

Effects of Carbon Source on Performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Cathode Materials Synthesized via Carbon Thermal Reduction for Li-ion Batteries

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Effects of the source of carbon on properties and performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode materials were studied using five different carbon containing materials (sucrose, graphite, carbon nanotubes, citric acid, and carbon black) in synthesis via the carbothermal reduction method. It was found that the electrochemical performance of the cathode material was greatly dependent on particle size, carbon content, and electron conductivity, which were all functions of the carbon source. When the ratio of carbon to vanadium was tentatively fixed at 1.25, $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ synthesized with carbon nanotubes showed the best electrochemical performance due to a high carbon content and uniformly distributed small particle size. In the further optimization of the ratio of carbon to vanadium in sucrose-synthesized cathode materials, sucrose was verified as more suitable carbon source and able to achieve to higher cathode performance.

Keywords: Lithium ion batteries; lithium vanadium phosphate; carbothermal reduction method; carbon nanotubes; sucrose

1. INTRODUCTION

Amongst commercial secondary batteries, Li-ion batteries have the highest power density and have attracted great interest for potential application in electric vehicles (EV) and hybrid electric vehicles (HEV) [1, 2]. Significant progress in anode electrode materials has been made during last decade through the introduction of nanocomposite carbon anodes with Si, Sn and Co, leading to major

battery performance improvements. Safe cathode materials capable of high specific capacity and good cyclic properties are essential to successful commercialization of Li-ion batteries for vehicles. Even though most of the lithium ion cells used in portable electronic devices such as cell phones and laptop computers are based on layered LiCoO_2 cathode materials, the chemical instability and safety concerns prevent the use of cobalt-rich cathode materials in large batteries for EV [3].

Recently, polyanion-based materials $(\text{PO}_4)^{y-}$ have emerged as the most promising candidates for the cathode material. They not only have high redox potentials and energy density, also exhibit excellent thermal and electrochemical stabilities [4-6]. In this family, the advantages in using Fe-based compounds are abundant, low cost, and stability against overcharge or discharge, whereas lithium iron phosphate (LiFePO_4) has been found to be limited by low electron conductivity and low Li^+ ion diffusion rate, resulting in poor performance. Some recent research indicates that there might be some ways to overcome this limitation, such as carbon coating and metal doping (Al, Cu, Ti, Zr, and Nb) [7-9]. Another promising cathode material for lithium ion batteries is $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, which exhibits different characteristics from LiFePO_4 . It has been found that there are three different Li sites with different coordination environments in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ structure according to a ^7Li NMR study [10,11]. The theoretical capacity based on extraction of three Li^+ ions is 197 mAh g^{-1} , which, currently, is the highest in all phosphate cathode materials [12-14]. Also, unlike the one-dimensional channels in LiFePO_4 , in the case of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, the three-dimensional framework is favorable to structural stabilization, and allows for fast Li^+ ion diffusion [15]. Like other phosphates, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ also is a safe cathode material. So, these advantages make it become an ideal cathode material for lithium ion batteries [16, 17]. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders can be synthesized via various methods such as solid-state reaction, sol-gel process [18], and solid state method [19-24]. Instead of using H_2 , N_2H_4 [25] or other reducing agents, carbon enable to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with a doping of carbon into the cathode material, thereby improving electronic conductivity and cyclic stability. Also, this synthesis method is more feasible to scale up in industry manufacture.

When similar carbothermal methods were used by other researchers to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, electrochemical performance was found to be greatly dependent on carbon sources used in synthesis [17, 20, 21]. Given the importance of understanding the key structure-performance relationship in materials synthesis, the effort in that area of research has been surprisingly limited, and has hampered progress in the development of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material for Li-ion battery technology in general. In this work, the carbothermal reduction method was further developed using five different carbon sources (sucrose, graphite, carbon nanotubes, citric acid, and carbon black) to synthesize the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ composite cathode material. The physical properties (morphology, particle size, carbon content, electron conductivity, and tap density) and electrochemical performance of the cathode materials synthesized from the five different carbon sources are systematically compared to provide an insight of structure-performance correlation for cathode material synthesis. Based on carbon contents of the as-prepared samples, the reaction equation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized by carbon thermal reduction is also discussed. Carbon to vanadium (C: V) ratio in synthesis is also proposed as an important factor to optimize cathode performance.

