Vanadium-based fluorophosphates are promising sodium-ion battery cathode materials. Different phases of NaVPO$_4$F and Na$_3$V$_2$(PO$_4$)$_2$F$_3$ are reported in the literature. However, experiments in this work suggest that there could be confusions about the single-phase NaVPO$_4$F in solid-state synthesis. Here, systematic investigation of the mechanism underlying structural and compositional evolution of solid-state synthesis (NaF:VPO$_4$ = 1:1) is determined by in situ and ex situ X-ray diffraction and electrochemical measurements. Three reactions—3NaF + VPO$_4$ → Na$_3$V$_2$(PO$_4$)$_2$F$_3$ + VPO$_4$ (up to 500 °C), Na$_3$V$_2$(PO$_4$)$_2$F$_3$ + VPO$_4$ → Na$_3$V$_2$(PO$_4$)$_3$ + VF$_3$ (600–800 °C), and 2Na$_3$V$_2$(PO$_4$)$_3$ → 2(VO)$_2$P$_2$O$_7$ + Na$_4$P$_2$O$_7$ + amorphous products (above 800 °C)—are validated by in situ XRD and thermogravimetric analysis/differential scanning calorimetry. None of the products reported in this work is consistent with single-phase NaVPO$_4$F at any temperature. It is speculated that the assignments of $I_4/mmm$ and $C2/c$ NaVPO$_4$F from solid-state synthesis are incorrect, which are instead multiphase mixtures of Le Meins’ Na$_3$V$_2$(PO$_4$)$_2$F$_3$, unreacted VPO$_4$, and hexagonal Na$_3$V$_2$(PO$_4$)$_3$. Liquid-electrolyte-based electrochemical ion exchange of LiVPO$_4$F produces a favorable NaVPO$_4$F structure, which is very different from Le Meins’ family of Na$_3$Al$_2$(PO$_4$)$_3$F$_3$ polymorphs.

1. Introduction

Sodium-ion batteries (SIBs) are promising alternatives to lithium-ion batteries (LIBs) for large-scale energy storage.[1] Due to the high operating voltage and thermal stability, vanadium-based fluorophosphates have aroused great interest as potential cathode materials for rechargeable SIBs.[1,2] Among these structures, NaVPO$_4$F (NaF:VPO$_4$ = 1:1) and Na$_3$V$_2$(PO$_4$)$_2$F$_3$ (NaF:VPO$_4$ = 3:2) were first shown by the Barker group in 2003 and 2006, respectively, as reversible insertion hosts for SIBs.[3] Both were obtained by solid-state synthesis with stoichiometric proportions of reactants, namely, NaF-VPO$_4$ = 1:1 feedstock for NaVPO$_4$F, and NaF-VPO$_4$ = 3:2 feedstock for Na$_3$V$_2$(PO$_4$)$_2$F$_3$. Barker’s original 2003 reference described the thus-obtained NaVPO$_4$F compound as tetragonal $I4/mmm$; but, it was mentioned in the same reference that the XRD pattern was “also in good accordance with the structural analysis of the related compound, Na$_3$Al$_2$(PO$_4$)$_2$F$_3$” (sic, the authors meant $\alpha$-Na$_3$Al$_2$(PO$_4$)$_2$F$_3$) despite the obvious difference in stoichiometry, also $I4/mmm$, first described by Le Meins and co-workers in 1999, with $a = 6.206$ Å and $c = 10.418$ Å.[3a,4] This allegedly $I4/mmm$ NaVPO$_4$F was reported with a high average discharge potential of 3.7 V (vs hard carbon) and a specific capacity of 82 mAh g$^{-1}$ (theoretical capacity should be 143 mAh g$^{-1}$ if V$^{3+}$/V$^{4+}$ is fully utilized), which might be comparable to the commercial cathode material LiFePO$_4$ (3.4 V vs Li/Li$^+$ and theoretical capacity 170 mAh g$^{-1}$) of LIBs.[3a,5] Since then, many groups have attempted to synthesize NaVPO$_4$F to improve its electrochemical performance.

