Sodium Citrate Induced Sol-gel Synthesis of Rhombohedral Structure $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ Composite with High Capacity and Stability as Cathode for Lithium-ion Batteries

Liping QIN,^{a,*} Shuquan LIANG,^b Xiaoping TAN,^b Weimin GUO,^c and Shunfeng CHEN^a

^a Department of Science & Technology, Guangxi University of Science and Technology, Liuzhou, Guangxi 545006, China

^b School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China

^c School of Biological and Chemical Engineering, Guangxi University of Science and Technology, Liuzhou, Guangxi 545006, China

* Corresponding author: qinlp2005@126.com

ABSTRACT

The rhombohedral structure $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ composites were successfully synthesized by a sodium citrate induced sol-gel method. The $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ consists of microplates roughly 80–90 nm in thin. The carbon content in the LNVP/C is approximately 8.29 wt%. As cathode materials for lithium-ion batteries, a cathodic peak at 3.67 V and an anodic peak at 3.82 V can be seen in CV curves, corresponding to the redox couple of $\text{V}^{4+}/\text{V}^{3+}$. In addition, the electrode can deliver an initial discharge capacity of 111.4 mAh g⁻¹ at 1 C and about 96.4% of the initial capacity is maintained after 150 cycles. LNVP/C also exhibits high coulomb efficiency and good rate performance.

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1. Introduction

The demand for rechargeable batteries with longer cycle-lives and higher performance for modern electrical devices continues to increase. As one of the most popular commercial energy storage devices, lithium-ion batteries (LIBs) attract huge attention in both industries and academe due to their high energy density, fast charge/discharge rate, and excellent cycle performance. Cathode materials as the significant part in lithium ion batteries have been widely investigated to find the suitable candidates for replacing LiCoO_2 .^{1,2} Recently, alternative cathode materials such as LiFePO_4 , LiMnPO_4 , LiCoPO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ have attracted research interests owing to three dimensional frame-network structure stability and high operating potential and high thermal stability in the field of lithium-ion batteries.^{3–7} $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with NASICON-related structure has been received enormous attention for its high theoretical capacity, high operating potential, long cycle life. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has rhombohedral and monoclinic structure. Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with better structure stability has attracted much attention. Monoclinic LVP possesses three potential plateaus at around 4.04, 3.64, and 3.55 V in lithium charge/discharge progress in the range of 3.0–4.3 V with a theoretical specific capacity of 133 mAh g⁻¹.^{8–11} However, its multi potential plateaus hinder its practical application. The cathode must exhibit a single working potential so that electronic devices provide a stable output power in order to run well.^{12–14} Rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ exhibits a single voltage plateau during lithium charge/discharge progress in the range of 3.0–4.3 V as cathode materials for LIBs. However, rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was rarely researched due to its poor structural stability and lithium insertion/extraction performance.¹³

On this background, $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ (LNVP) has attracted attention and was researched by studies. LNVP has a rhombohedral structure similar to rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. In the crystal structure of LNVP, $[\text{V}_2(\text{PO}_4)_3]^{3-}$ unit aligned along the c axis and interconnected by a PO_4 tetrahedral along the a axis, each VO_6 octahedron is linked with three PO_4 tetrahedrons through common

