

Rational Design of Mixed Polyanion Electrodes $Na_xV_2P_{3-i}(Si/S)_iO_{12}$ for Sodium Batteries

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we explore the effect of changing polyanion groups on the redox voltages and the gravimetric capacities of polyanion electrodes. Using first-principles calculations, we examine the influence of polyanionic substitutions on the stability and electrochemical behavior of the $Na_3V_2(PO_4)_3$ electrode material, which adopts the prototype structure of the natrium superionic conductor (NaSICON). Starting from the $Na_3V_2(PO_4)_3$ structure, we explore



the partial or total substitution of PO_4^{3-} groups by SiO_4^{4-} or SO_4^{2-} moieties, unveiling the uncharted multicomponent Na-V-P-(Si/S)-O phase diagram. We show that small amounts of SiO_4^{4-} can activate the V^{V/IV} redox couple, which is not experimentally accessible in the PO_4^{3-} NaSICON analogue, thereby increasing the average Na intercalation voltage. In the case of SO_4^{2-} substitution, we observe an increase in voltage of each V redox couple (i.e., $V^{III/II}$, $V^{IV/III}$, and $V^{V/IV}$) but at the expense of the maximum amount of Na⁺ intercalated. We show that exploiting the varying inductive effects of different polyanion groups can be effective for tuning the energy density of NaSICON electrode materials.

1. INTRODUCTION

With their exceptional energy densities, lithium (Li)-ion batteries dominate the growing market of portable energy storage devices and electric vehicles. Yet, due to the geopolitically constrained supply chains of Li and crucial transition metals (e.g., cobalt and nickel), further expansion in the use of Li-ion cells is at risk.¹⁻³ To accommodate the ever increasing global energy consumption and a transition to clean energy, large-scale and cost-effective energy storage technologies that provide an alternative to Li-ion are needed.

With a "rocking chair" architecture analogous to that of Liion cells, the sodium (Na)-ion battery is a promising, beyond-Li-ion storage technology, with several advantages. The ubiquity of Na makes it approximately 50 times cheaper than Li.^{1,4} Also, Na-ion batteries utilize inexpensive aluminum current collectors. Na-ion cells can be fabricated using processes similar to those of Li-ion batteries, which may ease the transition toward the use of sodium.^{4,5} Thus, the development of Na-ion batteries has grown rapidly,^{4,6} accompanied by a surge of interest in safer solid-state batteries relying on Na ions.⁷⁻¹⁰ Nevertheless, Na has a lower (in magnitude) electrochemical potential of -2.71 V vs the standard hydrogen electrode (SHE) and a higher atomic mass of 22.99 a.m.u. compared to that of Li (-3.04 V vs SHE and 6.94 a.m.u., respectively), typically resulting in lower energy densities in Na-ion vs Li-ion cells.¹¹

To improve the electrochemical performance of Na-ion batteries, it is necessary to develop electrode materials with enhanced operating voltages and capacities and minimal structural changes during electrochemical cycling.¹¹ Due to a higher proportion of Na per formula unit, layered transition metal oxides may show the largest gravimetric capacities, but their practical use as an electrode is limited by irreversible structural phase transitions during electrochemical cycling.¹² In contrast, polyanionic frameworks incorporating SO_4^{2-} , PO_4^{3-} , and SiO_4^{4-} groups¹³⁻¹⁶ can reversibly intercalate Na ions at relatively high operating voltages (which is attributed to the

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inductive effect of the polyanionic moieties, see below)^{14,17,18} but yield lower capacities due to the additional mass of the polyanionic groups. Therefore, polyanion electrodes result in energy densities that are similar to or lower than those of layered oxide materials.^{13,14,19,20} However, polyanion compounds also display robust 3D frameworks, limiting their expansion/contraction during Na intercalation, thus increasing the safety and reversibility of the electrochemical setup^{21,22} and making them an important family of Na cathodes.

The natrium superionic conductor (NaSICON) is a class of polyanion materials of general formula $Na_xM_2(ZO_4)_3^{23,8,14,24-29}$ where M is a single (or multiple) redox-active transition metal(s) and ZO_4 is a polyanionic group (Z is usually Si⁴⁺, P^{S+}, and/or S⁶⁺, but other cations, such as Mo⁶⁺ and W⁶⁺, are possible).^{18,17,14,22,30,28} In Na_xM₂(ZO₄)₃, the Na concentration, *x*, can vary from 1 to 4, depending on the oxidation states of the cations M and Z.

Here, we explore strategies for tuning the ZO₄ groups to obtain high-energy-density NaSICON electrodes by enhancing the Na-intercalation voltage and/or the gravimetric capacity. We have considered the NaSICON framework of Na₃V₂(PO₄)₃ and explored the substitution of PO₄³⁻ groups with SiO₄⁴⁻ or SO₄²⁻. We chose Na₃V₂(PO₄)₃ due to the presence of multiple oxidation states of V (2+, 3+, 4+, and 5+), the highly reversible Na-ion (de)intercalation, namely, the reversible extraction of 2 Na⁺ at ~3.4 V (V^{IV/III}) to form Na₁V₂(PO₄)₃, and reversible insertion of 1 Na⁺ at ~1.6 V (V^{III/II}) forming Na₄V₂(PO₄)₃.^{31-33,26,34-36,29} We use the nomenclature Na_xVP₃ for Na_xV₂(PO₄)₃; for example, Na₃VP₃ indicates Na₃V₂(PO₄)₃ or Na₃V₂P₃O₁₂. Similarly, Na_xVP_{1.5}S_{1.5} indicates a composition of Na_xV₂P_{1.5}S_{1.5}O₁₂. We will refer to the Na_xVP₃ formula/structural unit as NaSICON.

