

# Kinetic Monte Carlo Simulations of Sodium Ion Transport in NaSICON Electrodes

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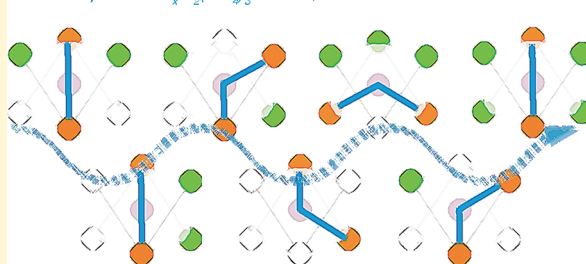
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Supporting Information

**ABSTRACT:** The development of high-performance sodium (Na) ion batteries requires improved electrode materials. The energy and power densities of Na superionic conductor (NaSICON) electrode materials are promising for large-scale energy storage applications. However, several practical issues limit the full utilization of the theoretical energy densities of the NaSICON electrodes. A pressing challenge lies in the limited sodium extraction in low Na content NaSICONs, e.g.,  $\text{Na}_1\text{V}^{\text{IV}}\text{V}^{\text{IV}}(\text{PO}_4)_3 \leftrightarrow \text{V}^{\text{V}}\text{V}^{\text{IV}}(\text{PO}_4)_3 + \text{e}^- + \text{Na}^+$ . Therefore, it is important to quantify the Na-ion mobility in a broad range of NaSICON electrodes. Using a kinetic Monte Carlo approach bearing the accuracy of first-principles calculations, we elucidate the variability of Na-ion transport vs Na content in three important NaSICON electrode materials,  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ . We show  $\text{Na}^+$  transport in NaSICON electrode materials is almost entirely determined by the local electrostatic and chemical environment set by the transition metals and the polyanionic scaffold. The competition with the ordering-disordering phenomena of Na vacancies also plays a role in influencing Na transport. We identify the Na content providing the highest room-temperature diffusivities in these electrodes, i.e.,  $\text{Na}_{2.7}\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_{2.9}\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_{2.6}\text{Cr}_2(\text{PO}_4)_3$ . We link the variations in the  $\text{Na}^+$  kinetic properties by analyzing the competition of ligand field stabilization transition metal ions and their ionic radii. We interpret the limited Na extraction at  $x = 1$  observed experimentally by gaining insights into the local Na vacancy interplay. Targeted chemical substitutions of transition metals disrupting local charge arrangements will be critical to reducing the occurrence of strong  $\text{Na}^+$ -vacancy orderings at low Na concentrations, thus expanding the accessible capacities of these electrode materials.

*$\text{Na}^+$  transport in  $\text{Na}_x\text{M}_2(\text{PO}_4)_3$   $\text{M} = \text{Ti}, \text{V}$  and  $\text{Cr}$  via kinetic Monte Carlo*



## 1. INTRODUCTION

Having achieved widespread commercialization, rechargeable lithium (Li)-ion batteries (LIBs) are now at the risk of geopolitically constrained supply chains of key raw materials, such as cobalt, nickel, and Li.<sup>1–3</sup> Sodium (Na)-ion batteries (SIBs) appear to be promising alternatives to the LIB analogs, as Na-metal can be harvested directly from seawater.<sup>4–6</sup> Extensive research is underway to optimize electrodes and electrolytes for SIBs.<sup>7–21</sup> One of the material classes for NIBs is the polyanionic sodium superionic conductor (NaSICON), discovered by Hong et al.,<sup>22,23</sup> a framework studied for its fast Na-conducting properties. Electrodes crystallizing in the NaSICON framework, with formula  $\text{Na}_x\text{M}_2(\text{PO}_4)_3$  (where  $\text{M}$  = transition metal), can be highly tuned to achieve promising energy densities,<sup>10,14,24</sup> by changing the ratio and types of transition metals in the NaSICON, such as  $\text{Na}_x\text{TiV}(\text{PO}_4)_3$ ,  $\text{Na}_x\text{TiMn}(\text{PO}_4)_3$ ,  $\text{Na}_x\text{VMn}(\text{PO}_4)_3$ , and  $\text{Na}_x\text{CrMn}(\text{PO}_4)_3$ .<sup>10,13</sup>

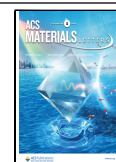
For most NaSICON electrodes, the accessible capacity is significantly lower than the theoretical value, which is linked to difficulties in reversibly extracting the entire available Na

content. For example, in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , the reversible extraction of four sodium ions entails the utilization of all vanadium redox states ( $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$ ,  $\text{V}^{\text{IV}}/\text{V}^{\text{III}}$ , and  $\text{V}^{\text{III}}/\text{V}^{\text{II}}$ ) with a theoretical gravimetric capacity of  $\sim 235 \text{ mAh g}^{-1}$ . In practice, only two sodium ions can be reversibly extracted from  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  up to  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ .<sup>14,15,24–26</sup> While Gopalakrishnan and Rangan suggested the possibility of chemically extracting the last  $\text{Na}^+$  forming  $\text{V}_2(\text{PO}_4)_3$ ,<sup>27</sup> successive endeavors have proven unsuccessful. Hence, understanding the factors that limit reversible Na extraction within NaSICONs and facilitating the same remains an active topic of research.

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In this Letter, using density functional theory (DFT) based kinetic Monte Carlo (kMC) simulations, we unveil the physical origins for the variation in  $\text{Na}^+$  transport properties in three NaSICON electrode materials, namely,  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ . Our analysis reveals the kinetic limits to reversibly extracting Na ions in these NaSICONs apart from identifying the Na-composition ranges to achieve a high  $\text{Na}^+$  diffusivity. The macroscopic  $\text{Na}^+$  transport is highly influenced by the interplay between Na-vacancy arrangements and transition metals. Our results shed light on the optimization of NaSICON electrodes for improved reversible capacities.

