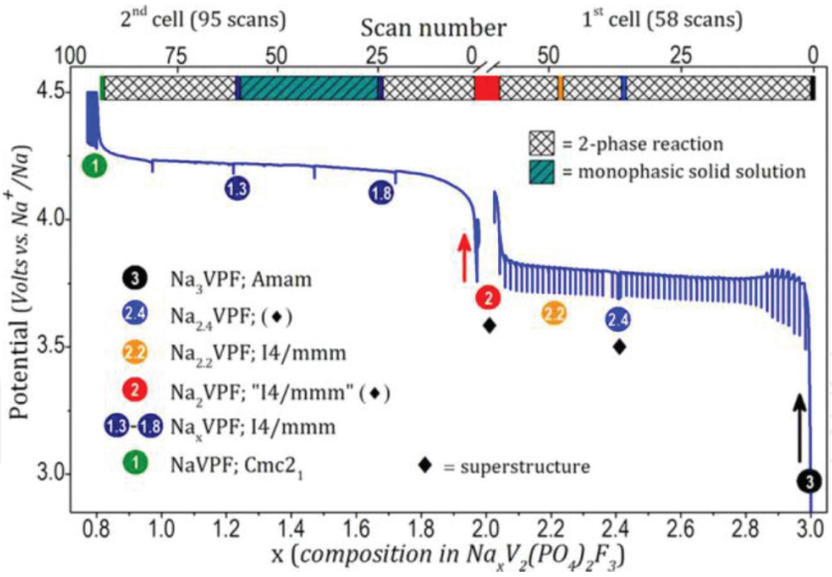


Figure 6. Potential–composition electrochemical curves obtained upon Na+ extraction from Na3VPF. The first cell was cycled (GITT) between the compositions Na_3VPF and Na_2VPF while recording 58 5 min diffraction scans; the second one (galvanostatic cycling) between the compositions Na_2VPF and Na_1VPF while recording 95 5 min scans. Significant single-phase compositions are highlighted by coloured circles. For the first cell they are obtained by the electrochemistry. Cycling of the second cell resulted in $\Delta x > 1$ because of electrolyte oxidation, hence in this case reported compositions are those obtained from Rietveld refinement. Top line describes the nature of the observed deintercalation mechanism. Reproduced from reference [34].

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energy density due to the high voltage provided by the adding inductive effect of fluorine. Moreover, these materials have demonstrated to be very stable and present outstanding electrochemical properties. V^{+3} $Na_3V_2(PO_4)_2F_3$, $V^{+3.8}$ $Na_3V_2O_{1.6}(PO_4)_2F_{1.4}$ and V^{+4} $Na_3V_2O_2(PO_4)_2F$ phases included in the family of compounds $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ have been structurally and electrochemically deeply analysed. Despite the similarity of all these materials, up to date studies show that the electrochemical behaviour of these electrode materials is clearly dependant not only on the sodium extraction/insertion mechanism, the occupancy and distribution of sodium and the electrochemical cycling history but also on the synthesis process employed for the obtaining of the starting material that determines its properties.

5. Future perspectives for sodium–vanadium fluorophosphates as cathodes for Na-ion batteries

As it has been presented, sodium–vanadium fluorophosphates are more than promising cathodic materials for near future commercial Na-ion batteries. However, the appearance of real commercial Na-ion batteries involves the development of the whole battery, that includes advancing in finding the appropriate components for a Na-ion cell based on a sodium–vanadium fluorophosphate cathode. In the first place, an anode matching this cathode must be chosen. This anode material should present relatively low operating voltage in order to provide the battery with the maximum available voltage. In the second place, the specific capacity of this anode and its rate capability should be in balance with the cathode performance in order to make an easier mass balance to prepare the cells. These two conditions will be necessary to assure that the battery, and thus its components, present the best possible performance in terms of battery voltage and power.

