Investigation of the Inorganic Compounds NaMV₂(PO₄)₃ (M = Fe, Co, Ni) as Anode Materials for Sodium-Ion Batteries

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ABSTRACT: The new compounds NaMV₂(PO₄)₃ (M = Fe, Co, Ni) were synthesized via a sol−gel synthesis route, and their crystal structures were refined using the Rietveld method from X-ray powder diffraction data. NaCoV₂(PO₄)₃ was also characterized by TGA, cyclic voltammetry, and galvanostatic cycling. The three phases crystallize with the orthorhombic symmetry and the space group Imma. The structures are isotypic to the studied α-CrPO₄-type structure and contain two vacant sites in which two sodium atoms can be intercalated. When NaCoV₂(PO₄)₃ is cycled at a 1C rate in the voltage ranges of 0.1−3 and 0.7−3 V vs Na⁺/Na, it delivers specific capacities of 190 and 75 mA h/g, respectively, with an average operation potential of ∼1.4 V. This attests to the electrochemical activity of this compound and indicates that the α-CrPO₄-type compounds could be suitable for hosting other guest ions.

1. INTRODUCTION

Nowadays, lithium-ion batteries (LIBs) are the most commonly used batteries in portable consumer electronic devices and in electric vehicles (EVs). With the population growth and the global warming, investments in renewable energies (solar, wind, or tidal power) are rising and the demand for LIBs is predicted to increase significantly in the future. This may cause disruption in the raw-material supply chain; therefore, since sodium is one of the most abundant and cheap elements on Earth and has similar electrochemical properties to lithium, sodium-ion batteries (NIBs) could be alternatives to LIBs, especially for large-scale storage applications.

Researchers have already developed a wide range of positive electrode materials for NIBs, namely, the layered oxides NaMO₂ and sulﬁdes NaMS₂; the polyanionic compounds NaMPO₄, Na₂MP₂O₇, Na₂MPO₄CO₃, Na₂M₃(PO₄)₂PO₄, Na₂M₅(PO₄)₃, Na₄M₂(SO₄)₂(PO₄), Na₂M₅(SO₄)₂, NaMPO₄F, Na₂MPO₄F, and Na₂M₅(PO₄)₂Fₓ; the ﬂuorides NaMFₓ; or the Prussian blue analogues Na₃M₆[Mₓ(CN)₆],nH₂O (M = divalent and/or trivalent transition metal). Among these intercalation compounds, NaMO₂ and Na₂V₃(PO₄)₂Fₓ are the best candidates for a practical application in NIBs. Furthermore, a large number of negative electrode materials also were investigated. These materials were classiﬁed into six main categories, namely, carbonaceous (e.g., hard carbon, soft carbon, N-graphene foam), conversion (e.g., Fe₂O₃, Co₃O₄, CuO), alloying (e.g., Ge, Sb, Si, Sn, Ni₃S₄, SnSb, SnGeSb, SnPₓ, SnFₓ, red P), conversion + alloying (e.g., SnO₂, SnO, SnS, SnS₂, Sb₂O₅, Sb₂O₃, Sb₂S₃), organic (e.g., Na₂C₈H₄O₄, Na₂C₆H₂O₄, Na₂C₁₄H₄O₄N₂, Schiff base polymers), and insertion materials (e.g., NaTiO₂, P₂Na₀.₆₆[Li₀.₂₂Ti₀.₇₈]O₂, Na₂Ti₃O₇, TiO₂, Li₄Ti₅O₁₂) (refs 19, 20, and references therein). To our knowledge, only a few polyanionic compounds have been investigated as anode materials for NIBs [e.g., NaTi₂(PO₄)₃ and Na₂V₃(PO₄)₂]; therefore, we decided to explore phosphates with multiple electron transfer to achieve high...
specific capacity with a relatively low potential. The Cr$_4$PO$_4$ family of compounds is particularly interesting since the β-CrPO$_4$ structure (α-CrVO$_4$-type) contains vacancies that may accommodate Li, Na, Ag, or Cu atoms. The α-CrPO$_4$ structure also contains large empty channels in which Li or Na atoms can be intercalated. Our research team was the first to report α-Na$_2$Ni$_2$Fe(PO$_4$)$_3$. NaCoCr$_2$(PO$_4$)$_3$, NaNiCr$_2$(PO$_4$)$_3$, and Na$_2$Ni$_2$Cr(PO$_4$)$_3$ crystallizing with the α-CrPO$_4$-type structure, as anode materials for NIBs. Following our results, other researchers investigated vanadium-based compounds such as NaV$_3$(PO$_4$)$_3$ and NaCoV$_2$(PO$_4$)$_3$ as anode materials for NIBs.

