Boron Substituted Na$_3$V$_2$(P$_{1-x}$B$_x$O$_4$)$_3$ Cathode Materials with Enhanced Performance for Sodium-Ion Batteries

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The development of excellent performance of Na-ion batteries remains great challenge owing to the poor stability and sluggish kinetics of cathode materials. Herein, B substituted Na$_3$V$_2$P$_{3-x}$B$_x$O$_{12}$ (0 ≤ x ≤ 1) as stable cathode materials for Na-ion battery is presented. A combined experimental and theoretical investigations on Na$_3$V$_2$P$_{3-x}$B$_x$O$_{12}$ (0 ≤ x ≤ 1) are undertaken to reveal the evolution of crystal and electronic structures and Na storage properties associated with various concentration of B. X-ray diffraction results indicate that the crystal structure of Na$_3$V$_2$P$_{3-x}$B$_x$O$_{12}$ (0 ≤ x ≤ 1/3) consisted of rhombohedral Na$_3$V$_2$(PO$_4$)$_3$ with tiny shrinkage of crystal lattice. X-ray absorption spectra and the calculated crystal structures all suggest that the detailed local structural distortion of substituted materials originates from the slight reduction of V–O distances. Na$_3$V$_2$P$_{3-1/6}$B$_{1/6}$O$_{12}$ significantly enhances the structural stability and electrochemical performance, giving remarkable enhanced capacity of 100 and 70 mAh g$^{-1}$ when the C-rate increases to 5 C and 10 C. Spin-polarized density functional theory (DFT) calculation reveals that, as compared with the pristine Na$_3$V$_2$(PO$_4$)$_3$, the superior electrochemical performance of the substituted materials can be attributed to the emergence of new boundary states near the band gap, lower Na$^+$ diffusion energy barriers, and higher structure stability.

1. Introduction

Sodium-ion batteries (SIBs) are attracting a significant attention as promising alternative to dominant lithium-ion batteries for the potential application in largescale grid storage and electrical vehicles due to the abundant reserves and cost advantages of Na as compared with Li.$^{[1,2]}$ However, electrochemical performances in terms of rate capability and cycling life associated with SIBs did not come up to those of the lithium counterparts for their practical application. As compared with lithium-ion, ionic radius of sodium-ion is much larger, which severely restricts the ion diffusion kinetics of Na$^+$ in host material, especially in cathode materials.$^{[3–6]}$ Therefore, to efficiently improve the diffusion kinetics of Na$^+$ is a significant issue for development of high performance electrode materials for SIBs.

In the past few years, many compounds including layer-structured oxide and polyanionic phosphates have been investigated to find a suitable cathode material for reversible and rapid intercalation/deintercalation of Na$^+$. Among them, sodium super ion conductor (NASICON) structured Na$_3$V$_2$(PO$_4$)$_3$ with 3D open framework and large tunnels for Na$^+$ migration has aroused an extensive interest as cathode materials for SIBs owing to its superiority of good stability, moderate potential plateau, high energy density, and so on.$^{[14–18]}$ However, the poor intrinsic electronic conductivity and structural stability of Na$_3$V$_2$(PO$_4$)$_3$ severely retard the cycling stability and rate capability of electrode in its practical application. To overcome such fundamental demerits, several strategies, including coating various carbon materials, reducing the particle size to nanoscale, and doping with the foreign ion, have been widely proposed in literature.$^{[19–21]}$