2. EXPERIMENT

2.1 Synthesis and characterization of cathode materials

LiOH·H₂O (AR, 99%), V₂O₅ (AR, 99%) and NH₄H₂PO₄ (AR, 99%) were used as starting materials. These raw materials were mixed at stoichiometric ratio with a fixed ratio of C: V for five different carbon source (sucrose, graphite, carbon nanotubes, citric acid, and carbon black), and ball-milled for six hours. Then pre-heat treatment was carried out at 300°C for four hours to release NH₃ and H₂O. After cooling and grinding, each sample was sintered at a temperature of 800°C for 16-24 hours in an argon atmosphere to synthesize the Li₃V₂(PO₄)₃/C composite cathode materials.

The morphology of Li₃V₂(PO₄)₃/C cathode materials as a function of carbon source was studied by a HITACHI S-4700 scanning electron microscope (SEM). The crystal structure of Li₃V₂(PO₄)₃ was characterized by X-ray diffraction (XRD) using a Rigaku D/max-β X-ray diffractometer with a Cu Kα radiation source ($\lambda = 0.154178$ nm, V=45 kV, I=50 mA, $2\theta = 10-90^\circ$). The particle size distribution of these samples was tested by a British Malvern Instruments LS900-V4.00B laser particle tester. The carbon content in composite cathode materials was determined with a Shimadzu TOC-VCPN-(SSM-5000A) analyzer. In order to measure electron conductivity of the synthesized composite cathode materials, a certain amount of sample was placed in a mold and pressed into a round cake with pressure of 16 MPa, then the resistance of the pressed round cake was analyzed with a Keithley four-probe conductivity meter (Model 2400 series).

2.2 Electrochemical tests

The synthesized Li₃V₂(PO₄)₃/C powders were mixed with acetylene black and polyvinylidene fluoride (PVDF 1300) at a mass ratio of 80:10:10. Then the mixture was dispersed into N-methyl pyrrolidone (NMP) solvent. After stirring for 12 hours, the paste was uniformly coated onto Al foil, and then dried under vacuum at 120°C for 24 hours. In an Ar-filled glove box, a model 2025 coin cell was used to assembly half-cell, in which metallic lithium foil was the counter electrode and Celgard 2400 microporous polyethylene membrane was used as the separator. Electrolyte was 1 mol·L⁻¹ LiPF₆ in a mixture of ethyl carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) with 1:1:1 volume ratio. Charge and discharge capacity and cycle performance for all of the half-cells were tested using a BTS-5V/5mA battery test system (Neware Inc.).

3. RESULTS AND DISCUSSION

3.1 Effect of carbon source on cathode performance

Even though a similar carbothermal method was used to synthesize the various Li₃V₂(PO₄)₃/C cathode materials, their electrochemical performance was found to be greatly dependent on the employed carbon source. In this work, five different carbon sources (sucrose, graphite, carbon nanotubes, citric acid, and carbon black) were used to synthesize Li₃V₂(PO₄)₃/C composite cathode

materials. The physical properties and electrochemical performance for these cathode materials were systematically compared. At first, the analysis indicates that sucrose and citric acid synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials contain much lower carbon content than those using the other carbon sources such as carbon nanotubes, carbon black and graphite, as shown in Fig. 1.

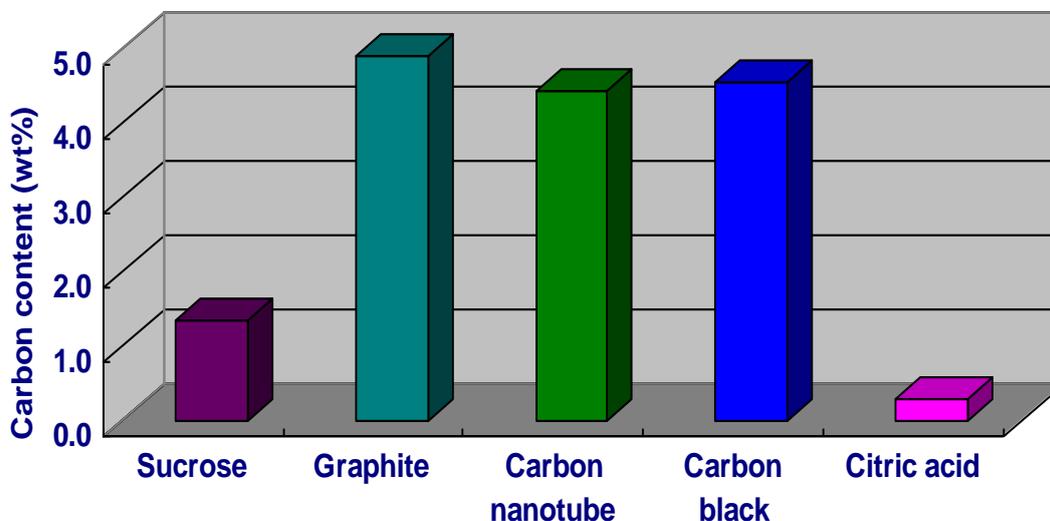
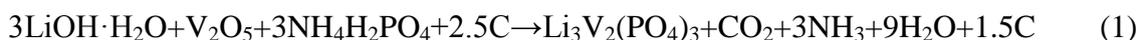


