

Phase Stability and Kinetics of Topotactic Dual Ca²⁺–Na⁺ Ion Electrochemistry in NaSICON NaV₂(PO₄)₃

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understood. In this work, we report on an investigation of the structure and/or Na⁺/Ca²⁺ environment(s) of a variety of chemically prepared NaSICON $Ca_xNa_yV_2(PO_4)_3$ phases which were characterized using synchrotron XRD, SEM-EDS, ²³Na NMR, and TEM. Highly calciated $CaV_2(PO_4)_3$, $Ca_{1.5}V_2(PO_4)_3$, and $CaNaV_2(PO_4)_3$ phases can be prepared at high temperature, but—unlike $Ca_{0.6}NaV_2(PO_4)_3$ —these materials are electrochemically inactive. To better understand the fundamental factors impacting successful Ca^{2+} electrochemistry in this system, DFT was employed to examine the $Ca_xNa_yV_2(PO_4)_3$ phase diagram and Ca^{2+} diffusion mechanism. Theoretical insights show that phase separation into Na-rich and Ca-rich phases is a reason for the capacity limitation and demonstrate that Na⁺ ions in the host materials assist the migration of neighboring Ca^{2+} ions, enabling reversible electrochemistry in $Ca_xNa_yV_2(PO_4)_3$. This investigation of fundamental principles affecting reversible Ca^{2+} (de)intercalation in $Ca_xNa_yV_2(PO_4)_3$ allows for the development of design principles to enable the discovery of a variety of successful cathodes for CIBs.

INTRODUCTION

Substantially reducing global dependence on fossil fuels relies on the development of a variety of efficient and cost-effective energy storage technologies. Thus far, the rapidly growing market for electric vehicles and grid electricity storage has been met by lithium-ion technology (lithium-ion batteries, LIBs). However, safety concerns, limited resources, and possible rising costs of these lithium-based storage systems have raised questions about the sustainability and suitability of this technology for the scale of future energy needs.^{1,2} In the hunt for alternative approaches, Ca-ion batteries (CIBs) have recently garnered recognition as promising next-generation energy storage systems.^{3,4} These batteries—utilizing the fifth most abundant element in the Earth's crust (2500 times more abundant than Li)-could be a sustainable energy storage alternative to Li systems.⁵ In addition to low materials cost, the production of CIBs could offer several recycling advantages since Ca salts are generally nontoxic and would not pose an environmental hazard during manufacturing. Furthermore, CIBs have the potential to offer large energy density since

Ca has a particularly low redox potential (-2.87 V vs SHE), and a Ca metal anode would offer high gravimetric/volumetric capacities relative to the graphite counter electrodes employed in commercial Li cells (>3-fold increase).⁶ Despite these advantages, much work is still needed to develop positive electrode (cathode) candidates for Ca-ion technology.

A variety of technological bottlenecks persist that prevent the implementation of Ca metal negative electrodes (anodes) for practical applications.⁷ Proof-of-concept demonstrations have shown reversible electrochemistry in Ca-ion cells with metal anodes,^{8–11} but such systems are hindered by low Coulombic efficiencies and poor cyclability due to parasitic side reactions and/or dendritic metal plating.¹² As a result,

Received: September 13, 2022 Revised: November 25, 2022



most studies investigating the electrochemical behavior of prospective cathode materials employ carbon-based counter electrodes to ensure that reversibility is not limited by dendritic shorts and/or the surface passivation of Ca.^{13,14} In this hunt for successful Ca cathode candidates, progress has been hampered by the major challenges plaguing all multivalent energy storage systems: sluggish solid-state diffusion;¹⁵ increased desolvation penalties due to strong contact-ion pairs;¹⁰ and a tendency toward conversion and/or parasitic side reactions at the interface.^{16,17} Additionally—owing to their large size—Ca²⁺ ions can cause large volume changes upon (de)insertion into/from host frameworks. Such transformations typically cause electrode active material to delaminate from current collectors and lose electrical contact within the cell, leading to capacity loss and limited reversibility.

To guide the design of Ca cathodes in this nascent technological field, much inspiration has been drawn from studies of Na-ion batteries due to the similarity in size between Na⁺ and Ca²⁺ ions (116 and 114 pm, respectively). Extensive Na-battery research has identified structures capable of accommodating large cations while simultaneously minimizing cathode strain during cycling, namely, layered materials with tunable basal spacing and/or open frameworks with large intercalant sites.¹⁸ Among potential candidates, Na super-ionic conductor (NaSICON) type materials-such as Na₃V₂(PO₄)₃ (Na₃VP) or Na₃V₂(PO₄)₂ $F_{3-\nu}O_{\nu}$ (NVPF)—have been intensively investigated due to their promising cyclability, chemical tunability, and high discharge voltages.^{19,20} These polyanionic frameworks boast remarkable structural stability as well as good ionic conductivity, and recent work has demonstrated their ability to reversibly host Ca²⁺ ions with promising electrochemical performance.²¹⁻²⁴

The classical NaSICON structure of Na₃VP is composed of a rhombohedral network of corner-sharing VO₆ octahedra and PO_4 tetrahedra. In this large open framework, VO_6 octahedra stacked along the *c*-axis are connected by a skirt of three PO_4 tetrahedra, creating 6-coordinate (CN) "lantern" positions (Wykoff 6b site or "M1" in $R\overline{3}c$, S.G. #167) partially occupied by Na⁺ cations. The 8 CN 18e (or "M2") sites surrounding these stacks host the remaining Na⁺ ions, and calculations have shown that diffusion through this NaSICON framework involves both of these sites.²⁵ Traditionally, Na₃VP structures have been reported to adopt this rhombohedral symmetry, particularly when parameters were refined from lab X-ray diffraction (XRD) data. However, high-resolution data collected at synchrotron facilities have proven that Na₃VP exhibits a monoclinic distortion at room temperature (C2/c, S.G. #15) and transitions through a variety of modulated structures at elevated temperatures before crystallizing into the classical rhombohedral cell at 180 °C.²⁶ In both $R\overline{3}c$ and C2/cstructures, Na⁺ cations partially occupy both 6 CN (M1) and 8 CN (M2) sites, however—below 180 °C—sodium ordering in the M2 sites breaks the 3-fold rotational symmetry of the rhombohedral system, resulting in the monoclinic structure.^{27,28} Upon extraction of two Na⁺ ions per formula unit, the resulting $NaV_2(PO_4)_3$ (NaVP) lattice adopts the highsymmetry rhombohedral framework, and the remaining Na⁺ cations fully occupy 6b-M1 sites while 18e-M2 sites remain vacant. During electrochemical cycling, the interconversion of Na₃VP toNaVP has been widely reported as a two-phase reaction, but recent studies have identified the existence of an intermediate $Na_2V_2(PO_4)_3$ (Na₂VP) phase that reduces the lattice mismatch between Na₃VP and NaVP phases and

enables a fast phase transition.^{28–30} This discovery has provided new insight into the excellent rate capabilities of Na₃VP and inspired detailed investigations into the complex electrochemical behavior of NaSICON electrodes. These NaSICON materials—with large interstitial sites available for cation intercalation—are successful hosts for divalent cations, exhibiting reversible Zn²⁺ and/or Mg²⁺ (de)insertion and significant promise for long-term cycling stability.^{31–34}

To date, there have been two reports of reversible Ca²⁺ electrochemistry in a NaSICON Ca_xNaV₂(PO₄)₃ host. Kim et al. demonstrated excellent electrochemical activity at room temperature, maintaining an 80 mAh·g⁻¹ capacity at 3.2 V for 40 cycles.²¹ At the same time, Jeon et al. reported a $Ca_x NaV_2(PO_4)_3$ cathode with similar capacity and operating potential, but different electrochemical behavior.²² In latter case, very small capacities were obtained during early cycling and a gradual increase in capacity was observed. This activation process was accelerated at elevated temperatures, and a significant (80 mAh·g⁻¹) capacity was achieved after only 3 cycles at 75 °C. Single phase Ca_{0.8}NaV₂(PO₄)₃ was prepared through chemical calciation, and the Rietveld refined composition of this sample shows that Ca²⁺ occupies 6b while Na⁺ occupies 18e sites. During cycling, Ca²⁺ inserts into 6b sites on discharge, but Na⁺ is removed on charge, as the composition of charged material was Ca_{0.9}Na_{0.4}V₂(PO₄)₃ according to ICP-OES. Both studies showed good cyclability of Ca^{2+} in the $NaV_2(PO_4)_3$ host, but due to the presence of multiple closely related phases, it is extremely difficult to understand the charge storage mechanism of Ca^{2+} (de)intercalation. Moreover, both works show that Ca2+ ions preferentially occupy 6b sites and apparently "push" Na⁺ ions to 18e sites, but the role that Na⁺ plays in modifying the Ca²⁺ mobility remains unknown. Finally, despite the good cyclability with Ca, these materials are unable to achieve the specific capacity that the host material achieves when used in Na cells $(Na_1VP \leftrightarrow Na_3VP, 120 \text{ mAh}\cdot\text{g}^{-1})$ and are only able to discharge Ca^{2+} ions up to 80 mAh·g⁻¹. The presence of multiple NaSICON phases upon discharge and the apparent capacity limitation indicate that the charge storage mechanism for Ca²⁺ ions may be different from that of a pure Na-NaSICON.