corners, forming the open three-dimensional framework structure. Each formula unit of LNVP contains one A1 site occupied by Na ion and two A2 sites occupied by two Na ions. The A1 site could maintain the rhombohedral structure because the larger ion radius of Na^+ ion is suitable at this site.¹⁵ LNVP with a single $\text{V}^{4+}/\text{V}^{3+}$ potential plateau at 3.7 V has a theoretical specific capacity of 133 mAh g⁻¹ between 3.0–4.3 V along with two lithium ions extraction/insertion in the charge/discharge process.¹⁶ This advantage of having only one voltage platform, which can provide electronic devices a stable output power, and having a high theoretical specific capacity make the LNVP an attractive cathode material for lithium-ion batteries. Rhombohedral LNVP was firstly synthesized by Goodenough¹⁷ via chemical ion exchange reaction from rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, and applied to lithium-ion batteries as cathode materials. The LNVP exhibits a specific discharge capacity of ~96 mAh g⁻¹ at a current density of 0.50 mA cm⁻² with a clear plateau near 3.7 V versus lithium metal. However, approximately 10% of the capacity is lost through the first 50 cycles, showing low reversible capacity. Then, Tang et al.¹⁸ developed a composite $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ by a simple solid state reaction utilizing the aforementioned mechanism. The material comprises of Rhom-LVP, Mono-LVP and Rhom-NVP, coexistent with a ratio of 59:10:31. According to discharge capacity, ~91.4% is contributed from rhombohedral phase. The composite delivers a discharge capacity of 119.1 mAh g⁻¹ at 0.05 C. In recent years, LNVP was synthesized by sol-gel method and carbon thermal reduction method to replace the ion exchange process. Mao et al.¹⁹ synthesized high performance hybrid phase $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ composite consist of rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (60.9%), rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (31.6%) and monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (7.5%) via a sol-gel method. The H-LNVP exhibits a discharge capacity of 123.3 mAh g⁻¹ at 0.5 C. Tang and Mao's studies proved that rhombohedral LNVP could be formed directly when Li^+ ions are partially substituted by Na^+ ions. However, multiple voltage plateaus could still be observed in the charge–discharge curves because the monoclinic LVP was generated simultaneously during the reaction. Recently, Zhang et al.¹²

synthesized a single rhombohedral NASICON-structured LNVP with better electrochemical performance through a sol–gel route and suggested that the Na^+ sources could induce the Na^+ ions to occupy all of the A1 sites in formula unit $[\text{V}_2(\text{PO}_4)_3]^{3-}$. As a phosphate-based compound, pure LNVP have poor conductivity. Carbon addition is an effective method to improve the conductivity of materials and enhance the cycle stability and the rate performance for lithium-ion batteries. Alfuruqi et al.¹⁴ prepared carbon-coated rhombohedral $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$ nanoflake using a pyro-synthesis technique. The cathode showed the first charge and discharge capacities of 103 and 92 mAh g^{-1} at 0.4 C, respectively, and demonstrated long cycle stability equaling to 100% of the initial discharge capacity during the 300th cycle.

The single phase rhombohedral structure LNVP/C exhibits a single working potential in favour of electronic devices providing a stable output power in order to run well. The synthesis process and the sodium source affect the product phase. The anionic surfactants can induce the structural transformation from the monoclinic phase into the rhombohedral phase of $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$. Sol-gel method is a simple and easy operating method of synthesizing solid materials. In this study, an attempt is made to synthesized single phase rhombohedral structure LNVP/C using sodium citrate as Na^+ source and sucrose as carbon source via a sol–gel route. The electrochemical performance was examined as cathode materials for lithium-ion batteries.

2. Experiments

The LNVP/C sample was synthesized by a sol-gel method with V_2O_5 , $\text{H}_2\text{C}_2\text{O}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{LiC}_2\text{H}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$ as raw materials, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ as Na^+ source and sucrose as carbon source. Firstly, V_2O_5 , $\text{H}_2\text{C}_2\text{O}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{LiC}_2\text{H}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ in the molar ratio of 1:3:3:2:1/3 were dissolved in 40 mL of deionized water under vigorous stirring at 70°C to obtain a clear blue solution. Secondly, sucrose was added to the solution, and the mixed solution was stirred continually till the precursor gel was obtained. The obtained precursor gel was heated at 100°C in a vacuum oven to achieve a dry gel. Finally, the gel precursor was pre-heated at 350°C for 4 h and calcined at 750°C for 8 h under Ar/H_2 flow to yield black product.