Ion-doping can be considered as an effective way to enhance the electronic conductivity of electrode material for improving the electrochemical performance of lithium and/or sodium ion batteries. Various metallic ions with different valence states and ionic sizes (such as K$^+$, Fe$^{2+}$, Mg$^{2+}$, and so on)$^{[23–25]}$ were introduced to partly substitute Na and/or V of Na$_3$V$_2$(PO$_4$)$_3$ units, and hence a modified Na$_3$V$_2$(PO$_4$)$_3$ with high capacity and excellent rate property can be achieved. So far, research on nonmetal substitution of Na$_3$V$_2$(PO$_4$)$_3$ at P-site and/or O-site is rare, except some cases on Na$_3$V$_2$(PO$_4$)$_3$-F$_{3x0}$ in which F...
atoms were utilized to replace the whole PO₄⁻³. Actually, the strategy of doping nonmetal element in polyanion cathode materials of LIBs to improve the electrochemical property has been studied.[29–31] For example, Sin et al. reported that boron polyanion substituted LiFe₀.₄Mn₀.₆(PO₄)₃ showed a high initial capacity and low over potential during cycling. [32] Similar enhancement of electrochemical performance can also be observed in olivine LiMnPPO₄ and LiFePPO₄ cathode, NASICON-type Li₃V₂(PO₄)₃ cathode and solid-state electrolyte LiTi₂(PO₄)₃ with an optimum amount of B. [33,34] They believed that replacement of B not only introduces the p-type conductivity, but also significantly increases Li⁺ diffusion kinetics and structure stability.

Inspired by the positive effects of B doped compounds with enhancement of electrochemical performance in LIBs, we herein presented B substituted Na₃V₂P₃–xO₁₂ (0 ≤ x ≤ 1) as cathode materials for SIB. A combined experimental and theoretical study on Na₃V₂P₃–xO₁₂ (0 ≤ x ≤ 1) were undertaken to reveal the evolution of crystal and electronic structure and Na-ion diffusion properties associated with various amount of B. Electrochemical properties of Na₃V₂P₃–xO₁₂ were optimized by adjusting B contents. Na₃V₂P₃–(1/6)xB₁/₆O₁₂ shows an obvious enhancement in cycling stability, fast rate capability, and Na-ion diffusion kinetics. DFT calculations revealed that the enhancement of Na⁺ migration derives from the optimized crystal structure and the decreases of the bad gap are due to the appearance of the new bound states by B substitution.

2. Results and Discussion

Phase purity of the Na₃V₂P₃–xO₁₂ (0 ≤ x ≤ 1) with various B concentrations was examined by X-ray diffraction (XRD) patterns. As shown in Figure 1, A series of Na₃V₂P₃–xBₓO₁₂ (0 ≤ x ≤ 1/3) with various amount of B can be observed in the rhombohedral crystal structure, which could be well-indexed into the NASICON Na₃V₂(PO₄)₃ with R-3c space group, indicating the substituted B in the range of 0 ≤ x ≤ 1/3 did not change the crystal framework of parent material. Moreover, the continuous shift of peak position to higher angle with increased x in Na₃V₂P₃–xBₓO₁₂ (0 ≤ x ≤ 1/3) implies a solid solution over this composition range, and a shrink of crystal size affected by the substitution of B. This observation is in agreement with previous report concerning variations of crystal volume of the B doped Li₃V₂(PO₄)₃.

Moreover, the half-height width of the peak changes to broaden with the increasing of B contents. The average crystallite sizes of Na₃V₂P₃–xBₓO₁₂ with x = 0, 1/10, 1/6, and 1/3 calculated by Scherrer’s equation are 205, 110, 80, and 64 nm, respectively, indicate that doping B can prevent the growth of nanoparticles, which is favorable for improving the kinetics of Na⁺ diffusion in bulk materials. Nevertheless, substantial changes in the B substitution in a Na₃V₂P₃–xBₓO₁₂ (0 ≤ x ≤ 1) procure the formation of impurities of Na₂V(PO₄)₂ while x > 1/2 (Figure S1, Supporting Information). The particle size and morphologies of Na₃V₂P₃–xBₓO₁₂ (0 ≤ x ≤ 1/3) were explored by scanning electron microscopy (SEM) (Figure S2, Supporting Information), showing sphere-like morphologies with similar particle size range of 0.5–2 μm. The high resolution transmission electron microscopy (HR-TEM) images (Figure 2) of Na₃V₂P₃–xBₓO₁₂ with x = 0 and x = 1/6 shows that both particles are coated uniformly by carbon layer with around 3 nm. It is believed that modification with carbon could endow the Na₃V₂P₃–xBₓO₁₂ higher electronic conductivity. Interplanar spacing of 3.7 Å corresponded to the (113) planes of Na₃V₂(PO₄)₃.

