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Improving the energy density of Na$_3$V$_2$(PO$_4$)$_3$ – based positive electrodes through V / Al substitution

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Abstract

The crystal chemistry and the electrochemical properties upon Na$^+$ extraction/insertion of NASICON-type Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ compositions ($y = 0.1$, $0.25$ and $0.5$) were investigated. It was found that this family of V/Al substituted NASICON materials undergoes multiple reversible phase transitions between -50°C and 250°C upon heating, from monoclinic to rhombohedral symmetry, related to progressive disordering of the Na$^+$ ions within the framework. The Na$^+$ insertion/extraction mechanisms were monitored by operando X-ray diffraction. It is shown for the first time that substitution of aluminum for vanadium in Na$_3$Al$_{0.5}$V$_{1.5}$(PO$_4$)$_3$ increases significantly the theoretical energy density of these promising positive electrodes (425 Wh/kg) due to a lighter molecular weight and to the possibility of reversible operation on the V$^{4+}$/V$^{5+}$ redox couple at 3.95 V vs. Na$^+$/Na.
Introduction

NASICON-type vanadium phosphate Na$_3$V$_{2/3}$(PO$_4$)$_3$ (NVP) is an attractive cathode material for sodium-ion batteries, presently investigated in particular for its high power rate capabilities [1-7]. The reversible extraction of sodium occurs as a two-phase reaction at 3.37 V vs. Na$^+/Na$ (V$^{3+}$ oxidized to V$^{4+}$) for a theoretical gravimetric capacity of 117.6 mA.h/g yielding an energy density of 396 W.h/kg. To our knowledge, the first electrochemical investigation of this material was reported in 2002 [8] but only very recently Saravanan et al. [1] demonstrated excellent cyclability of NVP even at very high current rate thanks to the presence of a thin layer of carbon coating that compensates for the low electrical conductivity. Since then, several high-profile studies were conducted in order to obtain optimized performances [1-7].

Gopalakrishnan [9] was the first to report on the chemical oxidation of NASICON Na$_3$V$_{2/3}$(PO$_4$)$_3$ (Na$^+$ extraction) to yield a new Na-free mixed-valence V$^V$V$^{IV}$(PO$_4$)$_3$ composition, suggesting the theoretical extraction of 3 Na$^+$ per 2 vanadium (i.e. 1.5 e$^-$ exchanged per transition metal). Later on, the electrochemical extraction of Na$^+$ from Na$_3$V$_2$(PO$_4$)$_3$ to NaV$_2$(PO$_4$)$_3$ was shown to occur following a two-phase reaction at 3.37 V versus Na$^+/Na$ (Fig. 1) [10] the latter phase being isotypical with NaTi$_2$(PO$_4$)$_3$ [11-13]. Moreover, as shown by Yamaki et al. [8] and Patoux et al. [10], V$^{3+}$ may be reduced to V$^{2+}$ through the electrochemical or chemical insertion of one sodium per formula unit, towards Na$_4$V$_2$(PO$_4$)$_3$ at 1.65 V vs. Na$^+/Na$ (for a theoretical capacity of 58.8 mA.h/g). These particular features offer the possibility of building symmetrical NVP / electrolyte / NVP batteries operating at 1.8 V, as recently demonstrated [14-16]. Up to now, to the best of our knowledge, no demonstration of reversible electrochemical extraction of Na$^+$ towards V$_2$(PO$_4$)$_3$ was demonstrated, similar to what was reported for the Li$^+$ counterpart NASICON B-Li$_3$V$_2$(PO$_4$)$_3$ [17, 18].