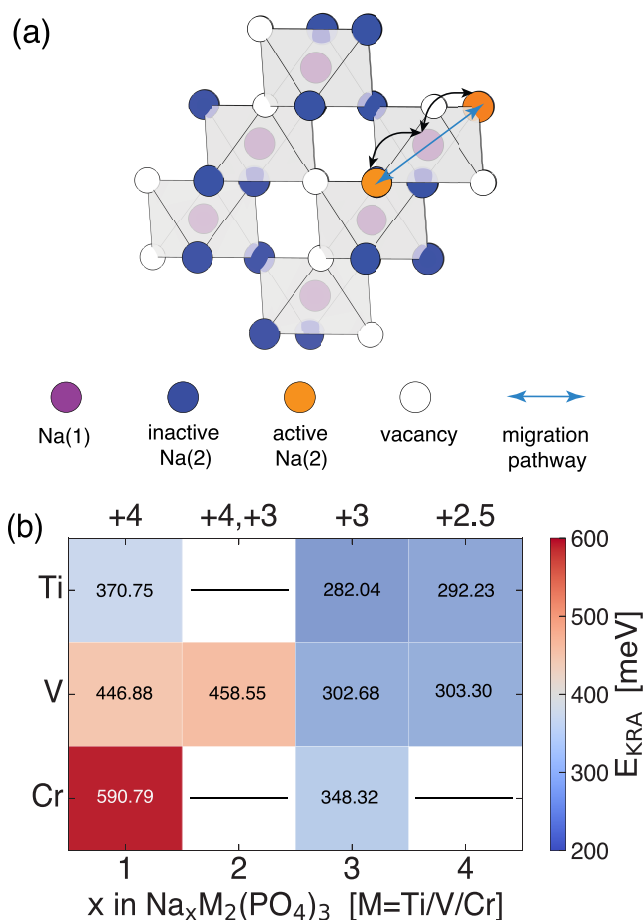
## 2. RESULTS

To investigate the  $\text{Na}^+$  transport in  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ , we rely on a combination of DFT calculations, constructing a cluster expansion Hamiltonian, and performing kinetic Monte Carlo simulations (*vide infra*).<sup>28,29</sup> The ground-state structures representing specific Na-vacancy arrangements at different Na compositions of the  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$  NaSICON were taken from refs 10 and 14. To estimate the  $\text{Na}^+$  migration barriers in the three NaSICONs, we selected several sodium compositions, including  $x = 1, 3$ , and 4 in  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ;  $x = 1, 2, 3$ , and 4 in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ ; and  $x = 1$  and 3 in  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ .

At  $x = 1$  and 4, all three NaSICONs crystallize in the rhombohedral space group ( $R\bar{3}c$  or  $R\bar{3}$ ). While  $\text{Na}_4\text{Cr}_2(\text{PO}_4)_3$  is included for completeness in this investigation, it is not expected to be stable (due to the instability of  $\text{Cr}^{\text{II}}$  in the solid state<sup>30</sup>) and has never been reported experimentally.  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  configurations with monoclinic ( $Cc$  or  $C2/c$ ) symmetry represent the compositions with the lowest formation energies in the  $\text{Na}_x\text{M}_2(\text{PO}_4)_3$  pseudobinary tie line of all the three NaSICONs.<sup>10,14</sup> Recent investigations predicted the mixed-valence  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  as a thermodynamically stable phase.<sup>14,24</sup>

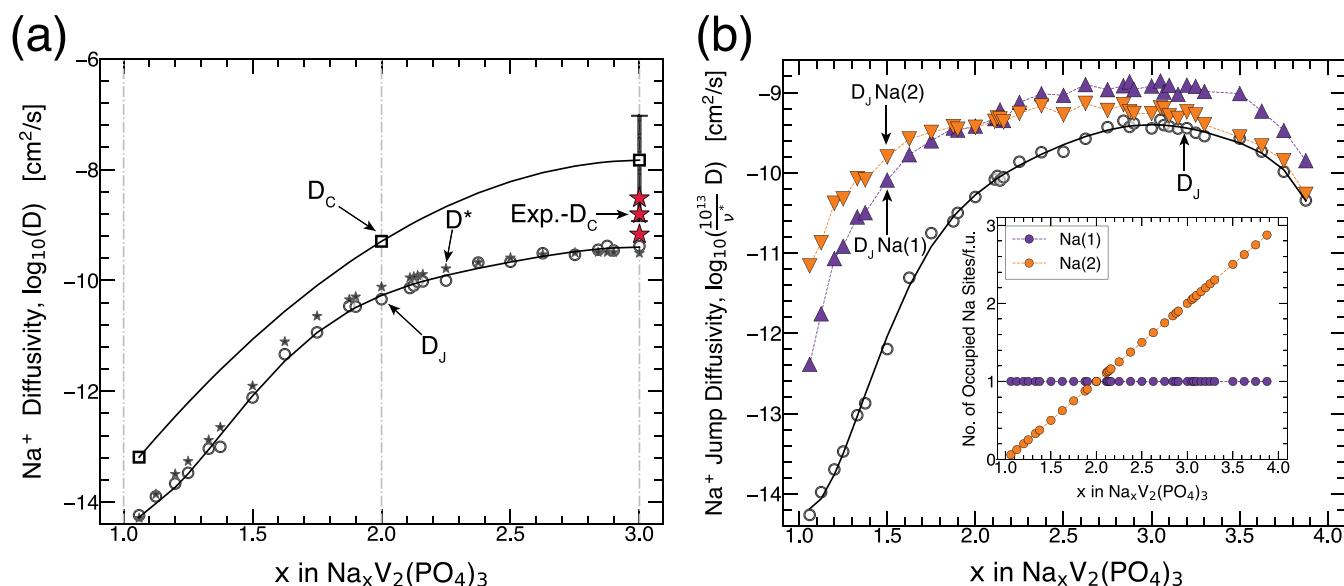
Each Na-vacancy (Va) configuration at the above Na compositions was optimized using the strongly constrained and appropriately normed exchange and correlation functional within DFT.<sup>31</sup> A Hubbard  $U$  correction (SCAN+ $U$ ) was applied, which has been confirmed to accurately predict the redox electrochemistry during Na (de)intercalation.<sup>14,29,30,32,33</sup> We use the nudged elastic band (NEB) method to simulate the  $\text{Na}^+$  migration barriers.<sup>34</sup>

Typically, the migration mechanism of ions in fast conductors is ascribed to be a local property of the immediate chemical environment of the migrating species, which is strongly influenced by the local ion-vacancy configuration(s).<sup>28,29,35,36</sup> Figure 1 shows the relevant local portion of the NaSICON structure—the migration unit (MU)—that is sufficient to capture the Na migration with variations in the local configurations of Na and vacancies. Figure 1a represents the general MU in  $\text{Na}_x\text{M}_2(\text{PO}_4)_3$ , where groups of corner-shared octahedra contain six Na(2) sites centered around a Na(1) site. For the sake of visualization, the  $\text{MO}_6$  and the  $\text{PO}_4^{3-}$  groups are not shown. Within each MU octahedron, two Na(2) sites will be “active”, taking part in the  $\text{Na}(2) \leftrightarrow \text{Na}(1) \leftrightarrow \text{Na}(2)$  migration event, whereas the remaining four Na(2) sites and/or vacancies will be “inactive” (Figure 1a) and spectating the process of Na migration. Herein, we consider a single Na migration hop  $\text{Na}(2) \leftrightarrow \text{Na}(1)$  as the fundamental Na-ion migration event in a single MU.<sup>22,23,26,29,37,38</sup>