Figure 1. Carbon content in $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material as a function of carbon source

In this comparison, the ratio of C: V is fixed at 1.25 for each carbon source. It also can be inferred that the reaction equation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized by carbon thermal reduction is as follows [26]:



or



As the stoichiometric carbon content of reaction (1) is 4.23 wt %, while that of reaction (2) is only 1.47 wt %, the reaction (1) is more likely in the carbothermal reduction (CTR) method for synthesis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials. It is worth noting that even though the same amount of carbon was used in cathode material synthesis for each carbon source, the different carbon content found in various cathode materials suggests a different level of carbon utilization during synthesis at the elevated temperatures. Higher carbon content in the cathode material would have positive effects on electron conductivity of cathode materials, particle size and Li^+ ion diffusion [27]. But the fraction of active lithium vanadium phosphate in the cathode material would be reduced due to the higher carbon content, thereby decreasing the specific capacity of cathode material.

In addition, surface morphology of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode materials were studied as a function of carbon source using SEM, as shown in Fig. 2. It can be clearly seen that bigger particle sizes were observed with sucrose and citric acid synthesized cathode materials. Obvious agglomeration appears in the case of graphite. On the other hand, uniform morphology and smaller particle size were obtained when carbon nanotubes and nanosized carbon black were used as carbon sources. Generally, carbon dispersed among the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles could restrain particle growth. The different

morphology and particle size are related to varying carbon contents, resulting from different carbon sources at a fixed synthesis temperature.

