



# Lithium sodium vanadium phosphate and its phase transition as cathode material for lithium ion batteries



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## ABSTRACT

In this work,  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  is successfully synthesized by using a simple solid-state reaction method. Structural analysis shows that this sample is a hybrid product consisted of rhombohedral  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  phase and rhombohedral  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  phase. As a cathode material for lithium ion batteries,  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  exhibits an initial reversible capacity of  $108.9 \text{ mAh g}^{-1}$  at  $35 \text{ mA g}^{-1}$  in the potential range between 3.0 and 4.3 V, with an average working potential at 3.75 V. The lithium-ion diffusion coefficient in  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  is measured to be  $1.86\text{--}3.27 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ . In addition, the electrochemical reaction between  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  and Li is also investigated by various *in-situ* and *ex-situ* techniques. Viewed from the *in-situ* and *ex-situ* results, it is concluded that the electrochemical reactions of  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  with Li are associated with the formation of rhombohedral  $\text{LiV}_2(\text{PO}_4)_3$  phase and rhombohedral  $\text{NaV}_2(\text{PO}_4)_3$  phase during the lithium ion extraction process and its reverse lithium insertion process is reversible for structural evolution. The highly stable structure ensures the electrochemical reversibility of  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  cathode material in lithium ion batteries.

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## 1. Introduction

Recently, phosphates have been widely considered as promising cathode materials for lithium ion batteries due to their low cost, excellent thermal stability and cycle performance [1–3]. Among these phosphates, NASICON ( $\text{Na}^+$  superionic conductor) structured  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  have been received enormous attention for its high theoretical capacity, high operating potential, long cycle life and reliable safety [4,5]. However, the low intrinsic electronic conductivity of monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  restricts its practical application. In order to overcome the restriction, many studies have been carried out to improve the electrochemical activity of monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , such as coating with carbon [6–9] and doping with other metal elements [10–14]. Besides, its multi potential plateaus also hinder its practical application.

Compared with monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , rhombohedral product is another existent phase of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . Rhombohedral  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  (Rhom-LVP) can also deliver a theoretical capacity of  $133 \text{ mAh g}^{-1}$  with only one potential plateau at about 3.7 V in the potential range of 3.0–4.3 V due to two lithium ions extraction/insertion. However, it is difficult to prepare rhombohedral

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$  since its structural stability is poorer than that of monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . In contrast, the monoclinic structure of  $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3$  can totally transform into rhombohedral structure with large amount of Li-site Na substitutions [14]. Although the as-prepared Na-doped product may consist of a single phase or hybrid phases, it still reveals a single rhombohedral structure and excellent electrochemical properties [14–18]. For instances, whether the rhombohedral NASICON-structured  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  is a single-phase or hybrid-phase product, it still exhibits flat working potential platform at about 3.75 V. Usually, single-phase  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  is always synthesized by a complex chemical ion exchange reaction [15]. In a typical ion exchange process, rhombohedral  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (Rhom-NVP) was firstly prepared via a traditional solid state reaction and then the ion exchange of rhombohedral  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  was performed in  $\text{LiNO}_3$  solution at  $40^\circ\text{C}$  to form single-phase  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ . To replace the complex preparation method, sol-gel route has been proposed to synthesize the single rhombohedral NASICON-structured  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  in recent years [16]. The anionic surfactants (such as sodium dodecyl benzene sulfonate) can induce the structural transformation from the monoclinic phase into the rhombohedral phase of  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ . As a result, the sol-gel formed  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  nanoparticles exhibit better electrochemical performance (7 % capacity fade after 500 cycles) than that of ion exchanged samples (10 % capacity after 50 cycles). However, sol-gel method is also a multi-

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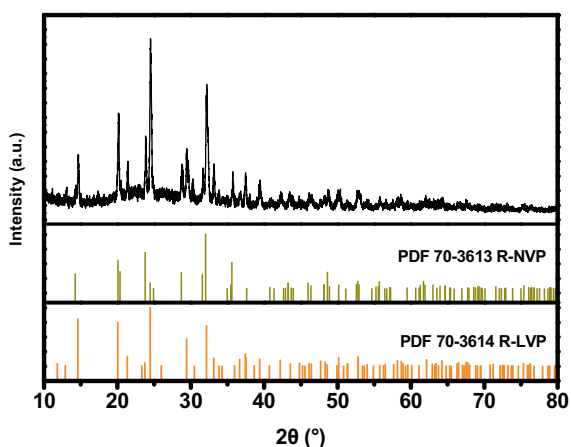


Fig. 1. XRD pattern of  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ .

step process with high cost. For comparison, hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  (H-LNVP) can be facilely synthesized by a simple solid state method [17]. Hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  not only exhibits flat working platform at 3.75 V but also shows higher reversible capacity than single-phase  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ , which makes hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  become a promising cathode material for lithium-ion batteries.