Zhao and co-workers proposed a monoclinic Cr-doped NaVPO$_4$F phase with space group $C2/c$ that provides 83.3 mAh g$^{-1}$ reversible capacity, by solid-state synthesis.[6] However, thereupon they also mentioned that “The proposed structure is in good accordance with the structural analysis of the related compound, Na$_3$Al$_2$(PO$_4$)$_2$F$_3$” (sic, the authors meant Na$_3$M$_2$(PO$_4$)$_2$F$_3$ of Le Meins’ family).[4,6] The work was then widely cited as NaVPO$_4$F, for example, Zhao and co-workers reported a phase transition of NaVPO$_4$F from monoclinic to tetragonal structure during high-temperature processing by sol–gel method.[5] Xu and co-workers synthesized tetragonal NaVPO$_4$F by hydrothermal method, and found that the obtained compound transformed into monoclinic phase after heating at 750 or 800 °C in Ar atmosphere.[5] Ruan and co-workers prepared graphene-modified tetragonal NaVPO$_4$F, and Jin and co-workers obtained monoclinic NaVPO$_4$F nanofiber through electrospinning method.[9] Recently, Law and Balaya synthesized monoclinic NaVPO$_4$F by a facile one-step soft
template method which delivered high cycling stability.[10] Details of the crystal structures and phase transition between tetragonal and monoclinic NaVPO$_4$F are confusing. Many of the works after Barker and co-workers and Zhuo and co-workers were based on the belief that monoclinic C$_{2}$/c and tetragonal I$_{4}$/mmn forms of NaVPO$_4$F exist as single-phase compound after 1:1 stoichiometric solid-state synthesis.[3a,6,11]

Recently, Boivin and co-workers proposed a nontavorite-type NaVPO$_4$F by liquid-phase hydrothermal synthesis.[12] This structure is also monoclinic with space group of C$_{2}$/c. However, different from the previously stated structures with acclamed (but puzzling) similarity to Le Meins family of Na$_3$Al$_2$(PO$_4$)$_2$F$_3$[3a,4,6,11] Boivin’s structure is built up by VO$_4$F$_2$ octahedra chains connected to each other via PO$_4$ tetrahedra, similar to other nontavorite compounds, such as LiVPO$_4$F, LiVPO$_4$OH, and HYPO$_4$OH. For clarity, in this paper we will denote the monoclinic structure pinned down by Boivin and co-workers as “nontavorite type,” and the other monoclinic structure(s) as “nontavorite monoclinic” NaVPO$_4$F. Note that while the crystal drawing of nontavorite NaVPO$_4$F was given by Boivin and co-workers,[12] the crystal drawing of nontavorite C$_{2}$/c NaVPO$_4$F was not provided[6,11] nor was that of tetragonal I$_{4}$/mmn NaVPO$_4$F.[3a] Thus, the nontavorite C$_{2}$/c and the tetragonal I$_{4}$/mmn forms of NaVPO$_4$F are mysterious to us.[3a,6,11]

Barker and co-workers demonstrated in 2006 that Na$_3$V$_2$(PO$_4$)$_2$F$_3$ can provide 115–120 mA h g$^{-1}$ reversible capacity,[15] and was later solved to be tetragonal P4$_2$/mmm,[16] belonging to Le Meins’ family of Na$_3$Al$_2$(PO$_4$)$_2$F$_3$ polymorphs that include the tetragonal I$_{4}$/mmn α-Na$_3$Al$_2$(PO$_4$)$_2$F$_3$, and can undergo temperature-driven massive transformations within this family.[15] But its symmetry has been later revised and established as subtle orthorhombic (b/a = 1.002) space group Am$ar{a}$m by Bianchini and co-workers by using a high angular resolution synchrotron diffraction, “preserving the global geometry of the P4$_2$/mmm framework but showing a different distribution of sodium ions:”[13] This crystal structure consists of pairs of corner-sharing VO$_4$F$_2$ octahedra, which are equatorially connected to PO$_4$ tetrahedra via O atoms. The doubt about the structural parallels between NaVPO$_4$F and Na$_3$Al$_2$(PO$_4$)$_2$F$_3$ despite obvious stoichiometry difference was suggested by Sauvage and co-workers[14] Moreover, the clear difference in acclaimed lattice motifs in the two monoclinic NaVPO$_4$F with same materials stoichiometry and space group (Zhuo et al’s and Boivin et al’s) also fed our suspicion. Therefore, we initially seek to understand the formation mechanism and define the structure of NaVPO$_4$F.

Both powder and tablet samples were prepared via conventional solid-state synthesis method at temperatures from 550 to 750 °C. In situ X-ray diffraction (XRD) and thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) measurements were employed to investigate the structural evolution details upon the heating process. The structural and compositional changes can be detected and quantified by recording spectra at a certain interval temperature. FT-IR, X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM) measurements were carried out to complement the XRD data. The structural and compositional evolution accompanied by detailed heating mechanisms during the electrochemical process was further evaluated.

