

Unlocking the Inaccessible Energy Density of Sodium Vanadium Fluorophosphate Electrode Materials by Transition Metal Mixing

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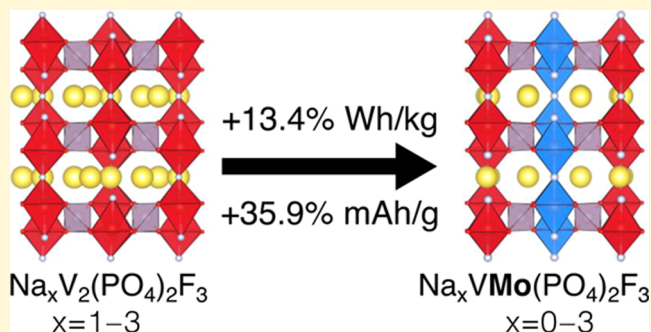


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ABSTRACT: Sodium (Na) vanadium (V) fluorophosphate $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) is a highly attractive intercalation electrode material due to its high operation voltage, large capacity, and long cycle life. However, several practical issues limit the full utilization of NVPF's energy density: (1) the high voltage plateau associated with extracting the "third" Na ion in the reaction $\text{N}_1\text{VPF} \rightarrow \text{VPF}$ (~ 4.9 V vs Na/Na^+) appears above the electrochemical stability window (ESW) of most practical electrolytes (~ 4.5 V vs Na/Na^+); and (2) a sudden drop in Na-ion diffusivity is observed near composition $\text{Na}_1\text{V}_2(\text{PO}_4)_2\text{F}_3$. Therefore, it is important to investigate the potential substitution of V by other transition metals (TMs) in NVPF derivatives, which can practically access the extraction of the third Na-ion. In this work, we investigate the partial substitution of V with molybdenum (Mo), niobium (Nb), or tungsten (W) in NVPF to improve its energy density. Using first-principles calculations, we examine the structural and electrochemical behaviors of $\text{Na}_x\text{V}_{2-y}\text{Mo}_y(\text{PO}_4)_2\text{F}_3$, $\text{Na}_x\text{V}_{2-y}\text{Nb}_y(\text{PO}_4)_2\text{F}_3$, and $\text{Na}_x\text{W}_2(\text{PO}_4)_2\text{F}_3$ across the whole Na composition region of $0 \leq x \leq 4$, and at various transition metal (TM) substitution levels, namely, $y = 0.5, 1.0, 1.5,$ and 2.0 for Mo, and $y = 1.0$ and 2.0 for Nb. We found that partial substitution of 50% V by Mo in NVPF reduces the voltage plateau for extracting the third Na ion by 0.6 volts, which enables further Na extraction from $\text{Na}_1\text{VMo}(\text{PO}_4)_2\text{F}_3$ and increases the theoretical gravimetric capacity from ~ 128 to ~ 174 mAh/g. Analysis of the migration barriers for Na-ions in $\text{Na}_x\text{VMo}(\text{PO}_4)_2\text{F}_3$ unveils improved kinetic properties over NVPF. The proposed $\text{Na}_x\text{VMo}(\text{PO}_4)_2\text{F}_3$ material provides an optimal gravimetric energy density of ~ 577.3 Wh/kg vs ~ 507 Wh/kg for the pristine NVPF, which amounts to an increase of $\sim 13.9\%$.



INTRODUCTION

With a higher natural abundance of sodium (Na) and lower raw material costs, sodium-ion batteries offer a promising alternative to lithium-ion batteries.¹⁻³ However, the higher reduction potential for Na (-2.71 volts vs standard hydrogen electrode, SHE) than for Li (-3.04 volts vs SHE), larger ionic size, and greater mass of Na contribute to a lower theoretical energy density.^{1,2} Therefore, developing energy-dense electrode materials based on sustainable constituents is a key challenge.

Polyanion-type materials are widely investigated as positive electrode hosts for Na-ion batteries due to their high voltages arising from inductive effects.⁴⁻⁸ The sodium vanadium fluorophosphate $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) is one of the most attractive positive electrodes for Na-ion batteries due to its high operation voltage (~ 3.95 V vs Na/Na^+ on average),⁹ large capacity (~ 128 mAh/g),¹⁰ and long cycle life of 100% specific capacity retention after 10,000 cycles.¹¹⁻¹⁴ In practice, two Na-ions can be reversibly extracted/inserted between $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (N_3VPF) and $\text{Na}_1\text{V}_2(\text{PO}_4)_2\text{F}_3$ (N_1VPF), giving a gravimetric energy density of ~ 507 Wh/kg.^{10,15-17}

The potential extraction of three Na-ions from N_3VPF to $\text{V}_2(\text{PO}_4)_2\text{F}_3$ (VPF) (instead of N_1VPF) would increase the

theoretical gravimetric capacity from 128 mAh/g to ~ 198 mAh/g. However, extraction of the third Na^+ from N_1VPF activates the $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ redox couple at a voltage plateau of ~ 4.9 V vs Na/Na^+ .¹⁸ This voltage appears above the electrochemical stability window (ESW) for most sodium electrolytes,¹⁹ rendering the third Na-ion electrochemically inaccessible. Furthermore, NVPF exhibits a rapid decline in Na^+ diffusivity as the Na content (per formula unit, f.u.) approaches 1, which has been attributed to additional energies required to create vacancies and to disrupt strong Na-vacancy orderings at N_1VPF .^{17,20,21} Recently, the group of Tarascon has demonstrated that the reversible extraction of the third Na-ion in NVPF is possible via the formation of a disordered tetragonal NVPF phase (space group $I4/mmm$). This disordered structure can reversibly uptake three Na-ions but at a lower

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potential than NVPF in the original ordered state, resulting in a 14% improvement in energy density.¹⁰ Achieving reversible three Na⁺ cycling with further optimization of the energy density in NVPF remains an open challenge.

Here, we demonstrate that the energy density of the NVPF positive electrode can be optimized via transition metal (TM) substitution, which replaces the high-potential V^{IV}/V^V at $0 \leq x \leq 1$ of NVPF by alternative TM redox couples and enables the reversible cycling of three Na-ions. Using first-principles calculations, we investigate the effect of replacing vanadium species with niobium (Nb), molybdenum (Mo), and tungsten (W) at different substitution levels, forming Na_xV_{2-y}M_y(PO₄)₂F₃ (M = Nb, Mo, or W, and $0 \leq x \leq 4$). We have studied the structural, electrochemical, and kinetic properties of these novel Na_xV_{2-y}M_y(PO₄)₂F₃ compositions upon Na-ion intercalation. Nb and Mo were selected based on a high-throughput *ab initio* study by Hautier et al., which demonstrated the average voltage of the Nb^{IV}/Nb^V and Mo^{IV}/Mo^V redox couples to be lower than V^{IV}/V^V by ~ 2.0 and ~ 0.6 V, respectively.²² W was included because it is isoelectronic to Mo and has recently been used as a dopant for enhancing the electrochemical performance of the NVPF cathode (Na₃V_{1.96}W_{0.04}(PO₄)₂F₃) material.²³

By replacing 50% of V in NVPF with Mo as in Na_xVMo(PO₄)₂F₃ (NVMoPF), we found that the voltage plateau associated with the extraction of the third Na-ion from Na₁VMo(PO₄)₂F₃ (N₁VMoPF) is reduced from 4.53 vs Na/Na⁺ to 3.93 V vs Na/Na⁺, which is practical for current nonaqueous electrolytes.¹⁹ The decreased voltage may enable the reversible extraction of three Na-ions and lead to an increase in capacity from 128 mAh/g for NVPF to 173.7 mAh/g for NVMoPF.

Further in-depth studies into the kinetic properties of NVMoPF reveal the favorable mechanism of extracting the third Na-ion from N₁VMoPF due to superior Na⁺ mobility, making NVMoPF a promising candidate for increasing the reversible capacity in comparison to NVPF. The increased capacity contributes to a boost of gravimetric energy density from ~ 507 Wh/kg for NVPF ($1 \leq x \leq 3$)¹⁵ to ~ 577.3 Wh/kg for NVMoPF ($0 \leq x \leq 3$), corresponding to a rise of $\sim 13.9\%$.