Importantly, these observations tend to indicate a strong discrepancy between the original result of Gopalakrishnan and the experimental electrochemical oxidation of V$^{3+}$ to V$^{4+}$ through the extraction of only two Na$^+$ out of three. As shown by Song et al. [19], galvanostatic extraction of Na$^+$ from pure Na$_3$V$_2$(PO$_4$)$_3$ up to 4.5 V vs. Na does not permit of extracting more than two Na$^+$. Therefore, part of the “heavy” vanadium in the structural formula Na$_3$V$_2$(PO$_4$)$_3$ appears to be
useless and we undertook chemical substitutions within the NASICON framework so as to better understand the reasons for such limitation. In other words, we wanted to precisely determine if the final composition NaV$_2$(PO$_4$)$_3$ reached was due either to the impossibility of oxidizing V$^{4+}$ to V$^{5+}$ within the NASICON framework or to the impossibility of yielding a composition with less than one Na$^+$ in the framework. For this purpose, we investigated the possible substitution of part of vanadium by aluminum according to the structural formula Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ ($0 \leq y \leq 0.5$). Such M/Al substitution has been shown previously to be possible into lithium- and sodium-based NASICON phases as an efficient method for improving the ionic conductivity [20]. The substitution of vanadium by aluminum has already been reported for the anti-NASICON composition A-Li$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ (up to $y = 0.5$) [21-23] and for the NASICON B-Li$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ obtained by ion exchange with the sodium analog B-Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ (with $y = 0.1$) [24]. Up to now, no electrochemical investigation of these systems as positive electrodes in Na batteries has been reported. We report here on the synthesis, on the crystal structure and on the electrochemical activity of Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ compositions : $y = 0, 0.1, 0.25$ and $0.5$.

**Experimental:**

NASICON Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ powders were prepared by solid state reaction in stoichiometric proportions from NH$_4$VO$_3$, NaH$_2$PO$_4$ and Al[OC(CH$_3$)$_3$]$_3$ precursors for $y = 0, 0.1, 0.25, 0.5$. NH$_4$VO$_3$ (Sigma-Aldrich 99%) and NaH$_2$PO$_4$ (Sigma-Aldrich 99%) were mixed and dissolved in hot water before aluminum tert-butoxide Al[OC(CH$_3$)$_3$]$_3$ (Sigma-Aldrich 99%), previously dissolved in absolute ethanol, was added dropwise. After slow evaporation of solvents, the remaining solid was successively grinded and gently heated up to 300°C as a pre-treatment to avoid uncontrolled volumetric expansion of the powder. After grinding the powder, a two steps heat treatment was performed in a tubular furnace under argon-hydrogen (90:10 vol.%) atmosphere at 400°C for 5 hours and at 750°C for 12 hours in order to reduce V$^{5+}$ into V$^{3+}$.

X-ray powder diffraction (XRD) diagrams were collected at 223K and 243K for Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ compositions and Na$_3$V$_2$(PO$_4$)$_3$ respectively. The samples were placed under primary vacuum within an Anton Paar TTK450 chamber mounted in a Bruker D8 diffractometer.
using the Cu-K$_{\alpha 1}$/K$_{\alpha 2}$ radiations and mounted in \( \theta \)-\( \theta \) configuration. High quality diffraction patterns were recorded overnight between \( 2\theta = 10^\circ \) and \( 2\theta = 100^\circ \) by steps of 4.5 s/0.01°. Part of the same samples were also sealed inside 0.5 mm diameter glass capillaries under argon atmosphere, and sent to the 11-BM at the APS Argonne, USA, for high resolution synchrotron X-ray diffraction data acquisition at 473 K. To this end, a constant wavelength of 0.413355 Å was used in the range 1-50°, with a step size of 0.001°.

*Operando* X-ray diffraction patterns, recorded during electrochemical cycling, were obtained from a Bruker D8 diffractometer using the Cu-K$_{\alpha 1}$/K$_{\alpha 2}$ radiations, mounted in \( \theta \)-\( \theta \) configuration between \( 2\theta = 10^\circ \) and \( 2\theta = 45^\circ \) for various acquisition times depending on the current rate and using the Be-containing electrochemical cell described in [25]. Data treatment and sequential Rietveld refinements were performed using the FullProf Suite [26].

Differential Scanning Calorimetry (DSC) measurements were performed using a Mettler Toledo DSC1 apparatus operating at heating/cooling rates of 10 K/min between -30 and 250°C under argon atmosphere.