Herein, a wide variety of analytical techniques are employed to elucidate the Ca-discharge process and to identify fundamental factors affecting reversible Ca²⁺ (de)insertion in $Ca_x Na_v V_2 (PO_4)_3$. For the first time, single-phase calciated and completely desodiated-materials are prepared, and we use this to create a controlled series of discharge products. We furthermore report on the crystal structure of $CaV_2(PO_4)_3$ (CaVP) and $Ca_{1.5}V_2(PO_4)_3$ (Ca_{1.5}VP). We find that the structures are closely related to their respective Na analogues, except that Ca²⁺ ions exhibit a stronger preference for 6 CN 6b-M1 sites relative to Na⁺ cations. We also report the structure of CaNaV₂(PO₄)₃ (CaNaVP), finding that—like Na₃VP and Ca_{1.5}VP-this structure exhibits a monoclinic distortion of the classical rhombohedral NaSICON framework. For $Ca_x Na_y V_2 (PO_4)_3$, we show that Ca^{2+} (de)insertion is only reversible when x < 0.65. In contrast, Ca²⁺ cannot be extracted from deeply calciated material (where x > 0.65) making the CaVP, Ca15VP, and CaNaVP phases all largely redox inactive. A computational construction of the ternary phase diagram in the Ca-Na-VP system suggests that phase separation into Na- and Ca-rich regions halts electrochemistry when electrochemically active material becomes surrounded by fully

reduced phases. Ab initio computations are also used to explore the cation diffusion mechanism in detail, revealing the key role of Na⁺ ions to enable Ca²⁺ electrochemistry at room temperature. We find that Na⁺ ions on 18e sites are crucial for neighboring Ca²⁺ ions to hop from a 6b site to an 18e site, and that independent Na⁺ diffusion enables 3D migration of Ca²⁺ that is otherwise impossible (without the presence of a sufficient number of mobile cations in the lattice). Our findings clarify important design principles for functional CIB cathodes, and we hope that this work will inspire the development of a variety of new hosts for Ca²⁺ and/or other divalent cations.

EXPERIMENTAL SECTION

Material Synthesis. All chemical reagents were purchased from Sigma-Aldrich and used as received unless noted otherwise. The parent Na₃V₂(PO₄)₃ NaSICON phase was prepared using a sol-gel (SG) method modified from a previously reported approach.³⁵ In a typical synthesis, 3 mmol of vanadium(V) oxide and 9 mmol of oxalic acid dihydrate were first dissolved in 50 mL of deionized water and stirred at room temperature until a translucent green solution formed. Then 9 mmol of ammonium dihydrogen phosphate and 4.59 mmol of sodium acetate were added into the above solution, and it was vigorously stirred for 1 h. Finally, Ketjenblack carbon (10 wt %) was added to the solution, and the mixture was stirred at 70 °C overnight until a gel formed which was then transferred to an oven and thoroughly dried at 80 °C. The obtained solid sample was then ground using a mortar and pestle for 15 min and pelletized at 2 tons in a die with a diameter of 13 mm. The pellets were transferred to an alumina crucible and heated in a tube furnace at 350 °C for 4 h and then 800 °C for 8 h at a heating rate of 5 °C·min⁻¹ under a constant flow of Ar gas. The obtained powder contained 7% carbon according to TGA (Figure S1), and this SG-Na₃V₂(PO₄)₃ material was used as the precursor for all subsequent chemical modifications.

All solvents required for the remaining chemical treatments were thoroughly dried after purchase. Ethanol (EtOH, 99%) was distilled over magnesium and stored over 4 Å sieves. Ethylene glycol (EG, 99.8%) was purged under Ar at 80 °C immediately before use, and acetonitrile (ACN) was washed with sodium hydroxide, distilled over calcium hydride, and stored over 4 Å sieves. To prepare $NaV_2(PO_4)_3$ (NaVP), SG-Na₃VP was added to a solution of 2.5 mol equiv of nitrosonium tetrafluoroborate (NOBF₄) in ACN and allowed to stir for 10 h at room temperature (RT). The obtained powder was washed with ACN three times and dried under vacuum at 120 °C. This NaVP material was mixed with a 3-fold excess of calcium iodide (CaI₂) in EtOH and stirred at RT for 16 days. The RT-Ca_xNaVP powder obtained from this brown solution was washed with EtOH multiple times and dried under vacuum at 120 °C. To prepare $CaV_2(PO_4)_3$ (CaVP), NaVP was mixed with 1 equiv of CaI₂ in EG, immediately heated to 200 °C, and held at that temperature for 1 week. Similarly, $\text{Ca}_{1.5}\text{V}_2(\text{PO}_4)_3~(\text{Ca}_{1.5}\text{VP})$ was obtained by mixing NaVP with excess CaI₂ (4.5 equiv) in EG; however, this solution was first held at RT until it turned brown prior to the subsequent high temperature (HT) treatment. Ion exchanges were carried out by mixing SG-Na₃VP with either 0.5 or 1 equiv of CaI₂ in EG and heating to 200 °C. Ca_{0.5}Na₂V₂(PO₄)₃ (Ca_{0.5}Na₂VP) was obtained after heating for 2 days, while CaNaV₂(PO₄)₃ (CaNaVP) was refluxed for 1 week prior to washing. Following reflux in EG, all powders were washed with methanol several times and dried at 150 °C under a vacuum. Chemical oxidations were then performed by mixing calciated materials with a slight excess of NOBF₄ in ACN at RT. For CaNaVP-where the treatment using NOBF₄ resulted in no detectable cation removal-the material was mixed with nitronium tetrafluoroborate (NO₂BF₄) in ACN and heated to 70 $^{\circ}$ C for 2 days prior to washing. Both NOBF4 and NO2BF4 oxidizing agents were used to attempt to remove Ca²⁺ ions from CaVP and/or Ca_{1.5}VP materials. However, no change in the Ca:V ratio could be detected in either powder following these chemical oxidations.

Material Characterization. X-ray diffraction (XRD) analysis was carried out on a PANalytical Empyrean diffractometer with Cu K α radiation. Powder samples were packed and sealed in glass capillary tubes, and the data were recorded in Debye-Scherrer geometry. For a variety of Ca_xNa_yVP samples, additional high-resolution synchrotron XRD was collected on 11-BM at the Advanced Photon Source located at the Argonne national laboratory. For clarity of comparison between data collected at a variety of wavelengths, all diffraction patterns are plotted versus Q (rather than 2θ). Rietveld analysis³⁶ was carried out on the diffraction patterns of single-phase materials by sequentially refining the scale factor, zero point, background, lattice parameters, fractional coordinates, occupancies, and atomic displacement parameters using TOPAS version 6 (Bruker, AXS). After preliminary refinements, if the occupancy of atoms did not deviate significantly from full occupancy, then those occupancies were fixed to 1.0 for subsequent refinements. Material morphologies and elemental compositions were examined using a Zeiss field emission scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. Samples were transferred to the instrument with minimal exposure to air and scans were collected at an accelerating voltage of 20 keV. Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 $^{\circ}C \cdot min^{-1}$ on a TA Instruments SDT Q500.

²³Na magic-angle spinning (MAS) NMR spectra were collected at spinning speeds between 40 and 67 kHz using Bruker 1.3 mm MAS HX probes. Static and variable temperature experiments were collected using a Bruker wide line static single channel probe. All experiments were performed using Bruker Avance III spectrometers, corresponding to ²³Na Larmor frequencies of 79.39 and 132.29 MHz (7.02 and 11.7 T, respectively). Chemical shifts were referenced to 1 M NaCl in H₂O ($\delta = 0$ ppm). Spectra were acquired with rotor synchronized spin–echo experiments (90°– τ –180°– τ) where $\tau = n/\nu_r$ (ν_r : spinning speed in Hz). 90° pulse lengths of 1.75 and 2.22 μs were used for MAS experiments at 7.02 and 11.7 T, respectively, and 2.7 μs for static experiments at 7.02 T. T₁ relaxation measurements were collected with inversion and saturation recovery experiments. Sufficiently long pulse recycle delays between 0.5 and 2.0 s were used for a quantitative NMR study.

The nanoscale visualization and compositional characterization of the calciated electrode was carried out using transmission electron microscopy (TEM). The ground nanoparticles of the cathode were deposited on Lacey Formvar/carbon mesh copper grids. Analysis was performed using a probe-corrected FEI Titan 80-300 STEM instrument operated at 300 kV. Scanning TEM (STEM) mode with a high-angle annular dark-field (HAADF) detector and Aztec's EDS data collection and analysis system for compositional analysis were used.

Electrochemical Investigations. $Ca_x Na_y V_2 (PO_4)_3$ electrodes were prepared with a 9:1 weight ratio of active material and polyvinylidene difluoride (PVDF) binder. The electrode slurry was ground in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich 99.5%) and subsequently doctor-bladed on to the carbon-coated aluminum foil. Electrodes with an active material loading of 2.5 $mg \cdot cm^{-2}$ were punched into 11 mm disks and dried at 110 °C under vacuum overnight prior to cell preparation. The counter electrode was prepared by mixing high surface area carbon (BP-2000) in an 8:1:1 ratio with Super P and PVDF. After the mixture was ground in NMP, the slurry was doctor bladed on carbon paper (AVCarb P50), punched into 16 mm disks and dried at 110 °C under vacuum overnight. The electrochemistry of these cells was examined using a VMP3 potentiostat/galvanostat (Biologic). Coin cells (2325) were assembled with an activated carbon counter electrode and 0.5 M $Ca(B(Ohfip)_4)_2$ in diglyme (G2) electrolyte.

