



# Self-combustion synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ nanoparticles coated with carbon shell as cathode materials for sodium-ion batteries



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## ABSTRACT

The real applications of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cathode material for sodium batteries have been hindered by low-cost and facile synthesis method. Herein, we report a facile self-combustion method to synthesize  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  nanoparticles coated with carbon shell (NVP/C). Using as the cathode, the NVP/C is capable of delivering the initial discharge and charge capacities of 100.72 and 111.3 mAh  $\text{g}^{-1}$  at the current of 0.1 C in a voltage of 2.5–3.8 V, and the capacity retention of the sample is approximately 95% of its initial specific capacity after 50th cycles. The first-principles simulation results show that the Na ions migration route prefers between two adjacent tetrahedral sites with the vacancy-hopping mechanism in a curved way, with the lowest activation energy of 0.292 eV. The diffusion coefficients  $D_{\text{Na}^+}$  at room temperature was also calculated as higher as  $2.38 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ . The results suggest great potential of self-combustion synthesized NVP/C as cathode materials for Na-ion batteries.

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## 1. Introduction

Na ion superionic conductor ( $\text{Na}_3\text{M}_2(\text{XO}_4)_3$ ; X =  $\text{Si}^{4+}$ ,  $\text{P}^{5+}$ ,  $\text{S}^{6+}$ ,  $\text{Mo}^{6+}$ ,  $\text{As}^{5+}$ ) framework materials have attracted much attention for sodium-ion batteries (NIBs) [1]. Amongst various materials with the NASICON structure, rhombohedral  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) has been regarded as the highly promising cathode materials, due to its high theoretical energy density (117.6 mAh/g  $\times$  3.4 V for the  $\text{V}^{3+}/\text{V}^{4+}$  redox couple) [2], its superior high-rate capability [3,4], as well as its excellent thermal-stability [5]. Therefore, many approaches have been developed to explore the extraordinary electrochemical properties of such materials. Jian et al. first synthesized carbon-coated NVP powders by a one-step solid state reaction, which delivered initial discharge capacity of 93.0 mAh  $\text{g}^{-1}$  at the current rate of 0.05 C, while rate capacities and cycle performance still have room to be improved [6]. Jung et al. employed a sol-gel method to synthesize graphene-supported NVP, which exhibited the decent discharge capacity of 90.6 mAh  $\text{g}^{-1}$  at the current rate of 0.2 C [7]. Jiang et al. has reported that the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  from solid state reaction exhibited an initial specific discharge capacity of 98.17 mAh  $\text{g}^{-1}$  at 0.1 C for potentials ranging from 2.5 to 3.8 V [2]. Palaniet al. adopted a novel soft template method to synthesis carbon-coated NVP nano-grains, which demonstrated the excellent cycling stability and superior rate capability, although it has

complicated synthesis process [8]. Hence, finding a facile, low-cost and efficient synthesis process is one of the main concerns for further research of this cathode material for use.

Using the most commonly used metal nitrates as oxidizer and citric acid as fuels [9], self-combustion method has been considered to be a cheap and efficient method to produce homogeneous nano-sized materials. Many cathode materials, such as  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  [10],  $\text{LiVP}_2\text{O}_7$  [11],  $\text{Li}_2\text{FeSiO}_4$  [9],  $\text{Na}_x\text{MO}_2$  [12], and  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  [13], which were prepared using the combustion process, have showed an improved electrochemical performance.

In this manuscript, we first employ self-combustion method – one featuring ease of processing and low cost – to synthesize nanoparticles coated with carbon shell (NVP/C), by which we were able to experimentally assess this material. The results suggest that NVP/C demonstrates the high initial discharge/charge capacities of 100.72 and 111.3 mAh  $\text{g}^{-1}$ . The capacity retention of the sample is approximately 95% of its initial specific capacity after 50th cycles. In the meantime, first-principles simulations were performed to illustrate the Na ion diffusion properties, which play an important role in the electrochemical performance for rechargeable batteries.

## 2. Experimental Details

### 2.1. Synthesis

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$  samples were prepared by the self-combustion method using  $\text{NaNO}_3$  as the oxidant precursors, citric acid as fuel,

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$\text{NH}_4\text{VO}_3$  as vanadium source, and  $\text{NH}_4\text{H}_2\text{PO}_4$  as phosphorus source, respectively. Primarily, the stoichiometric amounts of  $\text{NaNO}_3$ ,  $\text{NH}_4\text{VO}_3$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$  were dissolved in the minimum amount of distilled water along with citric acid as fuel on an electric heater and constantly stirred to get a homogenous solution. On continue stirring and heating, slow evaporation of the homogenous solution produced highly viscous gel; further heating resulted in firing spontaneously, producing finally voluminous superfine powders. We also performed the corresponding carbon-coating experiments to improve the poor intrinsic electronic conductivity of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  [14]. The obtained precursors were mixed with a balanced amount of glucose and ball milled for 2 h. Then, the obtained powders were transferred into a tube furnace and calcined at  $900^\circ\text{C}$  for 4 h under an Ar atmosphere to form the NVP/C particle composites, which is benefitted for enhancing the crystalline and obtaining carbon shell.