**Figure 1.** Model of  $\text{Na}^+$  migration in the NaSICON  $\text{Na}_x\text{M}_2(\text{PO}_4)_3$ , identifying the migration unit (MU) and associated Na-ion migration barriers. (a) A representation of the Na-vacancy sublattice in NaSICON, illustrated by the corner-sharing octahedra. Two Wyckoff positions, the Na(1) (6b) sites, are shown by purple circles and the Na(2) (18e) sites by orange or blue circles, depending on the participation of the Na(2) site in a migration event. Empty circles denote vacancies. Each Na(1) site is surrounded by six nearest neighbor Na(2) sites. In each octahedron, two Na(2) sites participate in the Na-ion migration pathway (orange circles connected by blue line), whereas every single hop  $\text{Na}(2) \leftrightarrow \text{Na}(1)$  is denoted by the black double-arrows. (b) Computed  $E_{\text{KRA}}$ 's for the migration event  $\text{Na}(2) \leftrightarrow \text{Na}(1)$  in the MU (values are indicated in each box), with varied Na compositions ( $x$ ) and transition metals (M). Black lines indicate compositions where migration barriers were not computed (see the main text). Na compositions are shown in the bottom  $x$  axis, and the formal oxidation states of the transition metals are in the top  $x$  axis.

The collective diffusion of Na ions in the NaSICON electrodes can be captured by our lattice model, which is composed of thousands of MUs, with different Na-vacancy orderings. Indeed, ensembles of MUs are used to tessellate periodically the  $\text{Na}_x\text{M}_2(\text{PO}_4)_3$  structures in the composition range  $1 \leq x \leq 4$ . At intermediate compositions ( $1 < x < 4$ ), a variety of MUs with different local Na vacancy arrangements is sufficient to approximate the migrating environments of the Na ions. The subsets of crystallographic sites of the migrating Na ions are fully encompassed by an ensemble of MUs incorporating all possible Na-vacancy occupation arrangements. Therefore, the partial occupations of Na sites as refined



**Figure 2.** Predicted diffusivities of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  at 300 K. Panel a plots  $D_J$  (circles),  $D^*$  (stars), and  $D_C$  (squares). The pre-exponential factor is assumed as  $1 \times 10^{13}$  Hz.<sup>35</sup> Vertical lines represent the phase boundaries derived from the phase diagram at  $\sim 300$  K.<sup>14</sup> Values of  $D_C$  are only in the single-phase regions, i.e.,  $x = 1, 2$ , and  $3$ . At intermediate compositions (two-phase regions), the thermodynamic factor  $\Theta = 0$  leads to zero  $D_C$ . In the two-phase regions,  $D_C$  is approximated using Vegard's law. The standard deviation of our predictions is shown at  $x = 3.0$ . Solid lines in black are the polynomial model fitted on the predictions. The experimental values of chemical diffusivity (exp.- $D_C$ , red stars) are from ref 47 at  $x = 3$ . Panel b plots  $D_J$  (black circles),  $D_J\text{Na}(1)$ , which arises from the Na(1)-ion movement (purple triangles), and  $D_J\text{Na}(2)$  from the Na(2)-ion movement (orange triangles). In panel b, all  $D_J$ 's are renormalized with a  $10^{13}/\nu^*$  factor, due to the uncertainty in the prefactor  $\nu^*$ .<sup>35,48</sup> The inset shows the computed occupation number of Na(1) (in purple) and Na(2) (in yellow) sites per formula unit vs.  $x$  extracted from the kMC simulations at 300 K.

from experimental techniques, such as X-ray diffraction,<sup>14,24,39,40</sup> can be described by the 3D networks formed by thousands of MUs.

Based on the assumption that the transport property relies mainly on the local Na-vacancy orderings, all possible migration pathways within the MUs were extensively simulated using the NEB method combined with SCAN+*U* calculations. The computed migration barriers are reported in Section 1 of the Supporting Information (SI). We did not evaluate the migration energy of  $\text{Na}^+$  at  $x = 2$  in  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$  and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ , as well as at  $x = 4$  in  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ , since they have not been reported experimentally.

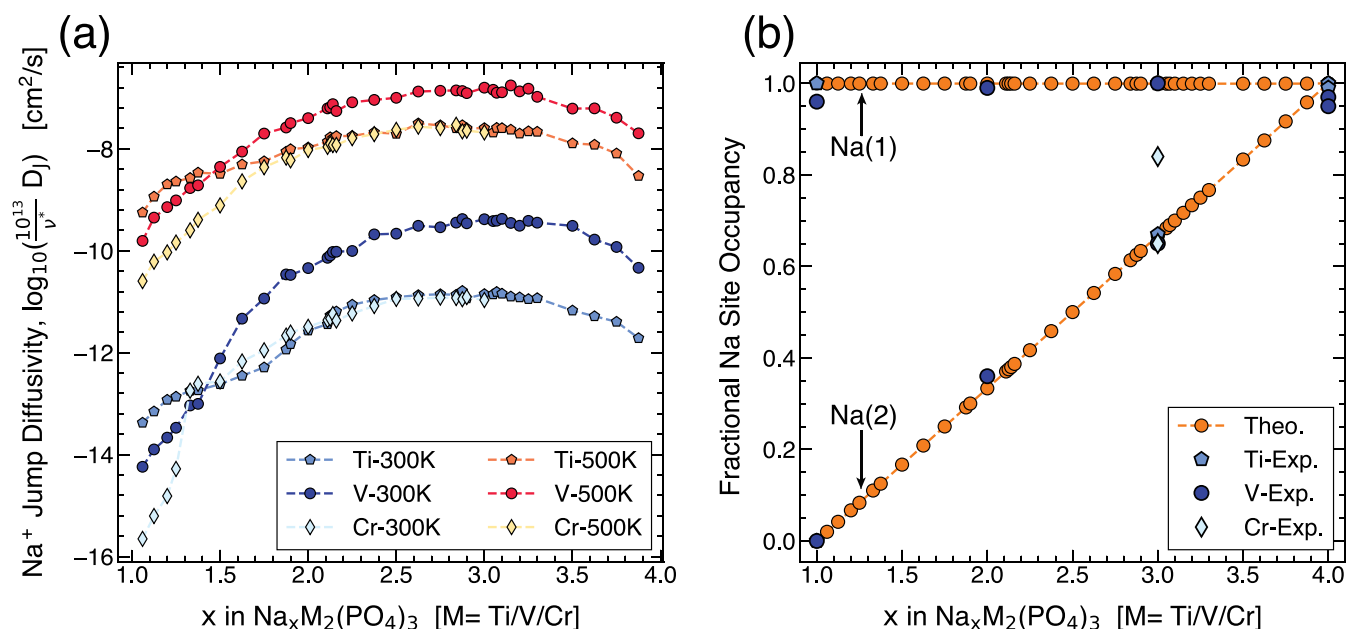
The computed migration barrier ( $E_{\text{barrier}}$ ) results are in good agreement with prior computational and experimental studies (see section 1 of the SI). For example, for  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$ , the  $E_{\text{barrier}} \sim 621$  meV agrees well with the  $\sim 620$  meV experimental value for the  $\alpha$  phase of the same system.<sup>16</sup> Similarly, for  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , we predict an  $E_{\text{barrier}} \sim 455$  meV, which is comparable with the range of values 353–513 meV computed with the HSE06 functional.<sup>41</sup> In the case of  $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ , the predicted  $E_{\text{barrier}} \sim 530$  meV underestimates the experimental value of  $\sim 750$  meV from ref 39.