In the present work, we describe the synthesis and crystal structures of NaMV$_2$(PO$_4$)$_3$ (M = Fe, Co, Ni) determined by X-ray powder diffraction. We then describe the thermal and electrochemical properties of NaCoV$_2$(PO$_4$)$_3$ determined by TGA, cyclic voltammetry, and galvanostatic cycling measurements.

2. RESULTS AND DISCUSSION

2.1. Structure Refinement. The crystal structure of NaCoV$_2$(PO$_4$)$_3$ was solved using the structure of NaCoCr$_2$(PO$_4$)$_3$ as a starting model. A statistical disorder of Co/V atoms was introduced, and constraints on their occupancies and atomic displacement parameters (ADPs) were applied. Since few ADP tensors displayed negative values, atoms of the same nature were restricted to have the same ADPs. The same constraints applied during the structural refinement of NaCoV$_2$(PO$_4$)$_3$ were also applied to NaCoNi$_2$VPO$_7$. The Rietveld analysis of the XRPD data collected at 293 K led to the reliability factors listed in Table 1. The atomic positions are given in Table 2. Figure 1 shows good agreement between the experimental and calculated patterns. Only one unindexed peak (see the inset of Figure 4). Therefore, a search-match process within the ICDD database was performed to identify the impurity phase that corresponds to Ni$_2$P$_5$. Consequently, the atomic positions of NaCoV$_2$(PO$_4$)$_3$ and Ni$_2$P$_5$ were used for the Rietveld refinement of NaCoV$_2$(PO$_4$)$_3$ (1) and Ni$_2$P$_5$ (2) structures, respectively. The same constraints applied during the structural refinement of NaCoV$_2$(PO$_4$)$_3$ were also applied to NaNi$_2$VPO$_7$.

2.2. Crystal Structure. The NaMV$_2$(PO$_4$)$_3$ (M = Fe, Co, Ni) compounds are isostructural to NaCoCr$_2$(PO$_4$)$_3$, which crystallizes with the α-CrPO$_4$-type structure. The structure consists of layers of [(M$_2$/V$_2$)O$_{10}$] dimer units (M = Fe, Co, Ni) sharing corners and edges with the [P$_2$O$_4$] tetrahedra (Figure 6d). These layers are bridged by oxygen atoms. The [V$_1$O$_6$] and [(Co$_2$/V$_2$)O$_6$] terahedra (Figure 6c) give rise to a three-dimensional framework with channels along the $a$ and $b$ axes, within which the sodium atoms are located (Figure 6a,b). Interatomic distances and bond valence sums (BVs) are listed in Table 3.

2.2.1. Crystal Structure of NaCoV$_2$(PO$_4$)$_3$. The vanadium atoms V1 and V2 occupy the atomic positions 4a (0,0,0) and 8g (1/4, 1/4, 3/4), respectively, and are octahedrally coordinated to oxygen atoms. The [V$_{18}$O$_8$] and [Co$_2$/V$_2$]O$_{10}$ octahedra are strongly distorted. In [V$_{18}$] octahedra, the

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**Table 1. Crystallographic Data and Structure Refinements for NaMV$_2$(PO$_4$)$_3$ (M = Fe, Co, Ni)**

| Crystal data | NaFeV$_2$P$_3$O$_{12}$ | NaCoV$_2$P$_3$O$_{12}$ | NaNiV$_2$P$_3$O$_{12}$ |
|--------------|-----------------------|-----------------------|-----------------------|
| Chemical formula | NaFeV$_2$P$_3$O$_{12}$ | NaCoV$_2$P$_3$O$_{12}$ | NaNiV$_2$P$_3$O$_{12}$ |
| $M_a$ | 465.6 | 468.7 | 468.5 |
| Space group | Imma | Imma | Imma |
| Temperature (K) | 293 | 293 | 293 |
| $a$, $b$, $c$ (Å) | 10.5067 (4) | 10.4947 (10) | 10.5091 (5) |
| $V$ (Å$^3$) | 889.80 (6) | 884.42 (14) | 876.16 (6) |
| $Z$ | 4 | 4 | 4 |