Electrochemical tests were performed on a 83:17 wt% mixture of the active material and Super P carbon, obtained by ball-milling in a SPEX 8000 mixer (2 stainless steel balls of 2g, 15min). In Swagelok\textsuperscript{®}-type cells, about 10-15 mg of the electrochemically active mixture were used as the positive electrode, separated from a sodium disk by two sheets of Whatman\textsuperscript{®} GF/D borosilicate glass fiber soaked in a 1 M molar solution of NaPF$_6$ in EC/DMC 1:1. Galvanostatic tests were conducted with a Biologic\textsuperscript{®} VMP potentiostat controlled by means of the EC-Lab\textsuperscript{®} software. For *operando* XRD measurements, 25-30 mg of the active mixture were loaded in our *in situ* cell behind an Al-protected Be window [25]. Galvanostatic tests were conducted with an Apple\textsuperscript{®} Mac Pile potentiostat.

**Results and Discussion**

**a - Structural considerations**
The most common space group encountered for describing the crystal structure of NASICON compositions is rhombohedral, $R$-3$c$. In certain conditions, low temperature and/or specific composition ranges for instance, the lattice may be distorted to a lower symmetry (monoclinic in most cases) due to $Na^+$ ordering on both M(1) and M(2) crystallographic sites, as extensively documented in the literature of the mid 70’s - early 80’s [11, 27, 28]. This is the case, as well, for $Na_3V_2(PO_4)_3$ (NVP) [10, 15, 17], $Na_3Ti_2(PO_4)_3$ [11, 29], and $Na_3Al_2(PO_4)_3$ [30]. Contrary to what is reported in many recent publications (which refer to a rhombohedral indexation of the diffraction patterns), we wish to stress that $Na_3V_2(PO_4)_3$ indeed crystallizes in a distorted monoclinic unit-cell at room temperature with complex phenomena of $Na^+$ ion ordering [15, 17]. This leads to a set of superstructure diffraction peaks, indicated in figure 2, that disappear upon heating at moderate temperature ($\sim$200°C) in full accordance with reversible thermal effects observed by DSC [15, 31]. Order-disorder transitions within the $Na^+$ sub-lattice are typical of Natrium Super Ionic CONductors (NASICON) and are associated with a randomization of the $Na^+$ positions and a lowering of the activation energy for ionic conduction.

The overnight XRD data collected at low temperature (from -30°C to -50°C) are reported in Figure 2 for $y = 0, 0.1, 0.25$ and 0.5 in $Na_3Al_yV_{2-y}(PO_4)_3$ together with the synchrotron pattern of $Na_3Al_{0.5}V_{1.5}(PO_4)_3$ at 200°C. As a first observation, we show here that the $Na_3Al_yV_{2-y}(PO_4)_3$ solid solution can be extended up to $\sim 0.5$ with a progressive shift of most of the diffraction peaks towards higher 2θ angles, as a result of progressive unit-cell contraction when Al substitutes for V in $Na_3Al_yV_{2-y}(PO_4)_3$ (Table 1). As demonstrated by temperature-controlled experiments the series of “new” small-intensity diffraction peaks encountered for the low temperature forms of $Na_3Al_yV_{2-y}(PO_4)_3$ are not related with impurities within our powders but characteristic of their crystal structure as they disappear upon heating (and come back under subsequent cooling). As a result, the XRD pattern of $Na_3Al_{0.5}V_{1.5}(PO_4)_3$ recorded at 200°C can be fully indexed in the $R$-3$c$ space group (Table 1).

These structural considerations obtained through X-ray diffraction data can be nicely correlated with the DSC data recorded for the three compositions $y = 0.1, 0.25, 0.5$ in $Na_3Al_yV_{2-y}(PO_4)_3$, plotted in figure 3 together with high resolution XRD data. Below room temperature, all the
compositions show pronounced monoclinic distortions (indexed in space group \(C2\)) while they can all be fully indexed in the rhombohedral space group \(R-3c\) at 200°C (Table 1). Upon increasing the Al content, the temperature at which the \(R-3c\) is stabilized is lowered, from 180°C for \(Na_3V_2(PO_4)_3\) [15] down to ~145°C for \(Na_3V_{1.75}Al_{0.25}(PO_4)_3\). Noticeably, the crystallinity of our powders seems to decrease with Al content increasing, as witnessed by a continuous increase of the FWHM of the diffraction peaks, from \(Na_3V_2(PO_4)_3\) to \(Na_3V_{1.5}Al_{0.5}(PO_4)_3\). This may be the reason why the order-disorder transition upon heating \(Na_3V_{1.5}Al_{0.5}(PO_4)_3\) is hardly detectable by DSC.