Computational Methods. Density functional theory (DFT) was used as implemented in the Vienna Ab Initio Simulation Package (VASP)³⁷ using the projector augmented-wave method^{38,39} and the generalized gradient approximation as formulated by Perdew, Burke, and Ernzerhof.⁴⁰ For all thermodynamic calculations, the energy cutoff was set to 520 eV, and at least 1000 k-points were used per reciprocal atom. For geometry optimizations, energies were converged



Figure 1. Electrochemical performance of $Ca_xNaV_2(PO_4)_3$ paired with an activated carbon counter electrode using 0.5 M $Ca(B(Ohfp)_4)_2$ in G2 electrolyte showing the (a) (dis)charge capacity after an activation cycle at room temperature and (b) cycling performance at a C/30 rate. (c) Lab XRD diffraction patterns of $Ca_xNaV_2(PO_4)_3$ materials at the various states of charge (indicated in panel a), showing a pristine $Ca_0.5NaV_2(PO_4)_3$ cathode (wine), charged electrode (red), discharged $Ca_xNa_yV_2(PO_4)_3$ (blue), and a desodiated $NaV_2(PO_4)_3$ reference (black). In the labels, VP refers to a $V_2(PO_4)_3$ formula unit.

to 10^{-5} eV for electronic steps and 0.01 eV·Å⁻¹ for ionic steps. The Hubbard U correction was used for the electronic states of V to account for the self-interaction error of semilocal density functionals.⁴¹ The U parameter was chosen to be consistent with the Materials Project database,⁴² as reported by Jain et al. (V: 3.25 eV).⁴³

When studying topotactic Na/Ca migration and insertion, the rhombohedral NaSICON structure $(\overrightarrow{R3c})$ with 72 oxygen ions $(Ca_{r}Na_{v}V_{12}(PO_{4})_{18})$ was used for all calculations, and the ionic positions, cell shape, and volume were allowed to locally optimize during relaxations. To be consistent with previous findings for the preferential site occupancy,²¹ the sites occupied by Ca and Na were chosen based on the following approach: The 6b site is lower in energy than the 18e site for both Ca and Na, but the difference in energy is larger for Ca. Therefore, 6b sites were occupied with Ca as much as possible before introducing Na. The lowest symmetrically distinct electrostatic orderings of Ca, Na, and empty sites were then sampled within these constraints using the Ewald method. In total, 72 different structures were calculated at varying levels of calciation and sodiation to determine the thermodynamic stability of phases in the NaSICON structure. Thermodynamic stability was determined using the convex hull method⁴⁴ in two different approximations. Overall stability of the NaSICON compounds was determined with respect to the entire Ca-Na-V-P-O chemical space including all competing phases from the Materials Project database. Stability within the topotactic NaSICON framework was also calculated by using $Ca_{1.5}V_2(PO_4)_3$, $Na_3V_2(PO_4)_3$, and $V_2(PO_4)_3$ in the NaSICON structure as stable endmembers. Such topotactic stability is often relevant when cycling cations in and out the structure at room temperature, as many known intercalation systems pass through metastable states but do not transform to the more stable (nontopotactic) competing phases. However, when the driving force for conversion to another host structure is very large, which is most common in reduction, nontopotactic transformations can start from the surface.⁴⁵ Only compositions of Ca_xNa_yV₂(PO₄)₃ for which the average V oxidation state is between (and including) V^{3+} and $V^{4.5+}$ were considered in the topotactic phase diagram $(2x + y \le 3)$. The

pymatgen library was used to set up and analyze the calculations in this work. $^{\rm 46}$

The climbing image Nudged Elastic Band (NEB) method⁴⁷ was used to calculate Ca and Na migration energies. The barriers were calculated in cells with 72 oxygen ions for single-ion hops and cells with 144 oxygen ions when multiple ions were allowed to hop. In addition to initial and final end points, NEB calculations were performed with five intermediate images generated to capture the energy along the migration trajectory. For the NEB images, energies were converged to 5×10^{-4} eV for electronic steps and 0.01 eV·Å⁻¹ for ionic steps.

RESULTS AND DISCUSSION

Experiments. To gain insight into key factors affecting reversible Ca²⁺ ingress/egress within a NaSICON framework, a large survey of Ca_xNa_yV₂(PO₄)₃ phases was conducted, and these materials were characterized using a variety of analytical techniques. The pristine Na₃V₂(PO₄)₃ parent phase was first synthesized by a sol-gel method $(\overline{SG}-Na_3\overline{VP})$ and then desodiated through chemical oxidation using NOBF₄ in acetonitrile (ACN) to form $NaV_2(PO_4)_3$ (NaVP). This synthetic method created a lightly carbon-coated material composed of nanosized crystallizes (~100s nm in diameter) that form porous, micrometer-sized agglomerates. The morphology of SG-Na₃VP is largely retained after removing Na⁺ ions to form NaVP (Figure S2). Electrochemically active $Ca_rNaV_2(PO_4)_3$ was prepared through a room temperature (RT) chemical calciation of NaVP using CaI₂ in ethanol (EtOH). According to SEM-EDS, the average composition of this product was Ca_{0.5(3)}Na_{1.0(4)}V₂(PO₄)₃; however, synchrotron XRD revealed the presence of multiple NaSICON phases that likely contain different relative fractions of Ca²⁺ and Na⁺ cations (Figure S3).

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When this material (" $Ca_{0.5}NaV_2(PO_4)_3$ " or $Ca_{0.5}NaVP$) was paired versus a carbon counter electrode in a cell with 0.5 M $Ca(B(Ohfip)_4)_2$ in G2 electrolyte, cations can be electrochemically extracted. It exhibits similar performance to previous reports, achieving an 85 mAh \cdot g⁻¹ capacity after discharge at a C/30 rate (Figure 1a).^{21,22} The diffraction patterns of Ca_{0.5}NaVP cathodes at various states of (dis)charge show that—as expected—a mixture of multiple larger-volume (calciated) phases is formed after discharge, but a single-phase material closely resembling NaVP is obtained after charge (Figure 1c). This process exhibits good reversibility during subsequent cycling, maintaining 70% of the initial capacity after 75 cycles (Figure 1b), albeit with increased polarization during cycling (in contrast to previous publications). It is likely that this electrochemical performance could have been significantly improved using a variety of techniques to further increase the conductivity of the active material and/or structural integrity of the electrode composite. However, no effort to optimize the material's electrochemical performance was made here, as these investigations instead focused on determining the structures of the calciated phases to identify factors affecting the charge storage mechanism during (dis)charge.

Previous experimental and theoretical investigations have suggested that-relative to Na⁺-Ca²⁺ ions have a stronger preference for 6b sites in the NaSICON framework, but neither report prepared nor considered the structure of a calciated framework that was completely desodiated.^{21,22} In our work, two materials were synthesized that contained no significant trace of residual Na after calciation, as detected by EDS elemental analysis (Figure 2). $CaV_2(PO_4)_3$ (CaVP) was prepared by mixing NaVP with one equivalent of calcium iodide (CaI_2) in refluxing ethylene glycol (EG) for 1 week prior to washing. Its structure closely resembles the NaVP analogue, where Ca²⁺ ions fully occupy the 6b Wykoff site in the R3c framework (Figure 2a and Table S1). Fully calciated $Ca_{1.5}V_2(PO_4)_3$ ($Ca_{1.5}VP$) was prepared using excess CaI_2 , and-like Na₃VP-this material exhibits a monoclinic distortion of the rhombohedral framework at room temperature (Figure 2b). In the monoclinic C2/c lattice, cations partially occupy 6-coordinate 4d sites (similar to 6b sites in the rhombohedral framework) along with 8f and 4e sites (pseudo 18e sites) in both Ca1.5VP and Na3VP. However, the distribution of cations differs significantly. In Na₃VP, Na⁺ ions have roughly equal occupancy on all three sites, but Ca²⁺ ions show a much stronger preference for the 4d (pseudo 6b) site relative to the sodiated structure.²¹ Unlike Na₃VP, the 4d site is fully occupied in $Ca_{1.5}VP_{1.5}VP_{1.5}$ and the remaining Ca^{2+} ions are evenly distributed between the 8f and 4e sites with occupancies of 0.17 and 0.13, respectively (Table S2).

