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Na1 sites. Our results indicate that the three-Na+ extraction is limited due to the high voltage and the large activation energy. We also from Na3V2(PO4)3 by charging the cathode material, an electrochemical three-Na+ extraction has not been reported yet, to the best of our knowledge. In this work, we studied factors that limit the three-Na+ extraction from Na3V2(PO4)3. In DFT calculations, the voltage of the third-Na+ extraction is predicted to be more than 4.5 V vs. Na+/Na0, which is above the potential windows of the conventional organic electrolytes. Our study of NaV1.5Al0.5(PO4)3 reveals that such a high voltage is required when Na ions are extracted from Na1 sites in the NASICON structure. From NEB calculations, the activation energy of the Na+ extraction from the Na1 site is predicted to be 753 meV for Na3V2(PO4)3. Ab-initio molecular dynamics simulations also suggest that the Na ions which remain in Na3V2(PO4)3 are kinetically locked up in Na1 sites. Our results indicate that the three-Na+ extraction is limited due to the high voltage and the large activation energy. We also compare Na3V2(PO4)3 with Li2V3(PO4)3, in which the three-Li+ extraction has been reported.

ABSTRACT
NASICON-type Na3V2(PO4)3 is a promising cathode material for Na-ion batteries. Although it is well known that two Na+ can be extracted from Na3V2(PO4)3 by charging the cathode material, an electrochemical three-Na+ extraction has not been reported yet, to the best of our knowledge. In this work, we studied factors that limit the three-Na+ extraction from Na3V2(PO4)3. In DFT calculations, the voltage of the third-Na+ extraction is predicted to be more than 4.5 V vs. Na+/Na0, which is above the potential windows of the conventional organic electrolytes. Our study of NaV1.5Al0.5(PO4)3 reveals that such a high voltage is required when Na ions are extracted from Na1 sites in the NASICON structure. From NEB calculations, the activation energy of the Na+ extraction from the Na1 site is predicted to be 753 meV for Na3V2(PO4)3. Ab-initio molecular dynamics simulations also suggest that the Na ions which remain in Na3V2(PO4)3 are kinetically locked up in Na1 sites. Our results indicate that the three-Na+ extraction is limited due to the high voltage and the large activation energy. We also compare Na3V2(PO4)3 with Li2V3(PO4)3, in which the three-Li+ extraction has been reported.

Keywords : Sodium Ion Batteries, Cathode Material, NASICON, Density Functional Theory

1. Introduction
Lithium-ion batteries (LIBs) have been widely used for various applications such as electric vehicles, smartphones, and large-scale energy storage systems due to their high energy density and excellent cycle performance. However, the growing demands for LIBs pose a risk of future depletion of the natural resources of lithium. The exhaustion of lithium resources could lead to limited availability and a severe increase in the price of LIBs. As one of the promising alternatives to the LIBs, sodium-ion batteries (NIBs) have attracted research interest due to the abundance and low cost of sodium resources. Various compounds such as layered transition-metal oxides, pyrite-type transition-metal sulfides, alluaudite-type sulfides, NASICON-type sulfates, NASICON-type phosphates, pyrophosphates, fluoro phosphates, perovskite-type fluorides, and organic compounds have been extensively studied as possible cathode materials for NIBs.

Among them, Na3V2(PO4)3 is one of the promising cathode materials due to its higher energy density (~400 Wh g⁻¹), low overpotential, rate capability, and good cyclability. This material has a NASICON (NA-Super-Ionic-CONductor) structure, as shown in Fig. 1a. In the NASICON structure, there are two Na sites, namely Na1 and Na2. The Na1 site is located in a distorted octahedron, and the Na2 site is located in an eight-fold coordinated polyhedron (Figs. 1b and 1c). Na3V2(PO4)3 exhibits a voltage plateau of V⁺³/V⁺⁴ redox at 3.4 V vs. Na⁺/Na⁰ with a capacity of 118 mAh g⁻¹, which corresponds to the theoretical capacity of two-Na⁺ extraction/insertion per formula unit. Na3V2(PO4)3 also exhibits additional two-Na⁺ insertion with a V⁺⁴/V⁺⁵ redox reaction, resulting in Na5V2(PO4)3. Since the voltage of V⁺³/V⁺⁴ redox is too low (~1.6 V), only the two-Na⁺ extraction/insertion reaction between Na3V2(PO4)3 and NaV2(PO4)3 can be utilized as a cathode.