2. Results and Discussion

The XRD pattern with Rietveld refinement of the precursor phase (R$_p$ = 2.3%, R$_wp$ = 3.2%) is presented in Figure S1a in the Supporting Information. VPO$_4$ (ICDD PDF No. 01-086-1196) without any impurities is indeed formed according to Equation (M1) in methods. The ex situ XRD patterns of the tablet samples (NaF:VPO$_4$ = 1:1) treated at various temperatures (TS550, TS600, TS650, TS700, and TS750) are shown in Figure 1a. XRD patterns are measured by mixing 5% silicon (ICDD PDF No. 01-089-2749) powder in these products to determine the exact composition of tablet samples. The results indicate that these samples are mainly composed of tetragonal Na$_3$V$_2$(PO$_4$)$_2$F$_3$ (ICDD PDF No. 01-089-8485) and VPO$_4$ below 650 °C. A new set of diffraction peaks of tablet samples can be indexed as the hexagonal crystalline Na$_3$V$_2$(PO$_4$)$_3$ (ICDD PDF No. 00-053-0188) above 600 °C, with a small amount of (VO)$_2$P$_2$O$_7$ (ICDD PDF No. 01-085-2281) and Na$_3$P$_2$O$_7$ (ICDD PDF No. 00-001-0356) byproducts. Upon further heating, a marked drop in the intensity of VPO$_4$ peaks and a gradual decline in Na$_3$V$_2$(PO$_4$)$_2$F$_3$ are also observed. Figure 1b depicts the Rietveld refinement of TS600 on the basis of the XRD data, revealing that TS600 consists of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$ with space group of P4$_2$/mmm and Cmmm (R$_p$ = 3.9%, R$_wp$ = 5.5%), respectively. We are not able to confirm or deny the subtle orthorhombic space group Am$ar{a}$m assignment to Na$_3$V$_2$(PO$_4$)$_2$F$_3$ by Bianchini and co-workers (b/a = 1.002) due to the resolution of our instrument.[13] Therefore, here we speculate that NaVPO$_4$F cannot be synthesized by solid-state synthesis at any temperature, and Na$_3$V$_2$(PO$_4$)$_3$ is part of the reaction products between Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$. The schematic crystal structures of the tetragonal P4$_2$/mmm/ sublattice orthorhombic (b/a = 1.002) Am$ar{a}$m Na$_3$V$_2$(PO$_4$)$_3$F$_3$ and hexagonal R$ar{3}$c Na$_3$V$_2$(PO$_4$)$_3$ are shown in Figure 1c. Different from Na$_3$V$_2$(PO$_4$)$_3$F$_3$ with 3D structure of V$_2$O$_4$F$_3$ biocatheda bridged by PO$_4$ tetrahedra, Na$_3$V$_2$(PO$_4$)$_3$ is built by isolated VO$_6$ octahedra and PO$_4$ tetrahedra interlinked via corners to establish the framework anion [V$_2$(PO$_4$)$_3$]$^{3-}$.[15] To further confirm our speculation, a powder raw materials mixture (NaF:VPO$_4$ = 1:1) is also calcined at similar temperatures. XRD patterns of these powder samples (PS550, PS600, PS650, PS700, PS750, and PS800) are shown in Figure S1b in the Supporting Information. The graph shows that there has been a sharper decreasing trend in the intensities of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ peaks until they disappeared altogether in PS800, suggesting that the tablet sample impeded volatilization of fluorine and reaction between Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$. To further confirm the synthetic products, samples with increasing ratio of feedstock NaF to VPO$_4$ (1.0:1 to 1.5:1) are calcined at 600 °C. As shown in Figure S1 in the Supporting Information, there is a steady downward trend in the intensity of XRD peaks related to VPO$_4$ until it disappears eventually upon increasing NaF to VPO$_4$ ratio, demonstrating that only Na$_3$V$_2$(PO$_4$)$_2$F$_3$ could be synthesized in solid-state synthesis.

To further understand crystal structure changes of the raw materials (NaF:VPO$_4$ = 1:1) from 25 to 950 °C, in situ XRD and TGA/DSC measurements are conducted (Figure 2). The heating process can be divided into four regimes by magenta lines in Figure 2: R1 for the preparation stage before solid-state reactions of raw materials below 400 °C, R2 for synthetic reaction.
of feedstock materials from 400 to 700 °C, R3 for chemical reaction between Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$ from 700 to 850 °C, and R4 for decomposition reaction of Na$_3$V$_2$(PO$_4$)$_3$ above 850 °C.