The average voltages of NaSICON frameworks follow the standard reduction potentials of the transition metals present,^{14,24} with the intercalation voltage increasing as the higher (possible) oxidation states of the transition metals accessed (e.g., $V^{IV/III}$ exhibits a higher voltage than $V^{III/II}$). Alternatively, the voltage of an existing transition metal redox couple (e.g., V^{IV/III}) can be increased by reducing the degree of covalency of the V-O bond via modification of the polyanion units, i.e., by changing the Z–O bonding in ZO₄. This voltage increase is caused by the inductive effect exerted by the Z cation on the Z–O bond, as defined in the framework of molecular orbital theory. 18,37 Specifically, Z cations with higher oxidation states draw O electrons away from the M atom, thus lowering the covalency (or increasing the ionicity) of the M-O bonds and raising the redox voltages upon Na (de)intercalation. Therefore, one can modulate the intercalation voltage by changing the Z cation. Only a handful of studies have been performed on varying the Z species, for example, by substituting PO_4^{3-} groups by SiO_4^{4-} in $Na_x VP_3^{8,38-40,16,41}$ However, the effects of substitution of diverse polyanion units on the phase stability of Na₃VP₃, the electrochemical behavior, and the Na ion kinetics are far from being fully addressed.

Our study systematically explores the phase stability of Na_xVP_3 upon partial (or full) exchange of the P⁵⁺ sites with other cation species, specifically Si⁴⁺ or S⁶⁺. Our choice of replacing P with Si is largely motivated by the work of Hong and Goodenough, where the authors mixed Si and P to enhance the Na-ion conductivity in Zr-based NaSICON solid electrolytes.^{8,23} We consider S substitution since previous studies have shown that the SO₄²⁻ group enhances the redox voltage of the Fe^{III/II} redox couple from 2.8 V (for SiO₄⁴⁻) to

3.6 V vs Li/Li⁺ (for SO₄²⁻) in Li-based NaSICON cathodes. 17,37

We use density functional theory (DFT) calculations coupled with a robust thermodynamic framework to reveal the effects of Si or S substitutions on the Na_xVP₃ structure, namely, its thermodynamic stability and Na intercalation voltages.^{42,43} The computed multicomponent phase diagrams of Na–V–P–Si/S–O are used to examine the synthesizability of Si/S substituted Na_xVP₃ at varying Na contents. Before analyzing the effects of Si/S substitution, we provide an overview of the structure and Na intercalation properties in Na_xVP₃. Our analysis provides important guiding principles for future experimental synthesis of mixed polyanion NaSICON materials for high-energy-density Na-ion batteries.

STRUCTURE AND Na INTERCALATION IN Na_xV₂(PO₄)₃

To benchmark our methodology and provide context for the study of mixed polyanion vanadium NaSICONs, we briefly revisit the mechanism of Na intercalation in Na_xVP₃. The rhombohedral ($R\overline{3}c$) and monoclinic (C2/c) NaSICON phases of Na_xVP₃ can be understood as networks of "lantern" units stacked into columns perpendicular to the basal plane to form the NaSICON framework (Figure S2).^{23,31,44,45} Each lantern unit (see inset of Figure 1) consists of two VO₆ octahedra



Figure 1. Comparison of the experimental (Exp) and predicted voltage curves of Na_xVP_3 .^{24,31} Theoretical predictions with the PBE +*U* (blue lines and symbols) and the HSE06 hybrid (orange lines and symbols) functionals. The inset displays the lantern units of the NaSICON framework for Na_xVP_3 , which are made up of VO₆ octahedra (cyan) and PO₄ tetrahedra (gray).

corner-sharing with O atoms of three PO_4 tetrahedra. Each O atom in the structure is shared between VO_6 and PO_4 in this manner, forming a three-dimensional (3-D) framework with V–O–P bonding.

In the rhombohedral NaSICON, Na ions intercalate in two different sites: Na1 (6 coordinated) between the lantern units running along the *c*-axis and Na2 (8 coordinated) occupying interstitial spaces between parallel columns of lantern units. There are 1 Na1 and 3 Na2 sites per formula unit of Na_xVP_3 . At room temperature, the rhombohedral Na_3VP_3 phase distorts into the monoclinic structure, which gives rise to site splitting among the Na2 sites.^{25,46}

The average Na intercalation voltage curves, as calculated with the Hubbard U corrected Perdew–Burke–Ernzerhof

(PBE+U)^{47,48} functional and the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional⁴⁹ (see Theoretical Methods section), are compared in Figure 1 with experimental curves at room temperature across the composition range $1 \le x \le 4$ in $Na_x VP_3$.³¹ The predicted voltages underestimate the experimental voltages, with the degree of underestimation being lower for PBE+U in the $3 \le x \le 4$ range. In general, from Figure 1 the average voltage and voltage difference are better predicted by the HSE06 hybrid functional. However, both functionals do obtain the correct qualitative trends in voltages, namely, the voltage plateaus between x = 1 and x = 3and between x = 3 and x = 4, both of which are indicative of two-phase behavior.^{50,51} So, given the higher computational costs of the hybrid DFT HSE06, we have used the PBE+Ufunctional for the remaining DFT calculations presented in this work.