RESULTS

Structural Features of the Na_xV₂(PO₄)₂F₃ Skeleton.

Chemical formulae are abbreviated to the first letter of their chemical group throughout this manuscript. For example, Na_xMo₂(PO₄)₂F₃ is abbreviated as NMoPF, and Na_xVMo(PO₄)₂F₃ is abbreviated as NVMoPF. When necessary, the sodium composition x is specified by the subscript, e.g., Na₁VMo(PO₄)₂F₃ is written as N₁VMoPF. The Na-ion that is extracted from Na₁ to Na₀ will be referred to as the third Na⁺.

The host structure of NVPF is composed of V₂O₈F₃ bioctahedral units corner-shared by PO₄ tetrahedra, resulting in a three-dimensional framework (see Figure 1a) and several Na-ion "interstitial" sites.^{15,24,25} As shown in Figure 1, PO₄ polyanionic groups separate the two-dimensional Na layers, which lie in the *ab*-plane of the structure.

The pristine N₃VPF phase comprises three distinct sodium positions that arrange into a "circle" around fluorine centers^{9,13,15,24} as shown in Figure 1b. The sodium ions can occupy the [010], [100], and [110] sites, which are indexed as Na(1) (4c), Na(2) (8f), and Na(3) (8f), respectively.

The Na(1) sites are fully occupied, whereas Na(2) and Na(3) sites are ~ 80 and $\sim 20\%$ occupied, respectively, for

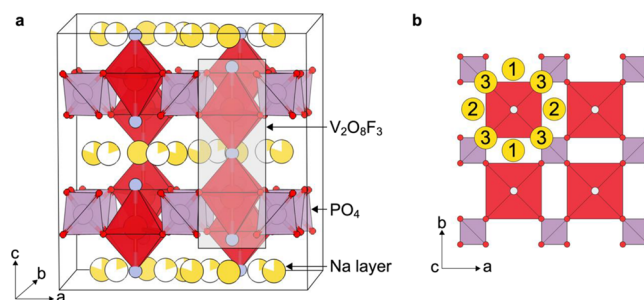


Figure 1. Crystal structure of the pristine Na₃V₂(PO₄)₂F₃ phase in the orthorhombic *Amam* space group is shown in panel (a). The V₂O₈F₃ bioctahedral unit (red) contains three fluorine atoms (gray) that are aligned along the [001] direction. The bioctahedral units are corner-shared with PO₄³⁻ tetrahedra (purple) that are aligned in parallel within the (001) plane, creating two-dimensional Na layers (yellow) in the *ab*-plane of the structure. Panel (b) shows the top view of the *ab*-plane for Na_xV₂(PO₄)₂F₃ and the available Na sites and their indexing. Three distinct sodium sites with their Wyckoff labels, i.e., Na(1) (4c), Na(2) (8f), and Na(3) (8f) sites (yellow circles) are indexed with 1, 2, and 3, respectively.

N₃VPF at room temperature.^{15,24,26} At the other Na contents in N_xVPF, specific Na-vacancy ordering or disordering will occur among the three Na sites (Figure 1b) and thus lead to different symmetries.^{15,25} Here, we will extend the same indexing convention of Na positions to NVPF systems where V is (partly) replaced by Mo.

Phase Stabilities and Voltage Curves of Mo- and Nb-Substituted Na_xV₂(PO₄)₂F₃. Using density functional theory (DFT, see Methods section), we computed the energy of mixing (i.e., the formation energy E_f) with Na of a substantial number of Na-vacancy orderings for N_xVPF ($x = 0\sim 4$ in a step size of increment = 0.5), N_xVMoPF ($x = 0\sim 4$ with increments $\Delta x = 1$), and N_xMoPF ($x = 0\sim 4$ with $\Delta x = 1$), which amounted to 202, 243, and 99 unique DFT-relaxations (atom coordinates + model cell shape + model cell volume) for NVPF, NVMoPF, and NMoPF, respectively. The computed energies of mixing are shown in Figure 2a–c as the Na concentration x is varied. Figure 2d–f shows the corresponding intercalation voltages vs Na/Na⁺ as a function of Na concentration for the parent NVPF and Mo-substituted NVPF systems, namely NVMoPF and NMoPF.

From the analysis of Figure 2a–c, we identified the phase diagrams at 0 K—the convex hulls—by the lower envelopes formed by the most stable Na-vacancy orderings in each tie-line considered. Structures with Na-vacancy orderings above the convex hull are metastable or unstable and likely to decompose into the nearest ground-state compositions. The ground-state structures representing Na-vacancy orderings for NVPF, NVMoPF, and NMoPF were identified at specific Na content $x = 0, 1, 2, 3$, and 4. These ground-state structures feature in the voltage curves of Figure 2d–f.

The green shading domains in Figure 2d–f indicate the practical Na composition range in which Na-ions are predicted to be accessible for reversible cycling. We consider the Na composition in the range of $0 \leq x \leq 3$ to be accessible if their voltage plateau is below 4.5 V vs Na/Na⁺, which is a common threshold for existing nonaqueous electrolyte stability.^{13,19,21} Note that the exact onset potential for electrolyte decomposition depends on the type of salt(s) and solvent(s).¹⁹ For example, Ponrouch et al. reported an average value of approximately 4.6 V vs Na/Na⁺ for NaClO₄ in 10 different

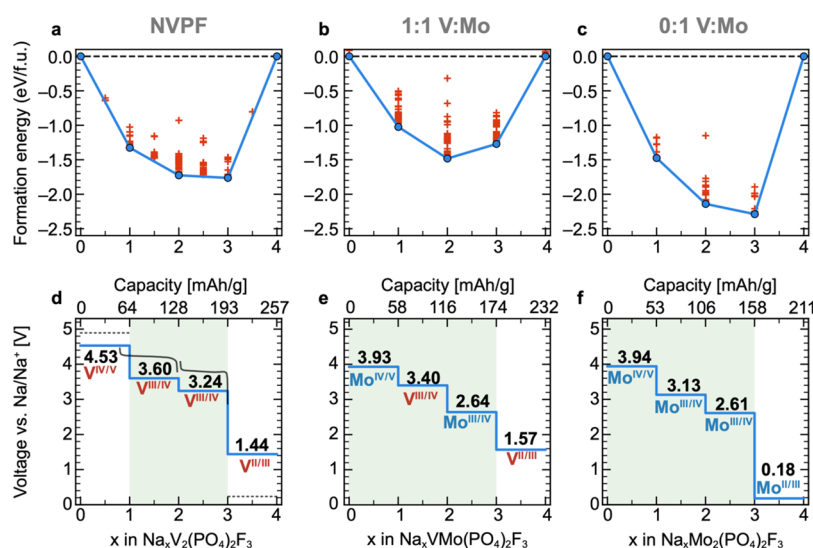


Figure 2. Panels (a–c) show the computed mixing energies (approximated by formation energy) with GGA + U as a function of Na concentration x for N_xVPF (a), N_xVMoPF (b), and N_xMoPF (c). Unstable Na-vacancy orderings are shown by red crosses, whereas ground-state orderings (blue dots) form the phase diagram at 0 K—the convex hull. Panels (d–f) depict the corresponding intercalation voltages vs Na/Na^+ as a function of Na concentration x for N_xVPF (d), N_xVMoPF (e), and N_xMoPF (f). The values of computed voltages and the activated redox couples for each step are reported. The experimental voltage of NVPF is superimposed with solid black lines in (d), depicting the (de)intercalation step of Na_1 - Na_2 and Na_2 - Na_3 ¹⁵ (reproduced and adapted with permission from ref 15. Copyright 2015 American Chemical Society). For the impractical high-voltage step at Na_0 - Na_1 ¹⁸ (reproduced and adapted with permission from ref 18. Copyright 2014 American Chemical Society) and low-voltage step at Na_3 - Na_4 for NVPF^{26,27} (reproduced and adapted with permission under a Creative Commons 4 from ref 26. Copyright 2016 Springer Nature. Reproduced and adapted with permission from ref 27, 2017 John Wiley and Sons), only the average voltages are schematically shown with dashed black lines for visualization (d). All capacities are normalized using the mass of each fluorophosphate structure at $x = 3$. The Na composition region with accessible capacity is indicated by green shades. Voltage curves and convex hulls of the $N_xV_{1.5}Mo_{0.5}PF$ and $N_xV_{0.5}Mo_{1.5}PF$ systems are in Supporting Figure S1.