According to the reports on the ion doping, the incorporation of impurity is more likely to replace those ions which have the similar valence states and the closer ionic radii.[37] Therefore, the boron prefers to substitute phosphorus or vanadium. To explore the effect of B doped Na₃V₂(PO₄)₃, a spin-polarized density functional theory (DFT) calculation was performed to investigate the crystal structure change while phosphorus or vanadium is replaced by boron. Figure 1c shows the lowest total energy configuration of Na₃V₂P₃–(1/6)xB₁/₆O₁₂, in which boron atom occupies the tetrahedral interstitial site. It can be clearly observed that a small amount of boron doping does not alter the framework of the material (Figure S3, Supporting Information). The corresponding lattice constants before and after doping are listed in Table S1 in the Supporting Information. The changes in the lattice parameter of the calculated Na₃V₂(PO₄)₃ with reference to the experimental value are less than 2%. The optimization results show that the lattice constant of Na₃V₂P₃–xBₓO₁₂ (0 ≤ x ≤ 1/3) decreases with the increase of boron concentration and a slight deformation of initial rhombohedral structure.

Figure 1. a) XRD patterns of Na₃V₂P₃–xBₓO₁₂ (x = 0, 1/10, 1/6, 1/3) powders, b) magnified view, and c) calculated crystal structure of Na₃V₂P₃–xBₓO₁₂ (x = 1/6).
which is owing to the smaller ion radius of $B^{3+}$ (0.27 Å) relative to $P^{5+}$ (0.38 Å). This is in good agreement with the XRD results. In addition, due to the weaker Coulomb interaction, the strength of the B–O bond is weaker than that of the P–O bond which can provide larger Na$^+$ diffusion channel. However, the lattice parameter $c$ elongates and volume expands significantly when the boron substitutes vanadium site, which are not conform to the experimental results, indicating that boron prefers to substitute for phosphorus.

To identify the local structural change and enhance the comprehension of the shrink of crystal volume affected by B substitution, X-ray absorption spectra including X-ray absorption fine structure (EXAFS) were carried out. According to XANES (Figure 3a) at V K-edge, the edge of B substituted sample shifts to higher energy compared to pristine sample, indicating a higher oxidation state of V in Na$_3$V$_2$P$_{3-x/6}$B$_{x/6}$O$_{12}$, which is consistent with the fact that replacing $P^{5+}$ with aliovalent ion $B^{3+}$ accompanies partly charge compensation of $V$ in the compound. X-ray photoelectron spectroscopy (XPS) of V 2p further confirms the formation of $V^{4+}$ (Figure S4, Supporting Information) and demonstrates that boron successfully a substitute for phosphorus as expected. As Park et al. noted, $V^{4+}$ usually exhibits a short vanadyl V–O bond length, which trends toward a distorted VO$_6$ octahedron. XANES spectra at V K-edge reveal the local environment surrounding V atom. The variation of peak intensity for the samples may be caused by the distortion of VO$_6$ octahedron and other local structural changes after incorporation of B in crystal. Moreover, the V–O distances of the B substituted sample Na$_3$V$_2$P$_{3-x/6}$B$_{x/6}$O$_{12}$ and pristine Na$_3$V$_2$P$_{3}$O$_{12}$ determined from the EXAFS data (Figure 3b) was 1.964 Å and 1.971 Å, suggesting that V–O distances were slightly reduced by substitution of B.