According to previous experimental and computational investigations in Na_xVP₃, the stable phases are at x = 1, 3, and 4, which are the ground state structures in the convex hull of Figure S1 in the Supporting Information (SI). The voltage plateau between x = 1 and x = 3 is associated with the V^{IV/III} redox couple, while the V^{III/II} redox is active between x = 3 and x = 4. Our PBE+U voltage plateaus, which are at ~2.9 V and ~1.5 V vs Na/Na⁺, verify the $V^{IV/III}$ and $V^{III/II}$ redox couples (while being lower than the experimental values of \sim 3.4 V and \sim 1.6 V).³¹ We use the computed magnetic moments to verify the existence of different oxidation states of V in our calculations. For example, at x = 1, we observe all V atoms in the Na₁VP₃ structure to exhibit a magnetic moment of 1.03 μ_B reflecting V^{IV}, while at x = 3, the uniform magnetic moment of 1.89 μ_B corresponds to V^{III}. At x = 4, Na₄VP₃ turns metallic and electronic delocalization occurs over all of the vanadium redox centers, preventing us from distinguishing V^{III} and V^{II.26}

Recent studies using SCAN+U functionals^{26,29} have isolated, both computationally and experimentally, an intermediate Na₂VP₃ phase, which challenges the notion of a two-phase reaction between Na_3VP_3 and Na_1VP_3 , as predicted by PBE+U. However, our DFT calculations are consistent with those of Wang et al.²⁶ in suggesting that the extraction of Na between x= 4 and 1 occurs exclusively from the Na2 sites, with the Na1 sites being electrochemically inactive. Further, the extraction of the last Na from Na₁VP₃ occurs through the V^{V/IV} redox pair and corresponds to the extraction of sodium from the Na1 site in the structure. The extraction of the final Na has been claimed experimentally by chemical oxidation, but the experiment has never been reproduced.52 The extraction of the last sodium (at the Na1 site) from Na₁VP₃ has never been observed electrochemically due to the unfeasibly high voltage of >4.7 V vs Na/Na $^{+53}$ (the computationally predicted voltage is \sim 4.3 V, Figure 1).

3. RATIONAL DESIGN OF HIGH-ENERGY DENSITY NaSICON ELECTRODES

Using Na₃VP₃ as a starting compound, we have explored the composition space with respect to partial and full aliovalent substitution of P⁵⁺ with Si⁴⁺ or S⁶⁺, respectively, as illustrated in Figure 2. When tetrahedrally coordinated by O, Si⁴⁺ and S⁶⁺ exhibit markedly different ionic radii ($r[Si^{4+}] \sim 26 \text{ pm}, r[S^{6+}] \sim 12 \text{ pm}$) compared to that of P ($r[P^{5+}] \sim 17 \text{ pm}$).⁵⁴ Previous studies suggest that Si or S can replace P partially without introducing a significant degree of structural distortion in the NaSICON framework.^{8,23} Nevertheless, the maximum amount



Figure 2. Physically accessible oxidation states and the electronic configurations of the t_{2g} orbitals of the vanadium centers as a function of Na concentration (*x*) in Na_xVP₃ with respect to the substitution of P with Si or S.

of Si or S that can be experimentally incorporated, specifically in $Na_x VP_3$, remains unclear.^{16,38-40}

The physically plausible oxidation states of vanadium in its binary oxides, e.g., VO, V₂O₃, VO₂, and V₂O₅, vary from V²⁺ to V^{5+, 55,56} Although the V⁵⁺ state is not observed electrochemically in Na_xVP₃,⁵⁷ it can be accessed in mixed transition metal NaSICON phosphates, such as Na_xVMn(PO₄)₃, Na_xVCr-(PO₄)₃, and Na_xNbTi(PO₄)₃,^{31,58-61} indicating the possibility of its accessibility in mixed polyanion NaSICONs as well. Figure 2 maps the physically accessible regions of Na concentrations and the corresponding V oxidation states at varying contents of PO₄³⁻, SiO₄⁴⁻, and SO₄²⁻ groups (*x*-axis) in the V-based NaSICON framework.

In Figure 2, an increase of SiO_4^{4-} concentration in the Na_xVP₃ scaffold unsurprisingly favors higher Na concentrations (to compensate for the higher negative charge of SiO_4^{4-} groups compared to PO_4^{3-}), whereas the opposite trend is observed with SO_4^{2-} substitution. Therefore, the accessible Na content, electrochemically, will decrease from a maximum of 3 in Na_rVP₃ (Na₁VP₃ \leftrightarrow Na₄VP₃) to 2 in Na_rVSi₃ (Na₂VSi₃ \leftrightarrow Na_4VSi_3) or Na_xVS_3 ($Na_0VS_3 \leftrightarrow Na_2VS_3$), resulting in a decrease in capacity as well. Thus, scenarios where PO_4^{3-} is moderately substituted by SiO_4^{4-} (or SO_4^{2-}) could provide the maximum possible extractable capacity for Na exchange in the V-based NaSICON system. If Si substitution in Na₃VP₃ can enable the extraction of the "last Na ion", high voltages are to be expected (Figure 1), which will require appropriate choices (and design) of electrolytes with high anodic stability.⁶ Furthermore, for similar substitution levels, the lower weight (Figure 2) of SiO_4^{4-} can slightly increase the gravimetric capacities as compared to PO_4^{3-} and SO_4^{2-} .