For clarity, only the characteristic diffraction peak areas of the phases: (002) peak of NaF (ICDD PDF No. 01-070-2508); (111) and (112) peaks of VPO$_4$; (002) peak of Na$_3$V$_2$(PO$_4$)$_2$F$_3$; (113), (116), and (226) peaks of Na$_3$V$_2$(PO$_4$)$_3$; (113) peak of (VO)$_2$P$_2$O$_7$; and (005) peak of Na$_4$P$_2$O$_7$ are shown. Figure 2a displays the stacked in situ XRD patterns corresponding to TGA/DSC curves. Figure 2b shows the color-coded and temperature-resolved intensity plots. The reference color bar is located under each XRD peak/peak pair, respectively. In addition, specific proportions of different components during the compositional evolution by semiquantitative calculation are displayed versus temperature in Figure 3 and Table S1 in the Supporting Information.

In R1 regime, with the temperature increasing up to 300 °C, all diffraction peaks of NaF and VPO$_4$ shift toward low angles. This phenomenon results from lattice expansion triggered by the atomic diffusion. When temperature increases up to 400 °C, intensity of NaF (002) peak weakens prominently while intensity of VPO$_4$ (111) and (112) peaks declines as well but much slower, indicating the reaction between NaF and VPO$_4$ occurs and the consumption rate of NaF is greater than VPO$_4$. The appearance of the new peak at 16.55° and the residual peaks of unreacted VPO$_4$ affirms the tetragonal/orthorhombic Na$_3$V$_2$(PO$_4$)$_2$F$_3$ as a result of 3:2 reaction in a feedstock of 1:1 NaF and VPO$_4$.

In R2 regime, the peak intensity of NaF keeps weakening until it disappears at 500 °C, while (002) peak of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ continues to increase, indicating the synthetic reaction keeps proceeding until NaF runs out. It should be noted that the ratio of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$ remains 1:1 until both of them exhausted at 800 °C, which matches the expected proportion after 3:2 synthetic reaction of Na$_3$V$_2$(PO$_4$)$_2$F$_3$, confirming the reaction product is Na$_3$V$_2$(PO$_4$)$_2$F$_3$ instead of tetragonal NaVPO$_4$F.

In R3 regime, from both stacked linear diffraction pattern and color-coded intensity plots in Figure 2, it is clear that the peak intensities of both Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$ significantly decline when temperature rises to 700 °C, whereas another series of new and strong peaks emerge, whose peak positions are nearly the same as the proposed monoclinic NaVPO$_4$F phase reported by many previous works.$^{[6,7,9b,11,16]}$ To further investigate the new crystal structure, the TGA/DSC measurement corresponding to in situ XRD was employed. As shown in Figures 2 and 3, there are a remarkable weight loss (~6.6%) and a strong endothermic peak from 650 to 800 °C corresponding to the generation of the new peaks. This weight loss precludes the possibility of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ + VPO$_4$ = 3NaVPO$_4$F. After careful comparison, these new peaks can be attributed to hexagonal
Na₃V₂(PO₄)₂F₃ (space group R3c), with weight loss attributed to volatile VF₃ (gas). The ≈ 6.6% weight loss is less than the theoretical proportion of VF₃ (≈ 17.5%) because part of the VF₃ is obstructed by the coating layer of amorphous carbon.[17] Therefore, tetragonal I₄/mmm and nontavorite monoclinic C₂/c NaVPO₄F may not exist. They might instead be tetragonal P₄2/2 multiple orthorhombic (b/a = 1.002) Amam Na₃V₂(PO₄)₂F₃ and R3c Na₃V₂(PO₄)₃, respectively, shown in Figure 1c, depending on the thermal treatment temperature. Because of the loss of VF₃, there can be no formation of or phase transition to nontavorite monoclinic C₂/c phase NaVPO₄F at still higher temperatures. Besides, pure rhombohedral Na₃V₂(PO₄)₂ are detected after complete chemical reaction at 800 °C.

In R₄, a progressive increase of several new peak intensities is observed at 850 °C, satisfying the mechanism of Equation (3) occurring at high temperature.[18] These new peaks can be attributed to the (VO)₂P₂O₇ (113) reflection and Na₃P₂O₇ (005) peak after rigorous analysis. Therefore, rhombohedral Na₃V₂(PO₄)₂ cannot sustain temperature above 800 °C and will decompose to (VO)₂P₂O₇, Na₃P₂O₇, and maybe other amorphous products (APs) that we have not clarified yet.[19] Due to tableting of raw materials and gaseous reaction product, chemical reaction between Na₃V₂(PO₄)₂F₃ and VPO₄ is far from completed in TS750. To summarize, the structural and compositional evolution in synthesis process of raw materials can be described as follows

\[
3\text{NaF} + 3\text{VPO}_4 \rightarrow \text{Na}_3\text{V}_2(\text{PO}_4)_3 \quad (\text{up to 500 °C}) \quad (1)
\]

\[
\text{Na}_3\text{V}_2(\text{PO}_4)_3 \text{F}_3 + \text{VPO}_4 \rightarrow \text{Na}_3\text{V}_2(\text{PO}_4)_3 + \text{VF}_3 \quad (600 \text{ to} 800 \text{ °C}) \quad (2)
\]

\[
2\text{Na}_3\text{V}_2(\text{PO}_4)_3 \rightarrow 2(\text{VO})_2\text{P}_2\text{O}_7 + \text{Na}_3\text{P}_2\text{O}_7 + \text{AP} \quad (\text{above 800 °C}) \quad (3)
\]