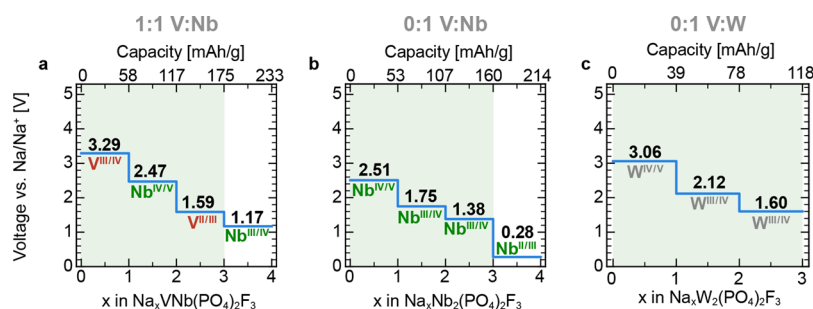


Figure 3. DFT + U computed intercalation voltages vs Na/Na^+ as a function of Na concentration x for (a) N_xVNbPF , (b) N_xNbPF , and (c) N_xWPF . The voltage profile of Na_3 - Na_4 in NWPF is omitted because the electronic state of N_4WPF is not correctly described by the GGA + U framework, leading to unphysical oxidation states and thus an inaccurate prediction of the electronic structure. All the gravimetric capacities are calculated using the masses of composition $x = 3$. The active redox couples are indicated in red for V, green for Nb, and silver for W. The accessible capacity is indicated by green shades.

organic solvents in the range of 3.7 to 5.2 V vs Na/Na^+ .¹⁹ The Na-ion associated with the reversible insertion step in the composition range of $3 \leq x \leq 4$ is considered inaccessible due to (1) the limited concentration of vacancies when approaching the fully discharged Na_4 composition, which prevents Na^+ mobility,¹⁷ and (2) the low voltage plateaus (~ 0 V) that fall below the electrolyte stability window.^{26,27}

We start by comparing the computed voltage profiles to the available experimental voltages for NVPF.^{18,19,28} Our results show two voltage plateaus at ~ 3.24 and ~ 3.60 V vs Na/Na^+ , respectively, which are associated with the reversible Na^+ extraction from N_3VPF to N_1VPF , and one voltage plateau at ~ 4.53 V vs Na/Na^+ that is associated with the extraction of the third Na^+ from N_1VPF to VPF , which is not reversible in experiments (Figure 2d).^{15,18} These plateaus were observed in

previous experiments at ~ 3.6 , ~ 4.2 , and ~ 4.9 V vs Na/Na^+ , respectively.^{18,19,28} The discrepancy between the theoretical and experimental value of voltage has previously been attributed to the Hubbard- U correction of 3.1 eV for V centers, which causes a constant voltage underestimation of approximately ~ 0.4 V.²¹ Importantly, the intercalation trends predicted in our calculations are in line with the experimental results, which underlines the reliability of our method for predicting the electrochemical properties.

Following the reaction of $N_1VPF \rightarrow VPF$, the voltage associated with the third Na^+ extraction from N_1VPF appears above the ESW of most common nonaqueous electrolytes for Na-ion batteries,^{13,19,21} thus making the extraction of this Na^+ inaccessible.¹⁹ As shown in Figure 8 and Supporting Table S1, extracting two Na-ions at the

predicted voltages of ~ 3.60 and ~ 3.24 V vs Na/Na⁺ results in a theoretical energy density of ~ 439.1 Wh/kg for NVPF (~ 507 Wh/kg as observed in experiments).¹⁵

The replacement of all V with Mo (giving NMoPF) decreases the values of the voltage plateaus by ~ 1.26 , ~ 0.63 , ~ 0.47 , and ~ 0.59 V in comparison to NVPF upon Na⁺ extraction from the hypothetical fully discharged N₄MoPF phase to the empty MoPF structure, respectively. From our calculations, we observe that the third Na⁺ extraction from N₁MoPF to MoPF activates the Mo^{IV}/Mo^V redox couple at a voltage of ~ 3.94 V vs Na/Na⁺. This is clearly below the threshold electrolyte stability window of the most common electrolytes.¹⁹

When substituting 50% of Mo for V, forming NVMoPF, the Na⁺ extraction from N₃VMoPF to the empty VMoPF occurs through the activation of the redox couples of Mo^{III}/Mo^{IV}, V^{III}/V^{IV}, and Mo^{IV}/Mo^V (see Figure 2e). The extraction of the third Na⁺ from N₁VMoPF shows a voltage of ~ 3.93 V vs Na/Na⁺, which is similar in magnitude to the same redox process in the all-Mo-containing electrode (~ 3.94 vs Na/Na⁺). The theoretical energy density of NVMoPF ($x = 0\sim 3$) is 577.3 Wh/kg, which is $\sim 13.9\%$ higher than NVPF (considering the third Na⁺ extraction an irreversible process for NVPF, see Supporting Table S1).

We also investigated the structural and electrochemical properties of Na⁺ extraction from the NNbPF, NVNbPF, and NWPF systems, whose voltage curves are shown in Figure 3. The corresponding mixing energy profiles are given in Supporting Figure S2.

On average, the voltage plateaus for the Nb-containing system NNbPF are nearly 2 V lower from $x = 0$ to $x = 3$ and over 1 V lower from $x = 3$ to $x = 4$ compared to NVPF. The extraction of the third Na-ion from $x = 1$ is predicted to occur at ~ 2.51 V vs Na/Na⁺ via Nb^{IV}/Nb^V. Assuming a potential extraction of three Na-ions, NNbPF could provide almost a 20% increased capacity (160 mAh/g) compared to NVPF (128 mAh/g). However, the higher capacity of NNbPF cannot compensate for the substantially lower intercalation voltages of NNbPF, which reduces the gravimetric energy density for NNbPF (~ 301 Wh/kg) by 40.6% compared to NVPF.

Surprisingly, in the mixed Nb/V fluorophosphate (i.e., NVNbPF), the extraction of the third Na⁺ from N₁VNbPF to VNbPF activates the V^{III}/V^{IV} redox couple at ~ 3.29 V (Figure 3a), which has a much lower voltage than the V^{IV}/V^V redox couple in NVPF (~ 4.53 V vs Na/Na⁺ at Na₀–Na₁, Figure 2d). Reversible cycling between Na₁ and Na₂ and between Na₂ and Na₃ in NVNbPF activates the Nb^{IV}/Nb^V and V^{II}/V^{III} redox couples at a voltage of 2.47 and 1.59 V vs Na/Na⁺, respectively. The resulting gravimetric energy density of NVNbPF is 428.5 Wh/kg, which is 15.5% lower than that of NVPF.

A commonality of NMoPF and NNbPF is the low value of the computed intercalation voltage (0.18 V and 0.28 V vs Na/Na⁺) for the insertion of the fourth Na-ion in the composition range $3 \leq x \leq 4$. To this end, we recomputed the “ground-state” structures of N₃MoPF, and N₄MoPF, as well as N₃NbPF, and N₄NbPF, with the same settings implemented by Materials Project.²⁹ We combined these new data with all the available phases in the respective Na–Mo–P–O–F and Na–Nb–P–O–F quinary composition spaces that we used to derive the thermodynamic stabilities of N₃MoPF, N₄MoPF, N₃NbPF, and N₄NbPF. Surprisingly, both N₃MoPF and N₄MoPF are stable compounds in the Na–Mo–P–O–F

phase field, with appreciable formation energies of ~ -2.59 and ~ -2.44 eV/atom, respectively. In contrast, the computed Na–Nb–P–O–F quinary space suggests that both N₃NbPF and N₄NbPF appear highly unstable, with the energy above the convex hull of ~ 245 and ~ 318 meV/atom, respectively.