b – Electrochemical insertion of Na\(^+\) into \(Na_3Al_yV_{2-y}(PO_4)_3\)

As already mentioned in the recent literature, the electrochemical insertion of Na\(^+\) into \(Na_3V^{III}_{2}(PO_4)_3\) leads to \(Na_4V^{III}V^{II}(PO_4)_3\) through a biphasic mechanism at 1.65 V vs. Na\(^+\)/Na for a limited theoretical gravimetric capacity of 58.8 mA.h/g (figure 1). The reason for such a low capacity is nested in the limited interstitial space available for Na\(^+\) in the NASICON framework, equal to a maximum of 4 Na\(^+\) per \(M_2(XO_4)_3\) structural formula [12, 13, 28, 32]. In other words, only half of vanadium is utilized upon electrochemical reduction and its partial substitution would not, then, induce a penalty in terms of theoretical capacity. As displayed on the right part of figure 4, one sodium ion per structural formula was successfully inserted (at a regime of C/20) in each of the \(Na_3Al_yV_{2-y}(PO_4)_3\) compositions, upon two sets of poorly separated (~50 mV) \(dx/dV\) derivative peaks in approximate ratios of 1/10 (figure S1). The experimental gravimetric capacities obtained slightly increase with the Al content but the most prominent feature is that the energy of the \(V^{3+}/V^{2+}\) redox couple is progressively shifted to higher values, i.e. lower operating voltage vs. Na\(^+\)/Na, when the Al content increases (1.6 V vs. Na\(^+\)/Na for \(Na_3V_{1.5}Al_{0.5}(PO_4)_3\) and 1.65 V for \(Na_3V_2(PO_4)_3\)). This may be correlated with the observed decrease of the V-O bond lengths when V is substituted by Al (hence with stronger covalency and as a consequence higher position of the \(V^{3+}/V^{2+}\) redox couple).

One of the above mentioned compositions, \(Na_3Al_{0.25}V_{1.75}(PO_4)_3\), was selected to perform an operando X-ray diffraction experiment during full discharge / charge of the battery. As displayed in figure 5, the insertion / extraction of 1 Na\(^+\) into \(Na_3Al_{0.25}V_{1.75}(PO_4)_3\) is fully reversible, through
a biphasic mechanism, mostly. Careful examination of the *operando* XRD data reveals a small solid solution domain, for the first region of $\text{Na}^+$ insertion, up to $\sim\text{Na}_{3.1}\text{Al}_{0.25}\text{V}_{1.75}(\text{PO}_4)_3$ (see Fig. 5, scan 3). Subsequently, two phases coexist for the entire discharge, the proportions of which varying continuously up to the final single phase $\text{Na}_4\text{Al}_{0.25}\text{V}_{1.75}(\text{PO}_4)_3$ (Table 1). However, the peaks positions of each phase are moving slightly during the process so that at mid-(dis)charge, the pattern is not a linear combination of both end members. This kind of unusual behavior was also observed for other chemical systems such as $\text{Li}_x\text{VPO}_4\text{O}$ [33] and $\text{Li}_y\text{Mn}_2\text{O}_4$ [34]. Overall, the insertion of one $\text{Na}^+$ within $\text{Na}_3\text{Al}_{0.25}\text{V}_{1.75}(\text{PO}_4)_3$ yields a unit-cell expansion of $\Delta V/V = +3\%$ with a sharp decrease of the c/a ratio, as commonly encountered in NASICON compositions upon filling the Na(2) crystallographic site.