With these hypotheses in mind, we performed DFT calculations to demonstrate the Na (de)intercalation characteristics in Na_xV₂P_i(Si/S)_{3-i}O₁₂, where the extent of polyanion mixing varies in the range $0.0 \le i \le 3.0$ in steps of 0.5. For each



Figure 3. a. Map of computed voltage curves (using PBE+*U*) in mixed $Na_xV_2P_i(Si/S)_{3-i}O_{12}$ compounds. The *x*-axis represents the polyanion compositions with the degree of mixing given indicated by $P_i(Si/S)_{3-i}$ in the $Na_xV_2P_i(Si/S)_{3-i}O_{12}$ formula unit, with *i* varying in steps of 0.5. The *y*-axis represents the Na content per formula unit from x = 0 to x = 4, also in steps of 0.5. The gray regions correspond to inaccessible vanadium oxidation states, i.e., below V²⁺ or above V⁵⁺. The voltage at each stage of (de)intercalation is indicated by the color bar. b. Calculated voltage curve of selected mixed polyanion compositions of P_2S_1 . Each voltage step in panel b is labeled and mapped to areas in panel a (via labels a–h).

polyanion composition, we also calculated the Na deintercalation voltages from the change in Na chemical potential as its content is varied within the corresponding NaSICON (see Theoretical Methods section for additional details).

Figure 3a shows the predicted voltages (using PBE+U) as a function of Na (de)intercalation at various substitution levels of PO_4^{3-} by SiO_4^{4-} or SO_4^{2-} . Each column represents a single substitution of $P_i(Si/S)_{3-i}$ in $Na_xV_2P_i(Si/S)_{3-i}O_{12}$. The value of each voltage-the color of each box-represents a plateau in the computed voltage curve, similar to those displayed in Figure 1, where each voltage plateau extends over a Na composition range (Δx) of at least 0.5. Therefore, at a given $Na_{x}V_{2}P_{i}(Si/S)_{3-i}O_{12}$, a change in color moving from a box to another along the y-axis corresponds to a step in a typical "staircase"-type voltage curve. In general, we observe higher voltages (red boxes) at low Na contents within the NaSICON (x < 1) and lower voltages at higher Na contents (x > 3). Similarly, large S (Si) substitution at the same Na content tends to decrease (increase) the average voltages, as denoted by the increasing frequency of green (orange) boxes toward the right (left) side of Figure 3a.

To facilitate the reading of Figure 3a, we show the voltage staircase plot for Na (de)intercalation of two selected compositions, Na_xVP₂Si₁ (P₂Si₁) and Na_xVP₂S₁ (P₂S₁), in Figure 3b. The two selected mixed polyanion systems display the maximum feasible range of Na (de)intercalation, i.e., the whole $0 \le x \le 4$ range (Figure 2). Note that, at Si/S substitution levels beyond P₂(Si/S)₁, the feasible range of Na content in the NaSICON structure reduces since V cannot exhibit stable oxidation states above +5 and below +2. The voltage plateaus in Figure 3b are mapped into Figure 3a through labels from "a" to "h". Steps at specific Na concentrations in the voltage curves (Figure 3b) correspond to stable compositions in the predicted pseudobinary (i.e., Navacancy pseudobinary within Na_xV₂P_i(Si/S)_{3-i}O₁₂) phase diagram.

While the V^{III/II} redox pair is accessed in Na_xVP₃ at compositions 3 < x < 4, the V^{III/II} redox couple is not active in Na_xVP₂Si₁ (i.e., 33% substitution of P by Si). Specifically, the P₂Si₁ composition involves V^{V/IV} and V^{IV/III} in the regions of 0 < x < 2 and 2 < x < 4, respectively, indicating higher average

Na intercalation voltages than those of Na_xVP₃ (Figure 1) for similar ranges of Na (de)intercalation. As the V^{IV/III} redox pair can be accessed in both Na_xVP₃ (1 < *x* < 3) and Na_xVP₂Si₁ (2 < *x* < 4) by sodium extraction from the Na2 site,²⁶ the difference in the average voltage of V^{IV/III} for these compounds can be used to accurately determine the effect played by Si on the redox voltage. Specifically, the average voltage of the V^{IV/III} redox for Na_xVP₂Si₁ (~2.67 V vs Na/Na⁺, (*a* + *b*)/2 in Figure 2) is ~280 mV lower than the corresponding voltage for Na_xVP₃ (~2.95 V), which can be attributed to the stronger inductive effect of P than of Si.

In Na_xVP₂Si₁, the step in the voltage curve with Na removal at x = 2 (~0.68 V) is due to the transition from the V^{IV/III} to the V^{V/IV} redox pair. The voltage difference from V^{IV/III} to $V^{V/IV}$ redox in $Na_x VP_2 Si_1$ is almost half of that between the corresponding voltage step for $Na_x VP_3$ (~1.33 V at x = 1, Figure 1). In Na₁VP₃, the large difference in the voltage steps of the V^{IV/III} to the V^{V/IV} redox is also partly due to the extraction of Na from the Na1 site, pushing the voltage beyond the anodic stability of conventional liquid electrolytes (>4 V), resulting in the VV/IV redox not being electrochemically accessible.²⁹ On the other hand, the lower voltage in P_2Si_1 may facilitate the extraction of Na from the electrochemically active Na2 site, while the $V^{V/IV}$ redox is active, as indicated by the average voltage of \sim 3.42 V vs Na/Na⁺ for 1 < *x* < 2 (Figure 3b). However, extraction of Na from the Na1 site, which continues to utilize the V^{V/IV} redox in P₂Si₁ (x < 1), requires a higher voltage (\sim 3.96 V), similar to the observation in Na_xVP₃ but marginally within the anodic stability (<4 V) of conventional liquid electrolytes. The activation of the V^{V/IV} redox and the extraction of Na from the Na1 site in P₂Si₁ produces a combined voltage step of 0.68 + 0.54 = 1.22 V (i.e., between labels d and b in Figure 3b), which is marginally lower than the ~1.33 V jump observed in $Na_x VP_3$. This difference in the voltage steps between the V^{IV/III} and the V^{V/IV} redox pairs $(\sim 1.22 \text{ V vs} \sim 1.33 \text{ V vs} \text{ Na/Na}^+)$ can also be attributed to the weaker inductive effect in Si than in P.