Replacing all V atoms with W, giving NWPF, substantially lowers the voltage plateaus of NVPF. In the Na composition range $0 \leq x \leq 3$, we find three voltage plateaus at ~ 3.06 , ~ 2.12 , and ~ 1.60 V vs Na/Na⁺ for NWPF. This voltage lowering results in a theoretical gravimetric energy density of only 265.9 Wh/kg in NWPF, which is $\sim 47.6\%$ lower than NVPF.

Sodium-Vacancy and TM Ordering in Na_xV₂(PO₄)₂F₃ Derivatives. Having established that Mo gives the largest increase in energy density, the remainder of this paper will focus on the structural and kinetic properties of Mo-substituted NVPF systems (Na_xV_{2–y}Mo_y(PO₄)₂F₃ with $y = 0, 1$, and 2).

Figure 4a shows the change in lattice parameters a and c as a function of the Na content in the NVPF, NMoPF, and

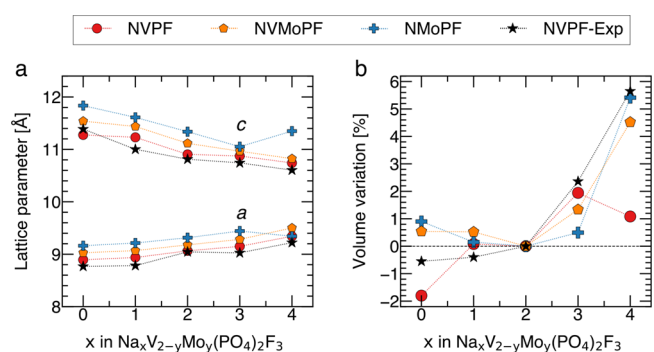


Figure 4. Calculated lattice parameters a and c (panel (a)), and volume variation (panel (b)) for Na_xV₂(PO₄)₂F₃ (red circles), Na_xVMo(PO₄)₂F₃ (yellow pentagons), and Na_xMo₂(PO₄)₂F₃ (blue crosses) systems. The volume variations are benchmarked to the volume of composition Na₂ as denoted by the horizontal dotted line in panel (b). Experimental values (NVPF-Exp)^{10,15,26} of lattice parameters and volumes are denoted by black stars in panels (a) and (b) (reproduced and adapted with permission under a Creative Commons 4 from ref 10. Copyright 2019 Springer Nature. Reproduced and adapted with permission from ref 15, 2015 American Chemical Society. Reproduced and adapted with permission under a Creative Commons 4 from ref 26. Copyright 2016 Springer Nature). The Na₂ composition was chosen as the reference as it is speculated to be the pristine composition in the NVMoPF (V/Mo = 1:1) system, see Figure 2b. Dashed lines are shown for visual guidance.

NVMoPF systems. Figure 4b illustrates the relative volume change of NVPF, NVMoPF, and NMoPF, with the Na₂ composition serving as the reference point. All structural parameters are in Supporting Table S2.

Quantitatively, the computed values of the lattice parameters agree well with experimental data for NVPF, where the length of c generally decreases upon Na⁺ insertion (upper bundle in Figure 4a). This behavior is also consistent for N_xVMoPF and N_xMoPF, except for N₄MoPF, which is accompanied by an increase of the lattice parameter c . Such an increase is attributed to the distortion of the bioctahedral units (Supporting Figure S3), which is not observed in the fully discharged all-V or mixed V–Mo fluorophosphate materials. The electrochemical cycling of three Na-ions in NVPF (i.e., from Na₃ to Na₀) leads to a volume variation of $\sim 4\%$, whereas

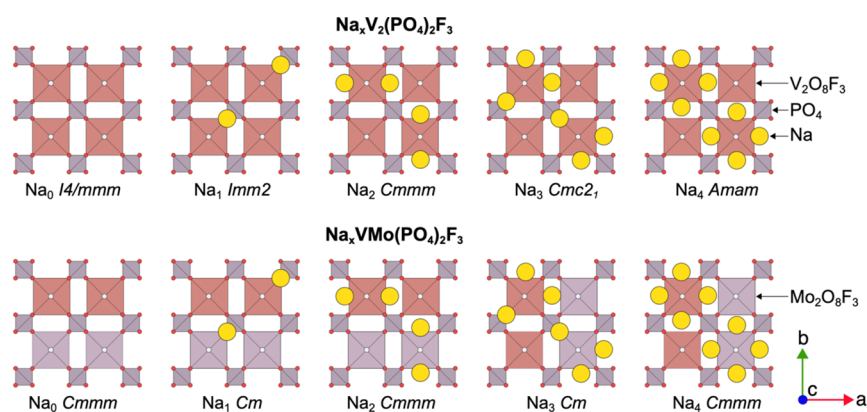


Figure 5. Na-vacancy orderings of the ground-state structures of N_x VPF (upper part) and N_x VMoPF (lower part) obtained at the GGA + U level of theory. Na ions (yellow), V biotahedral units (red), and Mo biotahedral units (violet) are shown. Phosphate groups are shown with smaller rectangles in magenta, while oxygen and fluorine atoms are in red and silver, respectively. All structures and space groups correspond to the computed lowest energy structures that form the convex hull (see Figure 2).

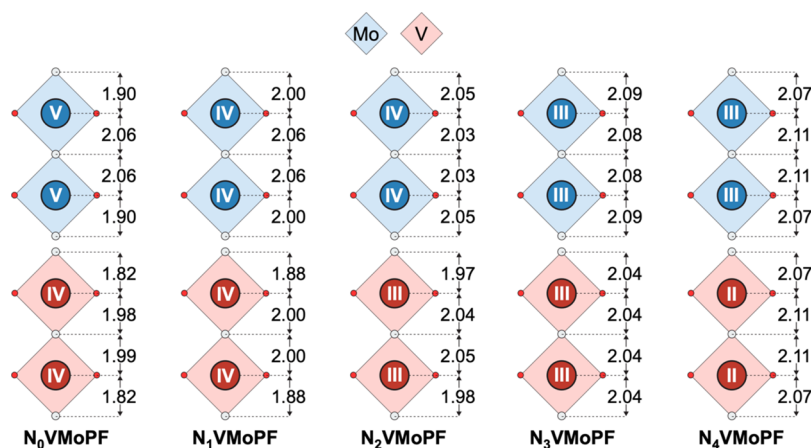


Figure 6. Biotahedral units for N_x VMoPF. The oxidation states of V (white text in red circles) and Mo (white text in blue circles) are obtained from DFT + U calculations. Bond lengths between the fluorine atoms and the transition metal atoms either V (F–V) or Mo (F–Mo) are shown in Å. The on-site magnetic moments used to derive the respective oxidation states are $\sim 1.0 \mu_B$ for V^{4+} and Mo^{5+} , $\sim 1.9 \mu_B$ for V^{3+} and Mo^{4+} , and $\sim 2.7 \mu_B$ for V^{2+} and Mo^{3+} .

for NVMoPF and NMoPF, the relative volume change at the same Na composition region is less than 1.5% (Figure 4b), indicating good structural stability of these Mo-substituted materials.

Changes of lattice constants and volumes upon (dis)charge of NVPF, NVMoPF, and NMoPF are the manifestation of specific spatial Na-vacancy orderings and transition metals (TMs) arrangements. The Na-vacancy orderings for the ground-state structures of NVPF and NVMoPF identified with DFT are displayed in Figure 5.

