

Short Communication

## Synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Composites as High-Performance Cathode Materials for Sodium Ion Batteries

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$\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) is a potential cathode material for sodium ion batteries (SIBs) due to its stable three-dimensional NASICON structure and high theoretical energy density. In this paper, the carbon-coated  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP/C) cathode materials using pitch as carbon source were synthesized by a simple solid-state reaction method combined with microwave calcinations. The electrode performance of as-prepared NVP/C materials were investigated and the results demonstrated that the NVP/C composite with 13.1 wt.% carbon shows the best electrochemical properties. It possesses a high initial discharge capacity of 108.2 mAh g<sup>-1</sup>, 90.5 mAh g<sup>-1</sup> at 0.2 C and 10 C. After 1000 cycles at the rate of 10 C, the discharge capacity remained almost unchanged, with no capacity fading.

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**Keywords:** Pitch, Carbon coating, Cathode material, Sodium ion battery

### 1. INTRODUCTION

Lithium ion batteries (LIBs) have been widely used in the industries of electronics, digital and transportation due to their high voltage, high energy density and long cycle life [1-5]. Unfortunately, with the increasing demand for LIBs, lithium reserves have been greatly reduced and the price continues to rise. Therefore, sodium ion batteries (SIBs) have attracted increasing attention for its abundant reserves and economic efficiency. However, the radius of Na ion is much larger than that of Li ion, which leads to lower ion insertion/extraction reversibility and grievous structural degradation along with huge volume change during the reduplicative insertion/extraction process [6-8]. Accordingly, it is a challenging task to find appropriate electrode materials for SIBs answering the requirements of long-term cycling stability and high rate capability.

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) with a three-dimensional NASICON structure is considered as one of the most potential cathode materials for SIBs, which possesses large interstitial space for fast Na ions insertion and extraction. Besides, NVP has impressive theoretical energy density ( $400 \text{ Wh kg}^{-1}$ ), moderate potential plateau ( $3.4 \text{ V vs Na/Na}^+$ ) and high thermal stability [9, 10]. Nevertheless, it is difficult to approach the theoretical electrochemical performance, mainly because pure NVP has poor intrinsic electronic conductivity [11-14]. Several strategies have been implemented to solve this problem, such as morphology designing [15, 16], particle size decreasing [17, 18], carbon coating [19-27] and metal ionic doping [28-31]. Among these ways, carbon coating has been verified to be an effective method to improve the electrochemical performance of NVP. Various carbon sources have been investigated to modify NVP, such as sugar [19], oxalic acid [21], glucose [26], folic acid [27], etc. In our previous study, we found that using the pitch as carbon source is an effective method to improve the electronic conductivity of electrode material for LIBs[32].

In this paper, we used pitch as a new carbon source to prepare NVP/C composites as cathode materials for SIBs and investigated the effect of pitch dosage on the electrochemical performance of NVP/C. The electrochemical tests show that the NVP/C composite with 13.1 wt.% carbon exhibits good rate capability and excellent cycle stability.