**Table 2.** The vanadium atoms V1 and V2 occupy the atomic positions 4a (0,0,0) and 8g (1/4, 1/4, 3/4), respectively, and are octahedrally coordinated to oxygen atoms. The [V$_{18}$O$_8$] and [Co$_2$/V$_2$]O$_{10}$ octahedra are strongly distorted. In [V$_{18}$] octahedra, the...
V1−O distances range from 1.927 to 2.030 Å with an average distance of 1.961 Å, whereas in [(Co2/V2)O6] octahedra, the V2−O distances are slightly larger. They range from 2.016 to 2.174 Å with an average value of 2.069 Å. This difference is mainly due to the presence of a statistical disorder of Co2+ and V3+ on the atomic position 8g (1/4, 0.6383, 1/4). Since the ionic radius of Co2+ (0.745 Å) is larger than that of V3+ (0.64 Å), dCo/V−O is larger than dV−O. The [PO4] and [P2O4] tetrahedra are regular in shape since the dP−O distances were constrained. The Na1+ ions are bonded to eight oxygen atoms belonging to six different [VO6] octahedra (Figure 6e). The Na1−O distances range from 2.606 to 2.718 Å with an average value of 2.689 Å. The BVS values of 0.73 for Na1 indicate that Na1 is under bonded.

2.2.2. Comparison of NaMV2(PO4)3 (M = Fe, Co, Ni).

The quantitative comparison between the three isotypic structures of NaMV2(PO4)3 (M = Fe, Co, Ni) was performed using the program Compstru. The numerical details of the comparison are given in Table 4. The crystal structures of the Ni and Co phases are highly similar with a measure of similarity \( \Delta = 0.031 \). The positions of the cations are essentially coincident, whereas large displacements were observed for the atom pairs O3 and O4, which are coordinated to the P2 atom. Our careful examination using the Vesta program indicates a slight tilt of the P2O4 tetrahedra (Figure S2). The crystal structures of the Fe and Co phases are also highly similar with a measure of similarity \( \Delta = 0.019 \). Furthermore, the atom pairs O3 and O4 show the largest displacements as in the case of Ni vs Co. The crystal structures of the Ni and Fe phases were also compared (\( \Delta = 0.025 \)). In this case, the largest atomic displacements were observed for the atom pairs Na1 and O2. Although the \( d_{Na1−O} \) distances were strongly shortened in the Fe phase (see Table 3), no major change in the coordination polyhedron of Na1 was observed (Figure S3). The decrease of the cell volume [894.52, 889.8 (6), 884.42 (14), 876.16 (6) Å3] when replacing V2+ with Fe2+, Co2+, or Ni2+, respectively, is

### Table 2. Fractional Atom Coordinates and Isotropic Atomic Displacement Parameters (Å²) for NaMV2(PO4)3 (M = Fe, Co, Ni)