Despite any structural similarities to their electrochemically active Na analogues, Ca^{2+} ions cannot be extracted from these calciated materials. EDS measurements detected no changes to the Ca:V ratios of either CaVP or $Ca_{1.5}VP$ after chemical oxidation (relative to pristine materials). Similarly, Ca^{2+} ions could not be electrochemically extracted from $Ca_{1.5}VP$, even when charged to high voltage in a Li cell. Figure S4 shows negligible capacity in the voltage regime where Ca^{2+} extraction is expected to take place (<4 V vs Li). The only redox activity observed—which takes place above 4.4 V vs Li—is likely indicative of electrolyte decomposition rather than cation removal, as there is no change in the XRD pattern or the Ca:V ratio of the $Ca_{1.5}VP$ electrode after charge. Although the



Figure 2. Rietveld refinement against the synchrotron XRD pattern of (a) rhombohedral $CaV_2(PO_4)_3$ and (b) monoclinically distorted $Ca_{1.5}V_2(PO_4)_3$ that shows the experimental data (black crosses), fitted profile (red line), difference map between the observed and calculated data (blue line), and Bragg positions (green ticks). Insets show the respective $R\overline{3}c$ and C2/c NaSICON structures composed of corner sharing VO₆ (red octahedra) and PO₄ (purple tetrahedra) along with Ca^{2+} occupying 6-coordinate (blue octahedra) and 8-coordinate (orange and yellow polyhedra) sites. (c) Elemental mapping of $Ca_{1.5}V_2(PO_4)_3$ that shows the presence of Ca-rich regions at the periphery of crystalline particles. In all figure labels, "VP" refers to a $V_2(PO_4)_3$ formula unit.

diffraction pattern of Ca1.5VP only detected a single phase, TEM analysis revealed the presence of an amorphous deposit on the periphery of the crystalline particles (Figure S5). Portions of this amorphous surface layer are carbon-rich and may resemble the surface coating present on the Na₃VP parent material (Figure S6). Other regions—rich in Ca—are likely insulating/passivating in nature (Figure 2c). The presence of these amorphous phases at the surface of Ca1.5VP particles may hinder Ca²⁺ extraction and inhibit electrochemical activity. However, it is unclear to what extent the observed electrochemical inactivity is a result of this surface passivation or if other factors—such as the lack of Na⁺ ions—negatively impact performance. To gain further insight into the role that Na⁺ ions play in the (de)insertion and/or migration of Ca²⁺ ions, the (electro)chemical behavior of a variety of structures containing both Ca²⁺ and Na⁺ cations was evaluated and compared.

To investigate whether the limited electrochemistry of $Ca_{1.5}VP$ is intrinsically hindered by the presence of passivating material formed at the surface of particles during the prolonged reaction either (1) at the higher temperature (HT) and/or (2) in the presence of highly reactive Ca^{2+} cations, sodiated materials were prepared using a similar method and their electrochemical performance was evaluated (Figure 3). HT-Na₃VP was obtained by refluxing NaVP with excess sodium iodide (NaI) in EG. When cycled at C/3 in a Na cell, this HT-Na₃VP material exhibited typical electrochemical behavior and achieves its theoretical capacity of 118 mAh·g⁻¹ (Figure S7). Similarly, $Ca_{0.46(1)}Na_{2.1(3)}V_2(PO_4)_3$ ($Ca_{0.5}Na_2VP$) obtained through ion exchange prepared a redox active material where Ca^{2+} ions are located at 6b sites in the $R\overline{3}c$ framework and Na⁺



Figure 3. Flowchart of various single- (black) and multiphase (red) NaSICON materials. The Na₃VP parent phase (yellow) was subjected to a series of chemical calciations (plain text) and/or oxidations (italics) to prepare the different $Ca_xNa_yV_2(PO_4)_3$ (Ca_xNa_yVP) compounds. Total ion content was determined by normalizing Ca and Na atomic fractions measured by EDS with respect to V and averaging across a wide variety of regions. Compositions with x < 0.65 were electrochemically active (blue), while more deeply calciated materials were largely inert with respect to (electro)chemical oxidation.



Figure 4. (a) Rietveld refinement against the synchrotron XRD pattern of $CaNaV_2(PO_4)_3$ that shows the experimental data (black crosses), fitted profile (red line), difference map between the observed and calculated data (blue line), and Bragg positions (green ticks). The inset shows the ²³Na NMR shift for Na⁺ in 4e (green) and 8f (purple) sites. (b) Crystal structure of the C2/c phase comprised of corner sharing VO₆ (red octahedra) and PO₄ (light purple tetrahedra) along with Ca²⁺ occupying 4d sites (blue octahedra), Na⁺ occupying 8f sites (dark purple polyhedra), and Na⁺ occupying 4e sites (green polyhedra).

ions are present at both 6b and 18e sites with partial occupancies of 0.39 and 0.54, respectively (Table S3 and Figure S8). Na⁺ cations are readily extracted from Ca_{0.5}Na₂VP to form Ca_{0.4}Na_{0.6}V₂(PO₄)₃ (Table S4), and Ca_{0.5}Na₂VP exhibits good electrochemical reversibility in a Na cell, albeit with a limited theoretical capacity relative to its Na counterpart since only 1.5 mol of Na⁺ can be extracted from the lattice in total (Figure S7). Unlike this reversible electrochemistry, when NaVP was treated with approximately 0.65 equiv of CaI₂, a largely redox inactive multiphase mixture with an average composition of Ca_{0.7(1)}Na_{0.76(9)}V₂(PO₄)₃ was formed (Figure S9); however, some Na⁺ ions could be removed, yielding a composition of Ca_{0.7(1)}Na_{0.21(5)}V₂(PO₄)₃ after chemical oxidation (Figure 3).

When SG-Na₃VP was mixed with 1 equiv of CaI₂ and refluxed at elevated temperature, a single-phase material was obtained with an average composition of $Ca_{0.98(2)}Na_{1.0(4)}V_2(PO_4)_3$ (CaNaVP). While lab XRD data for CaNaVP could be refined in the rhombohedral ($R\overline{3}c$) framework, the resulting stoichiometry was not consistent with the EDS analysis that agreed well with the targeted CaNaVP composition (Table SS). This anomaly was resolved by refining the synchrotron diffraction pattern of CaNaVP in the expected monoclinic structure. The Rietveld refinement against the synchrotron XRD pattern shows that Ca²⁺ solely

and fully occupies the 6 CN 4d (pseudo 6b) sites, whereas the Na⁺ ions occupy both the quasi-8 CN 4e and 8f sites (Figure 4a,b) with occupancies of 0.30 and 0.42, respectively (Table S6). To support this analysis, in parallel, ²³Na NMR data was collected for Na₃VP, NaVP, and CaNaVP to investigate the relative shifts of Na⁺ environments in these structures and confirm the Na site-occupation in the C2/c monoclinic structure (Figure S10 and Figure 4). The ²³Na NMR spectrum of $Na_1V^{4+}P$ shows that the signal for Na^+ in 6 CN sites exhibits a large Fermi contact shift relative to its position in Na₃V³⁺P as expected from the change in the d-electron configuration (Figure S10a,b), and the monoclinic distortion in Na₃VP broadens room temperature lineshapes (Figure S10c). Unlike Na₃VP, no intensity is observed at 27 ppm in the ²³Na NMR spectrum of CaNaVP, suggesting that Ca2+-rather than Na⁺-resides in the 6 CN (4d) sites in agreement with the Rietveld refinement. The two Na⁺ environments observed in the ²³Na NMR spectrum of CaNaVP at 178 and 92 ppm (Figure 4a) are assigned to the two 8 CN sites (4e and 8f, respectively) in the monoclinic lattice, with their relative integrated intensity (31% and 69%) being in very good accord with their relative fraction refined by XRD, taking into account the multiplicity (i.e., 26% and 74%). The much narrower ²³Na NMR lineshapes in CaNaVP compared to Na₃VP suggest lower mobility of the Na ions in the former, which can be



Figure 5. Comparison between the structure of $Ca_{0.5}Na_2V_2(PO_4)_3$ relative to $CaNaV_2(PO_4)_3$ and their respective electrochemical performances in Na cells. Unlike $Ca_{0.5}Na_2VP$ where some 6b sites remain vacant, deeply calciated material (with fully occupied 6b sites) is largely inert with respect to (electro)chemical oxidation. Although CaNaVP definitely (and $Ca_{0.5}Na_2VP$ likely) exhibits a monoclinic distortion at RT, the resolved rhombohedral structures are presented simply for clarity of comparison.



Figure 6. DFT-calculated topotactic ternary phase diagram of $Ca_xNa_yV_2(PO_4)_3$ in the NASICON host structure $(VP = V_2(PO_4)_3)$. The decomposition energy ΔE_d shown as a color map is the driving force for a composition to decompose to the more stable compositions. Stable compositions have a value of $\Delta E_d = 0$. The four chemical processes explored experimentally are plotted as arrows (electrochemical: NaVP \leftrightarrow $Ca_{0,6}NaVP$ (blue dotted line), $Ca_{0,5}Na_2VP \leftrightarrow Ca_{0,4}Na_{0,6}VP$ (red dotted line); chemical: $Ca_{0,7}Na_{0,8}VP \rightarrow Ca_{0,7}Na_{0,2}VP$ (black dotted line, left), $CaNaVP \rightarrow Ca_{0,93}Na_{0,65}VP$ (black dotted line, right)). The green hatched region is less relevant as the decomposition energy in that region is calculated based on a hypothetical VP phase.

explained by the fact that Ca^{2+} fully occupies the 6 CN 4d site, and likely blocks 4e \leftrightarrow 8f site exchange and reduces Na⁺ mobility. Thus, this more deeply calciated CaNaVP material is largely inert with respect to (electro)chemical oxidation (Figure 5), in stark contrast to the electrochemical behavior of Ca_{0.5}Na₂VP. Following chemical oxidation, no significant cation removal was observed after mixing with NOBF₄ at RT, and only a small quantity of (mostly) Na^+ cations was extracted using NO_2BF_4 at 70 °C, generating a multiphase mixture with an average composition of $Ca_{0.93(3)}Na_{0.7(2)}V_2(PO_4)_3$ (Figure 3).