In order to increase the energy density, it is desirable to extract more Na ions from Na3V2(PO4)3. Previously, Gopalakrishnan et al. reported a full Na⁺ extraction from Na3V2(PO4)3 by chemical oxidation. Moreover, Yan et al. recently demonstrated an electrochemical full Na⁺ extraction from Na3V2(PO4)3 by chemical oxidation.13 To the best of our knowledge, however, electrochemical three-Na⁺ extraction from Na3V2(PO4)3 has not been achieved, even though three-Li⁺ extraction has been achieved from Li3V2(PO4)3.15 Because of the difficulty of the three-Na⁺ extraction, alternative strategies have been employed to increase the energy density. One approach is to utilize V⁺³/V⁺⁴ redox and V⁺⁴/V⁺⁵ redox by substituting other trivalent elements for vanadium. For example, multi-redox reactions of V⁺³/V⁺⁴/V⁺⁵ were reported in previous studies of Na3V2−xAlx(PO4)3.16,17 and Na3V2−xCrx(P2O7)3.18,19 In addition to the activation of V⁺³/V⁺⁴ redox, another strategy is to increase the initial Na⁺ amount by substituting divalent elements for vanadium (e.g., Na3+V2−Mg−

Figure 1. (a) Crystal structure of NASICON-type Na3V2(PO4)3 (C2/c) and local environments of the (b) Na1 site and (c) Na2 site. The structure was visualized using VESTA.11
(PO₄)₃, Na₂V₃Mn(PO₄)₃). While the energy densities were improved in those materials, the last Na⁺ in the formula units still remained in the NASICON structures at the charged states.

In Na₂V₂(PO₄)₃, two Na⁺ were extracted from the Na₂ site during the charge reaction at 3.4 V, and the third Na⁺ remaining in Na₂V₂(PO₄)₃ occupied the Na₁ site, as reported by Jian et al. and Lim et al. The voltage of the third-Na⁺ extraction was predicted to be 4.64 V from the density functional theory (DFT) calculations. This voltage step from 3.4 V to 4.64 V originates from two factors. The first factor is the shift of the redox couples from V⁴⁺/V⁵⁺ to V⁴⁺/V⁵⁺, and the second is the Na⁺ extraction from the Na₁ site. Due to the overlap of the two contributions, it is difficult to point out the source of the limitation of the third-Na⁺ extraction. Partial substitution of electrochemically inactive elements for vanadium is an effective method to decouple the two contributions, as previously reported for Na₂V₂(PO₄)₃F.⁴,²⁴

In this work, we experimentally and computationally investigated factors limiting the three-Na⁺ extraction from Na₂V₂(PO₄)₃. Na₂V₁.₅Al₀.₅(PO₄)₃ was also studied in order to decouple the two contributions to the voltage step. The third-Na⁺ extractions were not observed in our electrochemical tests, and our DFT calculations predicted that a high voltage of more than 4.5 V is required to extract Na⁺ from the Na₁ site. Moreover, Na⁺ is locked up in the Na₁ site in Na₂V₂(PO₄)₃ due to the significant migration energy. The difference in voltage and alkali-ion diffusivities between Na₂V₂(PO₄)₃ and Li₁V₂(PO₄)₃ is also discussed.

2. Experimental

2.1 Materials synthesis and characterization

Carbon coated Na₃V₂(PO₄)₃ and Na₃V₁.₅Al₀.₅(PO₄)₃ were synthesized by a sol-gel method. Stoichiometric NaH₂PO₄ (≥99.0%, FUJIFILM Wako Pure Chemical Corporation) and NH₄VO₃ (≥99.0%, FUJIFILM Wako Pure Chemical Corporation) were added to ultrapure water (18.2 MΩ cm) purified with Direct-Q UV3 (Merck). For Na₃V₁.₅Al₀.₅(PO₄)₃, stoichiometric Al(NO₃)₃·9H₂O (≥98.0%, Kanto Chemical Co., Inc.) was also added. Then, citric acid (≥98.0%, FUJIFILM Wako Pure Chemical Corporation) as a carbon source was dissolved into the water. The molar ratio of citric acid to the metal ions (V and Al) was 3:2. The solution was dried at 120 °C. The dried precursors were ground and pelletized, then heated at 500 °C under an Ar-H₂ (95:5 vol.%) gas flow for 2 hours. The samples were ground and pelletized again, then heated at 750 °C under Ar-H₂ (95:5 vol.%) gas for 12 hours. The final products were obtained by grinding the samples after the calcination. X-ray diffraction (XRD) measurements were performed using a MiniFlex X-ray diffractometer (Rigaku Corporation) with Cu-Kα radiation. Rietveld refinements were carried out with RIETAN-EP.²⁵ The thermogravimetric (TG) analysis was performed with Thermo plus TGS8110 (Rigaku Corporation) in order to determine the carbon contents in the samples.