The directional dependence of  $E_{\text{barrier}}$  is removed by using the kinetically resolved activation barriers ( $E_{\text{KRA}}$ ), as defined in ref 35. Low values of  $E_{\text{KRA}}$  correspond to low migration barriers and vice versa. The computed  $E_{\text{KRA}}$  values of  $\text{Na}^+$  migration events of the type  $\text{Na}(2) \leftrightarrow \text{Na}(1)$  of an MU that best represents the ground state configurations at different  $x$  are shown in Figure 1b. The lowest values of  $E_{\text{KRA}}$  are calculated at compositions  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  and follow the order  $\text{Ti} \sim 282$  meV <  $\text{V} \sim 303$  meV <  $\text{Cr} \sim 348$  meV. In contrast, the maximum  $E_{\text{KRA}}$  values are observed at  $x \sim 1$ , in agreement with existing reports.<sup>16,26,39</sup> The barriers at  $x = 3$  across the

different NaSICONs follow the ligand field stabilization energies (LFSE) for  $\text{Ti}^{\text{III}}(d^1) < \text{V}^{\text{III}}(d^2) < \text{Cr}^{\text{III}}(d^3)$ , and the decreasing order of the transition metal sizes.<sup>42,43</sup> Note that LFSE also correlates with the NaSICON pseudobinary formation energies  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3 \gg \text{Na}_3\text{V}_2(\text{PO}_4)_3 > \text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ , thus increasing the Na migration barriers in the same order.<sup>10</sup>

Starting from the computed  $E_{\text{KRA}}$  encompassing several Na-vacancy arrangements in the MU (see section 2 of the SI), a local cluster expansion (LCE) Hamiltonian<sup>35</sup> was trained for each NaSICON system. We use the LCE together with our kinetic Monte Carlo simulation package<sup>44</sup> to investigate the  $\text{Na}^+$  transport within the NaSICON structures (see sections 2 and 3 in the SI), by performing long-time (on the order of milliseconds) and large-scale ( $8 \times 8 \times 8$  formula units corresponding to 4096 Na sites) simulations. The LCE Hamiltonian could investigate  $\text{Na}^+$  benchmarked on barriers obtained from first-principles calculations. The accuracy of predicted  $E_{\text{KRA}}$ 's, obtained from the LCE formalism is bound within root mean square (RMS) errors of  $\pm 31.75$  meV for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ ,  $\pm 25.29$  meV for  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ , and  $\pm 35.81$  meV for  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$  (see section 2 in the SI), which are within the perceived accuracy of migration barriers computed from first principles ( $\pm 50$  meV).<sup>45</sup>

By tracking all possible Na migration events of each NaSICON, we simulated the  $\text{Na}^+$  diffusion, quantified by (i) the jump diffusivity ( $D_J$ ), (ii) the tracer diffusivity ( $D^*$ ), and (iii) the chemical diffusivity ( $D_C$ ).<sup>36</sup> From the temperature vs composition phase diagrams of these NaSICON systems,<sup>14</sup> using canonical Monte Carlo simulations, 1850 initial Na-vacancy configurations for each system (50 different configurations at 37 unique Na compositions) with specific Na-vacancy arrangements were generated at  $\sim 973$  K, which is



**Figure 3.** Computed  $\text{Na}^+$   $D_j$  at 300 and 500 K (panel a) and fractional occupancy at 300 K (panel b) of Na(1) and Na(2) sites in  $\text{Na}_x\text{M}_2(\text{PO}_4)_3$  (M = Ti, V, or Cr). Due to the uncertainty in the prefactor  $\nu^*$ , all  $D_j$  values are normalized using a  $10^{13}/\nu^*$  factor. In panel a, data at 300 and 500 K are shown in blue and red/yellow symbols. For  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ , Na extraction can only occur for  $1 \leq x \leq 3$ .<sup>17</sup> The computed results (Theo.) in panel b are denoted by orange circles, with experimental values in blue shapes.<sup>15,18,24,52,53</sup> The computed Na-site occupancy does not show significant differences among the three NaSICONs within our predictions; hence, data for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  is plotted in panel b.

the typical synthesis temperature of these NaSICONs. Thus, these model structures mimic Na-vacancy configurations that are obtained postsynthesis<sup>17,22–24,26,46</sup> and are used in the kMC simulations as starting configurations. Subsequently, we performed 500 equilibration sweeps: one sweep is the total number of Na-vacancy sites in the simulation model, i.e., 4096 followed by 3000 kMC sampling sweeps of each configuration and statistically averaged the transport properties over a wide temperature range (300 to 900 K, see section 3 of the SI).

We used  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  to discuss the behavior of the diffusion coefficients predicted by our kMC simulations. Figure 2a shows the computed  $D_j$ ,  $D^*$ , and  $D_C$  values for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  at 300 K as a function of  $x$ .