Correlation of Computation with Experiment. The above experimental observations indicate that Ca^{2+} (de)-intercalation is not possible in the polyanionic framework if



Figure 7. XRD patterns of $Ca_xNa_yV_2(PO_4)_3$ obtained after chemical calciation at room temperature (cyan) and electrochemical discharge (black). These patterns consist of multiple phases and are plotted above the diffraction patterns of NaVP, CaNaVP, and Na₃VP for comparison. All diffraction patterns were collected using synchrotron radiation with the exception of electrochemically discharged Ca_xNa_yVP .

 Ca^{2+} is inserted beyond a critical amount ($x \sim 0.65$); however, fundamental aspects of the factors affecting electrochemical reversibility—such as the role of Na⁺ ions during (dis)charge—are still poorly understood. Thus, computational techniques were used to explore the ternary $Ca_xNa_yV_2(PO_4)_3$ phase diagram and elucidate the Ca^{2+}/Na^+ cation diffusion mechanism.

Density functional theory (DFT) calculations were used in an attempt to understand the multiple phase evolution processes upon chemical oxidation and electrochemical cycling of Na and Ca NaSICON materials. In Figure 6, we show the 0 K phase diagram and stability for topotactic Ca and Na insertion into the empty NaSICON structure. As we are studying topotactic Na/Ca changes, the analysis assumes that the VO₆ and PO₄ framework is maintained, so thermodynamic stability is computed only with respect to phases within the topotactic ternary phase diagram formed by Ca_{1.5}VP-Na₃VP-VP and not the entire Ca-Na-V-P-O structural space. In Figure S11, global stability allowing for decomposition into any structure in the entire 5-component space is also shown for comparison. All structures were fully relaxed in terms of ionic positions, cell shape, and volume allowing the symmetry to lower away from the rhombohedral symmetry of the framework.

In Figure 6, we also highlight some of the compositions that have been evaluated in chemical oxidation or electrochemical cycling experiments, distinguishing between compositions observed to exist as a single phase (blue stars) and compositions where multiple phases appear to coexist (red stars). NaVP, Na₃VP, CaVP, Ca_{1.5}VP, and CaNaVP have been observed as single phases in agreement with their calculated stability in this topotactic phase diagram. Ca_{0.5}Na₂VP was experimentally observed as a single phase but is calculated here to be 13.5 meV/atom higher than decomposition into Na₃VP and CaNaVP. Ca_{0.4}Na_{0.6}VP was observed as a single phase after electrochemical charging of Ca_{0.5}Na₂VP in a Na cell but is calculated here to be metastable by 7 meV/atom energy over decomposition into NaVP and CaVP, two phases that may be difficult to distinguish from one another by XRD, in particular when their domains are small. All compositions where multiple phases were observed experimentally (Ca_{0.5}NaVP, Ca_{0.6}NaVP, Ca_{0.7}Na_{0.8}VP, Ca_{0.7}Na_{0.2}VP, Ca_{0.93}Na_{0.65}VP) are indeed calculated to be unstable with respect to decomposition into two or more competing phases. For instance, XRD patterns of chemically calciated Ca_{0.5}NaVP at room temperature (Figure 7, cyan) show major peaks corresponding to Na₃VP, NaVP (CaVP), and Ca_xNa_yVP phases, supporting the calculated phase diagram. XRD patterns for electrochemically discharged Ca_{0.5}NaVP (Figure 7, black) also indicate multiple phases are present, but unlike the chemically calciated sample, there are no reflections corresponding to Na₃VP. This may indicate the formation of another Na-rich Ca_xNa_yVP phase in the Ca_{0.16}NaVP-Na₃VP-CaVP ternary region. Previous work on the Na_xVP NaSICON system has reported a Na₂VP phase to exist on the Na1-Na3VP tie line.28 Because of the very small energy difference of this phase compared to a Na₁VP and Na₃VP mixture, we cannot conclusively support the existence of this phase from theory. Different exchange-correlation functionals and + U values give different results for its stability. With our calculation settings the Na₂VP appeared as a slightly metastable phase (5 meV/atom above the convex hull). Moreover, the voltage step at Na₂VP ordering is too small to detect from experiment (\sim 50 meV). Considering that, we did not plot Na_2VP as a stable phase in Figure 6.

The pseudoternary phase diagram in Figure 6 can also be used to understand which processes occur during chemical oxidation and electrochemical cycling. The 0 K phase diagram indicates that Ca^{2+} discharged into NaVP would form a mixture of NaVP and $Ca_{0.16}$ NaVP. However, the formation energy variation between NaVP and $Ca_{0.16}$ NaVP is small, making it likely that at room temperature a solid solution forms between these two phases. Based on the small variation in formation energy in this area we expect this solid solution to persist until the $Ca_{0.16}$ NaVP composition is reached, though



Figure 8. (a) Local environment of 6b, 18e, and 36f sites in rhombohedral NASICON. (b) Schematic of the ion diffusion network in a NASICON structure and elementary Ca/Na hops. Each hexagon and octagon in the network represents a possible cation site labeled as 6(b) and 18(e). Unlabeled circle sites are 36f. Edges between two sites indicate that they are face-sharing. Blue (orange) denotes Ca (Na) occupation. (c) Ca hop from 6b to 18e in Ca_{0.083}VP. (d) Ca hop from 6b to 18e with preexisting Na in Ca_{0.17}Na_{0.83}VP. (e) Na hop from 6b to 18e in Na_{0.83}VP. (f) Minimum energy paths (MEPs) for the hops shown in (c), (d), and (e). Solid blue curve is (c), dotted blue curve is (d), and solid orange curve is (e).

slightly higher Ca compositions may also be possible for this solid solution region. When additional Ca²⁺ is inserted the formation energy rises rapidly making it likely that a threephase mixture of Ca_{0.16}NaVP-Na₃VP-CaVP forms. The dynamics of phase evolution as this three-phase region is traversed by further calciation are difficult to predict in detail as the 0 K phase diagram only gives qualitative information on the possible solid solution regions of each phase, but generally, the amount of Ca_{0.16}NaVP phase needs to decrease at the benefit of growing domains of Na₃VP and CaVP. If calciation proceeds in equilibrium Ca_{0.66}NaVP would be the terminal composition of this three-phase region (Point 4 in the phase diagram). This composition is calculated to be metastable on the tie line that connects Na₃VP and CaVP, suggesting phase separation into these separate Na- and Ca-rich compounds. The experimental results suggest that these are both inactive phases. CaVP was shown to be electrochemically inactive, and Ca²⁺ cannot be inserted into Na₃VP as this would require further V reduction below 3+. Note that this terminal composition consists of equilibrium between phases with average V valence of +3 (Na₃VP) and 3.5+ (CaVP). The predicted decomposition of Ca_{0.66}NaVP into inactive CaVP and Na₃VP therefore may explain the maximum experimentally observed capacity of ~0.65 mol of Ca^{2+} per $V_2(PO_4)_3$. In Figure S12, the computed voltage-capacity curve of Ca²⁺ intercalation into NaVP is plotted and shows voltage (3.11-3.25 V) and capacity (81 mAh·g⁻¹) to similar to those of published reports (Figure 1).^{21,2}

The chemical oxidation of $Ca_{0.7}Na_{0.8}VP$ that resulted in Na⁺ extraction to form $Ca_{0.7}Na_{0.2}VP$ (Figure 3) also begins in the same three-phase region where electrochemically discharging NaVP ends ($Ca_{0.16}NaVP-Na_3VP-CaVP$). From our calculated phase diagram, $Ca_{0.7}Na_{0.8}VP$ should phase separate with the major phases being Na₃VP and CaVP. Under the oxidizing conditions induced by NOBF₄ in ACN, we expect Na₃VP to be quickly oxidized to NaVP, while CaVP should be less prone to

oxidation (Figure 3). If the Ca_{0.7}Na_{0.8}VP composition occurs as a mixture of Na₃VP and CaVP as predicted by our calculations, the chemical oxidation of Ca_{0.7}Na_{0.8}VP to Ca_{0.7}Na_{0.2}VP can be attributed to Na⁺ extraction from Na₃VP, with CaVP remaining mostly chemically inactive.

It remains to be addressed why NaVP cannot be discharged past the nominal Ca_{0.66}NaVP composition (point 4 on the phase diagram). We believe that several issues conspire to limit this discharge. Converting the Na₃VP-CaVP two-phase mixture into the single endmember CaNaVP phase requires Na⁺ diffusion from Na₃VP into the CaVP and further Ca²⁺ insertion into the partially desodiated Na₃VP. Essentially, the CaVP phase should only discharge by taking up Na⁺ from the already formed Na₃VP phase, and any further Ca²⁺ uptake in the cathode should occur in the Na₃VP region that has lost Na⁺ ions. The high formation energies in the Na₃VP-CaVP-CaNaVP three-phase triangle indicate that the intermediate metastable solid solution states which need to be traversed to achieve this interdiffusion are high in energy. While in principle Na⁺/Ca²⁺ transport from one part of the material to another can occur through the electrolyte, the strong overpotentials in this system make that unlikely. Because of these thermodynamic and kinetic limitations, it is likely that the overpotential in discharge leads to some direct Ca²⁺ insertion into CaVP, creating the metastable Ca1.5VP. The global (nontopotactic) phase diagram indicates that this compound is unstable with respect to the formation of several phases including Ca pyrophosphates which likely have low Ca transport properties. Indeed, an amorphous calcium phosphate on the surface of Ca1.5VP formed by chemical calciation was detected by STEM/EDS analysis (Figure 2c and Figure S5).