Figure 4 shows Fourier transform-infrared spectrum (FT-IR) spectra between 2400 and 400 cm⁻¹ for as-synthesized products. The weak bands at 1650 and 1398 cm⁻¹ can be ascribed to O–H bending and O–H vibration of C–OH groups.[20] When the temperature rises, these two bands become weaker in powder samples (Figure S2, Supporting Information), but no such change occurs in the tablet samples. This phenomenon indicates tablet hinders the release of gases and the breakdown of C–OH groups. Strong broad band at 1060 cm⁻¹ can be attributed to asymmetric
absorbance of C–F bond (1178 cm$^{-1}$) becomes slightly stronger. It indicates that Equation (2) reaction is sustained and part of evaporable fluoride is captured by carbon coating layer. Furthermore, symmetric stretching of P–O bond (673 cm$^{-1}$) and asymmetric bending vibration $\nu$(F) of PO$_4^{3-}$ (556 cm$^{-1}$) keep lessening, whereas vibration of P$_2$O$_7^{4-}$ unit (602 cm$^{-1}$) intensifies along with the rising temperature above 650 °C. It means the V$_2$O$_4$F$_3$ bioctahedra in Na$_3$V$_2$(PO$_4$)$_2$F$_3$ transfers to isolated VO$_6$ octahedra in Na$_3$V$_2$(PO$_4$)$_3$ and the reaction product Na$_3$V$_2$(PO$_4$)$_3$ further decomposes as Na$_3$P$_2$O$_7$, (VO)$_2$P$_2$O$_7$, and other AP. The much weaker intensity of bands at 944 and 556 cm$^{-1}$ in powder samples obtained at 800 °C (Figure S2, Supporting Information) also demonstrates that compact tablet impedes the fluoride from fleeing the crystal lattice of Na$_3$V$_2$(PO$_4$)$_2$F$_3$. Overall, the peak shift and intensity in in situ and ex situ XRD patterns and the varying strength and position for bands in FT-IR spectra confirm that V–F bonds rupture in crystal, fluoride runs away from the Na$_3$V$_2$(PO$_4$)$_2$F$_3$, and part of PO$_4^{3-}$ unit transfers into P$_2$O$_7^{4-}$ group, affirming that feedstock materials undergo three reactions (Equations (1)–(3)) upon heating.

X-ray photoelectron spectroscopy (XPS) analysis of tablet samples is shown in Figure 5. In the F 1s spectra, two components of F–C bond at 687.0 eV and F–V bond at 684.0 eV are observed. The intensity of F–V bond is gradually and significantly reduced, and F–C bond increased much slower as resultant temperature increases, illustrating that the group related to F–V bond is tapered off and only part of fluoride has been captured by the coating carbon layer.[21] The C 1s region for tablet samples can be deconvoluted into five Gaussian peaks: C–C at 284.6 eV, C–O at 283.8 eV, C=O at 286.8 eV, O=C=O at 288.5 eV, and C–F at 289.0 eV.[20b,23a,24] The same trend as F–C bond in F 1s region confirms the speculation about the evolution of groups related to fluoride analyzed by in situ XRD and FT-IR measurement. The P 2p spectra are characterized by a broadened band which can be decomposed in two different components at 133.9 eV for P=O bond and 132.9 eV for P=O bond. The intensity of the broadened band suddenly weakens after 700 °C, in good agreement with the decomposition mechanism of Na$_3$V$_2$(PO$_4$)$_3$ at high temperature shown in Equation (3).