We derived the  $D_j$  by tracking the center-of-mass of all of the migrating  $\text{Na}^+$  species, including the cross-correlations between different Na ions, which are excluded in the tracer diffusivity  $D^*$ . For this reason, in Figure 2a,  $D_j$  and  $D^*$  are different, but of similar magnitude, highlighting minimal contributions from cross-correlations, similar to observations in other electrode materials.<sup>35</sup> From the statistical analysis of the computed diffusivities, we derived a standard deviation (Figure 2a) of approximately  $\pm 1$  order of magnitude in diffusivity ( $\pm 120$  meV in terms of  $E_{\text{barrier}}$ ).<sup>45</sup>

In  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , the  $\text{Na}^+$  jump diffusivities of Figure 2a increase progressively from low Na content ( $\sim 5.77 \times 10^{-15}$  cm<sup>2</sup> s<sup>-1</sup> at  $x \sim 1$ ) to high Na content ( $\sim 4.16 \times 10^{-10}$  cm<sup>2</sup> s<sup>-1</sup> at  $x = 3.0$ ). Diffusivities for  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  are in good agreement with existing measurements.<sup>26,38,49</sup>

We derive a fourth order polynomial fit for the monotonically increasing  $D_j$  across  $1 \leq x \leq 3$ , namely,  $D_j(x) = C + E_1x + E_2x^2 + E_3x^3 + E_4x^4$  (black line in Figure 2). The coefficients of the fit  $E_1$ ,  $E_2$ ,  $E_3$ , and  $E_4$  are reported in the SI. The fitted polynomial reflects the concentration dependence of  $D_j$ .

The chemical diffusivity  $D_C$  depends on the thermodynamic factor  $\Theta$ , as per  $D_C = D_j\Theta$ ; values of  $\Theta$  are from ref 14.  $D_j$  and  $\Theta$  contribute oppositely to  $D_C$ . As  $\Theta$  is related to the gradient of the Na chemical potential (eq 13 in SI),  $\Theta$  usually takes large values for highly ordered (stable) configurations (Supporting Figure 16 in the SI), increasing the  $D_C$  of the corresponding ordered phase. In contrast, low values of  $D_j$  are typically found in ordered phases due to a lack of accessible vacant sites controlled by strong ion-vacancy ordering interactions. In  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ ,  $D_C$  is dominated by  $D_j$ , as denoted by the relatively low values of room temperature chemical diffusivity at  $x = 1$  and 2 (instead of the large values as controlled by  $\Theta$ ).<sup>35</sup> Gray vertical lines in Figure 2a depict the phase boundaries for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  from ref 14 at 300 K. The predicted values of  $D_C$  at  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  ( $1.18 \times 10^{-9}$  to  $9.35 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>) are higher than the experimental values ( $4.59 \times 10^{-10}$  to  $2.0 \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup>) measured by electrochemical impedance spectroscopy (EIS).<sup>38,47</sup>

While some experimental values of  $D_C$ <sup>38,47</sup> fall within the standard deviations of our predictions, other experimental studies have reported significantly different  $D_C$  values, such as  $3 \times 10^{-15}$  and  $6 \times 10^{-13}$  cm<sup>2</sup> s<sup>-1</sup> measured using the galvanostatic intermittent titration technique (GITT),<sup>50</sup> and  $4 \times 10^{-14}$  to  $2.48 \times 10^{-13}$  cm<sup>2</sup> s<sup>-1</sup> measured by EIS.<sup>51</sup> Such large differences in experimental  $D_C$  values can be attributed to different synthesis procedures of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , which can affect the (im)purity of the particles, the particle sizes, and the defect concentrations, thus causing significant variations in transport properties.<sup>38</sup> Nevertheless, we expect our kMC simulations to yield an accurate value of  $D_C$  within bulk  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  given that our confidence interval of calculated  $D_C$  is quite narrow.

The computed  $D_C$  for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  at 300, 700, and 900 K (Supporting Figure 17 of the SI) is superimposed on the

temperature–composition phase diagram,<sup>14</sup> where the single-phase regions are always connected by dashed lines representing the two-phase regions. For all temperatures explored, we observe an increase in  $D_C$  in the composition range  $1 \leq x \leq 3$ . Unsurprisingly, the  $D_C$  values increase for increasing temperatures (i.e., at  $x = 3$  from  $1.48 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at 300 K to  $2.5 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  at 900 K), signifying high thermally activated motion of  $\text{Na}^+$ .

Given the dominating contributions of  $D_j$  to the effective chemical diffusivity,<sup>36</sup> we can gain valuable insights about the jump diffusivity ( $D_j$ ) of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  at 300 K by separating  $D_j$  into the specific contributions from each sodium site, i.e.,  $\text{Na}(1)$  and  $\text{Na}(2)$  in Figure 2b. Here, we obtain  $D_j\text{Na}(1)$  in the  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  structure by tracking all unique  $\text{Na}^+$  hopping events of the type  $\text{Na}(1) \rightarrow \text{Na}(2)$ , while we track  $\text{Na}(2) \rightarrow \text{Na}(1)$  for  $D_j\text{Na}(2)$ . The differences between the overall  $D_j$  and individual  $D_j\text{Na}(1)$  and  $D_j\text{Na}(2)$  originate mainly from the number of the  $\text{Na}(1)$  and  $\text{Na}(2)$  sites available (see eqs 8, 9, and 10 in SI).

Values of  $D_j\text{Na}(2)$  and  $D_j\text{Na}(1)$  show similar magnitudes and appear higher than the overall  $D_j$ , especially in the composition range  $1 \leq x \leq 3$ . Both the  $D_j\text{Na}(1)$  and  $D_j\text{Na}(2)$  achieve their maxima at intermediate Na compositions, specifically  $1.21 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  at  $x \approx 2.94$  for  $D_j\text{Na}(1)$  and  $1.15 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  at  $x \approx 2.71$  for  $D_j\text{Na}(2)$ . We observe a sharp decrease of Na diffusivity near  $x \sim 1$ , where values  $D_j\text{Na}(2)$  and  $D_j\text{Na}(1)$  are  $6.91 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  and  $4.11 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ , respectively.

The number of occupied Na sites extracted from kMC simulations (inset of Figure 2b) agrees well with existing site occupations at 300 K from experiment and theory.<sup>14,24</sup>  $\text{Na}(1)$  sites (purple line) are always fully occupied in the range  $1 \leq x \leq 3$ , whereas the  $\text{Na}(2)$  occupation (orange) varies from empty at  $x = 1$  to fully occupied, with three  $\text{Na}(2)$  sites per formula unit at  $x = 4$ . The number of occupied  $\text{Na}(2)$  sites is much lower than that of  $\text{Na}(1)$  at compositions around  $x = 1$ ,<sup>14</sup> reflecting the difference in stability of the two sites at  $x = 1$ , which results in boosting the  $D_j\text{Na}(2)$  over  $D_j\text{Na}(1)$ . Effects of cross-correlations among Na ions distributed between  $\text{Na}(1)$  and  $\text{Na}(2)$  sites remain convoluted in the computed values of  $D_j$ .