**c – Electrochemical extraction of $\text{Na}^+$ from $\text{Na}_3\text{Al}_y\text{V}_{2-y}(\text{PO}_4)_3$**

The electrochemical extraction of two sodium ions from $\text{Na}_3\text{V}^{\text{III}}_2(\text{PO}_4)_3$ leads to $\text{NaV}^{\text{IV}}_2(\text{PO}_4)_3$ through a biphasic mechanism at 3.37 vs. $\text{Na}^+$/Na for an overall theoretical gravimetric capacity of 117.6 mAh/g. As mentioned in the introduction part of this paper, vanadium is oxidized from $\text{V}^{3+}$ to $\text{V}^{4+}$ in $\text{NaV}^{\text{IV}}_2(\text{PO}_4)_3$ (Table 2) and the presence of one remaining $\text{Na}^+$ in the framework opens the door, theoretically, for the possible oxidation of $\text{V}^{4+}$ to $\text{V}^{5+}$ towards the final composition $\text{V}^{\text{IV}}\text{V}^{\text{IV}}(\text{PO}_4)_3$. Apart from the report of Gopalakrishnan [9], this phase has never been reported so far although $\text{V}^{5+}$-containing phosphates have been mentioned previously, such as for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [10, 17, 18, 35] and $\text{LiVOPO}_4$ [33, 36] positive electrodes in Li batteries. At this point, it is hence reasonable to argue that the capacity limitation in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ comes from a price to pay too high in energy for extracting the remaining $\text{Na}^+$ from the Na(1) site as the oxidation of $\text{V}^{3+}$ to $\text{V}^{4+}$ and then to $\text{V}^{5+}$ was previously observed in other structural units.

Consequently, mixed $\text{Na}_3\text{Al}_y\text{V}_{2-y}(\text{PO}_4)_3$ compositions are interesting to investigate as they may render the $\text{V}^{4+}/\text{V}^{5+}$ redox couple accessible. The reversible electrochemical oxidation (extraction of $\text{Na}^+$) of each $\text{Na}_3\text{Al}_y\text{V}_{2-y}(\text{PO}_4)_3$ composition ($y = 0.1, 0.25, 0.5$) within the 2.4 – 3.8 V voltage window is displayed on the left part of figure 4. Under these conditions, only the $\text{V}^{3+}/\text{V}^{4+}$ redox couple is active so that the charge capacity decreases progressively when the overall content of vanadium decreases (from 117.6 mAh/g for $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ down to 90.6 mAh/g for
Na₃Al₀.₂₅V₁.₇₅(PO₄)₃. Importantly, contrary to Na₃V₂(PO₄)₃ and Na₃Al₀.₅V₁.₅(PO₄)₃, the extraction of Na⁺ from Na₃Al₀.₂₅V₁.₇₅(PO₄)₃ and Na₃Al₀.₅V₁.₅(PO₄)₃ occurs through two distinct redox steps separated by ~0.04 V while the “average” V³⁺/V⁴⁺ remains at a value of 3.37 V vs. Na⁺/Na (Figure S1). These two redox steps are the signature of two biphasic reactions that occur upon charge / discharge for a given starting composition, as illustrated by the operando XRD experiment displayed in figure 6. The extraction of Na⁺ from Na₃Al₀.₂₅V₁.₇₅(PO₄)₃ towards Na₁.₂₅Al₀.₂₅V₁.₇₅(PO₄)₃ (Table 2) generates an intermediate single phase mixed valent (V³⁺ and V⁴⁺) composition of ~Na₂.₁Al₀.₂₅V₁.₇₅(PO₄)₃ whose lattice parameters vary slightly upon the two-phase domains as already witnessed in other systems [33, 34]. The overall charge / discharge electrochemical reaction is, structurally speaking, highly reversible as the XRD pattern of the pristine phase is fully recovered after one cycle.