Overall, our data indicate that the average voltage across the accessible Na concentration (0 < x < 4) in Na_xVP₂Si₁ is ~3.18 V vs Na/Na⁺, which is ~260 mV higher than the ~2.92 V in Na_xVP₃. Thus, the substitution of P by Si facilitates the



Figure 4. a. Stability heatmap in terms of energy above the convex hull (in meV/atom) of mixed polyanion NaSICONs as extracted from the quintenary phase diagrams, Na–V–P–Si–O and Na–V–P–S–O. The *x* and *y* axes are similar to those in Figure 3. The light-blue mark in the color bar represents the limit below which phases are expected to be stabilized by entropic effects and are likely to be synthetically viable. Gray boxes represent areas containing unstable vanadium oxidation states. Instability values higher than 50 meV/atom are also represented by dark red colored boxes. b. Projection of the energies above the hull of selected NaSICON compositions, namely, Na_xVSi₃ (light blue), Na_xVP₃ (orange), and Na_xVS₃ (green), as a function of Na content (*x*).

activation of higher-oxidation-state V redox couples at higher Na concentrations in Na_xVP₂Si₁, resulting in better intercalation voltages. Si substitution can also result in better capacities than the pure phosphate framework with the possibility of Na extraction from the Na1 site. In our computed (primitive unit cell) model containing 2 formula units of the Na_xVP₂Si₁ framework (total 42 atoms for x = 4), the thermodynamically stable ordering is made up of lantern units containing one SiO₄⁴⁻ and two PO₄³⁻ tetrahedra, as shown in Figure S2 of the SI. Thus, our model is limited in the number of SiO₄⁴⁻ and PO₄³⁻ arrangements enumerated, and this requires more investigation to verify whether other stable Si–P arrangements exist.

In contrast to P_2Si_1 , in $Na_rVP_2S_1$ (33% substitution of P by S) the V^{V/IV} redox pair is not active for 0 < x < 1. Additionally, the V^{IV/III} and V^{III/II} redox couples are active across 0 < x < 2and 2 < x < 4, respectively, in P_2S_1 , while the V^{V/IV} and V^{IV/III} are active for the corresponding Na contents in P₂Si₁, resulting in consistently lower average voltages for the $P_2 S_1$ structures, across all Na concentrations, compared to P_2Si_1 (Figure 3b). The stronger inductive effect of S^{6+} (vs P^{5+} or Si^{4+}) does cause the intercalation voltages to increase for the same active vanadium redox pair. For example, the average voltage of the $V^{IV/III}$ redox couple in P_2S_1 is ~3.37 V vs Na/Na⁺ (0 < x < 2), which is higher than the ~2.95 V in Na_xVP₃ (1 < x < 3) and ~2.67 V in P_2Si_1 (2 < x < 4). Also, the voltage for V^{IV/III} combined with Na removal from the Na2 site in P_2S_1 is ~3.01 V vs Na/Na⁺ (1 < x < 2), which is marginally higher than the corresponding voltage (~2.95 V) in Na_xVP₃ (1 < x < 2). Therefore, S substitution in Na_xVP enhances the voltage of each V redox couple, due to the inductive effect, but reduces the average voltage across the accessible Na concentration via activation of lower-oxidation-state V redox couples.

To assess the synthesizability of Si or S substituted NaSICONs with variable Si/S substitution levels in Na_xVP_3 , we have calculated the quintenary Na-V-P-Si-O and Na-V-P-S-O phase diagrams (or the 0 K convex hulls) of the $Na_xVP_i(Si/S)_{3-i}$ systems using DFT. The multicomponent phase diagrams provide insight into the thermodynamic stability (at 0 K) of the predicted compositions and constitute

a useful proxy for their synthesizability. The stabilities of each composition of $Na_x VP_{3-i}(Si/S)_i$ are computed with respect to all available elemental, binary, ternary, quaternary, and quinary entities obtained from the Materials Project and the inorganic crystal structure database (ICSD).^{63,64} The energies above the convex hull, for compositions considered in steps of Δx and Δi of 0.5, are presented in Figure 4a.

Figure 4b shows the computed energy above the hull as a function of Na content in Na_xVP_3 and the fully substituted Na_xVS_3 and Na_xVS_3 compositions. Other selected projections of the quinary phase diagrams of Figure 4a are shown in Figure S3 of the SI. Equation S1 in the SI explains how the formation energies and the stabilities of specific $Na_xVP_{3-i}(Si/S)_i$ compounds are assessed.

If we qualitatively assume that ~30 meV/atom is the (vibrational) entropic stabilization accessible at room temperature (see the blue line in the color bar of Figure 4a),⁶⁵⁻⁶⁷ our results suggest that only NaSICONs with low Si (0 < i < 0.5) and low S (0 < i < 1) contents might be experimentally accessible for specific ranges of Na concentrations.