We discuss the kMC predictions of two additional NaSICONs,  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ , with similar electrochemical behavior to  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ .<sup>10,14–18</sup> For  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ , the sodium composition ranges  $1 \leq x \leq 3$  and  $3 \leq x \leq 4$  are accessible electrochemically,<sup>10,18</sup> whereas for  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ , Na extraction only occurs in  $1 \leq x \leq 3$ .<sup>10,17</sup> Similar to  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$  show single phases at  $x = 1$  and  $x = 3$ .<sup>10,17,18,52,53</sup> Figure 3a shows the computed  $D_j$  of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$  at 300 and 500 K.

For all systems, we observe an increase of  $D_j$  in the composition range  $1 \leq x \leq 3$ , followed by a gradual decrease of  $D_j$  for  $3 < x \leq 4$  in  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$  and  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ . At 300 K,  $D_j$  reaches a maximum for all systems at  $x \sim 3$ , with  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  displaying a higher magnitude of  $D_j$  in the range  $1.5 \leq x \leq 4$  than  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$  and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ . At 500 K, in comparison, the  $D_j$  values of all three NaSICONs were of a similar order of magnitude, corresponding intuitively to higher diffusion rates with increasing temperatures.

The maximum values of  $D_j$  occur at similar compositions for all NaSICONs,  $4.09 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  at  $x \sim 2.9$ ,  $1.71 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$  at  $x \sim 2.7$ , and

$1.39 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$  at  $x \sim 2.6$ , respectively. Similarly, the lowest values of  $D_j$  occur at a low Na content (i.e.,  $x \sim 1$ ) for all NaSICONs. For example, the lowest  $D_j$  among the NaSICONs at  $x \sim 1$  is  $2.2 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Na}_1\text{Cr}_2(\text{PO}_4)_3$ . The low values of  $D_j$  at  $x \sim 1$  suggest that the reversible extraction of the “last” Na ion from NaSICON electrodes may be limited also by the poor kinetics at low Na contents.

To understand the  $\text{Na}^+$  distributions at 300 K, we extract the fractional occupancies of  $\text{Na}(1)$  and  $\text{Na}(2)$  sites (Figure 3b) and compare them with the experimental data of these NaSICON systems. At room temperature, we observe high stability of the  $\text{Na}(1)$  site across the entire Na concentration range ( $1 \leq x \leq 4$ ), where it remains fully occupied, while  $\text{Na}(2)$  occupancy monotonically increases with increasing  $x$ . Our kMC results agree quantitatively with the experimentally refined  $\text{Na}(1)/\text{Na}(2)$  occupations.<sup>15,18,24,52,53</sup> In the case of  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$ , the predicted occupation of  $\text{Na}(1)$  ( $\sim 1$ ) overestimates the experimental data ( $\sim 0.84$ ), which suggests that the nominal composition may deviate from the real composition of synthesized NaSICONs.<sup>53</sup>

### 3. DISCUSSION

In this Letter, using kMC simulations that bear the accuracy of DFT calculations, we investigated the variability of Na-ion transport vs Na content in three important NaSICON electrodes for Na-ion batteries:  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ . We demonstrated that the ion transport properties ( $D_j$ ,  $D^*$ , and  $D_C$ ) of NaSICONs have a configurational dependence on the local sodium vacancy arrangements near the migration events.

In the three NaSICONs, we observed an increase of  $D_j$  from low Na concentrations of  $x \sim 1$  to  $x \sim 3$ . For  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ , we observed a decrease in  $D_j$  in the composition range  $3 < x \leq 4$  (Figure 3a).

**Interplay of Ligand Field Stabilization and Ionic Radii of Transition Metals.** Two main factors: (i) the ligand field stabilization of transition metals and their (ii) ionic radii, can explain variations of migration barriers and diffusivities in these NaSICONs as a function of Na composition.

Different NaSICONs exhibit different migration barriers at the same Na content (see Figure 1b), with implications for the observed  $D_j$ . For example, at  $x \sim 1$ , the highest  $E_{\text{KRA}} \sim 591 \text{ meV}$  is exhibited by  $\text{Na}_1\text{Cr}_2(\text{PO}_4)_3$ , well exceeding  $447 \text{ meV}$  in  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ , and  $371 \text{ meV}$  in  $\text{Na}_1\text{Ti}_2(\text{PO}_4)_3$ . Since at  $x \sim 1$  all transition metals, Cr, Ti, and V, are tetra-valent (verified by the magnetic moments of Supporting Figure 7 in the SI), differences in migration energies in NaSICONs at this composition are controlled by the transition metal ionic radii, which will lead to different sizes of “bottlenecks” for the migrating Na ion.<sup>24</sup>

At  $x = 1$ , the transition metal ionic radii follow the trend of  $\text{Ti}^{\text{IV}} (\sim 0.61 \text{ \AA}) > \text{V}^{\text{IV}} (\sim 0.58 \text{ \AA}) > \text{Cr}^{\text{IV}} (\sim 0.55 \text{ \AA})$ , which causes a similar variation in the lattice parameters.<sup>10,24,52</sup> Thus, the sizes of the bottlenecks (i.e., the transition state) for the migrating  $\text{Na}^+$  reduce in the order of  $\text{Na}_1\text{Ti}_2(\text{PO}_4)_3 > \text{Na}_1\text{V}_2(\text{PO}_4)_3 > \text{Na}_1\text{Cr}_2(\text{PO}_4)_3$ ,<sup>24</sup> reflecting an identical trend in  $D_j$  values observed (see Figure 3a). Furthermore, the polyhedral volumes of transition-metal octahedra are  $\sim 9.80 \text{ \AA}^3$  for  $\text{TiO}_6$ ,  $\sim 9.33 \text{ \AA}^3$  for  $\text{VO}_6$ , and  $\sim 8.77 \text{ \AA}^3$  for  $\text{CrO}_6$ . The bond distance between the migrating  $\text{Na}^+$  at the transition state and nearby  $\text{O}^{2-}$  (which is linearly correlated with the migration barriers) follows a sequence of  $\text{Na}_1\text{Ti}_2(\text{PO}_4)_3 (\sim 2.36 \text{ \AA}) >$

$\text{Na}_1\text{V}_2(\text{PO}_4)_3$  ( $\sim 2.30$  Å)  $>$   $\text{Na}_1\text{Cr}_2(\text{PO}_4)_3$  ( $\sim 2.27$  Å). This sequence indicates the narrower sizes of the migration “bottleneck” from  $\text{Na}_1\text{Ti}_2(\text{PO}_4)_3$ , via  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ , to  $\text{Na}_1\text{Cr}_2(\text{PO}_4)_3$ , hence explaining the reduced values of  $D_j$  in Figure 3a.