2.2 Electrochemical tests

The Na₂V₂(PO₄)₃ and Na₃V₁.₅Al₀.₅(PO₄)₃ electrodes were prepared by coating slurries made of 80 wt.% of the active material, 10 wt.% of acetylene black (AB; Denka Co., Ltd.) and 10 wt.% of polyvinylidene fluoride (PVDF; KUREHA Corporation) in n-methyl-2-pyrrolidone (NMP; FUJIFILM Wako Pure Chemical Corporation) on Al foils. The slurries on the Al foils were dried in a vacuum at 80 °C. The typical loading mass of the active materials was 1.3 mg cm⁻². 2032 coin-type cells were fabricated in an Ar-filled glove box using the prepared positive electrodes, Na metal (99.9%; Sigma-Aldrich) as a negative electrode, 1 M NaPF₆ in EC:DMC (1:1 vol.%) as an electrolyte, and GA-55 glass fiber filter (Advantec) as a separator. Electrochemical tests were performed using BTH-2004H (NAGANO & Co., Ltd.).

2.3 Computational method

Density functional theory (DFT) calculations were performed with the Vienna Ab-initio Simulation Package (VASP).²⁶,²⁷ The projector augmented wave (PAW) method was used,²⁸,²⁹ and the plane-wave cutoff energy was set to 520 eV. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was adopted.³⁰ The Hubbard U value for vanadium was set to 5.0 eV,³¹ which was used for AVPO₄F (A = Li, Na, K) in a previous work.²⁵ For all DFT calculations, the Pymatgen package was used to generate input files and analyze the results.³²

The crystal structures of Na₃V₄(PO₄)₉ and Na₃V₁.₅Al₀.₅(PO₄)₉ were constructed from a unit cell (C2/c) reported by Chotard et al.,³³ and a Γ-centered 1 × 2 × 1 k-point mesh was used. All Na⁺ vacancy orderings and V-Al orderings in the unit cells were enumerated by the Supercell program.³⁴ For each composition, the 30 structures with the lowest electrostatic energies were subject to the DFT calculations, and the most stable configuration was determined.

For Li₃V₂(PO₄)₃, the crystal structures were constructed from monoclinic-Li₃V₂(PO₄)₃ (P2₁/n, ICSD No. 96962), and a gamma-centered 3 × 3 × 2 k-point mesh was used. Li⁺ vacancy orderings were selected following a previous report.³⁶

The average voltage between two phases was obtained using the following equation:³⁷

\[
V = \frac{-E(A₁M₂(PO₄)₃) - E(A₂M₂(PO₄)₃) - (x₁ - x₂)E(A)}{(x₁ - x₂)}
\]

where \(E(A₁M₂(PO₄)₃), E(A₂M₂(PO₄)₃),\) and \(E(A)\) are DFT energies of \(A₁M₂(PO₄)₃, A₂M₂(PO₄)₃\) and alkali metal (\(A = Na\) or \(Li\)), respectively. M in the chemical formula denotes V and Al.

To investigate the migration barriers of alkali ions, nudged elastic band (NEB) calculations were carried out using VASP Transition State Theory (VTST) tools.³⁸,³⁹

Ab-initio molecular dynamics (AIMD) simulations were also performed in the canonical (NVT) ensemble using VASP. The time step was set to 2.0 fs, and the simulations were run for 40 ps at 1000 K using the Nose-Hoover thermostat.⁴⁰,⁴¹ In order to reduce the computational cost, the plane-wave cutoff energy was set to 400 eV, and a single Γ point was used as a k-point mesh. Moreover, for Na₃V₂(PO₄)₃, a smaller unit cell (6 formula units) obtained from the Materials Project,⁴² (mp-77657), a core program of the Materials Genome Initiative, was used instead of the original unit cell (12 formula units) to reduce the computational cost.

