



Observation on the electrochemical reactions of $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3$ ($0 \leq x \leq 3$) as cathode materials for rechargeable batteries



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ABSTRACT

In this work, we propose a facile solid state reaction to prepare $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($0 \leq x \leq 3$), which are rarely explored as possible cathode materials in sodium-ion batteries. Their phase composition, surface morphology and electrochemical property are described and compared in detail by using various physical/chemical methods. Seen from phase analysis results, it is known that $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3$ is a three-phase mixture (monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$). In contrast, $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$, $\text{Li}_{1.5}\text{Na}_{1.5}\text{V}_2(\text{PO}_4)_3$, $\text{LiNa}_2\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_{0.5}\text{Na}_{2.5}\text{V}_2(\text{PO}_4)_3$ are two-phase mixtures consisting of rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Evaluated as cathode materials in half-cells, $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($0 \leq x \leq 3$) can deliver the initial reversible capacities of 94.3 mAh g^{-1} ($x = 0.0$), 103.6 mAh g^{-1} ($x = 0.5$), 115.1 mAh g^{-1} ($x = 1.0$), 112.7 mAh g^{-1} ($x = 1.5$), 99.6 mAh g^{-1} ($x = 2.0$), 94.0 mAh g^{-1} ($x = 2.5$) and 91.9 mAh g^{-1} ($x = 3.0$), respectively. After 45 cycles, the reversible capacities of 88.9 mAh g^{-1} ($x = 0.0$), 88.2 mAh g^{-1} ($x = 0.5$), 80.6 mAh g^{-1} ($x = 1.0$), 99.6 mAh g^{-1} ($x = 1.5$), 87.2 mAh g^{-1} ($x = 2.0$), 72.7 mAh g^{-1} ($x = 2.5$) and 72.3 mAh g^{-1} ($x = 3.0$) can be still kept for these samples. The electrochemical results suggest that Li/Na co-existence in $\text{M}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ may be beneficial to enhance the electrochemical performance. As a result, $\text{Li}_{1.5}\text{Na}_{1.5}\text{V}_2(\text{PO}_4)_3/\text{C}$ shows the best sodium storage capability as cathode material in sodium-ion batteries.

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1. Introduction

Energy production and storage, dominating the portable power market, have become key issues concerning our welfare in daily life [1–5]. Among various kinds of energy storage technologies, the electrochemical energy is one of the most appropriate forms of energy storage [6–10]. For this purpose, rechargeable lithium-ion batteries have been widely considered as the most advanced energy storage systems in the past three decades due to their environmental friendliness, long cycle life and high capacity retention. However, as the demand of grid-level stationary energy storage increases, sodium-ion batteries may be more suitable for large-scale grid applications in the near future due to the abundant

resources of sodium, its low price and the similarity of both Li and Na insertion chemistries.

In the past investigations, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is widely regarded as a promising cathode material for lithium-ion batteries owing to their low cost, high operating potential and great thermal stability [11–22]. However, no publications about the sodium storage capability of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode can be found in the previous work. In contrast, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ is always used as potential cathode material in sodium-ion batteries [19–30]. It has a three-dimensional framework, with VO_6 octahedra and PO_4 tetrahedra sharing oxygen vertices, which makes Na ions transport quickly in the electrode [27–33]. On the other hand, this polyanion structure also makes $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ suffer from poor intrinsic electronic conductivity. Thus, pristine $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cannot deliver satisfactory sodium storage capability. Recently, it is demonstrated that Li/Na co-existing $\text{M}_3\text{V}_2(\text{PO}_4)_3$ cathodes show enhanced electrochemical performance [34,35]. However, no systematical research has focused on the changes of sodium storage behaviors for these Li/Na

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co-existing $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3$ ($0 \leq x \leq 3$) cathodes in the past decades.

Herein, we employ a simple solid-state reaction method to synthesize $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($0 \leq x \leq 3$) and then they are applied as cathode materials for sodium-ion batteries. The phase composition, surface morphology and electrochemical property of the as-prepared compounds are investigated and compared via X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV) and charge/discharge tests. In addition, we also investigate the structural evolution of $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($x = 3$) by in-situ XRD observation. The results suggest that Li/Na co-existence in $\text{M}_3\text{V}_2(\text{PO}_4)_3$ is beneficial to achieve good sodium storage capability for $\text{M}_3\text{V}_2(\text{PO}_4)_3$ cathodes in rechargeable sodium-ion batteries.

2. Experimental

2.1. Synthesis

The $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($0 \leq x \leq 3$) were synthesized through a simple solid-state method and evaluated as cathode materials for sodium ion batteries. In a typical synthesis process, stoichiometric amount of V_2O_5 (Aladdin Chemical, AR), LiF (Aladdin Chemical, AR), NaF (Aladdin Chemical, AR) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Aladdin Chemical, AR) was ground and mixed by planetary ball-milling for 10 h with 15% mass excess of glucose (about 3% carbon after pyrolysis). Before ball-milling, the starting materials were dispersed into absolute ethanol, and mixed at a rotating speed of 400 r min^{-1} . After ball milling, the precursor was dried in an oven at 80°C for 12 h, and then preheated at 400°C for 4 h to expel H_2O and NH_3 . Finally, the pretreated precursor was ground and sintered for 12 h at 850°C in Ar atmosphere to yield the $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$.