If the cutoff voltage upon charge is set to an upper value of 4.2 V vs. Na⁺/Na, additional electrochemical activity is encountered at ~3.95 V vs. Na⁺/Na, for the V⁴⁺/V⁵⁺ redox couple. As shown in figure 7, the extraction of Na⁺ from Na₃Al₀.₅V₁.₅(PO₄)₃ first occurs at ~3.37 V through the oxidation of 1.5 vanadium from V³⁺ to V⁴⁺, i.e. towards the composition Na₁.₅Al³⁺₀.₅V⁴⁺₁.₅(PO₄)₃, then followed by the additional extraction of Na⁺ towards Na₁.₀Al³⁺₀.₅V⁴⁺₁.₀V⁵⁺₀.₅(PO₄)₃ upon oxidation of 0.5 vanadium from V⁴⁺ to V⁵⁺. Hence, concomitant with the slight increase in gravimetric capacity upon substitution of part of the inactive vanadium by aluminum in Na₃AlₙV₂₋ₙ(PO₄)₃, the Al substitution increases significantly the energy density of NVP-type NASICON electrodes, from 396.3 Wh/kg for Na₃V₂(PO₄)₃ to 424.6 Wh/kg for Na₃Al₀.₅V₁.₅(PO₄)₃. The corresponding operando XRD experiment up to 4.2 V vs. Na⁺/Na, is displayed in figure 8. As for Na₃Al₀.₂₅V₁.₇₅(PO₄)₃, two distinct bi-phasic regions at 3.34 V and 3.39 V vs. Na⁺/Na are first encountered at an average voltage of ~3.37 V vs. Na⁺/Na for the oxidation of V³⁺ into V⁴⁺. The operando experiment reveals, additionally, that the V⁴⁺ → V⁵⁺ electrochemical reaction occurs through a single phase mechanism centered at ~3.95 V vs. Na⁺/Na. From Na₁.₅Al³⁺₀.₅V⁴⁺₁.₅(PO₄)₃ to Na₁.₀Al³⁺₀.₅V⁴⁺₁.₀V⁵⁺₀.₅(PO₄)₃ at the end of oxidation, the lattice parameters vary continuously, as determined in the space group R-3c, to reach an overall V/Z value of 218.4 Å³.

Conclusions
This study, focused on the crystal chemistry of new compositions of general formula \( \text{Na}_{3-x} \text{Al}_y \text{V}_{2-y} (\text{PO}_4)_3 \) has shown, for the first time, that the extend of \( \text{V} / \text{Al} \) substitution in this NASICON framework, can be as high as \( y = \sim 0.5 \), which modifies significantly the electrochemical properties of this important family of materials as positive electrode for Na batteries. Compared with the \( \text{Na}_3 \text{V}_2 (\text{PO}_4)_3 \) composition, both the theoretical gravimetric capacity (due to substitution of \( \text{V} \) by lighter \( \text{Al} \)) and the average operating voltage (due to the access to the \( \text{V}^{4+}/\text{V}^{5+} \) redox couple) are higher. So far, we did not succeed to determine if the practical energy and power densities of these electrodes are indeed improved significantly compared with pure \( \text{Na}_3 \text{V}_2 (\text{PO}_4)_3 \). Future studies will focus on the evaluation of the rate capabilities and cycle efficiencies of this important class of new compositions.

Despite our repeated synthesis attempts, the hypothetical composition \( \text{Na}_3 \text{AlV}(\text{PO}_4)_3 \) could not be obtained, for which we envisage a theoretical capacity of 120.8 mAh/g operating for 50% of this capacity at 3.37 V vs. \( \text{Na} (\text{V}^{3+}/\text{V}^{4+}) \) and for the remaining 50% at 3.95 V vs. \( \text{Na} (\text{V}^{4+}/\text{V}^{5+}) \) for an overall expected energy density of 458.4 Wh/kg \( (\text{Na}_3 \text{V}^{3+}_{1}\text{Al}_{1}(\text{PO}_4)_3 \rightarrow \text{Na}_1 \text{V}^{5+}_{1}\text{Al}^{3+}_{1}(\text{PO}_4)_3) \)

**Acknowledgments**

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References:


Tables:

**Table 1:** Lattice parameters at -50°C (left) and at 200°C (right) of Na$_3$Al$_y$V$_{2.3}$(PO$_4$)$_3$ pristine compositions, determined by full pattern matching of XRD data.

<table>
<thead>
<tr>
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<th>223 K (-50°C) : C2</th>
<th>473 K (200°C) : R-3c</th>
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<td>$a$ (Å) $b$ (Å) $c$ (Å) $\beta$ (°) $V/Z$ (Å$^3$)</td>
<td>$a$ (Å) $c$ (Å) $c/a$ $V/Z$ (Å$^3$)</td>
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<td>0.1</td>
<td>15.134(3) 8.724(2) 21.624(6) 90.22(1) 237.94</td>
<td>8.7235(6) 21.883(3) 2.509 240.42</td>
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<td>8.7014(3) 21.866(2) 2.513 238.96</td>
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<td>0.5</td>
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<td>8.666(2) 21.769(6) 2.512 235.97</td>
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Table 2: Lattice parameters of Na$_x$Al$_y$V$_{2-y}$(PO$_4$)$_3$ compositions obtained upon Na$^+$ insertion or extraction (indexed in equivalent R-3c for comparison purpose)