## 2. EXPERIMENT

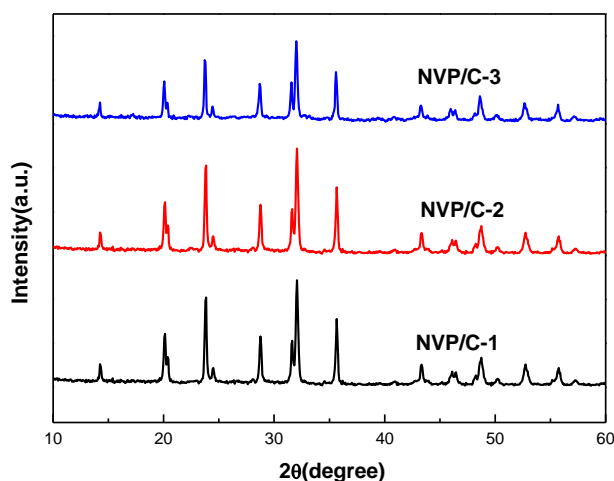
The NVP/C composites were prepared by a solid-state reaction method combined with microwave heating.  $\text{Na}_2\text{CO}_3$  (99.9%, Aladdin),  $\text{NH}_4\text{VO}_3$  (99.9%, Aladdin),  $\text{NH}_4\text{H}_2\text{PO}_4$  (99%, Aladdin) and pitch (high soften point coal pitch, Shenzheng China) were used as starting materials. Firstly, a certain amount of pitch (1 g, 1.5 g and 2 g, respectively), 0.0225 mol  $\text{Na}_2\text{CO}_3$ , 0.03 mol  $\text{NH}_4\text{VO}_3$  and 0.045 mol  $\text{NH}_4\text{H}_2\text{PO}_4$  were thoroughly mixed in acetone by a high-energy ball-mill machine to form the slurries. Then, the obtained slurries were dried at  $50 \text{ }^\circ\text{C}$  in a vacuum oven for 3 h. Finally, the as-prepared powders were pressed into pellets and calcined in a microwave tube furnace at  $750 \text{ }^\circ\text{C}$  for 10 min under flowing argon gas to obtain the final NVP/C composites. The NVP/C composites synthesized by using the amount of pitch of 1 g, 1.5 g and 2 g were denoted as NVP/C-1, NVP/C -2 and NVP/C -3, respectively.

The structure of the samples was investigated by the X-ray diffraction (DX-2700, Dandong Haoyuan) with a Cu K $\alpha$  radiation. The morphology was examined by the scanning electron microscope (SEM, Nova NanoSEM 230). The carbon content was detected by thermogravimetric analysis (TG-50, Shimadzu). The working electrode was prepared by mixing 80 wt% NVP/C activity material with 10 wt% Super-P carbon and 10 wt% LA-132 binder in the water. The mixed slurry was cast on aluminum foil to form the uniform film. The film was cut into discs with a diameter of 12 mm. The discs were dried at  $105 \text{ }^\circ\text{C}$  for 12 h in a vacuum oven. To assemble CR2032 coin cells, pure sodium foil was used as counter electrode, Whatman 1 M  $\text{NaClO}_4$  in EC/DMC/EMC (1:1:1, Vol% ) with 2 Vol% FEC as electrolyte, and glass fiber as the separator. Galvanostatic charge/discharge cycling tests were performed in the potential range of 2-4 V at  $25 \text{ }^\circ\text{C}$ . Both electrochemical impedance spectroscopy

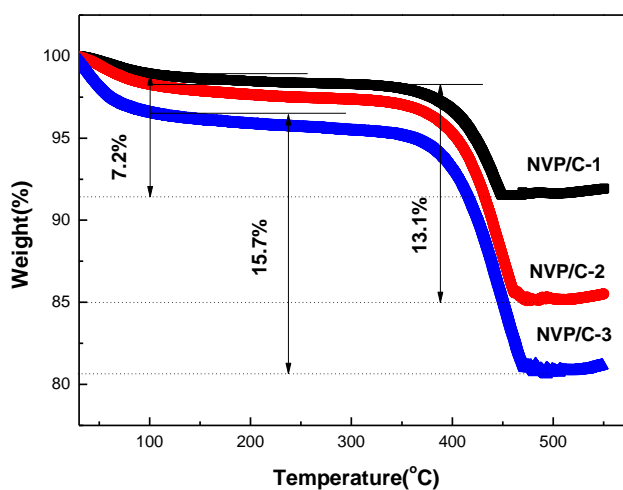
(EIS) measurements with a frequency range of 0.01 Hz to  $10^5$  Hz and cyclic voltammetry (CV) at a scan rate of  $0.2 \text{ mV s}^{-1}$  were performed by using CHI760E electrochemical station.

### 3. RESULTS AND DISCUSSION

The XRD patterns of three NVP/C samples are shown in Fig. 1. All the diffraction peaks of the samples are well indexed with the NASICON structure with R-3c space group (PDF#53-0018), indicating that all the samples are pure. There is no diffraction peaks for crystalline carbon observed in the XRD patterns, indicating that the residual carbon is mainly amorphous [33]. The carbon content in NVP/C-1, NVP/C-2 and NVP/C-3 is determined to be 7.2, 13.1 and 15.7 wt.%, which is measured by thermogravimetric analysis, and the results are shown in Fig. 2.