The characteristic Raman peaks are located at 1327, 1587, and 2654 cm$^{-1}$ (Figure S5a, Supporting Information), corresponding to the D, G, and 2D bands of carbonaceous materials, respectively. It has been reported that the relative intensity ratio of D and G bands (ID/IG) indicates degree of crystallinity in various carbon materials.[25] The ID/IG of each tablet samples is larger than 1, indicating the amorphous nature of carbon. The amount of carbon is estimated to be approximately 6% in the tablet samples (Figure S3b, Supporting Information) from the weight loss in air flow. The morphology of tablet samples is exhibited in Figure S3 in the Supporting Information. It is clear that all compounds composed of agglomerated nanoparticles, with secondary particle sizes mainly distributed around 1.5 μm. The nanoparticles clinging to secondary particles surface of tablet samples calcined above 600 °C might be ascribed to chemical reaction between Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$ and decomposition process of Na$_3$V$_2$(PO$_4$)$_3$. In contrast to stable P element, the amount of F element declines steadily after 600 °C (Figure S4, Supporting Information), in good agreement with Equation (2). HRTEM images confirm the composite structure of crystalline particles and
amorphous carbon. As shown in Figure 6, all sample surfaces are well coated by amorphous carbon layer thinner than 5 nm, especially in TS550 and TS650, revealing that the fluorine escaped from Na$_3$V$_2$(PO$_4$)$_2$F$_3$ lattice could be scavenged by the carbon layers. The lattice fringe of 5.35 Å can be observed inside the particles in TS550, consistent with the interplanar spacing of (002) plane of Na$_3$V$_2$(PO$_4$)$_2$F$_3$, which demonstrates that TS550 is mainly composed of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ particles. As for TS650, the crystallization region is obviously divided into two parts: a highly crystalline layered structure with a layer distance of 5.35 Å corresponding to interplanar spacing of (002) plane of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ on the left side, and another crystalline particle with fringe spacing of 3.73 Å consistent with (002) plane of Na$_3$V$_2$(PO$_4$)$_3$ on right side. Four divided parts of the multicomponent TS750 are shown in Figure 6c. On the basis of relevant fast Fourier transformation (FFT) images, crystal in part A can be ascribed to the newly formed Na$_3$V$_2$(PO$_4$)$_3$ particles; crystal in part B can be attributed to the residual Na$_3$V$_2$(PO$_4$)$_2$F$_3$ particles; amorphous layer in part C can be established as the coating carbon layer; and empty region in part D is gap of the transmission electron microscopy.

Figure 5. XPS spectra of F 1s, C 1s, and P 2p for tablet samples calcined at 550–750 °C.

Figure 6. HRTEM images of tablet samples calcined at a) 550, b) 650, and c) 750 °C and FFT pictures correspond to the selected areas. The abbreviations of NVPF and NVP correspond to Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and Na$_3$V$_2$(PO$_4$)$_3$. 

(TEM) micro grid copper network. These results have recorded the process of constant loss of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and new generation of Na$_3$V$_2$(PO$_4$)$_3$ crystals, consistent with Equations (1) and (2).

CR2016 coin cells with Na metal anode were assembled to investigate the detailed electrochemical performance of tablet and powder samples. Figure 7 shows the cyclic voltammetry (CV) curves of samples tested in potential range of 2.5–4.5 V (vs Na/Na$^+$) at a scan rate of 0.1 mV·s$^{-1}$. When the temperature is elevated up to 550 and 600 °C, the samples exhibit two couples of redox peaks (≈4.3 V/4.1 V and 3.8 V/3.6 V vs Na/Na$^+$) which belong to Na$_3$V$_2$(PO$_4$)$_2$F$_3$, and a couple of small redox peaks around 3.4 V/3.3 V (vs Na/Na$^+$) is attributed to Na$_3$V$_2$(PO$_4$)$_3$ for TS550. It demonstrates that the main active materials calcined below 650 °C is the well-established Na$_3$V$_2$(PO$_4$)$_2$F$_3$. However, a couple of strong redox peaks of ≈3.4 V/3.3 V (vs Na/Na$^+$) which belong to Na$_3$V$_2$(PO$_4$)$_3$ arise when temperature increased above 600 °C. Besides, another small and broad redox peaks around 2.9 V (vs Na/Na$^+$) are observed, belonging to the decomposition product of Na$_3$V$_2$(PO$_4$)$_2$F$_3$.$^{[18]}$ The redox peaks of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ (≈4.3 V/4.1 V and 3.8 V/3.6 V vs Na/Na$^+$) and Na$_3$V$_2$(PO$_4$)$_3$ (≈3.4 V/3.3 V vs Na/Na$^+$) become weaker during elevated sintering temperature above 650 °C, whereas the small redox peaks around 2.9 V (vs Na/Na$^+$) become even larger.$^{[18]}$ The corresponding charge/discharge curves at 0.1 C-rate (0.1 C means full charge/discharge in 10 h) are presented in Figure 7c,d. The initial charge/discharge curves of the test cells deliver an initial discharge capacity of 89.7, 86.7, 111.4, 105.3, and 94.9 mA h g$^{-1}$ of TS550, TS600, TS650, TS700, and TS750. The specific charge and discharge potential plateaus (3.5 V/3.3 V vs Na/Na$^+$) capacity of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ increases at first and then decreases at temperatures above 650 °C. These results indicate that chemical reaction between Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$ and decomposition reaction of Na$_3$V$_2$(PO$_4$)$_3$ occur at same time when the temperature increases up to 650 °C. The charge and discharge curves of powder samples (Figure S6, Supporting Information) show there is a diminishing trend in plateaus of Na$_3$V$_2$(PO$_4$)$_2$F$_3$. The difference of charge and discharge curves between tablet and powder samples illustrates that compacted tablet blocks the continuous reaction between Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and VPO$_4$ and hinders the fleeing of fluorine.