2.2. Materials characterization

The phase structures of the $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ samples were recorded on Bruker AXS D8 Focus X-ray diffraction (XRD) instrument with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$), operating at 40 kV and 40 mA. These samples were observed with a scan angle range from 10 to 80° at a step size of 0.02° . Carbon contents in $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ were determined by NXQ-2D carbon/sulfur determination instrument (Nanjing Nuoxin). The scanning electron microscopy (SEM) images were taken by using a Hitachi SU70 scanning electron microscopy (SEM) and Oxford Inca energy dispersive spectrometry (EDS). In-situ XRD patterns were conducted on the same Bruker XRD instrument based on the homemade technique. In-situ cell was fabricated by using metallic Be disk as X-ray window, which was also used as current collector for supporting active material. In-situ XRD patterns were recorded between 10 and 40° . We collected one XRD pattern for about 13 min at a step size of 0.02° and a count time of 1 s.

2.3. Electrochemical investigation

The working electrode ($\sim 2.0 \text{ mg cm}^{-2}$) was fabricated with the active material, conductive carbon black, and poly(vinylidene fluoride) binder in a weight ratio of 8:1:1 by using *N*-methyl-2-pyrrolidone as a solvent and aluminum foil as a current collector, followed by drying in a vacuum oven at 120°C for 10 h. After that, the dried thin film was punched into disks with a diameter of 15 mm and used as working electrode for electrochemical investigations. In a typical coin-type cell, sodium metal was used as the counter electrode and Whatman glass fiber was performed as the separator. The Na-containing electrolyte is 1 mol L^{-1} NaClO_4 dissolved in dimethyl carbonate/ethylene carbonate (1:1, v/v). All of

the coin-type cells were assembled in a glove box filled with argon gas and tested at room temperature (25°C). Galvanostatic charge/discharge measurements were carried out in the potential cut-offs of 2.8–4.1 V at a current density of 20 mA g^{-1} by using the Land CT2001A battery test system. Cyclic voltammetry (CV) tests were performed at a scan rate of 0.1 mV s^{-1} by using a Bio-Logic VSP-300 electrochemical workstation.

3. Results and discussion

The XRD patterns of as-synthesized $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($0 \leq x \leq 3$) are shown in Fig. 1. All the featured diffraction peaks observed for the prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ could be well assigned to the expected reflections of monoclinic phase with the space group of P21/n, which is in agreement with those previously reported [36–38]. With enhancing Na content in $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$, some diffraction peaks weaken gradually and some new diffraction peaks can be detected, suggesting that new phases appear in the as-prepared samples. With $x = 0.5$ in $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3$, $\text{Li}_{2.5}\text{Na}_{0.5}\text{V}_2(\text{PO}_4)_3$ can be identified as a three-phase mixture, including rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (PDF 70-3614), monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (PDF 47-0107) and rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (PDF 70-3613). For $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$, $\text{Li}_{1.5}\text{Na}_{1.5}\text{V}_2(\text{PO}_4)_3$, $\text{LiNa}_2\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_{0.5}\text{Na}_{2.5}\text{V}_2(\text{PO}_4)_3$, all of them are two-phase mixtures consisting of rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. With x reaching 3.0 in $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3$, the resulting product is a single-phase rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. It is clear that these XRD patterns of $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ are well-consistent with those previously reported [39,40]. In addition, carbon contents in $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ are also studied and corresponding results are 2.94 wt% ($x = 0.0$), 3.02 wt% ($x = 0.5$), 2.83 wt% ($x = 1.0$), 2.90 wt%

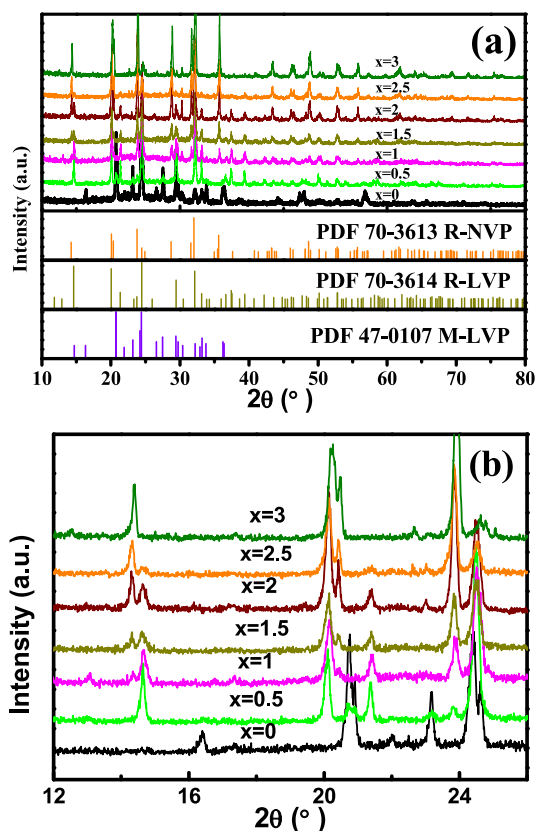


Fig. 1. XRD patterns of $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($0 \leq x \leq 3$), (a) $10^\circ \leq 2\theta \leq 80^\circ$ and (b) $12^\circ \leq 2\theta \leq 26^\circ$.

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