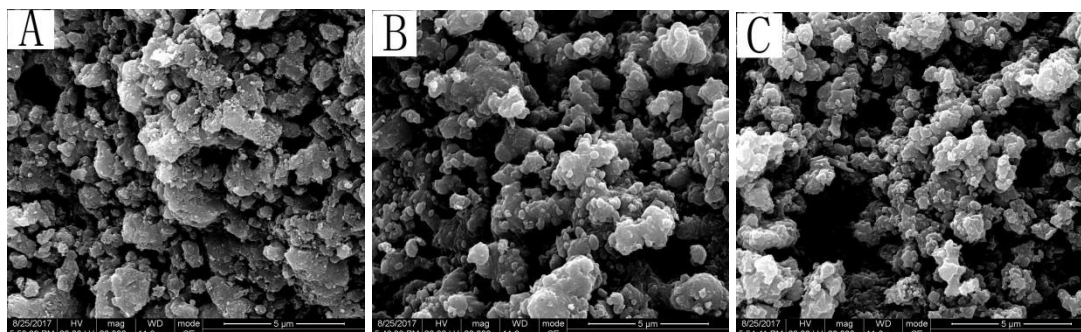


**Figure 1.** XRD patterns of NVP/C composites.



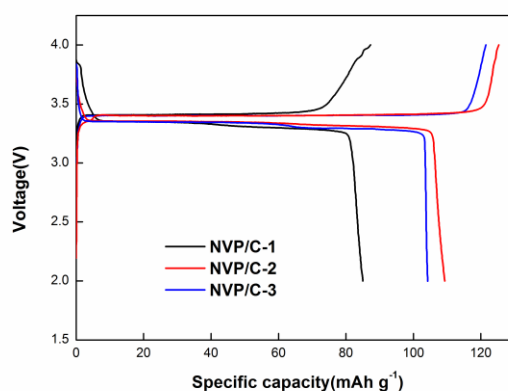
**Figure 2.** TG curves of NVP/C composites.

Fig. 3 shows the SEM images of three NVP/C samples. It can be seen that three samples are made up of irregular nanoparticles, and the particle size becomes smaller as the carbon content increases. The formation of nanoparticles may be related to the intense ball milling process. The thin coating carbon can improve the electronic conductivity, while it can alleviate vanadium dissolution in electrolyte but not hinder  $\text{Na}^+$  ion transmission[19, 26].



**Figure 3.** SEM images of NVP/C composites with various content carbon: (A) NVP/C-1, (B) NVP/C-2, (C) NVP/C-3.

The initial charge and discharge curves of three as-obtained NVP/C samples in the voltage range of 2-4 V at a scanning rate of 0.2C are presented in Fig. 4. It can be observed that the charge-discharge curves of all samples possess a flat potential plateau at approximately 3.4 V, demonstrating a two-phase reaction corresponding to  $\text{V}^{4+}/\text{V}^{3+}$  redox couple [34]. NVP/C-2 has a much higher discharge capacity of  $108.2 \text{ mAh g}^{-1}$ , while the capacity of NVP/C-1 and NVP/C-3 is 87 and  $106.1 \text{ mAh g}^{-1}$ , respectively. In addition, it is also interesting to see that NVP/C-2 has the smallest voltage gap between the charge and discharge voltage plateaus, indicating the least electrochemical polarization [35].



**Figure 4.** The first profile of charge-discharge curves at 0.2C for NVP/C composites.

Fig. 5 shows the rate capability for NVP/C-1, NVP/C-2 and NVP/C-3 at 0.2 C, 0.5 C, 1 C, 2 C, 5 C and 10C. The discharge capacity of all samples gradually decreases with the increasing of rate,