The local structure around the doping site was simulated to better understand the variation. As shown in Figure 3c,d, detail local environment for P and B illustrates that the bond length of B–O2 (O3, O4) in Na$_3$V$_2$P$_{3-x/6}$B$_{x/6}$O$_{12}$ is slightly shorter than that of P–O2 (O3, O4) in the corresponding position of pure Na$_3$V$_2$P$_{3}$O$_{12}$, while the bond length of B–O1 in Na$_3$V$_2$P$_{3-x/6}$B$_{x/6}$O$_{12}$ is slightly longer than that of P–O1 in pure Na$_3$V$_2$P$_{3}$O$_{12}$, which illustrates the local tetrahedral distortion after B doped Na$_3$V$_2$P$_{3}$O$_{12}$. In addition, as compared with the undoped samples, the V1–O1 and V3–O3 bond length of Na$_3$V$_2$P$_{3-x/6}$B$_{x/6}$O$_{12}$ is significantly shortened, while other V–O bond length only slight shrinkage (Table S2, Supporting Information), showing the same tendency with the experimental results. For the pure Na$_3$V$_2$(PO$_4$)$_3$ or Na$_3$V$_2$(PO$_4$)$_{3-}$, the calculated local magnetic moments of V ion are the same (1.98 or 1.103 $\mu_B$). However, the calculated local magnetic moment of V1 (1.179 $\mu_B$) and V3 (1.170 $\mu_B$) are quite different with other V ion (1.975–1.988 $\mu_B$) in Na$_3$V$_2$P$_{3-x/6}$B$_{x/6}$O$_{12}$, indicating that the V1 and V3 ions are oxidized when boron substitutes phosphorus. Therefore, the strong Coulomb interaction leads to the shrinkage of V1-O1 and V3-O3 when the oxidation state of V1 and V3 changes from $V^{3+}$ to $V^{4+}$. The change of local element valence induces the adjacent polyhedron geometry distortion.

The effects of substitution on intrinsic electronic conductivity were explored by calculating the density of state of Na$_3$V$_2$P$_{3-x/6}$B$_{x/6}$O$_{12}$. The spin up density of states (DOS) of Na$_3$V$_2$(PO$_4$)$_3$ and the projected DOS of atoms as labeled in Figure 3c are displayed in Figure S5 in the Supporting Information. It clearly shows that Na$_3$V$_2$(PO$_4$)$_3$ is a semiconductor with a large band gap of 2.57 eV and the high energy occupied regions in valence band are mainly ascribed to the V3d states with little contribution of O-2p states, while the low energy occupied regions in conduction band are mainly ascribed to the O-2p states with little contribution of V3d states, which are in agreement with the other theoretical calculation result using HSE06 hybrid function. All the V3d states and O-2p states are nearly the same. Due to the larger band gap, the electronic conductivity of Na$_3$V$_2$(PO$_4$)$_3$ is poor, which seriously affects its electrochemical performance. Therefore, the strong Coulomb interaction leads to the shrinkage of V1-O1 and V3-O3 when the oxidation state of V1 and V3 changes from $V^{3+}$ to $V^{4+}$. The change of local element valence induces the adjacent polyhedron geometry distortion.

![Figure 2](image-url)HR-TEM images of Na$_3$V$_2$P$_{3-x/6}$B$_{x/6}$O$_{12}$: a) $x=0$ and b) $x=1/6$.
to the 3d states of V1 and V3 atoms, while those near the top of the valence band are mainly ascribed to the 3d states of V2 and V4 atoms. There are two holes when B$^{5+}$ substituted P$^{5+}$, which may be transferred to the vicinity of the V1 and V3 atoms and induce the new energy states near the bottom of conduction band. Then the oxidation state of V1 and V3 changes from

![Figure 3.](image)

a) XANES and b) Fourier transformed EXAFS spectra of the Na$_3$V$_2$P$_3$–$xB_x$O$_{12}$ ($x=0$ and $x=1/3$). Local distortion around the doping site after structural optimization of Na$_3$V$_2$P$_3$–$xB_x$O$_{12}$ c) ($x=0$) and d) ($x=1/6$).

![Figure 4.](image)

Calculated a) total density of states (DOS) of Na$_3$V$_2$P$_3$–$xB_x$O$_{12}$ ($x=0$, $1/6$, $1/3$) and b) partial spin up density of states of Na$_3$V$_2$P$_{3-1/6}$B$_{1/6}$O$_{12}$. $E_f$ represents the Fermi energy level.
V\textsuperscript{3+} to V\textsuperscript{4+}, resulting the VO\textsubscript{6} octahedral distortion. The change of the local structure also affects the electronic structure of the adjacent atoms, such as V\textsubscript{2} and V\textsubscript{4}, and the appearance of the new energy states may improve the electrical properties of the materials.