The calculations summarized In Figure 6 address the thermodynamics of the various Na^+/Ca^{2+} insertion/extraction processes observed experimentally. Although we have discussed the thermodynamic implications of Ca^{2+} insertion/extraction, activating the diffusion of Ca^{2+} in the solid state is



Figure 9. Concerted hop mechanisms of (a) 6b-Ca, 18e-Na to 18e-Ca, 6b-Na in $Ca_{0.083}NaVP$, (b) 6b-Na, 18e-Na to 18e-Na, 6b-Na in $Ca_{0.083}NaVP$, and (c) 6b-Na, 18e-Na to 18e-Na, 6b-Na in $Na_{1.083}VP$. Corresponding NEB energy profile along the minimum energy path for paths 1, 2, and 3 in (d) Ca–Na hop in $Ca_{0.083}NaVP$ and (e) Na–Na hop in $Ca_{0.083}NaVP$ and (f) Na–Na hop in $Na_{1.083}VP$. 6, 18 label in the diagram refers to the 6b, 18e site, respectively.

nontrivial,^{48,49} so we also investigated Ca²⁺ migration in NaSICON phases using Nudged Elastic Band (NEB) calculations. In Figure 8a,b, the crystal structure of NaSICON is represented using a schematic 2D ion diffusion network.⁴⁸ Potential sites for Na⁺ and Ca²⁺ are shown as hexagons and octagons, with the 6b and 18e sites labeled respectively (note the tetrahedral 36f site shown as a circle lies between 6b and 18e but is not expected to be occupied by either Na⁺ or Ca²⁺). Edges between polygons/circles indicate face sharing between sites. The Na⁺/Ca²⁺ filled sites are each colored orange/blue, respectively. Only 6b-18e hops were calculated with NEB, as most diffusion in NaSICON structures propagates through 6b-18e-6b channels with 18e-18e hops expected to be <1.5% of all hops.⁵⁰

In Figure 8c-e, three single-cation hops with different local environments are presented. Figure 8c shows the Ca^{2+} hop from the more favorable 6b site to the less favorable 18e site in the dilute Ca^{2+} limit ($Ca_{0.083}V_2(PO_4)_3$), with the corresponding minimum energy path (MEP) shown in Figure 8f. The calculated activation barrier of 0.98 eV for this hop is high,⁵¹ suggesting Ca²⁺ is mostly immobile in the empty NaSICON framework. The energy difference between the end and beginning of the path indicates that the high barrier is related to the large site energy difference between 6b and 18e. This high barrier for dilute Ca2+ migration is consistent with our finding that all experiments where Ca²⁺ was observed to be active have at least 1 alkali cation per $V_2(PO_4)_3$ formula unit and hence require occupany of the 18e site. Note that if ≤ 1 alkali cation is present per $V_2(PO_4)_3$ unit, only 6b sites are expected to be occupied (Table S1, Figure S8). In Figure 8d, we consider the 6b–18e hop of Ca^{2+} in $Ca_{0.17}Na_{0.83}VP$ where all cations initially occupy 6b sites. DFT calculations suggest that both Ca²⁺ and Na⁺ prefer the 6b site, and the presence of Na⁺ on surrounding 6b sites increases the migration barrier for Ca^{2+} to 1.21 eV (Figure 8f). Considering that the Ca^{2+} 6b-18e site energy difference increased by ~0.4 eV with preexisting Na⁺, the increase in migration barrier going from the empty NaSICON (0.98 eV, Figure 8c) to the Na-containing NaSICON (1.21 eV, Figure 8d) mostly comes from

Coulombic repulsion between two neighboring Ca^{2+} (18e) and Na⁺ (6b) ions which raises the end state in the MEP. In contrast, Figure 8e shows Na⁺ diffusion in the absence of Ca^{2+} but with some surrounding Na⁺ ions in 6b sites. The calculated migration barrier for Na⁺ of 0.66 eV is substantially lower than for Ca²⁺ (Figure 8f), suggesting higher mobility of Na⁺ relative to Ca²⁺ in this framework.

In the NaSICON structure, it is known that if Na⁺ occupies neighboring 6b and 18e sites, both Na⁺ ions can hop simultaneously via a concerted ion migration mechanism.³ In Figure 9, we evaluate various concerted hopping mechanisms in Ca_{0.083}NaVP in which Na⁺ assists the Ca²⁴ migration (Figure 9a,d) and contrast them to Na-assisted Na⁺ migration at the same composition (Figure 9b,e). We additionally investigate Na-assisted Na⁺ migration in $Na_{1.083}VP$ to probe the effect of cation chemistry (Figure 9c,f). Concerted hopping in NaSICON can occur through three symmetrically distinct paths (shown in cyan, red-brown, and dark blue in Figure 9a,b,c, respectively), and the corresponding 3D structures are presented in Figure S13. The major difference between the three paths is the distance between the initial and final occupied 18e sites. Path 1 has the largest 18e-18e distance followed by path 2 and path 3. Figure 9d shows the MEPs for Na-assisted Ca²⁺ diffusion in Ca_{0.083}NaVP along the three migration paths. Path 1 has the lowest activation energy of 0.70 eV, while path 2 and path 3 have higher activation energies (>1 eV). Considering that a barrier of 0.6-0.75 eV or lower can permit reasonable diffusivity for multivalent-ion cathodes,^{45,51} this result indicates that each interstitial Ca²⁺ in NaV₂(PO₄)₃ can only diffuse via the Na-assisted path 1. While this might appear as 1D diffusion, which would be negatively impacted by channelblocking point defects⁵² and poor performance for large cathode particles, the direction of the Ca²⁺ diffusion is set by the vector between Na(18e) and Ca(6b), which can change when Na⁺ moves between the different 18e sites that surround a Ca²⁺ ion (6b). Recall that the calculated barrier for Na⁺ migration is much lower than Ca^{2+} migration (Figure 8f). Hence, the material is not truly a 1D diffuser, consistent with

Na-assisted Na⁺ diffusion in Ca_{0.083}NaVP is depicted in Figure 9b with the resulting MEPs shown in Figure 9e. The barriers for Na⁺-Na⁺ concerted hopping through paths 1, 2, and 3 are 0.47, 0.64, and 0.92 eV, respectively, all of which are much lower than those for the Ca²⁺–Na⁺ concerted hops. This result further supports that Na⁺ can hop on a much faster time scale than Ca²⁺. Moreover, in Figure 9c, the Na⁺-Na⁺ concerted hop without neighboring 6b Ca²⁺ is considered. This local environment depicts Na⁺-Na⁺ diffusion when there are no Ca²⁺ ions in the local structure. Figure 9f shows the barriers of Na⁺-Na⁺ concerted hop decreases to 0.41, 0.66, and 0.77 eV reflecting the smaller Columbic repulsion between Na⁺ ions than between Ca²⁺ and Na⁺. As a result, Na⁺ can hop to different 18e sites, which can in turn assist the 6b Ca²⁺ to hop in different directions via the path 1 mechanism, circumventing the issue of apparent 1D Ca²⁺ diffusion.

To further assess the nature of concerted hopping in NaSICON materials, we calculated NEB pathways for sequential (separate) Ca^{2+} and Na^+ hops via the same mechanism as shown in Figure 9a. The MEPs for these separated pathways are shown in Figure S14 and indicate that the activation barrier for sequential Ca^{2+} and Na^+ hops is comparable to the concerted mechanism. This similarity indicates that the presence of Na^+ at neighboring 18e sites is primarily stabilizing the site energy difference for Ca^{2+} in 6b and 18e and not the transition state for Ca^{2+} hopping between these two sites.

CONCLUSIONS

Our comprehensive investigation of the Ca-Na dual cation system has employed both experimental and computational methods to gain valuable insight into understanding the phase evolution that takes place during the cycling of Ca²⁺ in $Ca_x NaV_2(PO_4)_3$ (Ca_xNaVP). Rietveld refinement of the XRD patterns of single-phase materials confirms that Ca²⁺ ions exhibit a strong thermodynamic preference for the 6b site in the NaSICON framework relative to Na⁺ ions. Elevated temperatures promote the preparation of deeply calciated material (Ca > 0.65 per $V_2(PO_4)_3$); however, Ca²⁺ cannot be subsequently extracted so highly calciated NaSICONs are inert with respect to Ca²⁺ electrochemistry. In contrast, when the Ca^{2+} content is limited in $Ca_x NaVP$ to $x \approx 0.65$, good electrochemical reversibility is achieved during Ca2+ cycling where multiple closely related NaSICON phases are observed after (electro)chemical Ca²⁺ insertion. The 0 K topotactic ab initio phase diagram confirms that highly calciated NaSICON materials will phase-separate into Na₃VP, CaVP, and another VP phase. This phase separation prevents Ca_xNaVP from achieving the theoretical capacity on discharge when redoxactive material becomes surrounded by reduced phases, such as Na₃VP which cannot undergo further calciation or sodiation due to the limit in a typical voltage window. Also, based on the global phase diagram in the Ca-Na-V-P-O chemical space, the $Ca_x VP(x > 1)$ phase is likely to decompose into non-NaSICON materials under high overpotential. This process can lead to the formation of high Ca content passivation layers on the surface of Ca_xVP which negatively impacts electrochemical performance. Evidence of this surface passivation was observed by TEM and EDS analysis of Ca1.5VP particles, which shows patches of amorphous material rich in Ca on the surface of crystallites. Therefore, we conclude that the separation into

distinct cation-rich phases is the primary factor limiting the capacity for reversible Ca^{2+} cycling to $x \approx 0.65$ in $Ca_x NaVP$. NEB calculations show that for a dilute cation content in