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<thead>
<tr>
<th>Composition</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>V/Z (Å$^3$)</th>
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<td>21.36(2)</td>
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<td>V$^{3+}$</td>
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<td>Na$_3$V$_2$(PO$_4$)$_3$</td>
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<td>Na$<em>3$Al$</em>{0.5}$V$_{1.5}$(PO$_4$)$_3$</td>
<td>8.66(1)</td>
<td>21.67(3)</td>
<td>2.50</td>
<td>234.6</td>
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<td>V$^{4+}$/V$^{3+}$</td>
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<td>2.52</td>
<td>227.2</td>
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<td>Na$_{1.25}$V$_2$(PO$_4$)$_3$</td>
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<td>21.50(3)</td>
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Figures:

**Fig. 1**: Electrochemical signatures of Na$_3$V$_2$(PO$_4$)$_3$ electrodes upon Na$^+$ extraction (left) or Na$^+$ insertion (right). Galvanostatic data were recorded for a current rate corresponding to 1Na$^+$/20h.
Fig. 2: X-ray diffraction patterns of Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ compositions (0 ≤ y ≤ 0.5) recorded below room temperature and at 200°C for Na$_3$Al$_{0.5}$V$_{1.5}$(PO$_4$)$_3$ (top). The “new” diffraction peaks (•) refer to d$_{hkl}$ values not indexable in the rhombohedral R-3c space group. Bragg positions corresponding to the monoclinic C2 cell are given. Minor “Impurities” refer to traces of V$_2$O$_3$ or to the incommensurate form of NVP (see [31]).
Fig. 3: (left) Differential scanning calorimetry data recorded under Ar at 10°/min for \( \text{Na}_3\text{Al}_y\text{V}_{2-y}(\text{PO}_4)_3 \) compositions. (right) selected regions of X-ray diffraction patterns for the corresponding low- (C2) and high-temperature (R-3c) phases recorded at APS (200°C) and in-house (-50°C).
Fig. 4: Electrochemical signatures of Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ electrodes upon Na$^+$ extraction (left) or Na$^+$ insertion (right). Galvanostatic data were recorded for a current rate corresponding to 1Na$^+$/20h.
Fig. 5: (top) XRD patterns recorded *operando* for Na$_3$Al$_{0.25}$V$_{1.75}$(PO$_4$)$_3$ electrode upon galvanostatic discharge and charge (operating on the $V^{3+}/V^{2+}$ couple) at a current rate corresponding to 1 Na$^+$/30h. (down) an enlarged view of the 23-24$^\circ$ region.
Fig. 6: (top) *operando* XRD patterns of Na/NaPF<sub>6</sub> 1M in EC:DMC (1:1)/Na<sub>3</sub>Al<sub>0.25</sub>V<sub>1.75</sub>(PO<sub>4</sub>)<sub>3</sub> cell upon galvanostatic charge and discharge at a current rate corresponding to 1 Na<sup>+</sup>/20h up to 3.8 V and (down) an enlarged view of the 23.4-24.4° region.
Fig. 7: Electrochemical signature of $\text{Na}_3\text{Al}_{0.5}\text{V}_{1.5}\text{(PO}_4\text{)}_3$ electrode upon $\text{Na}^+$ extraction/insertion. Galvanostatic data were recorded for a current rate corresponding to $1\text{Na}^+/20\text{h}$. 
Fig. 8: (top) operando XRD patterns of Na//NaPF$_6$ 1M in EC:DMC (1:1)//Na$_3$Al$_{0.5}$V$_{1.5}$(PO$_4$)$_3$ cell upon galvanostatic charge at a current rate corresponding to 1 Na$^+$/15h up to 4.2 V and (down) an enlarged view of the 23.4-24.4° region.
Supplementary figures:

**Fig. S1**: Derivative electrochemical data upon Na$^+$ extraction/insertion from/into Na$_3$Al$_y$V$_{2-y}$(PO$_4$)$_3$ for $y = 0, 0.1, 0.25, 0.5$. 