To investigate the influence of B substitution on the cycling stability and rate capability of the batteries, half-cells were tested at various charge/discharge rates in the potential range of 2.5–4.0 V. Figure 5a compares the rate capability of the Na\textsubscript{3}V\textsubscript{2}P\textsubscript{3–x}B\textsubscript{x}O\textsubscript{12} (x = 0, 1/10, 1/6, 1/3) electrodes at charge–discharge rate increasing from 0.5 to 10 C. All the samples display the similar capacity of 105 mAh g\textsuperscript{−1} at lower C-rate of 1 C regardless of B content. However, samples with various B concentration shows distinct improvement of high C-rate capability above 3 C. Na\textsubscript{3}V\textsubscript{2}P\textsubscript{3–x}B\textsubscript{x}O\textsubscript{12} with x = 1/6 exhibits the highest rate capability, giving remarkable enhanced capacity of 100 and 70 mAh g\textsuperscript{−1} when the C-rate increases to 5 C and 10 C, respectively. The flat potential plateau displaying nearly theoretical capacity of 2 Na intercalation/deintercalation at around 3.4 V with weak polarization was observed at 1 C (Figure 5b). With the increase of C-rate, Na\textsubscript{3}V\textsubscript{2}P\textsubscript{3–1/6}B\textsubscript{1/6}O\textsubscript{12} delivers the lower capacity and larger potential gap as compared with that of Na\textsubscript{3}V\textsubscript{2}P\textsubscript{3} (Figure 5c). Na\textsubscript{3}V\textsubscript{2}P\textsubscript{3–1/6}B\textsubscript{1/6}O\textsubscript{12} maintained 98.4% of the initial discharge capacity after 200 cycles, whereas the Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} retained a lower portion of 97.2% of the initial discharge capacity after the same cycles, exhibiting the similar cycling stability of the electrodes.

Further kinetic analysis of the Na\textsubscript{3}V\textsubscript{2}P\textsubscript{3–x}B\textsubscript{x}O\textsubscript{12} (x = 0 and x = 1/6) was performed by cyclic voltammograms (CV). CV curves at a scan rate of 0.5 mV s\textsuperscript{−1} in potential range of 2.5–4.0 V versus Na\textsuperscript{+}/Na (Figure 6, Supporting Information) show that Na\textsubscript{3}V\textsubscript{2}P\textsubscript{3–1/6}B\textsubscript{1/6}O\textsubscript{12} exhibits a smaller potential polarization between cathodic and anodic peaks than pristine material, indicating weaker electrode polarization and faster ionic migration. With increasing of scan rates from 0.2 to 0.5 mV s\textsuperscript{−1} (Figure 6), slight shifts of potential of oxidation and reduction peaks at fast scan rate further suggest the existence of fast kinetics and weak polarization of the electrochemical reaction for electrode. A linear relationship between peak current (i\textsubscript{p}/m) and square root of potential scan rate indicates that the electrode reaction would be favored to be a diffusion-determining step. Diffusion coefficient of Na ions (D\textsubscript{Na}) can be calculated from the slope of the linear relationship using Randles–Sevcik equation.
of adjacent octahedral after B doping Na₃V₂(PO₄) may lead to shrinkage of tetrahedral of the doping site and the distortion longer. The diffusion routes of Na ion in Na₃V₂P₃₋⁵/₆B⁵/₆O₁₂ of Na₂–Na₁ (0.43 eV), the distance of Na₂–Na₂ is relative activation energy along Na₂–Na₂ (0.396 eV) is lower than that in Na₃V₂(PO₄)₃ (Figure 7c,d), Na₃V₂P₃₋⁵/₆B⁵/₆O₁₂ along Na₂–Na₁ (0.347 eV) and Na₂–Na₂ to a larger diffusion path. The energy barriers of Na ion in

The absolute values of slope for anodic and cathodic peaks of Na₃V₂P₃₋⁵/₆B⁵/₆O₁₂ are 48.17 and 47.55, higher than that of pristine Na₃V₂(PO₄)₃ (36.43 and 33.66) from the linear fitting results. Therefore, the Dₙa is ~1.7 and 1.9 times higher in Na₃V₂P₃₋⁵/₆B⁵/₆O₁₂ than those in pristine Na₃V₂(PO₄)₃ for anodic and cathodic process, respectively. Fast kinetics properties can be attributed to the enhanced ionic and electronic conductivities of the materials after B substitution.