3. Results and Discussion

3.1 Materials characterization

Figure 2 shows the results of the Rietveld refinements of as-prepared Na₂V₂(PO₄)₃ and Na₃V₁.₅Al₀.₅(PO₄)₃. The refined crystallographic data are shown in Table S1 and Table S2 in the Supporting Information. In both Na₂V₂(PO₄)₃ and Na₃V₁.₅Al₀.₅(PO₄)₃, all the diffraction peaks were indexed to a monoclinic lattice (C2/c), and no impurity phase was observed. While the structures of Na₂V₂(PO₄)₃ have been characterized as rhombohedral (R-3c) in many studies,²²,²³ Chotard et al. reported that Na₂V₂(PO₄)₃ forms a monoclinic structure (C2/c) below room temperature.³⁴ We performed the Rietveld refinements both with the monoclinic lattice and the rhombohedral lattice, and the former showed a better fitting. In the rhombohedral structure, there are only a Na₁ site and a Na₂ site. On the other hand, in the monoclinic structure, the Na₁ site splits into two distinct sites, namely Na₁ and Na₁b. The Na₂ site also splits into several sites (Na₂a, Na₂b, Na₂c, Na₂d, and Na₂e). These changes arise from the lower symmetry of the monoclinic structure. Since these split sites are essentially the same as the original sites, we refer to them as the Na₁ site or Na₂ site in this study unless otherwise specified.
The lattice constants of Na$_3$V$_2$(PO$_4$)$_3$ were $a = 15.1189(4)$ Å, $b = 8.7302(3)$ Å, $c = 21.8378(8)$ Å, $\alpha = \gamma = 90^\circ$, and $\beta = 90.123(3)^\circ$, respectively. The lattice constants of Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ were $a = 15.0604(4)$ Å, $b = 8.6609(2)$ Å, $c = 21.6551(4)$ Å, $\alpha = \gamma = 90^\circ$, and $\beta = 90.072(6)^\circ$, respectively. Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ has smaller lattice constants ($a$, $b$ and $c$) compared with Na$_3$V$_2$(PO$_4$)$_3$ because the ionic radius of Al$^{3+}$ (0.64 Å) is smaller than that of V$^{5+}$ (0.66 Å).

In Table S2, the occupancy of the Na$_{2d}$ site in Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ significantly decreased compared with Na$_3$V$_2$(PO$_4$)$_3$, and that of the other Na sites slightly increased instead. This is due to the partial stabilization of a Na ordering by the Al substitution. At $-10^\circ$C, Na$_3$V$_2$(PO$_4$)$_3$ has the Na ordering, where the Na$_{2d}$ and Na$_{2e}$ sites are completely vacant, and the other Na sites are fully occupied. While the Na ordering disappears at room temperature for Na$_3$V$_2$(PO$_4$)$_3$, Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ partially retained the Na ordering even at room temperature, as evidenced by the presence of the superstructure peak at 12.5° in the XRD pattern in Fig. 2b.

As shown in Fig. S1, TG analysis revealed that the carbon contents of Na$_3$V$_2$(PO$_4$)$_3$ and Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ were 7.89% and 6.13%, respectively.

### 3.2 Voltage profiles of Na$_3$V$_2$(PO$_4$)$_3$ and Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$

The voltage profiles of Na$_3$V$_2$(PO$_4$)$_3$ and Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ in the voltage range of 2.5–4.2 V at 0.1 C are shown in Fig. S2. For both Na$_3$V$_2$(PO$_4$)$_3$ and Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$, the obtained capacities almost correspond to two-Na$^+$ extraction/insertion. These results are in good agreement with the previous studies.

Figure 3 shows the calculated and experimental voltage profiles of Na$_3$V$_2$(PO$_4$)$_3$ and Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$. The experimental charge/discharge curves were measured in the voltage range of 2.5–4.7 V at 0.1 C. At the top of each figure, the redox couples corresponding to the range of $x$ in Na$_{3-x}$M$_2$(PO$_4$)$_3$ ($M = V$ and Al) are shown at the top of each plot.

From the DFT calculations, the voltage in $0 \leq x \leq 2$ is predicted to be 3.38 V, which is in good agreement with the experimental value. In the DFT calculations, the Na$^+$ is extracted from the Na$_2$ site in $0 \leq x \leq 2$ and all the Na$^+$ ions occupy the Na$_1$ site at $x = 2$. This result is consistent with the previous literature. A large voltage step from 3.38 V to 4.70 V is observed at $x = 2$. This voltage step is due to two contributions, namely the shift of the redox couples from V$^{3+}$/V$^{4+}$ to V$^{4+}$/V$^{5+}$ and the Na$^+$ extraction from the Na$_1$ site. Other minor voltage steps are also observed at $x = 2.67$. 

**Figure 2.** Rietveld refinements of XRD patterns of the as-prepared (a) Na$_3$V$_2$(PO$_4$)$_3$ and (b) Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$.

**Figure 3.** Experimental and calculated voltage profiles of (a) Na$_3$V$_2$(PO$_4$)$_3$ and (b) Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$. Redox couples corresponding to the range of $x$ in Na$_{3-x}$M$_2$(PO$_4$)$_3$ ($M = V$ and Al) are shown at the top of each plot.
and $x = 2.83$, respectively. They might be attributed to the change of the Na$^+$ ordering in the NASICON structure. Overall, the voltage for the third-Na$^+$ extraction from the Na1 site ($2 \leq x \leq 3$) is predicted to be more than 4.70 V, which is above the potential windows of the common organic electrolytes. Therefore, the electrolyte decompositions occur before the third-Na$^+$ extraction, as observed in our experiments.