The crystal phase of the sample was characterized by XRD (Rigaku D/max2500). The carbon structure of the sample was tested by Raman spectrum (LabRAM HR-800). The surface morphologies and microstructures of the samples were studied by SEM (Nova NanoSEM230) and TEM (HEM-2100F/UHR). TG was carried out on a DSC STA449C instrument from room temperature to 900°C at a heating ramping rate of 10°C min^{-1} in air.

The electrochemical measurements were conducted by assembling coin-type half cells. The working electrodes were prepared by mixing sample with acetylene black and poly(vinylidene fluoride) (PVDF) at weight ratio of 80:10:10 in N-methyl-2-pyrrolidone to form slurry. The resultant slurry was uniformly pasted on aluminum foil and dried. The cells were assembled in a glove box (Mbraun, Germany) filled with ultra-high purity argon using polypropylene membrane as the separator, and 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC) (EC:DMC = 1:1 v/v) as the electrolyte. Li foil was used as a counter electrode. The Cyclic voltammogram (CV) measurement was carried out on the CHI660C (CH Instrument Electrochemical workstation) in the potential range 3.0–4.3 V at a scan rate of 0.05 mV s^{-1} . The charge/discharge process and rate performance were tested on Land Battery Tester (Land CT 2001A, Wuhan, China) in 3.0–4.3 V.

3. Results and Discussion

Figure 1 shows the XRD patterns of as-prepared sample and the

Figure 1. XRD patterns of as-prepared sample.

standard patterns of rhombohedral LNVP. All the diffraction peaks of the sample are indexed to rhombohedral LNVP (PDF No. 54-0763) and consistent with previous reports.¹⁷ The sharp diffraction peaks illustrate the good crystallization of sample. No diffraction peaks of carbon are observed, indicating that the carbon in the sample may be amorphous or the content of carbon is too low to be detected. According to Goodenough¹⁷ and other researchers^{12,14} works, the rhombohedral LNVP has a three-dimensional framework structure and alkali metal ions can easily diffuse through the well-defined ion channels. In the crystal structure of LNVP, $[\text{V}_2(\text{PO}_4)_3]^{3-}$ unit aligned along the c axis and interconnected by a PO_4 tetrahedral along the a axis, each VO_6 octahedron is linked with three PO_4 tetrahedrons through common corners, forming the open three-dimensional framework structure. Each formula unit of LNVP contains one A1 site occupied by Na ion and two A2 sites occupied by two Na ions. The A1 site could maintain the rhombohedral structure because the radius of the Na ion is suitable at this site. The two Na ions could be exchanged by two Li ions to achieve the $\text{V}^{4+}/\text{V}^{3+}$ redox couple.

Raman spectroscopy is tested to study the carbon in the surface region of sample particles, as illustrated in Fig. 2(a). Two obvious bands at 1362 and 1573 cm^{-1} can be observed. The band at 1362 cm^{-1} is ascribed to defects like edges and disordered sp^3 bonded carbon, while the band at 1573 cm^{-1} is corresponded to in-plane stretching of ordered sp^2 bonded carbon. The results confirm the existence of carbon in sample. Carbon comes from the sucrose carbonization and improves the conductivity of samples. To estimate the amount of carbon in sample, TGA was carried out in air from room temperature to 900°C. As shown in Fig. 2(b), the weight loss below 120°C is attributed to the evaporation of the adsorbed water and moisture molecules. Then the weight loss of 8.29% between 400 and 600°C is mainly attributed to the oxidation of carbon in air. The weight increase after 600°C comes from the oxidation of sodium and vanadium elements in LNVP. Therefore, the weight percentage of carbon in LNVP/C is approximately 8.29 wt%.

SEM and TEM are employed to study morphologies and microstructures of the prepared materials. The typical SEM images of LNVP/C sample are illustrated in Fig. 3(a–b). The images reveal that the sample consists of microplates roughly 80–90 nm in thin and the microplates tend to be agglomerate. The presence of carbon in the sintering process will have a certain adhesive effect on the microplates. Layer of membrane materials may be carbon films, which can increase the conductivity of the sample and speed up the lithium ion transport, leading to lithium storage specific capacity increase. TEM images of sample are displayed in Fig. 3(c) and

Figure 2. Raman spectra (a) and TG curve (b) of as-prepared sample.