NaSICONs (Ca²⁺ < 1 per V₂(PO₄)₃), migration of Ca²⁺ is difficult due to the large site energy difference between the stable 6b site and the 18e site. Ca²⁺ migration is enabled when the site energy difference is reduced by the introduction of other cations to neighboring 18e sites, resembling the stuffing effect seen in Li-ion conductors.⁵³ The Ca²⁺ concentration must remain lower than ~ 1 per V₂(PO₄)₃ to prevent decomposition into non-NaSICON materials, which means that Na⁺ ions (rather than Ca²⁺) must be introduced to enable Ca²⁺ migration. Moreover, since Na⁺ has a lower site energy difference than Ca²⁺, the Na⁺ can move around in the structure freely, enabling pseudo-3D diffusion of Ca²⁺ ions. As a result, the Na⁺ ions present in the NaSICON framework are critical for successful electrochemistry of $Ca_x NaVP$ because (1) residual Na⁺ prevents overcalciation and the formation of redox-inactive phases during the preparation of active material, and (2) mobile cations are required to reduce site energy difference and enable 3D diffusion of relatively slow cations. Although our work here focused on the $Ca_x Na_y V_2 (PO_4)_3$ NaSICON system, this dual cation concept could be extended to aid the design of other multivalent cathodes. Host frameworks that contain two different symmetric sites of similar energy can participate in a similar concerted-hop process where monovalent cations enable sluggish multivalent cations to diffuse. This design strategy must be carefully employed with appropriate selection of electrode-electrolyte materials that allow for a selective ion to be extracted from the host framework during charging for consistent reversible electrochemistry.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c02816.

Additional TGA, SEM-EDS, XRD, TEM, and ²³Na-NMR experimental data and electrochemical measurements; DFT calculated pseudoternary diagram, capacity–voltage curve, concerted hopping pathway, and mechanism of sequential Ca^{2+} and Na^+ hops (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences. L.F.N. gratefully acknowledges the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Canada Research Chair and for platform support through the NSERC Discovery Grants program. This work made use of the NMR facilities and the Advanced Photon Source at the Argonne National Laboratory supported by the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This work utilized high-performance computing resources through the National Energy Research Scientific Computing Center (NERSC), a U.S. DOE Office of Science User Facility, operated under Contract No. DE-AC02-05CH11231 and the Savio computational cluster resource provided by the Berkeley Research Computing program at the University of California, Berkeley (supported by the UC Berkeley Chancellor, Vice Chancellor for Research, and Chief Information Officer). Computational resources were also provided by the Extreme Science and Engineering Discovery Environment (XSEDE) resource Stampede2 through allocation TG-DMR970008S, which is supported by the National Science Foundation Grant Number ACI1053575.

REFERENCES

(1) Mauger, A.; Julien, C. M. Critical Review on Lithium-Ion Batteries: Are They Safe? Sustainable? *Ionics* **2017**, 23 (8), 1933–1947.

(2) Olivetti, E. A.; Ceder, G.; Gaustad, G. G.; Fu, X. Lithium-Ion Battery Supply Chain Considerations: Analysis of Potential Bottlenecks in Critical Metals. *Joule* **2017**, *1* (2), 229–243.

(3) Liang, Y.; Dong, H.; Aurbach, D.; Yao, Y. Current Status and Future Directions of Multivalent Metal-Ion Batteries. *Nat. Energy* **2020**, 5 (9), 646–656.

(4) Muldoon, J.; Bucur, C. B.; Gregory, T. Quest for Nonaqueous Multivalent Secondary Batteries: Magnesium and Beyond. *Chem. Rev.* **2014**, *114* (23), 11683–11720.

(5) Gummow, R. J.; Vamvounis, G.; Kannan, M. B.; He, Y. Calcium-Ion Batteries: Current State-of-the-Art and Future Perspectives. *Adv. Mater.* **2018**, 30 (39), 1801702.

(6) Tian, Y.; Zeng, G.; Rutt, A.; Shi, T.; Kim, H.; Wang, J.; Koettgen, J.; Sun, Y.; Ouyang, B.; Chen, T.; Lun, Z.; Rong, Z.; Persson, K.; Ceder, G. Promises and Challenges of Next-Generation "Beyond Li-Ion" Batteries for Electric Vehicles and Grid Decarbonization. *Chem. Rev.* **2021**, *121* (3), 1623–1669.

(7) Ponrouch, A.; Bitenc, J.; Dominko, R.; Lindahl, N.; Johansson, P.; Palacin, M. R. Multivalent Rechargeable Batteries. *Energy Storage Mater.* **2019**, *20*, 253–262.

(8) Lipson, A. L.; Pan, B.; Lapidus, S. H.; Liao, C.; Vaughey, J. T.; Ingram, B. J. Rechargeable Ca-Ion Batteries: A New Energy Storage System. *Chem. Mater.* **2015**, *27* (24), 8442–8447.

(9) Verrelli, R.; Black, A. P.; Pattanathummasid, C.; Tchitchekova, D. S.; Ponrouch, A.; Oró-Solé, J.; Frontera, C.; Bardé, F.; Rozier, P.; Palacín, M. R. On the Strange Case of Divalent Ions Intercalation in V_2O_5 . J. Power Sources **2018**, 407, 162–172.

(10) Tchitchekova, D. S.; Ponrouch, A.; Verrelli, R.; Broux, T.; Frontera, C.; Sorrentino, A.; Bardé, F.; Biskup, N.; Arroyo-de Dompablo, M. E.; Palacín, M. R. Electrochemical Intercalation of Ca^{2+} Ions into TiS₂ in Organic Electrolytes at Room Temperature. *Chem. Mater.* **2018**, 30 (3), 847–856.

(11) Cabello, M.; Nacimiento, F.; Alcántara, R.; Lavela, P.; Pérez Vicente, C.; Tirado, J. L. Applicability of Molybdite as an Electrode Material in Calcium Batteries: A Structural Study of Layer-Type Ca_xMoO_3 . *Chem. Mater.* **2018**, *30* (17), 5853–5861.

(12) Arroyo-de Dompablo, M. E.; Ponrouch, A.; Johansson, P.; Palacín, M. R. Achievements, Challenges, and Prospects of Calcium Batteries. *Chem. Rev.* **2020**, *120* (14), 6331–6357.

(13) Liu, X.; Elia, G. A.; Passerini, S. Evaluation of Counter and Reference Electrodes for the Investigation of Ca Battery Materials. *J. Power Sources Adv.* **2020**, *2*, 100008.

(14) Park, J.; Xu, Z.-L.; Yoon, G.; Park, S. K.; Wang, J.; Hyun, H.; Park, H.; Lim, J.; Ko, Y.-J.; Yun, Y. S.; Kang, K. Stable and High-Power Calcium-Ion Batteries Enabled by Calcium Intercalation into Graphite. *Adv. Mater.* **2020**, *32* (4), 1904411.

(15) Rong, Z.; Malik, R.; Canepa, P.; Sai Gautam, G.; Liu, M.; Jain, A.; Persson, K.; Ceder, G. Materials Design Rules for Multivalent Ion Mobility in Intercalation Structures. *Chem. Mater.* **2015**, *27* (17), 6016–6021.

(16) Ponrouch, A.; Palacín, M. R. On the Road toward Calcium-Based Batteries. *Curr. Opin. Electrochem.* **2018**, *9*, 1–7.

(17) Hosein, I. D. The Promise of Calcium Batteries: Open Perspectives and Fair Comparisons. ACS Energy Lett. 2021, 6 (4), 1560–1565.

(18) Gupta, P.; Pushpakanth, S.; Haider, M. A.; Basu, S. Understanding the Design of Cathode Materials for Na-Ion Batteries. *ACS Omega* **2022**, *7* (7), 5605–5614.

(19) Zhou, Q.; Wang, L.; Li, W.; Zhao, K.; Liu, M.; Wu, Q.; Yang, Y.; He, G.; Parkin, I. P.; Shearing, P. R.; Brett, D. J. L.; Zhang, J.; Sun, X. Sodium Superionic Conductors (NASICONs) as Cathode Materials for Sodium-Ion Batteries. *Electrochem. Energy Rev.* **2021**, 4 (4), 793–823.

(20) Broux, T.; Bamine, T.; Fauth, F.; Simonelli, L.; Olszewski, W.; Marini, C.; Ménétrier, M.; Carlier, D.; Masquelier, C.; Croguennec, L. Strong Impact of the Oxygen Content in Na₃V₂(PO₄)₂F_{3-y}O_y ($0 \le y \le 0.5$) on Its Structural and Electrochemical Properties. *Chem. Mater.* **2016**, 28 (21), 7683–7692.

(21) Kim, S.; Yin, L.; Lee, M. H.; Parajuli, P.; Blanc, L.; Fister, T. T.; Park, H.; Kwon, B. J.; Ingram, B. J.; Zapol, P.; Klie, R. F.; Kang, K.; Nazar, L. F.; Lapidus, S. H.; Vaughey, J. T. High-Voltage Phosphate Cathodes for Rechargeable Ca-Ion Batteries. *ACS Energy Lett.* **2020**, 5 (10), 3203–3211.