To develop structure–property relationships in the Mo-containing fluorophosphate, it is important to benchmark our predictions to existing structural studies on the NVPF analog. For the empty vanadium fluorophosphate, Tarascon and co-workers¹⁰ determined the fully desodiated (N_0 VPF) structure via ex situ synchrotron powder X-ray (PXRD) measurements and found a tetragonal $I4/mmm$ space group. Our GGA + U calculations revealed the same tetragonal $I4/mmm$ spatial arrangement of atoms for N_0 VPF. Bianchini et al.¹⁵ described the N_1 VPF structure in the orthorhombic $Cmc2_1$ space group, where all Na-ions occupy the Na(1) positions. We predict a ground-state N_1 VPF structure with the same orthorhombic symmetry (in the $Imm2$ space group) with Na^+ occupying the

Na(3) position. However, we also identified a nearly degenerate structure at N_1 VPF with $Cmc2_1$ symmetry, where Na-ions occupy the Na(1) position (see Supporting Figure S4) which is only 2.12 meV/atom higher in energy than the ground-state structure. The fact that these two Na-vacancy orderings ($Imm2$ and $Cmc2_1$) show similar energies may indicate Na exchange between the Na(3) and Na(1) sites as also observed by previous first-principles calculations.²¹

For N_2 VPF, Bianchini et al.¹⁵ found a tetragonal structure ($I4/mmm$), which assumes an average distribution of four half-occupied Na positions on the [100] and [010] positions. We found instead an ordered Na-vacancy arrangement, resulting in the orthorhombic symmetry ($Cmmm$). In agreement with Bianchini et al.,¹⁵ our ground state at N_2 VPF shows that Na-ions occupy either the [100] or the [010] positions. Averaging out the different sodium arrangements of the [100] and the [010] positions from our DFT results can reproduce the same sodium orderings of Bianchini et al.

For N_3 VPF, Bianchini et al.¹⁵ found the orthorhombic $Amam$ space group. Our calculated ground-state structure exhibits the orthorhombic $Cmc2_1$ space group. The orthorhombic distortion calculated by our method ($b/a = 1.003$) is in close agreement with the experimental value of 1.002.²⁴ The

remaining discrepancy between the experimental (*Amam*) and calculated (*Cmc2₁*) space groups can be explained by considering that the experimental structure incorporates several different Na⁺ orderings at room temperature, resulting in partial occupancies of the Na-ions among available positions, whereas our 0 K computational models consider fully ordered structures. Furthermore, we identified five additional structures that are only 4 meV/f.u. or less above the ground-state energy (see Supporting Figure S5). The experimental structure that can be assumed as an average of these calculated structures coexisting at room temperature is accurately reproduced by our calculations if one considers the entropy scale of ~25 meV/atom at room temperature.

Finally, using the PXR measurements, Zhang et al. identified the *Amam* space group for the fully discharged compound N₄VPF with all Na(1) and Na(2) positions being fully occupied. Our calculations predict the same orthorhombic symmetry (*Amam*) with the same sodium occupancies of Na(1) and Na(2) as observed in the experiment.

In NVMoPF, we found identical Na-vacancy orderings as in the NVPF framework for all sodium compositions (i.e., $x = 0, 1, 2, 3,$ and 4). N₂VMoPF arranges in the same orthorhombic symmetry structure as the DFT-predicted ground state of N₂VPF, whereas the ground-state compositions of NVMoPF at $x = 0, 1, 3,$ and 4 are crystallized in different structures compared to NVPF (Figure 5). Specifically, the VMoPF, N₁VMoPF, N₃VMoPF, and N₄VMoPF ground-state structures have a lower symmetry than their NVPF analogs mainly due to the V-Mo arrangements with specific charges.

The different ionic radii of Mo and V and the additional valence electron in Mo will influence the polyanionic framework and the distributions of Na-ions. Hence, we gain more insights into the structural evolution of NVMoPF by analyzing the oxidation states of V and Mo, and the topologies of the bioctahedral units within NVMoPF, as shown in Figure 6.

As it is evident from Figure 6, the introduction of Mo into NVPF leads to ordered V–Mo arrangements in NVMoPF, where each bioctahedral unit is composed of either only V (V₂O₈F₃) or only Mo (V₂Mo₈F₃). Furthermore, within a single bioctahedral unit, both TMs (i.e., V or Mo) consistently exhibit the same oxidation state, suggesting ordered charges on V/Mo sites. When V and Mo do not exhibit the same oxidation state, i.e., at VMoPF, N₂VMoPF, and N₄VMoPF, the V ions always show a lower oxidation state than Mo. Specifically, for VMoPF, N₂VMoPF, and N₄VMoPF, the Mo bioctahedra are in V, IV, and III oxidation states, respectively, whereas the vanadium bioctahedra are in IV, III, and II oxidation states, respectively.

For NVPF, in contrast, our calculations reveal that the two vanadium ions within the same bioctahedral units exhibit two different oxidation states for VPF (V^{IV} and V^V) and N₄VPF (V^{II} and V^{III}, see Supporting Figure S6), suggesting that NVPF is more prone to charge disordering than NVMoPF. At specific Na compositions, experimental studies have revealed that vanadium may be further disproportionate in N₁VPF (via $2V^{4+} \rightarrow V^{3+} + V^{5+}$).^{9,30} Our calculations could not predict this disproportionation reaction in NVPF (see Supporting Figure S6) and by extension in NVMoPF.

Clearly, the occurrence of specific V and Mo oxidation states directly influences the structural features of the composition of the electrode materials at different state of (dis)charge. As can be seen in Figure 6, the F–V bond lengths are shorter than

their corresponding F–Mo bond lengths when the TMs share the same oxidation state, which is consistent with the larger ionic radius of Mo compared to V. We observed a general tendency for the F–TM bonds to elongate with lower oxidation states of the TM, which is evident from an increase in bond length during Na intercalation from VMoPF to N₄VMoPF. This bond elongation can be understood from the increase in ionic radius with lower TM oxidation states which leads to longer F–TM bond lengths,³¹ and is in line with experimental findings for parent NVPF (see Supporting Figure S7).^{10,15,24,26} The bond length increase with lower oxidation states is very similar for NVPF and NVMoPF (see Supporting Figure S7).

Sodium-Ion Mobility in Na_xV₂(PO₄)₂F₃ Derivatives. To understand the extent of the Na-ion mobility in Mo-substituted NVPF derivatives, we performed nudged elastic band (NEB) simulations coupled with GGA + *U* calculations. In these NEBs for NVMoPF, we assumed the V–Mo charge ordering provided by the ground-state N₂VMoPF. For parent NVPF, we used the host skeleton of the ground-state N₃VPF to evaluate Na⁺ mobility. Using these model structures, we studied the effect of Na content on the migration barriers by invoking the high-vacancy limit or charged state (one Na per f.u. of NVMoPF/NVPF) and the low-vacancy limit or discharged state (one vacancy per f.u. of NVMoPF/NVPF). The *ab*-plane view of Na₂VMo(PO₄)₂F₃ is shown in Figure 7a, with the three crystallographic distinct Na sites (i.e., Na(1), Na(2), and Na(3) as denoted in Figure 1) superimposed on the host skeleton.

Two typical Na⁺ migration pathways with two-dimensional character (i.e., within the *ab*-plane) can be defined in the structure of the NVPF derivatives, namely the intra-unit and inter-unit pathways. The intra-unit pathway adopts a ring-like shape surrounding four nearest-neighbor (NN) Na(1)/Na(2) sites and is indicated by the blue rings in Figure 7a. The inter-unit pathway is indicated by the green arrow in Figure 7a and accounts for the Na-ion migration across the intra-unit rings. These two migration pathways can be decoupled into three different Na⁺ migration paths, denoted as p1, p2, and p3 in Figure 7a.¹⁷ Path1 (p1) corresponds to the intra-unit migration which occurs between 2 NN Na(1) and Na(2) sites via an interstitial Na(3) site. Both path2 (p2) and path3 (p3) describe the hops that contribute to the macroscopic inter-unit pathway, where p2 occurs between one Na(1) site and one Na(2) site through two interstitial Na(3) sites, and p3 captures the migration mechanism between two Na(2) sites via the two interstitial Na(3) sites.