Figure 3. The SEM images: (a) and (b), the TEM images: (c) and (d) of LNVP/C.

(d). The images show the sample with agglomerate microplate morphology, and some flocculent carbon can be seen. The result is consistent with the SEM images, further confirms the morphologies of microplates for LNVP/C.

A typical set of charge–discharge voltage curves for the first cycle of the cell is presented in Fig. 4(a). The curves show a flat discharge voltage plateau and a flat charge voltage plateau at every

Figure 4. (a) Charge–discharge voltage curves of LNVP/C; (b) CV curves for the first two cycles of LNVP/C at 0.05 mV s^{-1} .

rate, corresponding to the redox couple of $\text{V}^{4+}/\text{V}^{3+}$. As the rate increases, the oxidation–reduction potential difference increases gradually, indicating that the polarization increases.

CV curves of LNVP/C electrode for the first two cycles at a scan rate of 0.05 mV s^{-1} in voltage range of 3–4.3 V are shown in Fig. 4(b). During the first charge, one anodic peak is observed at 3.82 V corresponding to the extraction of lithium from the rhombohedral LNVP/C structure, accompanied by oxidation of vanadium from V^{3+} to V^{4+} . In the subsequent cathodic scan, one cathodic peak can be seen at 3.67 V corresponding to the insertion of lithium into the rhombohedral LNVP/C structure, accompanied by the reduction of vanadium from V^{4+} to V^{3+} . The results are consistent with the analysis in Fig. 3(a) and reports in literature.¹² Following, the peak location and current of the two cycles almost coincide, indicating that the cycling performance tends to be stable.

For comparison, the LNVP sample was synthesized by method of adding sucrose no changing other parameters as the method of synthesizing LNVP/C. The discharge capacities of LNVP/C at 1 C and 2 C, and the discharge capacities of LNVP at 1 C are shown in Fig. 5(a). The electrode of LNVP/C delivers an initial discharge capacity of 111.4 mAh g^{-1} at 1 C. After 150 cycles, a capacity of 107.4 mAh g^{-1} is maintained, about 96.4% of the initial capacity. The capacity and capacity retention rate are both beyond the Tang's report.¹⁸ The electrode of LNVP/C delivers an initial discharge capacity of 106 mAh g^{-1} at 2 C, higher than the capacity Zhang's report.¹² After 150 cycles, about 86.8% of the initial capacity is maintained. However, the LNVP sample delivers an initial discharge capacity of 109 mAh g^{-1} with 24 mAh g^{-1} at 1 C after 150 cycles, showing poor cycling stability. Obviously, the cycling stability of LNVP/C is superior to the sample without carbon. Carbon enhanced the electric conductivity of the electrode, thus improved the electron transportation during charging and discharging. Coulomb efficiency of LNVP/C at 1 C and 2 C for the first 100 cycles are shown in

Figure 5. (a) The discharge capacities of LNVP/C at 1 C and 2 C, and the discharge capacities of LNVP at 1 C; (b) and (c) Coulomb efficiency of LNVP/C at 1 C and 2 C for the first 100 cycles; (d) charge/discharge capacities of LNVP/C at different rates.

Fig. 5(b) and (c). It can be seen that the first coulomb efficiency of LNVP/C electrode at 1 C and 2 C are 93.9% and 91%, respectively. The coulomb efficiency of the subsequent cycle is above 95%, indicating that the LNVP/C electrode has a higher reversibility in the process of charging and discharging.

Figure 5(d) shows the rate capability of the LNVP/C electrode. The electrode can deliver the capacities of 123, 112, 104, 96 and 79 mAh g^{-1} at 0.2 C, 0.5 C, 1 C, 2 C and 5 C, respectively. When the rate is reset to 0.2 C after 25 cycles, it delivers a high discharge capacity of 121 mAh g^{-1} . Above results shows that the sample has high discharge capacities, good rate performance and structural stability.