Based on our experience, with 1:1 NaF:VPO$_4$ feedstock and solid-state synthesis one cannot get single-phase NaVPO$_4$F compound at any temperature. Instead, one gets two-phase mixture of Na$_3$V$_2$(PO$_4$)$_2$F$_3$+VPO$_4$ up to 500 °C. The resulting tetragonal P4$_2$/mmm/subtle orthorhombic (b/a = 1.002) Na$_3$V$_2$(PO$_4$)$_2$F$_3$ may be easily mistaken to be tetragonal I4/mmm.$^{[3a]}$ And then from 600 to 800 °C, Na$_3$V$_2$(PO$_4$)$_2$F$_3$+VPO$_4$ → Na$_3$V$_2$(PO$_4$)$_3$ + VF$_3$↑. The degree of VF$_3$ volatilization depends on the temperature exposure and details of pelletization; however, some vaporization of VF$_3$ and mass loss are unavoidable after 650 °C. Since Na$_3$V$_2$(PO$_4$)$_3$ is rhombohedral R$3_c$, it may also be easily mistaken to be nontavorite monoclinic C$_2$/c NaVPO$_4$F.$^{[6,11]}$ Based on Barker and co-workers and Zhuo and co-workers.$^{[3a,6]}$ many researchers have quoted tetragonal I4/mmm and nontavorite monoclinic C$_2$/c NaVPO$_4$F from solid-state synthesis; for example, Zhao and co-workers reported a gradual phase transition of NaVPO$_4$F from monoclinic at 700 °C to tetragonal at 750 °C.$^{[7]}$ however, we believe these assignments of single-phase NaVPO$_4$F compound may often be mistaken.

Since we have not obtained NaVPO$_4$F with solid-state synthesis, we would like to form NaVPO$_4$F by another method, liquid-aided electrochemical ion exchange. We perform Li→Na ion exchange on LiVPO$_4$F, by introducing LiVPO$_4$F as cathode to cycle in a sodium half-cell to form NaVPO$_4$F electrochemically for
comparision. As shown in Figure 8, the XRD patterns of LiVPO$_4$F and the ion exchanged compound after 10, 30, and 50 cycles are well observed. After 10 cycles’ electrochemical ion exchange process, Na ions are expected to be the cations reinserted into VPO$_4$F framework due to preponderant Na ion concentration in sodium half-cell. The crystal structure has changed dramatically after 10 cycles which can be ascribed to the formation of NaVPO$_4$F. However, this new structure of NaVPO$_4$F by liquid-phase method is far different from the hypothetical tetragonal $I_4/mmm$ and nontavorite $C_2/c$ NaVPO$_4$F of previous reports (in the sense that although no explicit atomic coordinates were given and of a different stoichiometry, they were all acclaimed to be as similar to Le Meins’ family). These liquid-phase NaVPO$_4$F belongs to the Tavorite family instead. Furthermore, a unique and distinct charge/discharge plateaus at =3.9 V (vs Na/Na$^+$) is detected in charge and discharge curves (Figure 8b), which is different from the tetragonal (4.1 and 3.6 V vs Na/Na$^+$) and nontavorite monoclinic “NaVPO$_4$F” (3.4 V vs Na/Na$^+$). Moreover, due to the major weight loss, nontavorite monoclinic NaVPO$_4$F might be misleading. These structures might be multiphase mixtures of Le Meins’ Na$_3$V$_2$(PO$_4$)$_2$F$_3$, unreacted VPO$_4$ and nontavorite Na$_3$V$_2$(PO$_4$)$_3$. The understanding gained about the formation mechanism upon heating process of 1:1 NaF:VPO$_4$ raw materials we proposed may help us avoid future mislabeling of fluorophosphate SIB cathode materials.