In order to decouple the two contributions to the large voltage step at $x = 2$, we also investigated the electrochemical property of Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$. Figure 3b shows the experimental and calculated voltage profiles of Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$. In the experimental charge curve, a plateau which arises from V$^{3+/4+}$ redox was observed at 3.4 V in $0 \leq x \leq 1.5$. Compared to Na$_3$V$_2$(PO$_4$)$_3$, this plateau showed a decreased capacity, because the amount of V was reduced by the partial substitution of Al for V. In addition to the plateau at 3.4 V, a voltage slope was observed at $\sim$4.0 V in $1.5 \leq x \leq 2$. The voltage step at $x = 1.5$ is due to the shift of the redox couples from V$^{3+/4+}$ to V$^{4+/5+}$. This result is in good agreement with the previous report. Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ also exhibited a large charge capacity (196 mAh$^{-1}$), which is due to the oxidative decomposition of the electrolyte. In the discharge curve, only the voltage slope at $\sim$4.0 V and the voltage plateau at 3.4 V were observed, and no additional voltage slope or plateau was observed. Ex-situ XRD measurements of Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ were also carried out, as shown in Fig. S3b. The active material transformed from Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ to Na$_3$V$_2$(PO$_4$)$_3$ during charging to 4.2 V, and no additional phase transition was observed at the higher voltage. Therefore, like Na$_3$V$_2$(PO$_4$)$_3$, the third Na$^+$ was not extracted from Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$.

In the DFT calculations, the voltage profile has a plateau at 3.38 V in $0 \leq x \leq 2$ and another plateau at 3.86 V in $1.5 \leq x \leq 2$. Although the predicted voltage of the second plateau (3.86 V) is slightly smaller than the experimental value ($\sim$4.0 V), the calculated result is roughly consistent with the experimental result. From the DFT calculation, it is found that the Na$^+$ is extracted from the Na2 site in $0 \leq x \leq 2$, while the shift of the redox couples from V$^{3+/4+}$ to V$^{4+/5+}$ occurs at $x = 1.5$. At $x = 2$, another voltage step from 3.86 V to 4.54 V is predicted. This large voltage step is solely ascribable to the Na$^+$ extraction from the Na1 site, because the redox couple remains unchanged at $x = 2$. Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ has another minor voltage step at $x = 2.5$, which might originate from the change of Na+ orderings.

Our results revealed that the Na$^+$ extraction is limited due to the high voltage. Such a high voltage is likely to stem from destabilization of the desodiated NASICON structure. However, further studies are needed to elucidate a relationship between the desodiated structure and its stability.

### 3.3 NEB calculations and AIMD simulations of Na$_3$V$_{2–x}$V$_x$(PO$_4$)$_3$

It is possible that the third-Na$^+$ extraction is limited due to not only the high voltage but also kinetics. Therefore, we performed NEB calculations to study the Na$^+$ diffusivity in Na$_3$V$_2$(PO$_4$)$_3$ and Na$_3$V$_2$(PO$_4$)$_3$. In the NASICON structures, Na ions hop between the Na1 sites and Na2 sites, resulting in a Na1-Na2-Na1 di
diffusivity, the AIMD simulations

**Figure 4.** (a) Migration path and (b) migration barriers of Na ions in Na$_3$V$_2$(PO$_4$)$_3$ and NaV$_2$(PO$_4$)$_3$.

This substantial energy increase is attributed to destabilization of the Na2 site. At the Na2 site, a Na ion is repelled by four neighboring V ions while there are only two V ions near the Na1 site. In NaV$_2$(PO$_4$)$_3$, the oxidation state of V is 4+, whereas it is 3+ in Na$_3$V$_2$(PO$_4$)$_3$. Therefore, the Na2 site in Na$_3$V$_2$(PO$_4$)$_3$ is destabilized due to the stronger electrostatic repulsions from V$^{4+}$ ions. The shorter Na-V distances at the Na2 site also contribute to the destabilization of the Na2 site. In the AIMD calculations, the unit cell volumes of Na$_3$V$_2$(PO$_4$)$_3$ and NaV$_2$(PO$_4$)$_3$ are predicted to be 3008 Å$^3$ and 2780 Å$^3$, respectively. Because of this volume contraction after the two-Na$^+$ extraction, the average Na-V distance at the Na2 site is decreased from 3.73 Å for Na$_3$V$_2$(PO$_4$)$_3$ to 3.51 Å for NaV$_2$(PO$_4$)$_3$. This shorter Na-V distance also increases the electrostatic repulsions between Na ions and V ions, resulting in the destabilization of the Na2 site.

For Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$, Zhao et al. reported that the Al substitution increased the Na-ion migration energy due to the lattice contraction induced by the Al substitution. Therefore, we suspect that the Al substitution makes the third-Na$^+$ extraction further unfavorable although we have not carried out the NEB calculations for Na$_3$V$_{1.5}$Al$_{0.5}$(PO$_4$)$_3$ and Na$_3$V$_2$(PO$_4$)$_3$.