In the past decades, only two relevant reports about hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  cathode materials have been published [17,18]. Y.H. Tang initially prepared hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  with high ratio rhombohedral phase (90%) through a simple solid state reaction [17]. It could deliver a lithium storage capacity of  $119.1 \text{ mAh g}^{-1}$  with a main discharge at 3.7 V. They also found that monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , rhombohedral  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and rhombohedral  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  phases with a mole ratio of 10:59:31 coexisted in the same primary particle. This hybrid characteristic made as-prepared  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  exhibit better lithium storage capability than the mixed products ( $2\text{Li}_3\text{V}_2(\text{PO}_4)_3 \cdot \text{Na}_3\text{V}_2(\text{PO}_4)_3$ ) and single-phase samples ( $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  or  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ). Based on this report, W.F. Mao also prepared hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  with higher ratio rhombohedral phase (92.5 %) [18]. They compared the hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  with single-phase rhombohedral  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  in electrochemical behavior and structural stability. It can be found that the hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  could deliver better electrochemical performance, higher chemical diffusion coefficient and more stable structure than that of single-phase rhombohedral  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ . They speculated that the improved electrochemical property and structural stability is contributed to the existence of superionic phase  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  in hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ . However, no evidence was directly presented to support these results. Therefore, the comparison between  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ ,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  should be carried out in detail. Besides, previous investigations for  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  only focused on the phase

composition, electrochemical performance and structural stability. While, no  $\text{Li}^+$  extraction/insertion mechanism in  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  has been reported till now, especially for the use of in-situ observation.

In this paper, hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  with rhombohedral NASICON-structure is synthesized by a facile solid-state reaction method.  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  are also obtained via the same preparation method for comparison. These three samples are studied in detail and compared in chemical diffusion coefficient. Furthermore, we also utilize *in-situ* and *ex-situ* techniques to make a careful study of the structural evolutions and  $\text{Li}^+$  extraction/insertion mechanism of  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  during repeated electrochemical charge–discharge cycles. Besides, the differences in phase evolution during charge–discharge cycles are also presented by a comparison of in-situ observation between  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ ,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ .

## 2. Experimental

The chemicals used in the sample synthesis were analytical reagents and purchased from Aladdin Chemistry. Hybrid  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$  was prepared via a solid–state reaction method as follows: stoichiometric amounts of  $\text{V}_2\text{O}_5$ , LiF, NaF and  $\text{NH}_4\text{H}_2\text{PO}_4$  as well as a 15% mass excess of glucose were mixed by high energy ball milling for 10 h in ethanol medium. After ball milling, the slurry was dried at  $80^\circ\text{C}$  for 12 h. Then, the mixture was initially sintered at  $400^\circ\text{C}$  for 4 h and subsequently sintered at  $800^\circ\text{C}$  for 12 h under a following  $\text{N}_2$  atmosphere. For comparison, monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and rhombohedral  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  were also synthesized through a similar processing procedure.

For electrochemical evaluation, the working electrode was prepared by mixing the active material ( $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , 80 wt.%) with carbon back (10 wt.%) and poly-vinylidene fluoride (10 wt.%) in 1-methyl-2-pyrrolidinone, then coating the mixture onto an Al foil and drying at  $100^\circ\text{C}$  under vacuum condition for 12 h. The Swagelok batteries were assembled with the working electrode as cathode, metallic lithium as anode,  $1 \text{ mol L}^{-1}$  LiPF<sub>6</sub> (Tinci Materials Technology Co. Ltd.) in 1:1 dimethyl carbonate/ethylene carbonate as electrolyte and Whatman glass fiber as separator in an argon filled glove-box. For better comparison, all the working electrodes were selected with the same mass of active materials (2.4 mg) in the electrochemical tests.

The crystallographic structures of the resulting samples were characterized by the X-ray diffraction (XRD, Bruker AXS D8 Focus diffractometer) using  $\text{Cu K}\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ) radiation. *In-situ* XRD patterns were collected on the same instrument using metallic Be as X-ray window [19]. The surface morphology and microstructure of the samples were investigated by scanning electron microscopy (SEM, JEOL S3400). The lithiated and delithiated samples for X-ray photoelectron spectroscopy (XPS, PHI-Quantum 2000) measurement were washed by dimethyl carbonate and vacuumed for 5 h. The samples for *ex-situ* high-resolution transmission electron

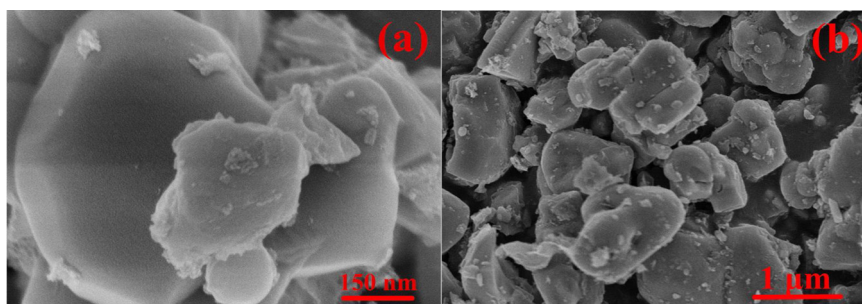


Fig. 2. SEM images of  $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ .

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