Na₃V₂(PO₄)₃ has two Na ion positions, namely Na1 and Na2, along the conduction channels and there are two typical ion transport pathways in the NASICON structure, namely Na₂-Na1-Na2 and Na₂-Na2.[40] In order to figure out the effect of doping on ionic conduction, the Na ion hopping barriers along the path of Na₂-Na1 and Na2-Na2 in Na₃V₂P₃₋⁵/₆B⁵/₆O₁₂ (x = 0 and x = 1/6) were calculated using the climbing image nudged elastic band (CINEB) method. The distances of neighboring Na₁-Na₂ (3.315 Å) and Na₂-Na₂ (4.358 Å) near the doping site in Na₃V₂P₃₋⁵/₆B¹/₆O₁₂ are shorter than those in Na₃V₂(PO₄)₃ (3.416 Å, 4.472 Å) respectively; however, the distances of Na₁-Na₂ and Na₂-Na₂ far from the doping site in Na₃V₂P₃₋⁵/₆B¹/₆O₁₂ are nearly the same as those in Na₃V₂(PO₄)₃. The diffusion trajectory in Na₃V₂(PO₄)₃ and the corresponding migration energy barriers for Na ion near the doping site along the path of Na₂-Na₁ and Na₂-Na₂ in Na₃V₂P₃₋⁵/₆B¹/₆O₁₂ (x = 0 and x = 1/6) are plotted in Figure 7. In pathway 1 and pathway 2, the Na ions diffuse through a bottleneck triangle and the migration trajectory are parallel to the two nearest VO₆ octahedral due to the strong electrostatic repulsion between V and Na ions (Figure 7a,b). Although the activation energy along Na₂–Na₂ (0.396 eV) is lower than that of Na₂–Na₁ (0.43 eV), the distance of Na₂–Na₂ is relative longer. The diffusion routes of Na ion in Na₃V₂P₃₋⁵/₆B¹/₆O₁₂ are similar to that in Na₃V₂(PO₄)₃. As discussed above, the shrinkage of tetrahedral of the doping site and the distortion of adjacent octahedral after B doping Na₃V₂(PO₄)₃ may lead to a larger diffusion path. The energy barriers of Na ion in Na₃V₂P₃₋⁵/₆B¹/₆O₁₂ along Na₂-Na₁ (0.347 eV) and Na₂-Na₂ (0.282 eV) are lower than that in Na₃V₂(PO₄)₃ (Figure 7c,d), indicating that Na ion is more likely to migrate after B substituted P as a result of the shorter distance of Na₁–Na₂ and the larger diffusion channel induced by the local structure distortion.

3. Conclusion

A series of B substituted Na₃V₂P₃₋xBₓO₁₂ (0 ≤ x ≤ 1) have been successfully prepared by a sol–gel process. The XRD and XAS characterizations demonstrated that B doping did not change the crystal framework of parent material in the range of 0 ≤ x ≤ 1/3, but aroused the local structure distortion with tiny shrink of crystal lattice. Confirmed from the results of DFT calculation, doping of B in material could change local element valence, resulting in the adjacent polyhedron geometry distortion, which narrow the band gap and facilitate the diffusion of Na⁺. B substituted Na₃V₂P₃₋xBₓO₁₂ significantly enhances the structure stability and electrochemical performance. Na₃V₂P₃₋xB¹/₆O₁₂ exhibits the best cycling stability and rate capability. The capacity retention of Na₃V₂P₃₋xB¹/₆O₁₂ (98.7%) is much higher than that of pristine materials (91.8%) after 200 cycles at 5 C.