Furthermore, the fully substituted Na_xVS₃ and Na_xVS₃ display large instabilities (>30 meV/atom), as seen in Figure 4a,b, suggesting difficulties in their experimental synthesis. To elaborate further, the convex hull of quaternary Na_xVP₃ (orange line in Figure 4b) shows that only Na_xVP₃ structures at x = 1 and x = 3 are stable, with x = 4 and x = 0 being metastable (~7.3 and ~14.6 meV/atom) at 0 K, respectively. This is in qualitative agreement with experimental reports that use Na₃VP to form Na₁VP₃ and Na₄VP₃ via electrochemical extraction/insertion.^{31,33} Although the fully deintercalated Na₀VP₃ shows only marginal instability (~14.6 meV/atom with the decomposition products of VP₂O₇ and VPO₅), it is not electrochemically accessible.²⁴

In the case of Na₄VSi₃, we predict that the NaSICON phase will decompose into stable NaV(SiO₃)₂, Na₂Si₂O₅, NaVO₃, and Na₃VO₄, where the decomposition involves disproportionation of V from its 4+ oxidation state in NaSICON to 3+ in NaV(SiO₃)₂ and 5+ in NaVO₃ and Na₃VO₄. The corresponding desodiated composition Na₂VSi₃ (with V⁵⁺) decomposes into NaVO₃ and SiO₂. The NaSICON with a low

concentration of Si, i.e., $Na_x VP_{2.5}Si_{0.5}$, shows low instabilities (7-32 meV/atom) across the whole range of Na concentrations $0 \le x \le 4$, indicating that low Si substitution may be accessible at room temperature. However, we do not expect higher Si content (i > 0.5) in $Na_x VP_{3-i}Si_i$ to be favorable for synthesis. Additionally, the minimum energy configurations (i.e., most negative formation energies with respect to elements or the lowest energy above convex hull values) shift from x = 3 in $Na_3 VP_3$ to higher Na contents, x = 3.5 and 4, when a fraction of Si (i = 0.5 and 1, respectively) substitutes for P. In general, compositions with Na contents between x = 1 and 3.5 remain metastable (<30 meV/atom) with small Si addition (up to i = 0.5), which may be accessible via high temperature synthesis.

In the case of S substitution, we predict that the NaSICON- Na_2VS_3 will decompose into stable Na_2SO_4 , SO_2 , and VO_2 , with oxidation of V from its 2+ oxidation state in NaSICON to 4+ in VO₂ accompanied by a reduction of S^{6+} in NaSICON to 4+ in SO₂. The corresponding desodiated composition Na_0VS_3 (with V^{III}) decomposes into VO₂ (V^{IV}), SO₃ (S⁶⁺), and SO₂ (S^{4+}) . In contrast to Si, the substitution of P by S shifts the minimum energy configurations to lower Na content (green boxes in Figure 4a). Specifically, Na concentrations near x = 1become energetically favorable (i.e., low instabilities) with increasing S content. Hence, S substitution will favor synthesizing NaSICONs with lower Na content compared to the pure phosphate or Si substituted versions. Nevertheless, large S substitutions (i > 1) result in high instabilities (>30)meV/atom) at most Na contents within the NaSICON, indicating synthesis difficulties and possible decomposition during electrochemical experiments.

4. DISCUSSION

 PO_4^{3-} substitution by SiO_4^{4-} or SO_4^{2-} in Na_xVP_3 modifies the redox voltages of the feasible V redox pairs, namely, V^{III/II}, $V^{IV/III}$, and $V^{V/IV}$. Due to the lower oxidation state of Si than P, the presence of Si decreases the average voltage of each V redox couple, while S shows the opposite trend (Figure 3). This behavior can be attributed to a progressive increase in inductive effect, in the order Si < P < S. However, with Si and S introduction into Na, VP, the shifts in the overall average voltages arise from the activation of the high voltage $V^{V/IV}$ redox pairs in the case of Si (resulting in overall higher average voltage than P) and the low voltage $V^{\rm III/II}$ redox pairs in S (lower overall average voltage). Importantly, the high voltage $V^{V/\text{IV}}$ redox can be accessed with Si substitution even without extraction from the Na1 site, which is not feasible in the parent Na_xVP₃ structure.²⁶ From our predictions, Si substitution appears to decouple the voltage required for the V^{V/IV} redox and the activation of the Na1 site (labels c and d in Figure 3), making the V^{V/IV} couple accessible within the practical stability windows of conventional electrolytes.

It is important to discuss the effects of vibrational and configurational entropy contributions in favoring the synthesizability of potential mixed $Na_xVP_{3-i}(Si/S)_i$ compositions. First, there cannot be a general criterion suggesting that any arbitrary phase will be stabilized by some amount vibrational entropy with respect to other competing phases. The entropic (vibrational) stabilization depends critically on how the target NaSICON composition of interest responds to temperature effects relative to all relevant competing phases for that target compound. The second important thermodynamic handle that controls the formation of mixed $Na_xVP_{3-i}(Si/S)_i$ compositions is the configurational entropy arising from both Na/vacancies and/or Si/P (or S/P) mixing. Previously, we have elucidated the role of configurational entropy linked to the Na/vacancy lattice in Na_xVP₃,²⁶ whose magnitude for compositions between Na₁VP₃ and Na₃VP₃ appears negligible (~1 J/K). This low value of configurational entropy is the result of the significant stability of specific Na/vacancy orderings at Na₁VP₃ and Na₃VP₃,^{26,29} which competes with the configurational entropy from the Si(S) mixing with P in Na_xVP_{3-i}(Si/S)_i. Here, using a simple model of ideal solution shown in Figure 5,