probably because the utilization of the active material decreases as the rate increases [36]. NVP/C-2 possesses a reversible capacity of 108.2, 104.8, 102.3, 100.6, 97.2, 90.5 mAh g<sup>-1</sup> at 0.2 C, 0.5 C, 1 C, 2 C, 5 C, 10C, respectively, While the capacity of NVP/C-1 and NVP/C-3 is 94.5, 90.1, 86.1, 85, 80.6, 76.9 mAh g<sup>-1</sup> and 106.1, 102.7, 99.8, 96.1, 90.1, 84.2 mAh g<sup>-1</sup>, respectively. Clearly, NVP/C-2 exhibits much higher discharge capacity at each rate than that of NVP/C-1 and NVP/C-3. Moreover, the electronic conductivity of NVP/C materials may increase when the carbon content enhances. Therefore, NVP/C-2 exhibits better rate performance than NVP/C-1. However, too high content carbon might hinder the penetration of electrolyte solution into the carbon layers and inward/outward diffusion of Na<sup>+</sup> ion through the carbon layers, which causes the rate performance of NVP/C-3 to be poorer than that of NVP/C-2[18, 27]. In the previous report[18], NVP/C only exhibits the discharge capacity of 97.9 mAh g<sup>-1</sup>, 93.5 mAh g<sup>-1</sup> at 0.2 C and 5 C.

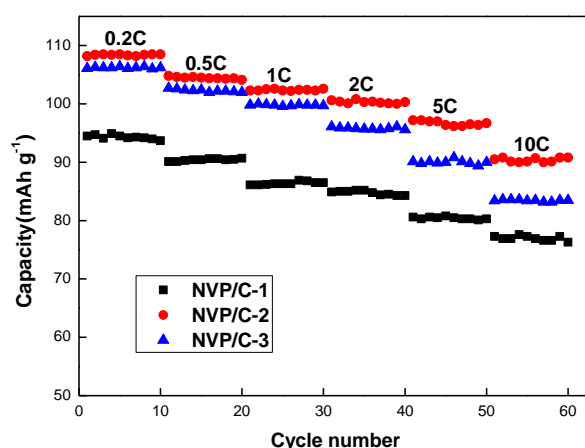


Figure 5. Rate capacity of NVP/C composites.

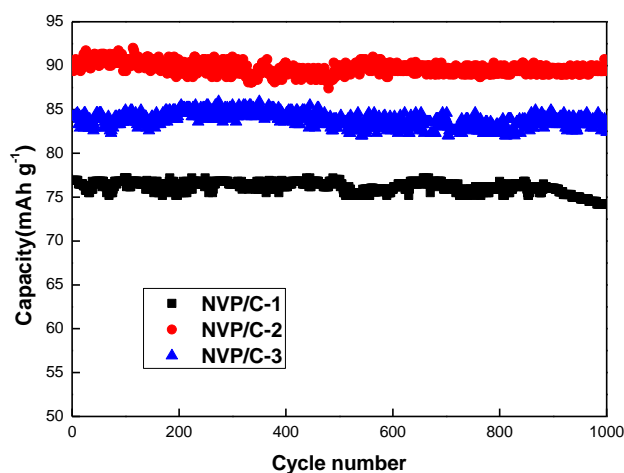


Figure 6. Cycling performance of NVP/C composites.

Fig. 6 displays the cycling performance of NVP/C-1, NVP/C-2, NVP/C-3 samples at 10C between 2 and 4 V. NVP/C-2 reveals a high initial discharge capacity of 90.5 mAh g<sup>-1</sup> with almost no capacity fading after 1000 cycles whereas NVP/C-1 and NVP/C-3 deliver an initial discharge capacity

of 76.9 mAh g<sup>-1</sup> and 84.2 mAh g<sup>-1</sup>, respectively, and the capacity remain 74.2 and 82.4 mAh g<sup>-1</sup> after 1000 cycles. Obviously, the cycle stability of NVP/C-2 is superior to that of NVP/C-1 and NVP/C-3.

#### 4. CONCLUSION

NVP/C cathode materials with pitch as carbon sources were synthesized by a solid-state reaction method combined with microwave calcinations. The results illustrate that the NVP/C cathode materials prepared with 13.1 wt. % carbon exhibits good rate capability and excellent cycle stability. The NVP/C-2 composite still delivers a high specific capacity of 89.7 mAh g<sup>-1</sup> after 1000 cycles at 10 C. Therefore, using pitch as carbon source for the preparation of NVP/C is a promising strategy, which may be further extended to other systems to prepare high performance cathode materials for SIBs.

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