The impact of transition metal ionic radii is lower at a higher Na content (i.e., at  $x \sim 3$ ), since the large ionic radius of  $\text{Na}^+$  (when six-coordinated) dictates lattice parameters more significantly. Thus, variations observed in  $E_{\text{barrier}}$  and  $D_j$  are to be linked to the electronic structure (and LFSE) of the transition metals involved than to changes in lattice parameters or bottleneck sizes. Specifically, LFSE stabilizes  $\text{Cr}^{\text{III}}$  ( $3d^3$ ) more than  $\text{V}^{\text{III}}$  ( $3d^2$ ; see Supporting Figure 8 in the SI), due to the high stability of the half-filled high-spin  $t_{2g}$  orbitals of  $\text{Cr}^{\text{III}}$ .<sup>10</sup> A higher  $\text{Na}^+$   $E_{\text{barrier}}$  in  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  compared to  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  is expected as more energy is required to oxidize a  $\text{Cr}^{\text{III}}$  that is near a migrating  $\text{Na}^+$  to  $\text{Cr}^{\text{IV}}$ , which is consistent with a lower value of  $D_j$  (Figure 3a) for  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  than that for  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ .

In the case of  $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}^+$  migration is penalized compared to  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  since the highly stable configuration of  $\text{Ti}^{\text{IV}}$  ( $3d^0$ ) needs to be reduced by the migrating  $\text{Na}^+$  to the unpreferred  $\text{Ti}^{\text{III}}$  ( $3d^1$ ) configuration. Thus, the energy cost associated with a local Ti reduction near a migrating Na causes the  $D_j$  for  $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$  to be lower than  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ . In general, at composition  $x > 2$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  shows consistently higher  $D_j$  compared to  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$  and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$  (Figure 3a).

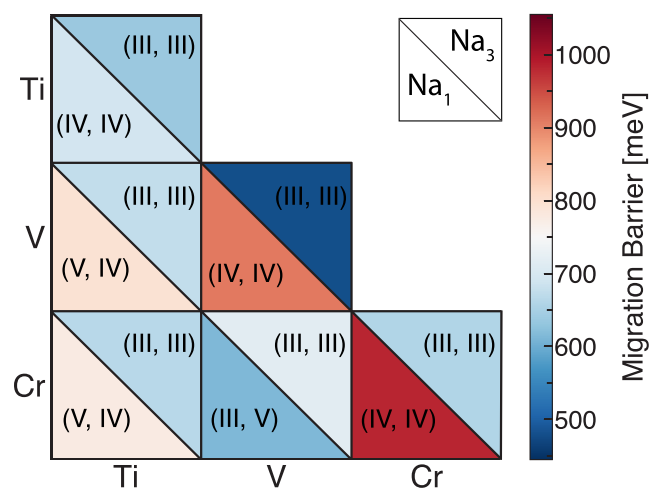
**Extracting the Last Na from  $\text{Na}_1\text{M}_2(\text{PO}_4)_3$ .** From the occupation of Na sites (Figure 3b) at  $x = 1$ , we identified that only Na(1) sites were fully occupied, whereas Na(2) sites were empty. Such an arrangement of the Na ions relates to the “structural integrity” of  $\text{Na}_1\text{M}_2(\text{PO}_4)_3$ , where only Na(1) is occupied and screens the electrostatic repulsions of nearby  $\text{MO}_6$  octahedra stacked along the  $c$  axis imparting stability to the  $\text{Na}_1\text{M}_2(\text{PO}_4)_3$ .<sup>24,54–56</sup> Furthermore, we observed a large site energy difference ( $\sim 880$  meV) between the lower energy Na(1) site and Na(2) at  $x \sim 1$  in  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  (see Supporting Figure 2 of the SI). These results indicate that Na(2) sites are thermodynamically unstable at  $x \sim 1$ , which hinders the ion transport in  $\text{Na}_1\text{M}_2(\text{PO}_4)_3$ .<sup>8</sup> We also observed an abrupt decline of  $D_j$  (i.e.,  $\sim 5.8 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ) in  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ , suggesting that further Na extraction  $x < 1$  is impractical. Such a drop of diffusivity at  $x = 1$  has also been commented on in prior reports.<sup>38,49,50,57</sup>

Low values of  $D_j$  at low Na concentrations limit the full utilization of NaSICON capacities. The extraction of the last Na-ion should happen via  $\text{Na}_1\text{V}^{\text{IV}}\text{V}^{\text{IV}}(\text{PO}_4)_3 \leftrightarrow \text{V}^{\text{V}}\text{V}^{\text{IV}}(\text{PO}_4)_3 + \text{e}^- + \text{Na}^+$ , in the case of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ . This reaction is not redox-limited, as the high-voltage  $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$  redox couple is reversibly accessible.<sup>19,58,59</sup> To date, the chemical Na extraction from  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  has been elusive.<sup>27</sup> The impractical extraction from  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  can be partially attributed to the low Na diffusivities (Figures 2 and 3).<sup>38,49,50</sup>

We propose that atomic substitutions on either Na sites, transition metal sites, or the inclusion of alternative polyanion groups may represent practical approaches to facilitate the extraction of the last Na ion in these NaSICONs. The feasibility of such a method has been confirmed in several studies.<sup>19,55,60,61</sup> The last Na ion can be extracted from  $\text{Na}_1\text{Nb}_2(\text{PO}_4)_3$  forming the mix-valence  $\text{Nb}_2(\text{PO}_4)_3$ ,<sup>62</sup> or from the mixed NaSICON  $\text{Na}_x\text{TiNb}(\text{PO}_4)_3$ .<sup>63,64</sup> Thus, mixing V with “softer” transition metals from the second and third rows,

bearing redox characteristics similar to those of vanadium, may unlock additional capacity in NaSICONs.

**Migration Barriers in Mixed-Transition-Metal NaSICONs.** On the one hand, at low Na content (i.e.,  $x = 1$ ) transition metals with higher oxidation states will tend to repel the Na ions at Na(1) electrostatically and hence destabilize the Na(1) site with an increase of the site energy at Na(1). In addition, the occurrence of transition metals with higher oxidation states will decrease the electron density on the surrounding  $\text{O}^{2-}$ , which will reduce their electrostatic attraction to Na ions and increase the repulsion between nearby “ $\text{O}_3$ ” faces of the  $\text{MO}_6$  octahedra. This will contribute to enlarging the Na-migration bottlenecks.<sup>24</sup> On the other hand, transition metals with a lower oxidation state will attract more Na ions around, resulting in the population of nearby Na(2) sites, which may lower the site energy difference between Na(1) and Na(2) sites at the composition  $x = 1$ . These considerations suggest that the local charge arrangement with higher/lower oxidation states of transition metals may introduce disorder on the Na vacancy lattice, which may decrease the  $E_{\text{barrier}}$  at  $x = 1$ . To quantify this aspect, we evaluated additional Na-migration barriers for NaSICONs with mixed transition metals in a 1:1 ratio (see Figure 4).