In the computed migration energies of Figure 7b, both NVMoPF and NVPF show significantly lower migration barriers for the intra-unit pathway p1 than for the inter-unit pathways p2 and p3 at both the discharged and charged limits. Therefore, the inter-unit p2 and p3 pathways appear as the rate-limiting steps for Na⁺ diffusion in NVMoPF and NVPF. The migration barriers of p2 and p3 increase with the intercalation of Na-ions for both NVPF and NVMoPF. For example, in the discharged limit, NVMoPF shows migration barriers of ~647 and ~779 meV for p2 and p3, respectively, whereas in the charged structure (i.e., high vacancy limit), the migration barriers are as low as ~270 and ~266 meV for p2 and p3, respectively. The higher migration barriers for the discharged limits are attributed to the stronger electrostatic repulsions of nearby Na-ions. Conversely, in the charged limit of NVMoPF, the migrating Na-ions benefit from a situation of

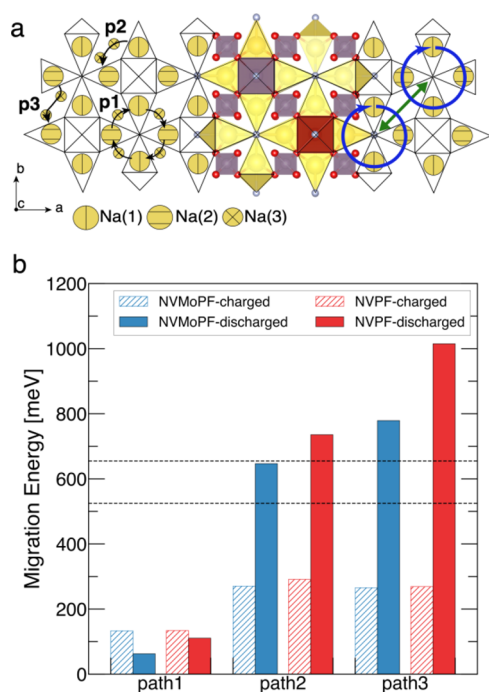


Figure 7. Computed Na^+ migration barriers in NVPF and NVMoPF. Panel (a) superimposes the three typical Na sites in the NVPF derivatives, i.e., Na(1), Na(2), and Na(3), and schematically represents the three symmetrically distinct Na^+ migration pathways, i.e., path1 (p1), path2 (p2), and path3 (p3). p1 corresponds to the intra-unit pathway (blue rings), whereas p2 and p3 contribute to the inter-unit pathway (green arrow). Panel (b) shows the Na-migration barrier energies as calculated by NEBs for the fully charged ($x = 0$) and fully discharged ($x = 4$) NVMoPF (blue) and NVPF (red). The migration energy thresholds of 525 and 650 meV set adequate battery operation in micro-size and nano-size particles, respectively³² (reproduced and adapted with permission from ref 32. Copyright 2015 American Chemical Society), are set by the horizontal lines.

reduced electrostatic repulsions. Note that the hopping mechanism between two Na(1) sites through two interstitial Na(3) sites can also be approximated by p3 with comparable barrier energies through the same divacancy mechanism (see Supporting Figure S8).

The migration barriers for p1 are comparable for NVMoPF and NVPF at both the discharged and charged limits. That is, 63–133 meV for NVMoPF, and 110–134 meV for NVPF. However, the migration barriers p2 and p3 were subjected to a further reduction when going from NVPF to NVMoPF. For example, the migration barrier of p3 at the discharged limit is ~1015 meV for NVPF, but only ~779 meV for NVMoPF, corresponding to a ~23% decrease. The Na migration barrier of p2 at the fully discharged limit also decreases by ~12% from 736 meV for NVPF to ~647 meV for NVMoPF. Note that the migration barriers of p2 for NVMoPF in the discharged limit are in the tolerable window of ~525 and ~650 meV for particle sizes of the active material ranging from micrometer to nanometer scales, respectively.³² These results suggest optimized kinetic properties and superior Na^+ diffusion with sustainable (dis)charge rate³² of NVMoPF compared to NVPF.

DISCUSSION

The energy density of the $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) electrode may be increased by ~50% by enabling the extraction of the

third Na-ion from N_1VPF . Here, we set the goal to identify substitution strategies of TMs on the vanadium centers in NVPF that may release the third Na^+ in sodium fluorophosphate-like electrode materials. Using DFT, we inspected the viability of replacing partially or entirely vanadium in NVPF with Mo, Nb, and W.

Relying on our computed voltages (Figure 2) at the GGA + U level of theory, we have inspected the characteristics of Na intercalation into NVPF substituted compounds. For example, we have investigated the partial (1:1 ratio) or complete substitution of Mo into NVPF. We found that the average voltage from Na_1 to Na_3 for NVMoPF is ~0.15 V higher than for the theoretically predicted NMoPF. This is mainly attributed to the voltage of the redox couple $\text{V}^{\text{III}}/\text{V}^{\text{IV}}$ at Na_1 – Na_2 in NVMoPF, which is ~0.27 V higher than the activated $\text{Mo}^{\text{III}}/\text{Mo}^{\text{IV}}$ at Na_1 – Na_2 in NMoPF.

When replacing 50% of V with Mo, the voltage plateau associated with the Na^+ extraction from $x = 1$ to $x = 0$ is lowered from 4.53 V vs Na/Na^+ in NVPF to 3.93 V vs Na/Na^+ in NVMoPF by activating the $\text{Mo}^{\text{IV}}/\text{Mo}^{\text{V}}$ (instead of the $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$) redox couple. Therefore, we speculate that the extraction of the third Na^+ is thermodynamically possible for the NVMoPF positive electrode using the most common electrolytes for Na-ion batteries.¹⁹ The extraction of the third Na^+ in NVMoPF results in an improved gravimetric capacity of 173.4 mAh/g and a predicted energy density of 577.3 Wh/kg for NVMoPF (see Supporting Table S1). This energy density represents a substantial increase (~13.9%) in comparison to NVPF (i.e., 507 Wh/kg as observed in experiments).¹⁵ Since GGA + U underestimates the voltage of NVPF (vide supra) at each step, the actual increase in energy density for NVMoPF is expected to be more substantial. Specifically, using the theoretically computed (rather than the experimentally reported) energy density of 439 Wh/kg for NVPF as the reference, we predict an increase in energy density of ~31.5% for NVMoPF. An in-depth analysis of the Mo–V spatial arrangements and oxidation states in NVMoPF suggests that Mo and V centers in the mixed fluorophosphate electrodes act entirely independently. Indeed, a closer look at the Mo–V arrangement in the stable ground-state ordering (Figure 6) may suggest a tendency for charge ordering of Mo and V bioctahedral units.

We contemplated the possibility of replacing all the V content in NVPF with Mo. Notably, the voltage associated with the full desodiation from N_1MoPF at 3.94 V vs Na/Na^+ is similar to N_1VMoPF (~3.93 V vs Na/Na^+). An increased capacity resulting from extracting the third Na^+ from N_1MoPF gives an energy density of ~511.1 Wh/kg for NMoPF (see Supporting Table S1)—accounting for an increase of ~0.8% for the experimental energy density of NVPF (~16.4% relative to the computed energy density of NVPF). Our results suggest that this electrochemical process ($\text{N}_1\text{MoPF} \sim \text{N}_0\text{MoPF}$) may be accessible in NMoPF electrode material.

Furthermore, we investigated the addition of Nb in NVPF (in a 1:1 ratio), as well as the full replacement of V with Nb. Unexpectedly, in NVNbPF, the extraction of the third Na-ion from N_1VNBPF to the empty VNBPF activates the $\text{V}^{\text{III}}/\text{V}^{\text{IV}}$ redox couple at ~3.29 V vs Na/Na^+ , which is more than 1 V lower than in the parent NVPF at $x = 0 \sim 1$ via $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ (~4.53 V vs Na/Na^+). Considering the reversible extraction of three Na-ions, we estimated that NVNbPF has a theoretical gravimetric energy density of ~428.5 Wh/kg, and 15.5% lower than NVPF. Furthermore, the estimated theoretical

energy density of NNbPF ($x = 0\sim 3$) is ~ 301.2 Wh/kg, resulting in a decrease of 40.6% compared with NVPF. Therefore, both NVNbPF and NNbPF do not chart as promising candidates for Na-ion battery positive electrodes.