To further investigate the Na$^+$ diffusivity, the AIMD simulations were also performed for Na$_3$V$_2$(PO$_4$)$_3$ and NaV$_2$(PO$_4$)$_3$. Figure 5 shows the isosurfaces of Na-ion probability densities for Na$_3$V$_2$(PO$_4$)$_3$ and NaV$_2$(PO$_4$)$_3$. Note that Na ions at the initial position are shown in Figs. 5a and 5c, and only the isosurfaces are displayed in (b) and (d). As shown in Figs. 5a and 5b, Na ions diffuse via the typical three-dimensional Na1-Na2-Na1 migration.
Figure 5. Isosurfaces (blue) of Na-ion probability densities obtained from AIMD simulations at 1000 K for (a), (b) Na$_3$V$_2$(PO$_4$)$_3$ and (c), (d) NaV$_2$(PO$_4$)$_3$. Na ions at the initial positions are also shown in (a) and (c). Only the isosurfaces are displayed in (b) and (d).

Figure 6. Calculated voltage profile of Li$_3$V$_2$(PO$_4$)$_3$. Redox couples corresponding to the range of $x$ in Li$_{3-x}$V$_2$(PO$_4$)$_3$ are shown at the top of the plot.

paths in the Na$_3$V$_2$(PO$_4$)$_3$ structure. In Na$_3$V$_2$(PO$_4$)$_3$, on the other hand, Na ions at the Na1 sites remain at their initial positions, as shown in Figs. 5c and 5d. This limited Na$^+$ diffusivity stems from the large migration energy from the Na1 site to the adjacent Na2 site. Our results from the NEB calculations and AIMD simulations suggest that the three-Na$^+$ extraction is hindered due to the large migration energy in NaV$_2$(PO$_4$)$_3$, as well as the high voltage.

3.4 Voltage profiles and AIMD results of Li$_3$V$_2$(PO$_4$)$_3$

In contrast to Na$_3$V$_2$(PO$_4$)$_3$, three Li$^+$ can be extracted from Li$_3$V$_2$(PO$_4$)$_3$. This discrepancy might originate from the fact that Li$_3$V$_2$(PO$_4$)$_3$ has an anti-NASICON structure whereas Na$_3$V$_2$(PO$_4$)$_3$ has a NASICON structure. Note that there are three Li sites (Li1, Li2, and Li3) in the Li$_3$V$_2$(PO$_4$)$_3$ structure. To compare the difference between the two compounds, we investigated the property of Li$_3$V$_2$(PO$_4$)$_3$ by the DFT calculations. Figure 6 shows the calculated voltage profile of Li$_3$V$_2$(PO$_4$)$_3$. There are four plateaus, as reported previously. The voltages of the first plateau in 0 $\leq x < 0.5$ and the second one in 0.5 $\leq x < 1$ are 3.85 V and 3.92 V, respectively. Note that these voltages are calculated against a Li metal anode. The calculated voltages are higher than the reported ones of 3.6 V and 3.7 V for the first and second plateaus, respectively. The third plateau in 1 $\leq x < 2$ is 4.12 V. This value is in good agreement with the reported one. Multiple voltage plateaus arise from the Li$^+$ orderings, and the redox couple remains V$^{3+}$/V$^{4+}$ in this range (0 $\leq x < 2$). At $x = 2$, all Li ions are located in Li2 sites, and the redox couples shift from V$^{3+}$/V$^{4+}$ to V$^{4+}$/V$^{5+}$. The voltage of the third-Li$^+$ extraction from Li2 sites (2 $\leq x < 3$) is predicted to be 4.45 V, which is consistent with the experimental results. The voltage is equal to approximately 4.2 V when it is calculated against a Na metal anode. This value is 0.5 V lower than the voltage of the third-Na$^+$ extraction from Na$_3$V$_2$(PO$_4$)$_3$. The relatively lower voltage enables the third-Li$^+$ extraction from LiV$_2$(PO$_4$)$_3$ without a significant electrolyte decomposition.

In order to investigate Li-ion diffusivity, AIMD simulations were also performed for Li$_3$V$_2$(PO$_4$)$_3$ and LiV$_2$(PO$_4$)$_3$. Figure 7 illustrates the isosurfaces of Li-ion probability densities in the two structures. For both compositions, it can be seen that Li ions diffuse three-dimensionally in the V$_2$(PO$_4$)$_3$ frameworks. This result suggests that the migration barriers from the Li2 site to another site are small enough, and the third-Li$^+$ extraction is not kinetically limited. The superior Li$^+$ diffusivity in Li$_3$V$_2$(PO$_4$)$_3$ contrasts with the case of Na$_3$V$_2$(PO$_4$)$_3$, in which the Na$^+$ is locked up in the Na1 site.