4. Experimental Section

Computation Methods: First-principles spin-polarized density functional theory (DFT) calculations[41] have been performed to investigate the Boron doping to the NASICON structured Na₃V₂(PO₄)₃ cathode materials using the Vienna ab initio simulation package[42] with the projector augmented waves (PAW) pseudopotentials[43] and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.[44] The plane-wave basis set was determined with a cutoff energy of 520 eV and the k-point sampling of Brillouin-zone integrals used a 2 × 2 × 1 Gamma grid. The simplified rotationally invariant approach introduced by Dudarev[45] to the Hubbard model corrections was used with a U-J parameter of 4.2 eV for vanadium atom, whereas the correction was not used for the other species. The U value of vanadium is a little higher than the experimental formation enthalpy of vanadium oxides as there are high inductive effects in vanadium phosphates.[46] The calculations were performed in a rhombohedral chemical cell consisting 6-f.u. Na₃V₂(PO₄)₃ and a sodium-ordered form was chosen in our models which had been demonstrated in other literatures.[47,48] Different boron substitution positions of Na₃V₂P₃₋xBₓO₁₂ (x = 1/6 and x = 2/6) and Na₃V₂P₃₋xB¹/₆O₁₂ were calculated, and the lowest energy structure was selected. The Na⁺-ion hopping barriers were obtained using the climbing image nudged elastic band (CINEB) method, which can determine the pathway for structure changes efficiently.

Figure 6. CV curves of the pristine a) Na₃V₂(PO₄)₃ and b) Na₃V₂P₃₋¹/₆B¹/₆O₁₂ at various sweep rates; b) Iₓ versus vₓ/2 and linear fitting curves of CV.
Sample Preparation: The NASICON structured Na$_3$V$_2$P$_3$–$x$B$_x$O$_{12}$ ($0 \leq x \leq 1$) was synthesized by a sol–gel process and followed by solid-state reaction. Typically, 2 mmol NH$_4$VO$_3$ and 4 mmol citric acid were added to 70 mL deionized water maintaining at 80 °C with continuous stirring to obtain a clear solution, and then stoichiometric amount of Na$_2$CO$_3$, NH$_4$H$_2$PO$_4$, and H$_3$BO$_3$ were added. After evaporation of water at 80 °C, the solution transforms from sol to gel. The gel was dried in an oven at 150 °C for 4 h, and heat-treated at 400 °C for 5 h under nitrogen atmosphere to remove CO$_2$, H$_2$O, and NH$_3$. Afterward, the powder was ground and annealed at 800 °C under Ar flow for 12 h to produce the final compound.

Structure Characterization: X-ray diffraction (XRD) patterns of the as-prepared samples were collected on a Bruker D8 diffractometer using Cu Kα radiation. The morphology of the materials was observed by Hitachi S-4800 field emission scanning electron microscope (FE-SEM). High resolution transmission electron microscope (HR-TEM) images were taken on a JEOLJEM-2010F microscope (JEOL, Japan) at an acceleration voltage of 200 kV. X-ray absorption spectroscopy (XAS) was measured at the V k-edge, at 12-BM at the advanced photon source (APS), Argonne national laboratory.

Electrochemical Characterization: The work electrode was prepared by coating a mixture of 80 wt% Na$_3$V$_2$P$_3$–$x$B$_x$O$_{12}$ ($0 \leq x \leq 1$), 10 wt% PVDF and 10 wt% Super P onto Al current collector. The electrode was then dried at 120 °C in vacuum for 12 h. The test cells were assembled into coin cell in an argon-filled glovebox. Sodium metal foil was used as the counter electrode and a glass fiber filter (Whatman) was used as the separator. A 1 M solution of NaClO$_4$ in EC/DMC (1:1 by volume) was prepared and used as the electrolyte. The charge/discharge, C-rate capacity and cycling ability of cells were recorded on a LAND battery test system. Cyclic voltammograms (CVs) were performed using a CHI 440A instrument (CHI Instrument Inc.) at a scanning rate from 0.2 to 0.6 mV s$^{-1}$.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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