| atom     | Wyck. | site   | occ. | x     | y     | z     | U^iso (Å²) |
|----------|-------|--------|------|-------|-------|-------|------------|
| NaFeV2P3O12 |      |        |      |       |       |       |            |
| Na1      | 4e    | mm2    | 1    | 0     | 1/4   | 0.405(2) | 0.004(5)   |
| V1       | 4a    | 2/m..  | 1    | 0     | 0     | 0     | 0.016(3)   |
| Fe2/V2   | 8g    | .      | 0.5/0.5 | 1/4 | 0.6338(4) | 1/4   | 0.0205(19) |
| P1       | 4e    | mm2    | 1    | 0     | 1/4   | 0.9199(16) | 0.010(3)  |
| P2       | 8g    | .      | 0.5/0.5 | 1/4 | 0.4255(5) | 1/4   | 0.010(3)  |
| O1       | 8h    | m.     | 1    | 0     | 0.1482 (6) | 1/4   | 0.004(2)   |
| O2       | 8i    | .      | 1    | 0.1105 (11) | 1/4 | 0.7642(15) | 0.004(2)  |
| O3       | 16j   | 1      | 1    | 0.2817 (8) | 0.3593(5) | 0.061(1) | 0.004(2)  |
| O4       | 16j   | 1      | 1    | 0.3596(7) | 0.5002(5) | 0.2816 (15) | 0.004(2)  |
| NaCoV2P3O12 |      |        |      |       |       |       |            |
| Na1      | 4e    | mm2    | 1    | 0     | 1/4   | 0.3934(19) | 0.004(5)  |
| V1       | 4a    | 2/m..  | 1    | 0     | 0     | 0     | 0.015(3)   |
| Co2/V2   | 8g    | .      | 0.5/0.5 | 1/4 | 0.6383(4) | 1/4   | 0.024(2)  |
| P1       | 4e    | mm2    | 1    | 0     | 1/4   | 0.9077(17) | 0.009(3)  |
| P2       | 8g    | .      | 0.5/0.5 | 1/4 | 0.4304(5) | 1/4   | 0.009(3)  |
| O1       | 8h    | m.     | 1    | 0     | 0.1528 (7) | 1/4   | 0.0105    |
| O2       | 8i    | .      | 1    | 0.1195 (11) | 1/4 | 0.7707(15) | 0.0105    |
| O3       | 16j   | 1      | 1    | 0.2906 (7) | 0.3689(5) | 0.0581(10) | 0.0105    |
| O4       | 16j   | 1      | 1    | 0.1393 (7) | 0.5014(4) | 0.1963 (15) | 0.0105    |
| NaNiV2P3O12 |      |        |      |       |       |       |            |
| Na1      | 4e    | mm2    | 1    | 0     | 1/4   | 0.387(3)  | 0.054(10)  |
| V1       | 4a    | 2/m..  | 1    | 0     | 0     | 0     | 0.000(2)   |
| Ni2/V2   | 8g    | .      | 0.5/0.5 | 1/4 | 0.6339(2) | 1/4   | 0.0062(15) |
| P1       | 4e    | mm2    | 1    | 0     | 1/4   | 0.9199(12) | 0.008(2)  |
| P2       | 8g    | .      | 0.5/0.5 | 1/4 | 0.4263(4) | 1/4   | 0.008(2)  |
| O1       | 8h    | m.     | 1    | 0     | 0.1497 (8) | 1/4   | 0.0105    |
| O2       | 8i    | .      | 1    | 0.1170 (8) | 1/4 | 0.7782(12) | 0.0105    |
| O3       | 16j   | 1      | 1    | 0.2838 (6) | 0.3592(4) | 0.0623(7) | 0.0105    |
| O4       | 16j   | 1      | 1    | 0.1384 (5) | 0.5001(4) | 0.2277 (12) | 0.0105    |

Figure 1. Observed, calculated, and difference plots from the Rietveld refinement of the XRPD (Cu Kα radiation) pattern of NaCoV2(PO4)3. The asterisk corresponds to the peak (022) of the impurity phase NaVP2O7.
in good agreement with the decrease of the ionic radii of the octahedral coordinated atoms (IR\(_V\) = 0.79, IR\(_Fe\) = 0.78, IR\(_Co\) = 0.745, IR\(_Ni\) = 0.69 Å) and explains the shift of the XRPD patterns toward high \(\theta\) angles (Figure S1). The formation of these four phases indicates that the \(\alpha\)-CrPO\(_4\)-type structure is very flexible and can accommodate small and large cations. It would be very interesting to test it as a host for magnesium and potassium.

2.3. Electrochemical Properties of NaCoV\(_2\)(PO\(_4\))\(_3\). The electrochemical measurements were performed on the NaCoV\(_2\)(PO\(_4\))\(_3\) sample since this phase was almost pure. Figure 7a shows the charge/discharge cycles of the [NaCoV\(_2\)(PO\(_4\))\(_3\)/electrolyte/Na] half-cell, between 0.1 and 3.0 V, at a 1C rate (1 e\(^-\) transfer \(\rightarrow\) 57 mA h/g). The charge/discharge profiles are nearly identical to those observed in NaV\(_3\)(PO\(_4\))\(_3\). NaCo\(^{2+}\)V\(^{2+}\)(PO\(_4\))\(_3\) and NaV\(^{2+}\)V\(^{2+}\)(PO\(_4\))\(_3\) are isostructural, and in both compounds, the electrochemical process involves the redox couple V\(^{3+}/V^{2+}\) as depicted in the equation below

\[
\square \, 2 \, \text{Na}^+ M^{2+}(V^{3+})_2(\text{PO}_4)_3 + 2 \, \text{Na}^+ + 2 \, e^- \rightleftharpoons 2 \, \text{Na}_3M^{2+}(V^{2+})_2(\text{PO}_4)_3 (M^{2+} = \text{V}, \text{Co}; \square = \text{vacancy})
\]