Figure 5. Estimated configurational entropy arising from in Si(S) in Na_xVP₃. The ideal solution model $\Delta S_{mixing} = -nR[i \times \ln(i)] + [(1 - i) \times \ln(1 - i)]$ was used, where *n* is the number of P atoms per f.u., *R* is the molar gas constant, and *i* is the amount of either Si or S mixed with P in Na_xVP₃.

we have estimated that the entropy stabilization form the Si/P (or S/P) mixing in $Na_xV_2(PO_4)_3$ reaches a maximum at i = 1.5 Si (S) in $Na_xVP_{3-i}(Si/S)_i$ of ~17 J K⁻¹. This finding demonstrates that Si/P or S/P mixing may favor the synthesis of these mixed NaSICON phases.

Indeed, the replacement of phosphate groups (PO_4^{3-}) by silicate groups (SiO_4^{4-}) in Na_3VP_3 to prepare the Na-rich $Na_{3+i}VP_{3-i}Si_i$ (with i = 0.1, 0.2, and 0.4) solid solutions has been reported by Aragón et al.³⁹ and more recently reinvestigated by Pal et al.¹⁶ The composition $Na_{3,4}VP_{2,6}Si_{0,4}$ included a large fraction of impurities that could not be assigned by the authors.^{16,39} Although our phase diagram in Figure 4 suggests that the Na-rich/Si-rich $Na_{3,5}VP_{2,5}Si_{0,5}$ is slightly metastable, it tends to decompose into the $Na_3V (PO_4)_2$, V_2O_3 , $NaV(SiO_3)_2$, and $Na_3V_2(PO_4)_3$ phases, which may have been the impurities in the synthesized $Na_{3,4}VP_{2,6}Si_{0,4}$.¹⁶ Thus, more experimental studies are required to ascertain the extent of solubility of Si in Na_xVP_3 . While a moderate capacity increase was reported for $Na_{3,1}VP_{2,9}Si_{0,1}$ (first discharge ~ 98 mAh/g at C/10) and $Na_{3,2}VP_{2,8}Si_{0,2}$ (first discharge \sim 98 mAh/g at C/10) in comparison to Na_3VP_3 (~88 mAh/g at C/10), ¹⁶ the authors did not explore the high-voltage domain of the $V^{V/IV}$ redox couple in the Si-

The predicted average voltage (vs Na/Na⁺) for Na_xVP_{3-i}(Si/S)_i compounds together with the corresponding theoretical gravimetric capacities provide the theoretical energy densities (see Figure S4). At lower Si or S substitutions for P (i < 0.5), as the accessible Na concentrations range remains unchanged for all the compositions (i.e., 1 < x < 4), the negligible difference in the gravimetric capacities only arises from the small differences in the masses of Si and S.

Additionally, a high degree of substitution of either Si or S (i > 1) for P significantly reduces the gravimetric capacity, and the energy density, due to the reduction in the feasible range for Na extraction per formula unit. Futhermore, our stability predictions (Figure 4) also point to increasing synthesis difficulties upon high degrees of Si/S substitution (i > 1) in Na_xVP_{3-i}(Si/S)_i.

Although the Na-intercalation voltage for each V redox couple increases with S substitution compared to Si due to the enhanced inductive effect of S, the average voltage for deintercalation, across the accessible Na range, is higher with Si substitution than with S. For example, a small degree of S substitution in Na_xVP₃ extends the activity of the low voltage $V^{III/II}\ redox$ pair over a larger Na content range, thereby reducing the overall average voltage. On the other hand, a small amount of Si extends the high voltage V^{V/IV} redox couple over a larger Na content range, thereby improving the overall average and the theoretical energy density. Thus, an improvement in the gravimetric capacity combined with the overall higher voltage through activation of the $V^{V/IV}$ redox couple achieved by $Na_x VP_{3-i}Si_i$ (at i < 1) offers an opportunity to increase the energy density of Na batteries that employ NaSICON electrodes. Furthermore, the replacement of P⁵⁺ by Si⁴⁺ may reduce the barriers for Na migration in NaSICON electrodes due to reduced electrostatic repulsions between migration of Na⁺ and Z cations.

5. CONCLUSIONS

In summary, by using DFT calculations combined with a robust thermodynamic analysis, we have explored the effect of polyanionic substitution on the structure, stability, and electrochemical behavior of the vanadium-based NaSICON, $Na_xV_2(PO_4)_3$. Although PO_4^{3-} substitution with SO_4^{2-} enhances the voltage of each V redox, it lowers the overall average voltage due to the extension of the low voltage $V^{\rm III/II}$ redox couple. In contrast, SiO_4^{4-} substitution is found to activate the high voltage V^{V/IV} redox couple without necessarily removing Na from the Na1 site, resulting in a higher overall average voltage. Note that activating the V^{V/IV} redox couple without Na extraction from the Na1 site is not possible in the parent Na_xVP₃ compound. The computed quinary phase diagrams of Na-V-P-(Si/S)-O indicate that small degrees of Si/S substitution should be experimentally feasible. Our computed theoretical energy densities highlight that incorporating low Si contents into Na_xVP₃ appears a feasible pathway for improving the energy densities of NaSICON cathodes.