4. Conclusions

In this study, we explored the factors that limit the three-Na$^+$ extraction from Na$_3$V$_2$(PO$_4$)$_3$. From the DFT calculations, it is found that Na$^+$ is located in the Na1 sites in both Na$_3$V$_2$(PO$_4$)$_3$ and NaV$_1.5$Al$_0.5$(PO$_4$)$_3$. The voltages of the third-Na$^+$ extractions from Na$_3$V$_2$(PO$_4$)$_3$ and NaV$_1.5$Al$_0.5$(PO$_4$)$_3$ are predicted to be more than 4.70 V and 4.54 V, respectively. These voltages are too high for the conventional organic electrolytes. Thus, the oxidative decomposition of the electrolytes occurs before the Na$^+$ extraction. For Na$_{3-x}$V$_2$Al$_x$(PO$_4$)$_3$, the voltage step was observed at $x = 1.5$ due to the shift of the redox couples from V$^{3+}$/V$^{4+}$ to V$^{4+}$/V$^{5+}$. Moreover, another large voltage step is predicted at $x = 2$ in the DFT calculation. The voltage step at $x = 2$ solely stems from the Na$^+$ extraction from the Na1 site since the redox couple remains V$^{4+}$/V$^{5+}$. Thus, the three-Na$^+$ extraction is limited because the high voltage is required to extract Na$^+$ ion from the Na1 site.

The NEB calculations revealed that the Na$^+$ migration energy from the Na1 site to Na2 site is 755 meV in Na$_3$V$_2$(PO$_4$)$_3$, while that in Na$_3$V$_2$(PO$_4$)$_3$ is 304 meV. The AIMD simulations also suggest that the third Na$^+$ is trapped in the Na1 site in Na$_3$V$_2$(PO$_4$)$_3$ due to the large migration energy. Therefore, the three-Na$^+$ extraction is also limited because of the kinetics.

In contrast to Na$_3$V$_2$(PO$_4$)$_3$, Li$_3$V$_2$(PO$_4$)$_3$ exhibits a lower voltage of the third-Li$^+$ extraction. Moreover, the AIMD simulations suggested that the Li$^+$ can easily diffuse three-dimensionally in Li$_3$V$_2$(PO$_4$)$_3$. Accordingly, the three Li$^+$ ions can be extracted from Li$_3$V$_2$(PO$_4$)$_3$ without a significant electrolyte decomposition or kinetic limitation.

In conclusion, the extraction of three Na ions from Na$_3$V$_2$(PO$_4$)$_3$ has proven challenging due to the high voltage and the substantial
migration energy. However, our findings indicate that the three-Na⁺ extraction might be achievable by using ionic liquids or solid electrolytes which are stable at high voltage and applying a low rate current. In addition, elemental substitutions for Na or V may alter the stability of the crystal structure and the Na site energies, and thereby enable the three-Na⁺ extraction. We believe this study provides important insights toward the design of new NASICON-type cathode materials with higher energy densities.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00080.