NaCoV\(_2\)(PO\(_4\))\(_3\) delivers an initial discharge and charge capacities of 290 and 180 mA h/g, respectively. An initial Coulombic efficiency of nearly 62% is due to the decomposition of the electrolyte and formation of the solid electrolyte interphase (SEI) layer [see the large irreversible peak around 0.5 V in the dQ/dV plot (Figure 7b)]. No
conversion reaction took place since the ex situ XRPD pattern of the electrode after the first cycle was almost identical to that of the initial electrode (Figure S4). In the subsequent cycles, NaCoV$_2$(PO$_4$)$_3$ delivers a reversible capacity of around 190 mA h/g that increases slightly during the first 40 cycles and then decreases to reach 75 mA h/g after 250 cycles (Figure 7c). This capacity fade is most probably due to the reduction of the electrolyte at low voltages.

It should be noted that a capacity of 190 mA h/g is much higher than 114 mA h/g expected for the intercalation/extraction of two sodium atoms. A similar phenomenon was observed in NaV$_2$(PO$_4$)$_3$, and the authors concluded based on impedance spectroscopic analyses that the electrochemical process involves two different mechanisms. $^{5,7}$ Similarly, we conclude that in the voltage range of 3–0.7 V, NaCoV$_2$(PO$_4$)$_3$ undergoes a multistep Na intercalation reaction with the insertion of two sodium atoms and the formation of Na$_3$CoV$_2$(PO$_4$)$_3$, and below 0.7 V, there is a pseudo-capacitive contribution. To confirm this, another cell was cycled between 0.7 and 3 V at a 1 C rate (Figure 8a). After the formation of the SEI layer during the first discharge, the cell can be cycled reversibly for 250 cycles delivering an average specific capacity of 75 mA h/g (Figure 8b). This confirms that the capacitive...
contribution was eliminated and the electrolyte decomposition was avoided when the lower cutoff voltage was limited to 0.7 V.

The rate capability of NaCoV₂(PO₄)₃ is depicted in Figure S5. In the voltage range of 0.1−3 V and at C/5 and 1C rates, the cell delivers ∼207 and 180 mA h/g, respectively. Meanwhile, at 5C, 10C, and 20C rates, no charge/discharge could take place. This slow charge discharge kinetic indicates that NaCoV₂(PO₄)₃ most probably requires a carbon coating to increase its electronic conductivity. Hu et al. have demonstrated that the introduction of carbon is effective to improve the rate capability of NaV₃(PO₄)₃.37

3. CONCLUSIONS

The new compounds NaMV₂(PO₄)₃ (M = Fe, Co, Ni), synthesized via a sol−gel reaction route, crystallize with the stuffed α-CrPO₄-type structure. Their structures, determined using XRPD data, are essentially coincident. These compounds are not stable at temperatures above 850 °C. Only the cobalt phase was almost pure when annealed at 750 °C for 24 h under argon. The structure of NaCoV₂(PO₄)₃ contains two vacant sites, which enables the intercalation of two sodium atoms leading to the reduction of both vanadium atoms from V⁵⁺ to V³⁺ and the formation of the new phase Na₃CoV₂(PO₄)₃. This mechanism takes place between 3 and 0.7 V; however, between 0.7 and 0.1 V, a capacitive contribution is observed. After the first cycle in the voltage range of 0.1 to 3 V, the cell can be cycled reversibly and delivers ∼190 mA h/g. This capacity increases slightly during the first 40 cycles and then fades quickly to 75 mA h/g after 250 cycles. If the cell is cycled between 0.7 and 3 V, NaCoV₂(PO₄)₃ exhibits good sodium uptake and removal behavior with a stable capacity of ∼75 mA h/g at a 1C rate and an operation potential around 1.4 V. These results indicate that the α-CrPO₄-type structure is very flexible and can accommodate a wide range of cations and therefore can be used as a host for sodium and most probably for other guest ions such as magnesium or potassium.