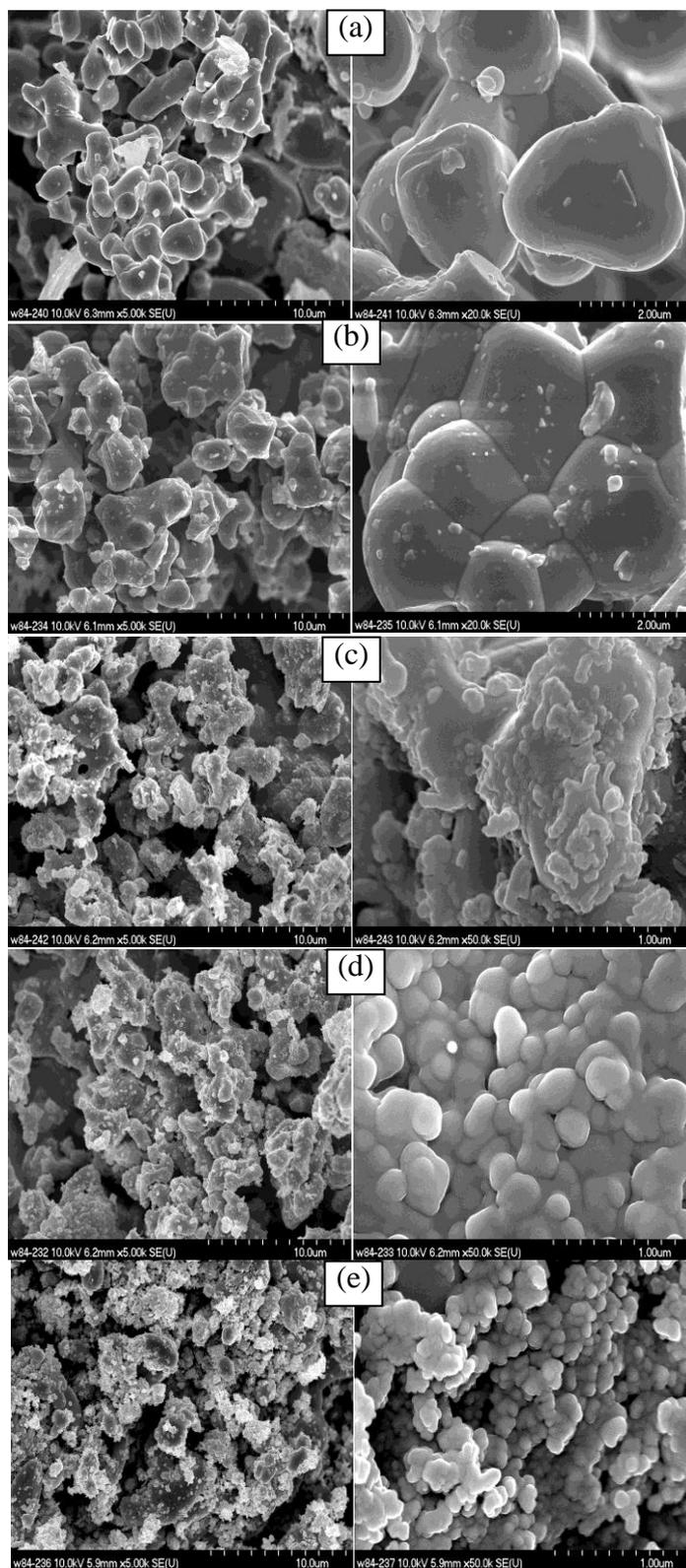


Figure 2. SEM images of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples: a) sucrose, b) citric acid, c) graphite, d) carbon nanotubes, d) carbon black

For each of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples synthesized from different carbon sources, similar XRD patterns could be indexed well to monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ structure with the space group of $\text{P}2_1/n$ [28, 29] (Fig. 3). This suggests that the crystal structures of cathode material are independent of the employed carbon source in synthesis. The various carbon contents derived from different carbon sources in cathode materials only have an influence on the morphology and particle size of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, but not on the crystal structures.

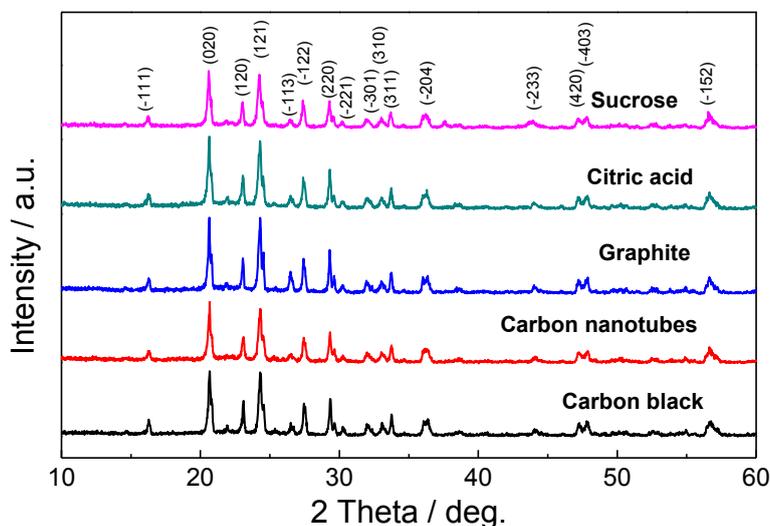


Figure 3. XRD patterns of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ synthesized from various carbon sources

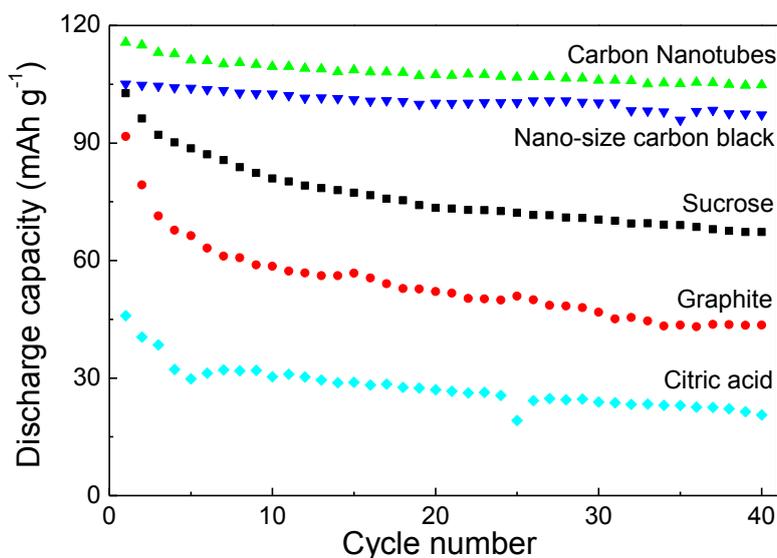


Figure 4. Cyclic performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as a function of carbon source