6. THEORETICAL METHODS

To determine the effect of Si and S substitution at the P site of Na_xVP₃, structures of Na_xV₂P_{3-i}(Si/S)_iO₁₂ with *i* ranging from 0 to 3 at step sizes of 0.5 were examined, providing Na_xV₂(PO₄)₃ (*i* = 0, P₃), Na_xV₂P_{2.5}(Si/S)_{0.5}O₁₂ (*i* = 0.5, P_{2.5}(Si/S)_{0.5}), Na_xV₂P₂(Si/S)₁O₁₂ (*i* = 1.0, P₂(Si/S)₁), Na_xV₂P_{1.5}(Si/S)_{1.5}O₁₂ (*i* = 1.5, P_{1.5}(Si/S)_{1.5}), Na_xV₂P_{1.5}(Si/S)_{2.5}), and Na_xV₂P_{0.5}(Si/S)_{2.5}O₁₂ (*i* = 2, S, P_{0.5}(Si/S)_{2.5}), and Na_xV₂(Si/S)₃O₁₂ (*i* = 3, (Si/S)₃), respectively. These compositions were studied with Na content *x* ranging from 0 to 4 with step sizes of 0.5 for *x*. Thus, the concentration steps of 0.5 along the *i* and *x* variables result in a total of 97 distinct compositions (number of nongray squares

in Figures 3 and 4). Fully Na ordered $Na_4VP_{3-i}(Si/S)_i$ structures were generated from a reference structure of the NaSICON, namely, the rhombohedral ($R\overline{3}c$) primitive cell containing 2 formula units per unit cell found in the ICSD database (id: 20340).⁶⁴

In this primitive structure, Si and S were partially (or fully) substituted onto P sites, and Na atoms were extracted to generate new configurations of $Na_x VP_{3-i}(Si/S)_i$, at different Na contents. Various Na/vacancy and Si/P (S/P) orderings were enumerated using the pymatgen package.⁶⁸ To minimize the number of orderings, we used a ranking scheme based on the Ewald energy,⁶⁹ where the electrostatic energy was computed after assigning integer point charges to each species (Na = +1, Si = +4, P = +5, S = +6, and O = -2, V charges assigned based on Na and Si/S content).⁶⁹ At each Na composition, 500 structures with the lowest Ewald energies were selected. The final number of structures computed was further reduced by symmetry considerations.

To ascertain the thermodynamic stability of the mixed polyanion phases, we computed the quinary phase diagrams. This implies that all known and ordered binary, ternary, quaternary, and quinary compounds for the Na–V–P–Si–O and Na–V–P–S–O systems found in the ICSD were calculated (apart from the pure elements) and complemented by structures available in the Materials Project.^{63,64}

The Vienna ab initio simulation package (version 5.4.4) software was used to perform DFT total energy calculations of the structures considered. The wave functions were described by planewaves extending to a maximum kinetic energy of 520 eV, which was combined with projector augmented wave (PAW) potentials for core electrons. The PAW potentials used were Na 08Apr2002 3s¹, V pv 07Sep2000 3p⁶3d⁴4s¹, P 17Jan2003 3s²3p³, Si 05Jan2001 3s²3p², S 17Jan2003 3s²3p⁴, and O 08Apr2002 2s²2p⁴. PBE-parametrized spin-polarized generalized gradient approximation (GGA) was used for the exchange and correlation energy, and the Dudarev method was introduced to account for the on-site Coulomb repulsions between 3d electrons of vanadium,⁷⁰ by incorporating a Hubbard U parameter of 3.1 eV.⁵⁰ The U parameter has been derived for oxide compounds, and it may be less accurate for polyanion compounds, as in this study. Hence, we also performed test calculations with the screened hybrid functional, HSE06.^{49,71} The irreducible Brillouin zone was sampled using a Γ -point-centered Monkhorst–Pack mesh with a minimum of 25 subdivisions along each reciprocal lattice vector. The total energies were considered converged when differences were less than 10^{-5} eV/structure, forces on atom less than 10^{-2} eV/Å, and stresses less than 0.29 GPa.

6.1. Calculation of Voltages for Na Extraction. The reversible extraction of Na ions from the NaSICON $Na_x VP_{3-i}(Si/S)_i$ framework can provide an intercalation battery according to the redox reaction of eq 1.

$$y \operatorname{Na} + \operatorname{Na}_{x} V_{2}(\operatorname{PO}_{4})_{3-i}(\operatorname{ZO}_{4})_{i} \stackrel{\Delta G}{\longleftrightarrow} \operatorname{Na}_{x+y} V_{2}(\operatorname{PO}_{4})_{3-i}(\operatorname{ZO}_{4})_{i}$$
(1)

The DFT total energy was used to approximate the Gibbs energy, *G*, of each compound in eq 1, and the average voltage $\langle V \rangle$ at each stage of intercalation is calculated following eq 2, with *F* being the Faraday constant.⁷²

(2)

$$\langle V \rangle = \frac{-\Delta G}{yF} = \frac{E[Na_{x+y}V_2(PO_4)_{3-i}(ZO_4)_i] - yE[Na] - yE[Na_xV_2(PO_4)_{3-i}(ZO_4)_i]}{yF}$$

In this approximation both the entropic contribution and the pV terms are neglected.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00230.

Theoretical framework to develop the NaSICON phase diagrams, phase diagrams of NaSICON $Na_xV_2(PO_4)_3$ and $Na_xV_2P_iSi_{3-i}O_{12}$, decomposition reactions of NaSICON $Na_xV_2P_iSi_{3-i}O_{12}$, and models of $Na_xV_2P_2Si_1O_{12}$ (PDF)

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Notes

The authors declare no competing financial interest.

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