We also investigated the effect of adding W into NVPF. Since W is a much heavier element (183.8 g/mol) than V, Nb, and Mo (50.9, 92.9, and 96.0 g/mol, respectively), the computed theoretical capacity of NWPF is only ~ 39.2 mAh/g per Na, which is substantially lower than the ~ 64.2 , ~ 52.8 , and ~ 53.4 mAh/g per Na for NVPF, NMoPF, and NNbPF electrode materials, respectively. Therefore, the predicted energy density using our voltages (Figure 3) for NWPF is only 265.9 Wh/kg, corresponding to a 47.6% decrease in comparison with NVPF (Table S1 of SI). Figure 8 summarizes the predicted voltages and energy densities for each intercalation step in $\text{Na}_x\text{V}_{2-y}\text{M}_y(\text{PO}_4)_2\text{F}_3$ at various substitution levels of Mo, Nb, and W.

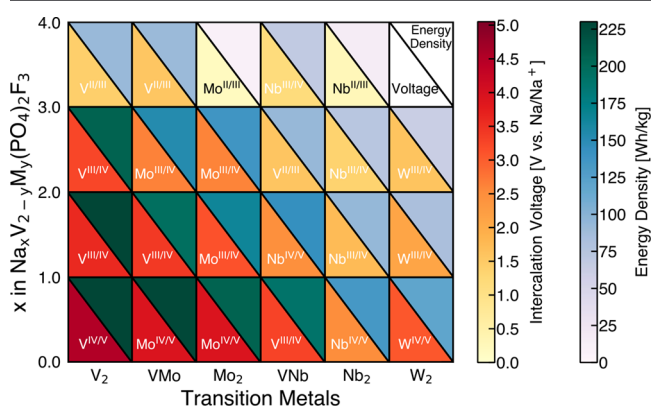


Figure 8. Map of computed intercalation voltages and energy densities for $\text{Na}_x\text{V}_{2-y}\text{M}_y(\text{PO}_4)_2\text{F}_3$ systems. The x -axis represents the different transition metal combinations of V and M, where M = Mo, Nb, and W. The y -axis represents the Na concentration x from $x = 0$ to $x = 4$. Each square is divided into lower and higher triangles, which are mapped onto the specific values of intercalation voltage and energy density, respectively. The redox couple for each intercalation step is superimposed on the lower triangle of each square.

To evaluate the synthesizability of Mo-containing NVPF compounds (appearing as the most promising Mo-, Nb-, and W-substituted NVPF studied here), we derived their thermodynamic phase stabilities from an analysis of the Na–Mo–P–F–O quinary phase diagram. Our results confirm that the N_3MoPF structure—the ground-state structure in the pseudo-binary N_0MoPF – N_4MoPF space (see Figure 2c)—appears as a stable phase. This stability is imparted by the highly stable high-spin t_{2g}^3 electronic configuration of the Mo^{III} species in N_3MoPF .^{33–37} Although the N_1MoPF structure containing Mo^{IV} appears slightly above the stability line (~ 8 meV/atom above the convex hull) in the quinary phase diagram, previous reports suggested that Mo^{IV} is accessible by reduction of Mo^{VI} precursors to obtain phosphate-like materials, e.g., $\text{NaMo}_2(\text{PO}_4)$. As N_3VPF and $\text{N}_3\text{V}_2(\text{PO}_4)_3$ are typically synthesized using VIII precursors,^{15,24,44–46} the synthesis of a mixed V/Mo $\text{N}_2\text{V}^{\text{III}}\text{Mo}^{\text{IV}}\text{PF}$ may require particular care in preserving Mo as Mo^{IV} (and V as V^{III}). These findings suggest that the predicted ground-state composition in the pseudo-binary N_0VMoPF – N_4VMoPF tie line (see Figures 2b and 6) may be accessible experimentally.

To elucidate the feasibility of extracting the third Na-ion from N_1VMoPF , we have studied the kinetic properties of NVMoPF . We established that the rate-determining steps are the inter-unit pathways, i.e., the p2 and p3 pathways (Figure 7) that contribute to the macroscopic diffusion of Na ions in fluorophosphate-like electrode materials. We found that the Na^+ migration energy barriers at the charged limit are ~ 270 meV (p2) and ~ 266 (p3) meV for NVMoPF , and ~ 291 meV (p2) and ~ 269 meV (p3) for NVPF , which are all below the tolerance limits of 525 and 650 meV (see Figure 7). These low values of migration barriers at low Na composition regions suggest no obvious kinetic limitations imposed on the migrating Na-ion in NVPF and NVMoPF .

Nevertheless, it has been shown experimentally that NVPF exhibits a rapid decline in Na^+ diffusivity as x approaches 1.²⁰ Therefore, we attribute the difficulty in extracting the third Na-ion (i.e., from $x = 1$ to $x = 0$) to the strong Na-vacancy orderings at $x = 1$. Such a strong interplay of Na-vacancy at low Na concentration hinders the creation of vacancies that are needed for Na-ion mobility, resulting in a higher migration energy penalty to promote Na^+ diffusion. Consequently, the Na^+ migration is impractical to occur at $x = 1$. As a measure for the Na-vacancy ordering at low Na content (charged state), one may examine the voltage step between $x = 0\sim 1$ and $x = 1\sim 2$. For NVPF (Figure 2d), we observe a steep decrease of ~ 0.93 V in the intercalation voltage (i.e., from 4.53 to 3.60 V vs Na/Na^+), suggesting a rather strong gain in stabilization induced by the effect of Na-vacancy ordering at N_1VPF .

Interestingly, the same voltage step in N_1VMoPF is only 0.53 V (Figure 2e), corresponding to a decrease of 43% compared to N_1VPF . A milder decrease in intercalation voltage is driven by mixing V with Mo, which weakens the strong tendency of Na-vacancy ordering, thereby facilitating Na-ion migration.^{21,38}

Importantly, Dacek et al. showed that vacancy formation energy in N_1VPF ²¹ is only favorable if sodium extraction occurs at the same voltage as the equilibrium oxidation potential. In practice, the high intercalation voltage of N_0VPF – N_1VPF , well above the electrolyte stability window (~ 4.5 V vs Na/Na^+), leads to a practical extraction potential that is lower than the equilibrium potential,¹⁹ resulting in poor kinetics for the NVPF system with high defect formation energies. According to our predictions, the extraction of the third Na-ion in NVMoPF occurs at a voltage that is below the stability window of most electrolytes for Na-ion batteries. This lower voltage may allow the third Na-ion to be extracted at the equilibrium oxidation voltage, and therefore, favorable kinetics are expected for the NVMoPF electrode.

Overall, both the lower migration barrier and weaker Na-vacancy orderings in NVMoPF as compared to NVPF indicate an improvement of the accessible capacity in the charged states. Specifically, the theoretical capacity of NVMoPF is evaluated to be ~ 174 mAh/g, corresponding to insertion/extraction between N_0VMoPF and N_3VMoPF , which is 35% higher than 128 mAh/g of NVPF (at $x = 1\sim 3$, see Supporting Table S1).

CONCLUSIONS

We investigated the substitution of vanadium (V) by molybdenum (Mo), niobium (Nb), and tungsten (W) in $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) to improve the gravimetric energy density of this promising electrode material for Na-ion batteries. Using first-principles calculations based on DFT,

we elucidated the electrochemical and structural properties of NVPF derivatives at different substitution levels.

The partial substitution of 50% V with Mo reduces the voltage plateau for extracting the third Na⁺ from ~4.5 to ~3.9 V vs Na/Na⁺, thus enabling the practical Na extraction from Na_xVMo(PO₄)₂F₃ and increasing the capacity from ~128 to ~174 mAh/g. Structural analysis revealed that Na_xVMo(PO₄)₂F₃ (NVMoPF) undergoes a minimal volume change of only 1.3% upon reversible Na extraction, suggesting good structural stability during cycling. An in-depth analysis of the Na-ion migration barriers showed that NVMoPF may have superior kinetic properties over NVPF, which was attributed to the disrupted Na⁺ orderings enabled by the extra entropy of mixing Mo with V in the fluorophosphate material. The mixing of Mo with V may deliver a gravimetric energy density of ~577.3 Wh/kg for Na_xVMo(PO₄)₂F₃ versus 507 Wh/kg for Na_xV₂(PO₄)₂F₃, corresponding to an increase of 13.9%. The high practical energy density combined with superior Na-ion kinetics of intercalation make NVMoPF a promising positive electrode material for Na-ion batteries.