## 2.2. Materials characterization

The phases and crystal structures of the samples were analyzed using a powder X-ray diffraction (XRD) analysis system (D/MAX2500V, Rigaku, Japan) equipped with a  $\text{Cu K}\alpha$  radiation source. The morphological features of the powder particles were analyzed by field-emission scanning electron microscopy (FESEM) (SU8020, Hitachi, Japan) and high-resolution field-emission transmission electron microscopy (HRTEM) (JEM-2100F, JEOL, Japan). The specific surface area and pore-size distribution were measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption-desorption measurement (SA3100, America). The thermogravimetric (TG) analysis of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  sample was carried out on a diamond TG thermo-analyzer.

## 2.3. Electrochemical performance tests

The working electrodes were prepared by casting the slurry of the active material (75 wt%), acetylene black (15 wt%), polyvinylidene fluoride (PVDF) (10 wt%) dissolved in appropriate amount N-methyl-2-pyrrolidone (NMP) as the binder on a clean Al foil. The resultant electrochemical cells were assembled in a glove box filled with high-purity argon where pure sodium foil, 1 M  $\text{NaClO}_4$  in propylene carbonate (PC) and glass fiber were used as the counter electrode, the electrolyte and the separator, respectively. The discharge and charge measurements were carried out on a NEWWARE battery test system (Shenzhen, China) in a voltage range of 2.5–3.8 V. For the cyclic voltammetry (CV) measurements, all the cells were performed using a CHI660D (Shanghai, China)

electrochemical workstation at the scan rate of  $0.05 \text{ mV s}^{-1}$  over potentials ranging from 2.5 to 3.8 V (vs.  $\text{Na}^+/\text{Na}$ ). For the electrochemical impedance spectroscopy (EIS) tests, all the cells were also performed using the above-mentioned electrochemical workstation over frequencies ranging from 100 kHz to 0.01 Hz during the discharge stage (2.5 V) by applying an AC signal of 5 mV.

## 2.4. DFT calculations

The calculations were performed using density functional theory with the projector-augmented wave method [15]. The generalized gradient approximation (GGA) functional of Perdew and Wang (PW91) was adopted to treat the exchange and correlation potential in all calculations [16]. The LST method was used to calculate the energy barrier. In view of the stronger inductive effect in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , a higher U parameter of 4.2 eV was used [5]. The norm-conserving pseudopotential was used for the electron-ion interactions, and the cut-off energy was set to 330 eV. The Brillouin zone sampling k-point set-mesh parameters were  $3 \times 3 \times 3$ .

## 3. Results and discussion

### 3.1. Structural and morphological analysis

Fig. 1a depicts the powder X-ray diffraction pattern (PXRD) of the as-synthesized NVP. All the diffraction peaks were indexed to the NASICON structure with the R-3c space group (167). The calculated pattern matches well with the measured profile with the low  $R_{\text{wp}}$  (7.78%) and  $R_{\text{p}}$  (6.02%), which suggests that the purity of the phase is high. The calculated lattice parameters of NVP are  $a = 8.7205 \text{ \AA}$ ,  $c = 21.7632 \text{ \AA}$ ,  $\alpha = 90^\circ$ , and  $\gamma = 120^\circ$ . These results were consistent well with those reported previously [6,7,17–20]. Further, no diffraction peaks related to crystalline or amorphous carbon were presented in the XRD patterns. However, the confirmation that the NVP particles were uniformly coated with amorphous carbon shell layer is shown in field-emission transmission electron microscopy (FETEM) images. Fig. 1b demonstrates the NASICON-type framework structure of rhombohedral  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  projected on the (211) plane. It can be noted that each  $\text{VO}_6$  octahedron corner-shares with  $\text{PO}_4$  tetrahedrons to establish the framework anion  $[\text{V}_2(\text{PO}_4)_3]^{3-}$  basic units along the c-axis direction,  $[\text{V}_2(\text{PO}_4)_3]^{3-}$  unit is interlinked to each other by the  $\text{PO}_4$  tetrahedron along the a-axis, and this established the open 3D framework structure [6,18,19]. The two independent sodium ions are located in the voids/channels of the framework with two

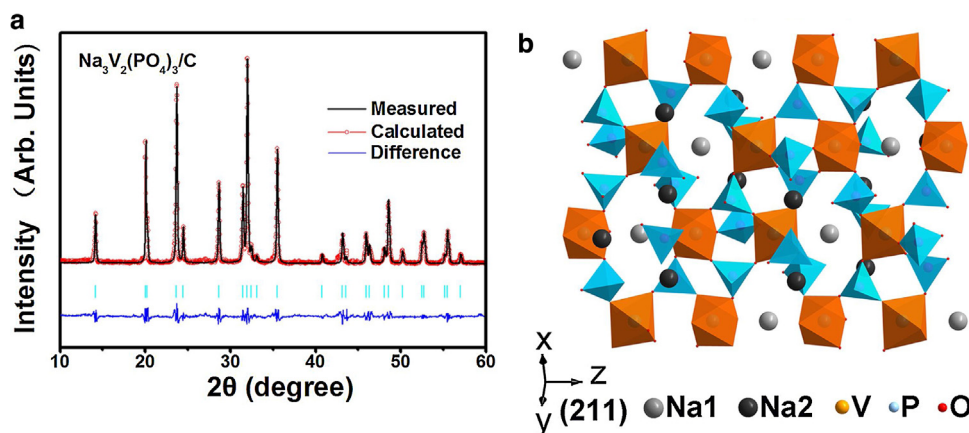


Fig. 1. (a) Rietveld refinement powder XRD patterns for the carbon-coated  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  samples with 25 wt% glucose content at  $900^\circ\text{C}$ . (b) View of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  NASICON structure on the (211) plane.

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