4. EXPERIMENTAL SECTION

4.1. Synthesis. The compound NaCoV₂(PO₄)₃ was prepared via a sol−gel reaction route, from a 1:1:2:3:2 molar ratio of sodium acetate CH₃COONa (Aldrich, ≥99%), cobalt acetate tetrahydrate Co(CH₃COO)₂·4H₂O (Aldrich, ≥99.995%), ammonium metavanadate NH₄VO₃ (Aldrich, ≥99%), ammonium dihydrogen phosphate NH₄H₂PO₄ (Aldrich, ≥99%), and citric acid C₃H₅O(COOH)₃ (Riedel-deHäen) (CA). First, NH₄VO₃ and CA with a 1:1 molar ratio were dissolved in 40 mL of water to form a clear blue solution, and then Co(CH₃COO)₂·4H₂O was dissolved in 20 mL of water and added to the blue solution (solution A). The CH₃COONa and NH₄H₂PO₄ precursors were dissolved together in 40 mL of water (solution B). Solution B was then added dropwise to solution A under continuous stirring. The solution was finally left to dry at 90 °C overnight. The resulting powder was pelletized, put into an alumina crucible, and heated at 500 °C for 3 h under argon to decompose the precursors and release the H₂O, NH₃, and CO₂ molecules. The pellet was then ground, pelletized, and annealed at 750 °C for
24 h under argon. The synthesis procedure mentioned above was also used to prepare NaFeV2(PO4)3 and NaNiV2(PO4)3. The progress of the reactions was followed by X-ray powder diffraction (XRPD). The three phases were formed since the XRPD patterns were very similar to the theoretical XRPD of NaV2(PO4)3; however, impurities were observed (Figure S1). Therefore, several other heat treatments were performed under different conditions. At temperatures below 750 °C, most of the samples were partly amorphous, whereas at temperatures above 750 °C, the amount of impurities increased and weight losses were noticed. It should be mentioned that the samples used in the current manuscript contain the least amount of impurities.

4.2. X-ray Powder Diffraction Measurement. To ensure the purity of our samples, XRPD measurements were performed. The data were collected at room temperature over the 2θ angle range of 5° ≤ 2θ ≤ 100° with a step size of 0.02° using a Bruker D8 advance diffractometer operating with Cu Kα radiation. Full-pattern matching refinements were performed with the Jana2006 program package. The backgrounds were estimated by Legendre functions, and the peak shapes were described by a pseudo-Voigt function. Rietveld refinements were then performed.

4.3. Electron Microprobe Analysis. Semiquantitative energy-dispersive X-ray spectroscopy (EDX) analyses of the prepared samples were carried out with a 7610F (JEOL) scanning electron microscope (SEM). The experimentally observed compositions were close to the ideal ones of NaMV2(PO4)3 (M = Fe, Co, Ni).

4.4. Thermal Analysis. Thermal gravimetric analysis (TGA) was carried out on the NaCoV2(PO4)3 sample using a TA Instruments Discovery Thermogravimetric Analyzer (Discovery TGA). The measurement was conducted between 25 and 1250 °C at a heating rate of 10 °C/min. The experiment was performed in an alumina crucible under an argon atmosphere.

4.5. Electrochemical Cycling. Positive electrodes were made from mixtures of NaCoV2(PO4)3 powder, acetylene black (AB), and polyvinylidene fluoride (PVDF) in a weight ratio of 80:12:8. The resulting electrode films were cut into discs (Φ = 14 mm) and dried at 120 °C for 12 h under vacuum. The electrolyte was 1 M NaPF6 dissolved in ethylene carbonate (EC) and propylene carbonate (PC) (1 M NaPF6 in EC/PC). Coin-type cells (CR2032) embedding Na-FeV2(PO4)3/NaPF6 + EC + PC/Na were assembled in an argon-filled glove box with a Whatman glass fiber separator (Grade GF/A = 14 mm) and dried at 120 °C for 12 h under vacuum. The resulting electrolyte was 1 M NaPF6 dissolved in ethylene carbonate (EC) and propylene carbonate (PC) (1 M NaPF6 in EC/PC).

4.6. Supporting Information. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01922.

Figure S1. Comparison of the XRPD patterns of NaMV2(PO4)3 (M = V, Fe, Co, Ni). Figure S2. The comparison between the structures of NaCoV2(PO4)3 and NaNiV2(PO4)3. Figure S3. The comparison between the structures of NaFeV2(PO4)3 and NaNiV2(PO4)3. Figure S4. XRPD patterns of the NaCoV2(PO4)3 electrodes before cycling (a) and after the first cycle in the voltage range of 0.1–3 V (b). Figure S5. Rate capability of NaCoV2(PO4)3 in the voltage range of 0.1–3 V (PDF).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01922.

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Notes

The authors declare no competing financial interest.

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