**Figure 4.** Migration barriers for  $\text{Na}_1\text{MM}'(\text{PO}_4)_3$  and  $\text{Na}_3\text{MM}'(\text{PO}_4)_3$ , where M and M' = Ti, V, or Cr mixed transition metals, where M, M' = Ti, V, or Cr. The ratio of the transition metals is kept at 1:1. The three diagonal squares are 1-transition-metal NaSICONs, where only consistent tetra-valent (IV) and trivalent (III) states were observed at  $\text{Na}_1$  and  $\text{Na}_3$  compositions. Each square is divided into a lower triangle and a higher triangle, corresponding to the migration barriers for  $\text{Na}_1$  and  $\text{Na}_3$  compositions, respectively. Within each triangle, we identify the oxidation states of the two transition metals, which provide the local charge ordering environment for migrating  $\text{Na}^+$  as  $(m, n)$ , where  $m$  and  $n$  correspond to the oxidation states of the transition metal labeled on the  $y$  axis and  $x$  axis, respectively. For example, (III, V) in the lower-triangle of the  $\text{Na}_1\text{CrV}(\text{PO}_4)_3$  square identifies the local charge arrangement of  $\text{Cr}^{\text{III}}$  and  $\text{V}^{\text{V}}$  oxidation states.

In  $\text{Na}_1\text{VTi}(\text{PO}_4)_3$  and  $\text{Na}_1\text{VCr}(\text{PO}_4)_3$ , we observed an  $E_{\text{barrier}}$  of  $\sim 794$  and  $\sim 613$  meV, respectively (see Supporting Figure 10 in the SI), lower than the  $\sim 910$  meV in  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ . Instead of the single oxidation state of  $\text{V}^{\text{IV}}$  observed at  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ , we found a local charge arrangement of  $\text{V}^{\text{V}}$  and  $\text{Ti}^{\text{IV}}$  redox states near the migrating Na ion in

$\text{Na}_1\text{VTi}(\text{PO}_4)_3$ . Similarly, in  $\text{Na}_1\text{VCr}(\text{PO}_4)_3$ , suggest an ordering of the  $\text{V}^{\text{V}}$  and  $\text{Cr}^{\text{III}}$  states (see Supporting Figure 9 in the SI) in agreement with existing experiments.<sup>55,65</sup> Furthermore, the site energy difference between Na(2) and Na(1) also decreased from  $\sim 880$  meV for  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  to 744 meV for  $\text{Na}_1\text{VTi}(\text{PO}_4)_3$  and from 576 meV for  $\text{Na}_1\text{VCr}(\text{PO}_4)_3$ .

The lower values of  $E_{\text{barrier}}$  for mixed transition-metal NaSICONs at  $x = 1$  will increase  $D_j$  for  $\text{Na}_1\text{VTi}(\text{PO}_4)_3$  and  $\text{Na}_1\text{VCr}(\text{PO}_4)_3$  by  $\sim 2$  and  $\sim 4$  orders of magnitude, respectively,<sup>45</sup> in comparison to a  $D_j$  of  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ . A lower  $E_{\text{barrier}}$  of 774 meV for  $\text{Na}_1\text{TiCr}(\text{PO}_4)_3$  will also increase its  $D_j$  by approximately 3 orders of magnitude compared to  $\text{Na}_1\text{Cr}_2(\text{PO}_4)_3$ .

In  $\text{Na}_3\text{VTi}(\text{PO}_4)_3$ ,  $\text{Na}_3\text{VCr}(\text{PO}_4)_3$ , and  $\text{Na}_3\text{TiCr}(\text{PO}_4)_3$ , the  $E_{\text{barrier}}$  values are  $\sim 676$  meV,  $\sim 719$  meV, and  $\sim 667$  meV, respectively (see Supporting Figure 12 in the SI). Only trivalent transition metals, such as  $\text{V}^{\text{III}}$ ,  $\text{Ti}^{\text{III}}$ , and  $\text{Cr}^{\text{III}}$ , were found in these systems (see Supporting Figure 11 in the SI), which set specific local charge arrangements for the migrating  $\text{Na}^+$ . Compared with the migration barriers for the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ,  $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ , and  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  NaSICON analogs at  $x = 3$ , which were  $\sim 485$ ,  $\sim 638$ , and  $\sim 659$  meV, respectively, the deviations between the  $E_{\text{barrier}}$  of single-transition-metal NaSICON and mixed-transition-metal NaSICON are as small as  $\sim 50$  meV, except  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , which exhibits a significantly lower  $E_{\text{barrier}}$ .

Our results in Figure 4 indicate that the local charge arrangements on the transition metal sites with higher/lower oxidation states may disrupt potentially stable Na–Va arrangements at  $\text{Na}_1\text{M}_2(\text{PO}_4)_3$ , thus lowering the migration barriers and enhancing the  $\text{Na}^+$   $D_j$ , which, in turn, may enable the extraction of the last Na. For example, in the case of the  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  system, if compositions with low Na content (i.e.,  $\text{Na}_{0+x}\text{V}_2(\text{PO}_4)_3$ ) were thermodynamically stable, the Na extraction from  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  would be highly facilitated because of the favorable local charge arrangement of the mixed-valence vanadium sites  $\text{V}^{\text{IV/V}}$ .

#### 4. CONCLUSION

In conclusion, our *ab initio*-based kMC approach revealed the complex relationships among Na-ion transport in  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$  NaSICON electrode materials as a function of Na content and temperatures. We identified optimal compositions providing maximum intrinsic  $\text{Na}^+$  diffusivity for  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$ . Our analysis demonstrated that the Na transport properties of NaSICON materials are highly dependent on the local chemical environments determined by the local arrangements of sodium ions and their vacancies as well as the oxidation states of transition metals. In particular, we elucidated that the environments favoring stable Na-vacancy orderings, typically in the fully charged region, should be disrupted to increase the energy density of NaSICON electrodes, such as  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ . The insights gained from this study into the  $\text{Na}^+$  diffusion properties in  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ ,  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_x\text{Cr}_2(\text{PO}_4)_3$  shed light on appropriately tailored combinations of transition metals that can be used to access swift Na transport in polyanionic electrodes for inexpensive Na-ion batteries.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.3c00610>.

Details of simulations of migration barriers with first-principles methods, the formalism of the local cluster expansion, and details of kinetic Monte Carlo simulations (PDF)

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## Notes

The authors declare no competing financial interest.

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