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References

1. J.-J. Braconnier, C. Delmas, C. Fouassier, and P. Hagenmüller, Mater. Res. Bull., 15, 1797 (1980).
2. A. Kitajou, J. Yamaguchi, S. Hara, and S. Okada, J. Power Sources, 247, 391 (2014).
3. P. Barpanda, G. Oyama, S. Nishimura, S.-C. Chung, and A. Yamada, Nat. Commun., 5, 4358 (2014).
4. S. Okada, H. Arai, and J. Yamaki, Denki Kagaku, 65, 802 (1997).
5. Y. Uebou, T. Kiyabu, S. Okada, and J. Yamaki, The Reports of Institute of Advanced Material Study, Kyushu University, 16, 1 (2002).
6. Y. Uebou, S. Okada, and J. Yamaki, Electrochemistry, 71, 308 (2003).
7. K. Chihara, A. Kitajou, I. Gocheva, S. Okada, and J. Yamaki, J. Power Sources, 227, 80 (2013).
8. I. Gocheva, M. Nishijima, T. Doi, S. Okada, J. Yamaki, and T. Nishida, J. Power Sources, 187, 247 (2009).
9. K. Chihara, N. Chuo, A. Kitajou, and S. Okada, Electrochem. Acta, 110, 240 (2013).
10. J. B. Goodenough, H. Y.-P. Hong, and J. A. Kafafas, Mater. Res. Bull., 11, 203 (1976).
11. K. Momma and F. Izumi, J. Appl. Crystallogr., 44, 1272 (2011).
12. Z. Jian, Y. Sun, and X. Ji, Chem. Commun., 51, 6381 (2015).
13. J. Gopalakrishnan and K. K. Rangan, Chem. Mater., 4, 745 (1992).
14. G. Yan, S. Mariyappan, G. Rouse, Q. Jacquet, M. Deschamps, R. David, B. Miriaux, J. W. Freeland, and J.-M. Tarascon, Nat. Commun., 10, 585 (2019).
15. H. Huang, S.-C. Yin, T. Kerr, N. Taylor, and L. F. Nazar, Adv. Mater., 14, 1525 (2002).
16. F. Lalère, V. Szemc, M. Courty, R. David, J.-N. Chotard, and C. Masquelier, J. Mater. Chem. A, 3, 16198 (2015).
17. M. J. Aragón, P. Lavela, R. Alcántara, and J. L. Tirado, Electrochim. Acta, 180, 824 (2015).
18. M. J. Aragón, P. Lavela, G. F. Ortiz, and J. L. Tirado, ChemElectroChem, 2, 995 (2015).
19. R. Liu, G. Xu, Q. Li, S. Zheng, G. Zheng, Y. Li, E. Kruszop, R. Fu, Z. Chen, K. Amine, and Y. Yang, ACS Appl. Mater. Interfaces, 9, 43632 (2017).
20. A. Inouishi, Y. Yoshikoa, L. Zhao, A. Kitajou, and S. Okada, ChemElectroChem, 4, 2755 (2017).
21. F. Chen, V. M. Kovalnug, R. David, O. Menrté, F. Fauth, J.-N. Chotard, and C. Masquelier, Small Methods, 3, 1800218 (2019).
22. Z. Jian, C. Yuan, W. Han, X. Lu, L. Ou, X. Xi, Y.-S. Jin, H. Li, W. Chen, D. Chen, Y. Xuhara, and L. Chen, Adv. Funct. Mater., 24, 4265 (2014).
23. S. Y. Lim, H. Kim, R. A. Shakoour, Y. Jung, and J. W. Choi, J. Electrochem. Soc., 159, A1393 (2012).
24. I. L. Marris, S. Ducéec, T. K. Pietrzak, R. Malik, and G. Ceder, Chem. Mater., 27, 6089 (2015).
25. F. Inumi and K. Momma, Solid State Phenom., 130, 15 (2007).
26. G. Kresse and J. Furthmüller, Comput. Mater. Sci., 6, 15 (1996).
27. G. Kresse and J. Furthmüller, Phys. Rev. B, 54, 11169 (1996).
28. P. E. Blöchl, Phys. Rev. B, 50, 17595 (1994).
29. G. Kresse and D. Joubert, Phys. Rev. B, 59, 1758 (1999).
30. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., 77, 3865 (1996).
31. S. L. Dudarev, G. A. Booth, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B, 57, 1505 (1998).
32. H. Kim, Y. Ishado, V. Tian, and G. Ceder, Adv. Funct. Mater., 29, 1902392 (2019).
33. S. P. Ong, W. D. Richards, A. Jain, G. Hautier, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson, and G. Ceder, Comput. Mater. Sci., 68, 314 (2013).
34. J.-N. Chotard, G. Rousse, R. David, O. Mentré, M. Courty, and C. Masquelier, Chem. Mater., 27, 5982 (2015).
35. K. Okhotinov, T. Charpentier, and S. Cadars, J. Cheminform., 8, 17 (2016).
36. S.-C. Yin, H. Gondrey, P. Strobel, M. Anne, and L. F. Nazar, J. Am. Chem. Soc., 125, 10402 (2003).
37. M. K. Aydinol, A. F. Kohan, G. K. Ceder, K. Cho, and J. Joannopoulos, Phys. Rev. B, 56, 1354 (1997).
38. G. Henkelman and H. Jónsson, J. Chem. Phys., 113, 9978 (2000).
39. D. Sheppard, P. Xiao, W. Chemeliledzwe, D. D. Johnson, and G. Henkelman, Adv. Energy Mater., 3, 156 (2013).
40. F. Deng, C. Eames, L. B. Nguyen, O. Pecher, J. Griffith, M. Courty, B. Fleutot, J.-N. Chotard, C. P. Grey, M. S. Islam, and G. Masquelier, Chem. Mater., 30, 2618 (2018).
41. K. M. Bui, V. A. Dinh, S. Okada, and T. Ohno, Phys. Chem. Chem. Phys., 17, 30433 (2015).
42. L. Zhao, H. Zhao, Z. Du, N. Chen, X. Chang, Z. Zhang, F. Gao, A. Tremczak, and K. Świerczek, Electrochim. Acta, 282, 510 (2018).
43. C. Masquelier and L. Croguennec, Chem. Rev., 113, 6552 (2013).