(22) Jeon, B.; Heo, J. W.; Hyoung, J.; Kwak, H. H.; Lee, D. M.; Hong, S.-T. Reversible Calcium-Ion Insertion in NASICON-Type $NaV_2(PO_4)_3$. Chem. Mater. 2020, 32 (20), 8772–8780.

(23) Xu, Z.-L.; Park, J.; Wang, J.; Moon, H.; Yoon, G.; Lim, J.; Ko, Y.-J.; Cho, S.-P.; Lee, S.-Y.; Kang, K. A New High-Voltage Calcium Intercalation Host for Ultra-Stable and High-Power Calcium Rechargeable Batteries. *Nat. Commun.* **2021**, *12* (1), 3369.

(24) Chen, C.; Shi, F.; Zhang, S.; Su, Y.; Xu, Z.-L. Ultrastable and High Energy Calcium Rechargeable Batteries Enabled by Calcium Intercalation in a NASICON Cathode. *Small* **2022**, *18* (14), 2107853.

(25) Wang, Q.; Zhang, M.; Zhou, C.; Chen, Y. Concerted Ion-Exchange Mechanism for Sodium Diffusion and Its Promotion in $Na_3V_2(PO_4)_3$ Framework. J. Phys. Chem. C 2018, 122 (29), 16649– 16654.

(26) Chotard, J.-N.; Rousse, G.; David, R.; Mentré, O.; Courty, M.; Masquelier, C. Discovery of a Sodium-Ordered Form of $Na_3V_2(PO_4)_3$ below Ambient Temperature. *Chem. Mater.* **2015**, 27 (17), 5982–5987.

(27) Deng, Z.; Sai Gautam, G.; Kolli, S. K.; Chotard, J.-N.; Cheetham, A. K.; Masquelier, C.; Canepa, P. Phase Behavior in Rhombohedral NaSiCON Electrolytes and Electrodes. *Chem. Mater.* **2020**, 32 (18), 7908–7920.

(28) Wang, Z.; Park, S.; Deng, Z.; Carlier, D.; Chotard, J.-N.; Croguennec, L.; Gautam, G. S.; Cheetham, A. K.; Masquelier, C.; Canepa, P. Phase Stability and Sodium-Vacancy Orderings in a NaSICON Electrode. J. Mater. Chem. A **2021**, 10 (1), 209–217. (29) Zakharkin, M. V.; Drozhzhin, O. A.; Ryazantsev, S. V.; Chernyshov, D.; Kirsanova, M. A.; Mikheev, I. V.; Pazhetnov, E. M.; Antipov, E. V.; Stevenson, K. J. Electrochemical Properties and Evolution of the Phase Transformation Behavior in the NASICON-Type Na_{3+x}Mn_xV_{2-x}(PO₄)₃ (0 $\leq x \leq 1$) Cathodes for Na-Ion Batteries. *J. Power Sources* **2020**, 470, 228231.

(30) Park, S.; Wang, Z.; Deng, Z.; Moog, I.; Canepa, P.; Fauth, F.; Carlier, D.; Croguennec, L.; Masquelier, C.; Chotard, J.-N. Crystal Structure of $Na_2V_2(PO_4)_3$, an Intriguing Phase Spotted in the $Na_3V_2(PO_4)_3$ - $Na_1V_2(PO_4)_3$ System. *Chem. Mater.* **2022**, 34 (1), 451–462.

(31) Cabello, M.; Alcántara, R.; Nacimiento, F.; Lavela, P.; Aragón, M. J.; Tirado, J. L. $Na_3V_2(PO_4)_3$ as Electrode Material for Rechargeable Magnesium Batteries: A Case of Sodium-Magnesium Hybrid Battery. *Electrochim. Acta* **2017**, *246*, 908–913.

(32) Hasegawa, G.; Akiyama, Y.; Tanaka, M.; Ishikawa, R.; Akamatsu, H.; Ikuhara, Y.; Hayashi, K. Reversible Electrochemical Insertion/Extraction of Magnesium Ion into/from Robust NASI-CON-Type Crystal Lattice in a $Mg(BF_4)_2$ -Based Electrolyte. ACS Appl. Energy Mater. **2020**, 3 (7), 6824–6833.

(33) Ko, J. S.; Paul, P. P.; Wan, G.; Seitzman, N.; DeBlock, R. H.; Dunn, B. S.; Toney, M. F.; Nelson Weker, J. NASICON $Na_3V_2(PO_4)_3$ Enables Quasi-Two-Stage Na^+ and Zn^{2+} Intercalation for Multivalent Zinc Batteries. *Chem. Mater.* **2020**, 32 (7), 3028–3035.

(34) Hu, P.; Zou, Z.; Sun, X.; Wang, D.; Ma, J.; Kong, Q.; Xiao, D.; Gu, L.; Zhou, X.; Zhao, J.; Dong, S.; He, B.; Avdeev, M.; Shi, S.; Cui, G.; Chen, L. Uncovering the Potential of M1-Site-Activated NASICON Cathodes for Zn-Ion Batteries. *Adv. Mater.* **2020**, *32* (14), 1907526.

(35) Pan, A.; Liu, J.; Zhang, J.-G.; Xu, W.; Cao, G.; Nie, Z.; Arey, B. W.; Liang, S. Nano-Structured $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Carbon}$ Composite for High-Rate Lithium-Ion Batteries. *Electrochem. Commun.* **2010**, *12* (12), 1674–1677.

(36) Rietveld, H. M. A Profile Refinement Method for Nuclear and Magnetic Structures. J. Appl. Crystallogr. 1969, 2 (2), 65–71.

(37) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6* (1), 15–50.

(38) Kresse, G.; Hafner, J. Norm-Conserving and Ultrasoft Pseudopotentials for First-Row and Transition Elements. *J. Phys.: Condens. Matter* **1994**, *6* (40), 8245–8257.

(39) Blöchl, P. E.; Jepsen, O.; Andersen, O. K. Improved Tetrahedron Method for Brillouin-Zone Integrations. *Phys. Rev. B* **1994**, 49 (23), 16223–16233.

(40) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865– 3868.

(41) Wang, L.; Maxisch, T.; Ceder, G. Oxidation Energies of Transition Metal Oxides within the $\operatorname{CGA}+\operatorname{U}\$ Framework. *Phys. Rev. B* **2006**, *73* (19), 195107.

(42) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* **2013**, *1* (1), 011002.

(43) Jain, A.; Hautier, G.; Ong, S. P.; Moore, C. J.; Fischer, C. C.; Persson, K. A.; Ceder, G. Formation Enthalpies by Mixing GGA and GGA \$+\$ \$U\$ Calculations. *Phys. Rev. B* **2011**, *84* (4), 045115.

(44) Bartel, C. J. Review of Computational Approaches to Predict the Thermodynamic Stability of Inorganic Solids. *J. Mater. Sci.* 2022, *57*, 10475.

(45) Sai Gautam, G.; Canepa, P.; Urban, A.; Bo, S.-H.; Ceder, G. Influence of Inversion on Mg Mobility and Electrochemistry in Spinels. *Chem. Mater.* **2017**, *29* (18), 7918–7930.

(46) Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G. Python Materials Genomics (Pymatgen): A Robust, Open-Source Python Library for Materials Analysis. *Comput. Mater. Sci.* **2013**, *68*, 314–319. (47) Henkelman, G.; Jónsson, H. Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points. *J. Chem. Phys.* **2000**, *113* (22), 9978–9985.

(48) Xiao, Y.; Jun, K.; Wang, Y.; Miara, L. J.; Tu, Q.; Ceder, G. Lithium Oxide Superionic Conductors Inspired by Garnet and NASICON Structures. *Adv. Energy Mater.* **2021**, *11* (37), 2101437.

(49) Kwon, B. J.; Yin, L.; Bartel, C. J.; Kumar, K.; Parajuli, P.; Gim, J.; Kim, S.; Wu, Y. A.; Klie, R. F.; Lapidus, S. H.; Key, B.; Ceder, G.; Cabana, J. Intercalation of Ca into a Highly Defective Manganese Oxide at Room Temperature. *Chem. Mater.* **2022**, *34* (2), 836–846. (50) Zou, Z.; Ma, N.; Wang, A.; Ran, Y.; Song, T.; Jiao, Y.; Liu, J.; Zhou, H.; Shi, W.; He, B.; Wang, D.; Li, Y.; Avdeev, M.; Shi, S. Relationships Between Na⁺ Distribution, Concerted Migration, and Diffusion Properties in Rhombohedral NASICON. *Adv. Energy Mater.* **2020**, *10* (30), 2001486.

(51) Canepa, P.; Sai Gautam, G.; Hannah, D. C.; Malik, R.; Liu, M.; Gallagher, K. G.; Persson, K. A.; Ceder, G. Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chem. Rev.* 2017, *117* (5), 4287–4341.

(52) Malik, R.; Burch, D.; Bazant, M.; Ceder, G. Particle Size Dependence of the Ionic Diffusivity. *Nano Lett.* **2010**, *10* (10), 4123–4127.

(53) Jun, K.; Sun, Y.; Xiao, Y.; Zeng, Y.; Kim, R.; Kim, H.; Miara, L. J.; Im, D.; Wang, Y.; Ceder, G. Lithium Superionic Conductors with Corner-Sharing Frameworks. *Nat. Mater.* **2022**, *21*, 924.