### 4. Experimental Section

#### Materials Preparation

The active materials calcined at different temperatures were prepared by a traditional two-step carbothermal reduction route. V$_2$O$_5$ and NH$_4$H$_2$PO$_4$ with a stoichiometric amount were first ball milled with acetylene black (20% excess) in 400 rpm for 6 h to get a uniform particles distribution. The mixture was calcined at 750 °C for 8 h in argon (Ar) atmosphere to obtain VPO$_4$. The active materials were prepared by mixing and tablet or not with proportion (1:1) of the intermediate VPO$_4$ and NaF, then sintered at 550, 600, 650, 700, and 750 °C under Ar flow for 8 h, respectively. The first step incorporation reaction may be summarized as

\[
\text{V}_2\text{O}_5 + 2\text{NH}_4\text{H}_2\text{PO}_4 + 2\text{C} \rightarrow 2\text{VPO}_4 + 2\text{NH}_3 + 3\text{H}_2\text{O} + 2\text{CO} \tag{M1}
\]

The unexhausted acetylene black was left as carbon coating on the surface of the active materials in the final product.

#### Characterization

In situ and ex situ XRD measurement was performed to characterize the structural and compositional evolution upon heating by using an X’pert Pro (PAAnalytical Ltd., Holland) with Cu Kr radiation ($\lambda = 1.5406$ Å). Characteristic weight loss and thermodynamic heat energy transmission of the second step mixture precursor were measured by TGA/DSC analyses using a Mettler Toledo (TGA/DSC 1) thermoanalyzer. The measurement was conducted from room temperature to 900 °C at a heating rate of 10 °C min$^{-1}$. The IR spectra were obtained by FTIR spectrometer (Nicolet, iS10, USA) under transmission mode based on the KBr pellet method in the range of 400–4000 cm$^{-1}$. XPS was collected by using a monochromatic Al Kr (1486.6 eV) radiation. Raman spectra were obtained on a HORIBA JOBIN YVON micro-Raman spectrometer.
The particle morphology of the active materials (heat treatment at 550–750 °C, at an interval of 50 °C, in the second step) was observed by field emission scanning electron microscopy (FE-SEM Quanta 250FEFG, FEI, USA). TEM (TEM, FEI TITAN G2, USA) was employed to characterize the morphology as well as the evolution of raw materials upon heating.

Electrochemical Measurement: The electrochemical performance was carried out with 2016 coin cells assembled in glove box filled with high-purity argon gas. In the sodium half-cells, the 70% active material, 20% conducting carbon (super P), and 10% polyvinylidene fluoride binder (PVDF) were used as the cathode, a microporous polymer (Celgard 2500) as separator, the sodium metal as the anode, and 1 M solution of NaClO4 in EC-DMC (50:50) as the electrolyte. The mass loading of active material in each coin cell is typically 1.0–1.5 mg cm−2, and the electrode footprint area is 2.01 cm2. The galvanostatic charge/discharge at the range of 2.5–4.2 V vs Na/Na+ was measured on a CT2001A Land Battery Testing System, while the CV was performed on a Versatile Multichannel.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
Na3V2(PO4)3, tavorite-type NaVPO4F, volatile VF3 gas

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Supplementary information

Fluorophosphates from Solid-State Synthesis and Electrochemical Ion Exchange: NaVPO$_4$F or Na$_3$V$_2$(PO$_4$)$_2$F$_3$?

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Figures

Figure S1 (a) Rietveld refinement based on the XRD pattern of the precursor phase. (b) XRD patterns of the powder samples calcined at 550 - 750 °C. (c) and (d) XRD patterns of raw materials with various ratio of NaF and VPO$_4$ calcined at 600 °C in 3D and 2D mode, respectively.
**Figure S2** FT-IR spectra of powder samples calcined at 550 - 750 °C.

![FT-IR spectra](image)

**Figure S3** (a) Raman spectra of tablet samples calcined at 550 - 750 °C. (b) TG curves of tablet samples from 50 °C to 600 °C at a heating rate of 10 °C min⁻¹ in Air flow.

![Raman spectra and TG curves](image)
Figure S4 FESEM images of tablet samples calcined at 550 - 750 °C.
**Figure S5** EDS element analysis (a) – (e) and the percentage of F and P element (f) of tablet samples calcined at 550 - 750 °C.

**Figure S6** The charge/discharge curves of powder samples calcined at 550 - 750 °C. The load density of the electrode is about 1.5 ~2.0 mg cm$^{-2}$, with the formulation of active materials: acetylene black: PVDF = 70: 20:10 (weight).
Tables

Table S1 The compositional changes of raw material upon heating calculated by semi-quantitative calculation of in situ XRD patterns.

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<th>VPO$_4$ (at%)</th>
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