4. Conclusion

The $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ material with rhombohedral structure was successfully synthesized by a sol-gel method. The SEM and TEM revealed that the $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ sample consists of microplates roughly 80–90 nm in thin and the microplates tend to be agglomerate. The carbon content in the $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ sample is approximately 8.29 wt%. A cathodic peak at 3.67 V and an anodic peak at 3.82 V can be seen in CV curves of $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ electrode, corresponding to the redox couple of $\text{V}^{4+}/\text{V}^{3+}$. In addition, the $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3/\text{C}$ electrode exhibits high discharge capacities, good cyclic stability and rate performance.

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References

1. K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, *Mater. Res. Bull.*, **15**, 783 (1980).
2. N. Nitta, F. Wu, J. T. Lee, and G. Yushin, *Mater. Today*, **18**, 252 (2015).
3. B. Xu, D. Qian, Z. Wang, and Y. S. Meng, *Mater. Sci. Eng. Rep.*, **73**, 51 (2012).
4. C. Zhang, Y. Liang, L. Yao, and Y. Qiu, *J. Alloys Compd.*, **627**, 91 (2015).
5. Z. Liu, X. Qin, H. Xu, and G. Chen, *J. Power Sources*, **293**, 562 (2015).
6. M. Chen, L.-L. Shao, H.-B. Yang, Q.-Y. Zhao, and Z.-Y. Yuan, *Electrochim. Acta*, **168**, 59 (2015).
7. Y. Gu, H. Wang, Y. Zhu, L. Wang, Y. Qian, and Y. Chu, *Solid State Ionics*, **274**, 106 (2015).
8. W. Zhang, Q. Liu, L. Feng, S. Wang, Y. Yang, and H. Wei, *New J. Chem.*, **38**, 2265 (2014).
9. A. K. Rai, T. V. Thi, J. Gim, S. Kim, and J. Kim, *Ceram. Int.*, **41**, 389 (2015).
10. L. F. Li, C. L. Fan, X. B. Huang, X. Zhang, and S. C. Han, *Energy Technol. (Weinheim)*, **3**, 955 (2015).
11. Q. Wei, Q. An, D. Chen, L. Mai, S. Chen, Y. Zhao, K. M. Hercule, L. Xu, A. Minhas-Khan, and Q. Zhang, *Nano Lett.*, **14**, 1042 (2014).
12. Y. Zhang, P. Nie, L. Shen, G. Xu, H. Deng, H. Luo, and X. Zhang, *RSC Advances*, **4**, 8627 (2014).
13. J. Mao, L. Shao, P. Li, X. Lin, M. Shui, N. Long, and J. Shu, *Electrochim. Acta*, **173**, 96 (2015).
14. M. H. Alfuruqi, S. Islam, J. Song, S. Kim, D. T. Pham, J. Jo, S. Kim, J. P. Baboo, D. Y. Putro, V. Mathew, and J. Kim, *Chem. Phys. Lett.*, **681**, 44 (2017).
15. P. Li, L. Shao, P. Wang, X. Zheng, H. Yu, S. Qian, M. Shui, N. Long, and J. Shu, *Electrochim. Acta*, **180**, 120 (2015).
16. J. Wang, X. Zhang, W. He, Y. Yue, Y. Wang, and C. Zhang, *RSC Advances*, **7**, 2658 (2017).
17. B. L. Cushing and J. B. Goodenough, *J. Solid State Chem.*, **162**, 176 (2001).
18. Y. Tang, C. Wang, J. Zhou, Y. Bi, Y. Liu, D. Wang, S. Shi, and G. Li, *J. Power Sources*, **227**, 199 (2013).
19. W. F. Mao, Y. Ma, S. K. Liu, Z. Y. Tang, and Y. B. Fu, *Electrochim. Acta*, **147**, 498 (2014).