On the other hand, a special effort must be done to search for a long-lasting and high-voltage working electrolyte for these systems. Since the recovery of Na-ion battery research, great efforts have been directed to the search of new electrode materials whereas studies dealing with the electrolyte are much scarcer. One of the reasons for this trend can be that it has been shown that the SEI formed on carbonaceous electrodes is markedly different for sodium- and lithium-based electrolytes even using the same solvent [57,58]. Non-aqueous Na electrolytes presently used are mainly based on $NaClO_4$ or $NaPF_6$ salts in propylene carbonate or other solvents and mixtures such as ethylene carbonate: dimethyl carbonate. In general, a good electrolyte should exhibit: i) good ionic conductivity, ii) a large electrochemical window (i.e., high and low onset potential for electrolyte decomposition through oxidation and reduction at high and low voltages, respectively), iii) no reactivity towards the cell components, iv) thermal stability (i.e. melting point and boiling point lower and higher than the standard temperatures for the cell utilization, respectively). Finally, it should be intrinsically safe, have as low toxicity as possible and meet cost requirements for the targeted applications. All these features are intrinsically dependent on the nature of the salt and the solvent(s) and the possible use of additives [59].

Another argument pointed out as a drawback for Na-ion batteries based on sodium–vanadium fluorophosphates is the use of a vanadium compound in them. It is said that vanadium is not

a green element that needs careful handling after battery life cycle, but the same can be said from the electrolytes used in both sodium- and lithium-based systems. In any case, a battery will always need to be collected to be treated as a residue after its cycle life, as it is nowadays done. Apart from that, it is also commented that vanadium cost is another drawback for the development of these batteries. But it must be recalled that there exist commercial vanadium-rich energy storage systems, such as redox flow batteries, that comprise the use of high amounts of vanadium for their two electrodes [60]. Thus, a careful cost analysis should be done to confirm or discard this statement once the appropriate anode and electrolyte materials are chosen and a viable cell prototype is proposed.

Finally, and now focusing our attention on the commercial development of only sodium–vanadium fluorophosphates compounds, a last challenge that must be overcome is to develop a synthetic method that allows an easy and economical mass production of these materials. For this purpose, different parameters will have to be taken into account: the different possible synthetic methods (hydrothermal, microwave or ceramic processing); the different possible vanadium starting reactants; and the yields obtained by crossing these latter two parameters (**Figure 7**).

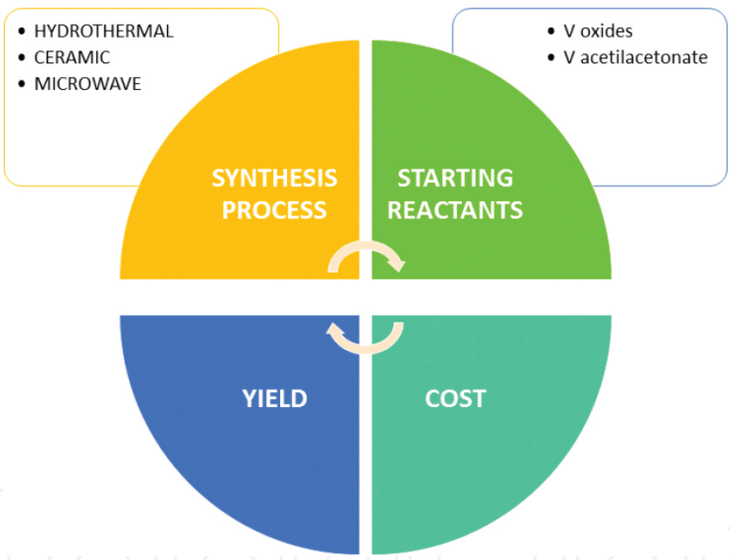


Figure 7. Main parameters that must be adjusted to get a commercially viable production method for sodium–vanadium fluorophosphates.

To sum up, sodium–vanadium fluorophosphates family is one of the main possible future cathodic materials for high-voltage Na-ion batteries. Their excellent electrochemical properties and performance have been perfectly well demonstrated by different research groups, as it has been told in this chapter. Now, the great defy for these materials lays on the industrial pace, that is, in the assembly and building of a real Na-ion full cell based on these materials and the development of a commercially viable process to produce these compounds in great amounts.

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