METHODS

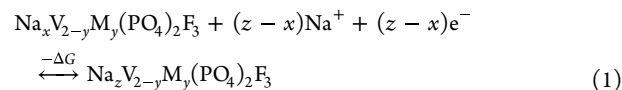
We used the DFT-based Vienna Ab initio Simulation Package (VASP)^{39,40} to evaluate the structural stability, total energy, and thermodynamic and electronic properties of Na_xV_{2-y}M_y(PO₄)₂F₃ positive electrode materials (0 ≤ x ≤ 4, y = 2, 1.5, 1, 0.5, and 0, and M = V, Mo, Nb, and W). The spin-polarized generalized gradient approximation (GGA)-type Perdew–Burke–Ernzerhof (PBE) functional was used to approximate the unknown exchange-correlation contribution in DFT.⁴¹ We also added a Hubbard *U* correction to address the strong on-site Coulomb correlation effects of the 3*d* electrons of V, the 4*d* electrons of Nb and Mo, and the 5*d* electrons of W.^{42,43} The effective *U* parameters applied in this study are 3.1 eV for V, 2.0 eV for Nb, 3.5 eV for Mo, and 4.0 eV for W.⁴⁴ A value of *U* of 3.1 eV for V was chosen because it gives reliable formation energies and redox reactions for V-based compounds.^{17,21,45,46}

The projected augmented wave (PAW) potentials were used for the description of core electrons,⁴⁷ namely, Na 08Apr2002 3s¹3p⁰, P 17Jan2003 3s²3p³, O 08Apr2002 2s²2p⁴, F 08Apr2002 2s²2p⁵, V_pv 07Sep2000 3p⁶3d⁴4s¹, Mo_pv 08Apr2002 4p5s4d, Nb_pv 08Apr2002 4p5s4d, and W_pv 06Sep2000 5p6s5d. Valence electrons were represented using plane waves up to an energy cutoff of 520 eV. In addition, a Γ -centered Monkhorst-Pack⁴⁸ *k*-point mesh with 25 subdivisions along each reciprocal lattice vector was applied to all structures. The total energy of each structure was converged to within 10⁻⁵ eV/cell and atomic forces within 10⁻² eV/Å.

To explore the Na (de)intercalation behaviors for all the selected Na_xV_{2-y}M_y(PO₄)₂F₃ systems, we used the experimentally observed Na₃V₂(PO₄)₂F₃/Na₄V₂(PO₄)₂F₃ phases²⁶ as the starting structures to study Na removal with different degrees of substitution of TMs (i.e., M = Mo, Nb, and W in Na_xV_{2-y}M_y(PO₄)₂F₃). Specifically, in NVPF, we substituted 25, 50, 75, and 100% of V by Mo, or 50 and 100% of V by Nb, or 100% of V by W, resulting in the chemical formulas Na_xV_{2-y}Mo_y(PO₄)₂F₃, Na_xV_{2-y}Nb_y(PO₄)₂F₃, and Na_xW₂(PO₄)₂F₃ with y = 0, 0.5, 1.0, 1.5, and 2.0 for Mo, and y = 1.0 and 2.0 for Nb, respectively. For each of the selected systems, we varied the Na content *x* in the range of 0 ≤ *x* ≤ 4 and with a step Δ*x* = 0.5 or 1.0. The possible Na-vacancies and TM configurations were enumerated using the pymatgen package.⁴⁹ At each Na content *x* of the specific Na_xV_{2-y}M₂(PO₄)₂F₃ system, we chose a maximum of 100 candidate structures with the lowest Ewald energy⁵⁰ based on integer charges (i.e., Na = +1, P = +5, O = -2, F = -1) and variable charges on the TM (+2 ~ +5) to limit the number of possible candidate structures and keep our calculations computationally tractable. DFT calculations were performed on the primitive cell (2 formula units of Na_xV_{2-y}M_y(PO₄)₂F₃ with 30 + 2*x* atoms) and supercells (2 × 1 × 1) of these enumerated configurations. The oxidation states of the TM-

ions were derived by tracking the magnetic moments on the TMs upon structural and electronic relaxation.

The (de)intercalation process for the Na_xV_{2-y}M_y(PO₄)₂F₃ positive electrode material can occur through the reversible Na⁺ insertion/extraction according to the redox eq 1.



where *x* and *z* represent the initial and final Na content, and Δ*G* is the change of Gibbs free energy at 0 K, which can be approximated by the DFT energy. The formation energies (*E_f*(*x*)), which are corresponding to the phase stability of Na_xV_{2-y}M_y(PO₄)₂F₃ with respect to the DFT-energies of fully charged (Na₀V_{2-y}M_y(PO₄)₂F₃) and discharged phase (Na₄V_{2-y}M_y(PO₄)₂F₃), can be computed using eq 2.

$$E_f(x) = E[\text{Na}_x\text{V}_{2-y}\text{M}_y(\text{PO}_4)_2\text{F}_3] - \left(\frac{4-x}{4}\right)E[\text{Na}_0\text{V}_{2-y}\text{M}_y(\text{PO}_4)_2\text{F}_3] - \left(\frac{x}{4}\right)E[\text{Na}_4\text{V}_{2-y}\text{M}_y(\text{PO}_4)_2\text{F}_3] \quad (2)$$

Note that we approximate the 0 K mixing energies using formation energies, neglecting the *pV* and entropic contributions. The intercalation voltage for the redox reaction of eq 1 can be approximated using eq 3.

$$V = -\frac{\Delta G}{(z-x)F} = -\{E[\text{Na}_z\text{V}_{2-y}\text{M}_y(\text{PO}_4)_2\text{F}_3] - (E[\text{Na}_x\text{V}_{2-y}\text{M}_y(\text{PO}_4)_2\text{F}_3] + (z-x)\mu_{\text{Na}})\}/\{(z-x)F\} \quad (3)$$

where μ_{Na} is the chemical potential of bulk Na metal and *F* is the Faraday constant. The corresponding theoretical capacity (*C*) for this intercalation step can be evaluated using eq 4.

$$C = \frac{(z-x)F}{m} \quad (4)$$

where *m* is set as the mass of the “pristine” Na₃V_{2-y}M_y(PO₄)₂F₃ composition to normalize the gravimetric specific capacity (mAh/g).

To investigate the Na ion migration in Na_xVMo(PO₄)₂F₃ (NVMoPF) and Na_xV₂(PO₄)₂F₃ (NVPF) systems, we employed the NEB method,^{51–53} with the same DFT settings discussed above. We reduced the *k*-point sampling to the Γ -point. For both NVMoPF and NVPF, we did NEB at the fully charged/desodiated (*x* = 0) and fully discharged/sodiated (*x* = 4) limits with the fixed TM (i.e., V, Mo) skeleton at these two limits, which are corresponding to the host skeleton of the V–Mo and V–V arrangements at the ground state of Na₂VMo(PO₄)₂F₃ and Na₃V₂(PO₄)₂F₃, respectively. In this way, we could approximate the topotactic Na⁺ migration during Na (de)-intercalation from/into the ground-state structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c00745>.

Formation energies and intercalation voltages for NV_{2-y}Mo_yPF with y = 0.5 and 1.5; formation energies for NVNbPF, NNbPF, and NWPF; biotetrahedral units with angular data for N₄VPF, N₄VMoPF, and N₄MoPF; Na-vacancy orderings for near-degenerate structures of N₁VPF and N₃VPF; biotetrahedral units with oxidation states and bond lengths for NVPF and NMoPF; TM–F bond length changes for NVPF, NVMoPF, and NMoPF; NEB energy paths for NVPF and NVMoPF; summary of

all intercalation properties in terms of voltages, capacities, and energy densities for NVPF, NVMoPF, NMoPF, NVNbPF, NNbPF, $NV_{1.5}Mo_{0.5}PF$, and $NV_{0.5}Mo_{1.5}PF$; and tabulated space group and lattice parameters for $NV_{2-y}Mo_yPF$ with $y = 0, 0.5, 1.0, 1.5,$ and 2.0 (PDF)

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Notes

The authors declare no competing financial interest.

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