In order to prepare the cathode electrodes and test their electrochemical performance in a half-cell, the synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials were assembled with a metallic lithium counter

electrode, electrolyte, and separator. The specific capacity and cycle performance for each of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material synthesized from different carbon sources were compared at a 0.1C charge-discharge rate as shown in Fig 4. The results indicate that the carbon nanotubes and nanosized carbon black synthesized cathode materials have the highest specific capacity (around 110 mAh g^{-1}) and better charge-discharge cycle performance. The possible explanation is related to their different physical properties. Carbon nanotubes and carbon black precursors led to uniform and small particle size distributions in cathode materials, thus having higher surface area, good contact for each particle, and a better environment for Li^+ ion diffusion. This comparison suggests that electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ is greatly dependent on its physical characteristics such as carbon content, morphology, and particle size.

3.2 Carbon nanotubes as carbon source

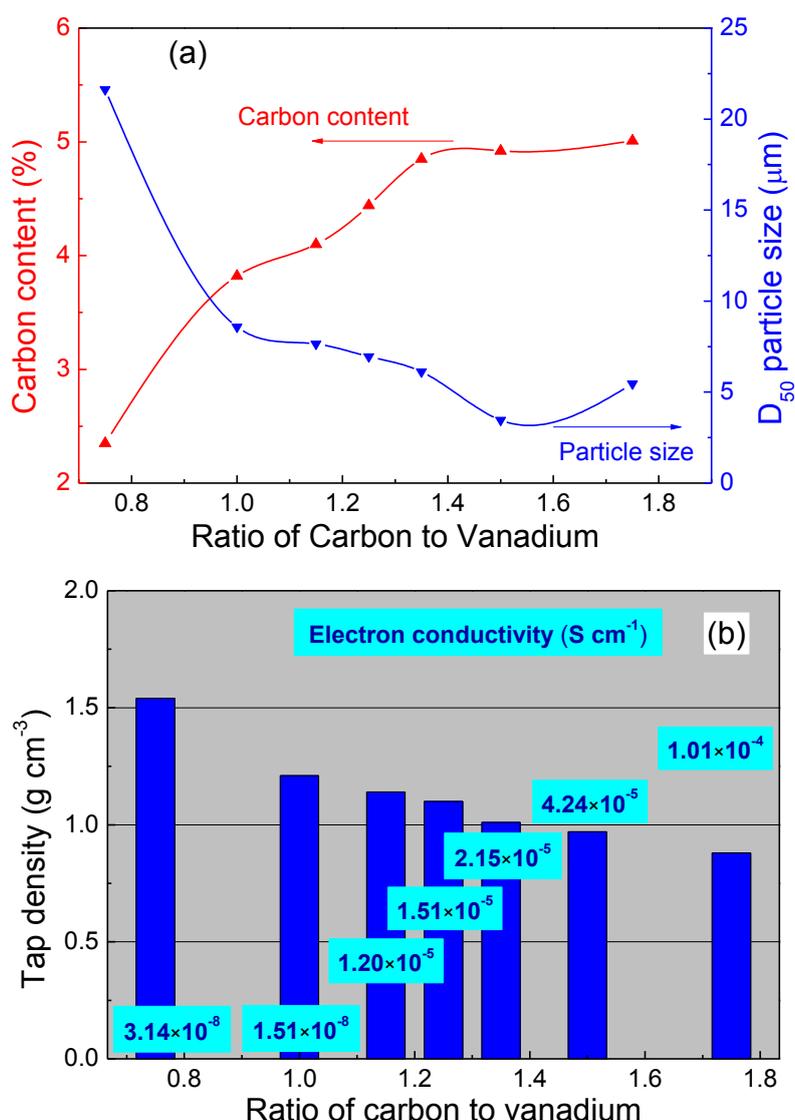


Figure 5. Effect of C:V ratios on (a) carbon content and particle size, and (b) electron conductivity and tap density of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material synthesized from carbon nanotubes

The carbon nanotube synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material shows the highest performance at 0.1C charge-discharge rates when the ratio of carbon to vanadium (C:V) is tentatively fixed at 1.25, therefore further optimization in terms of the amount of carbon nanotube used in synthesis was conducted to achieve higher performance. At first, the physical properties including carbon content, particle size, electron conductivity and tap density were studied as a function of ratio of C: V in a range from 0.75 to 1.75.

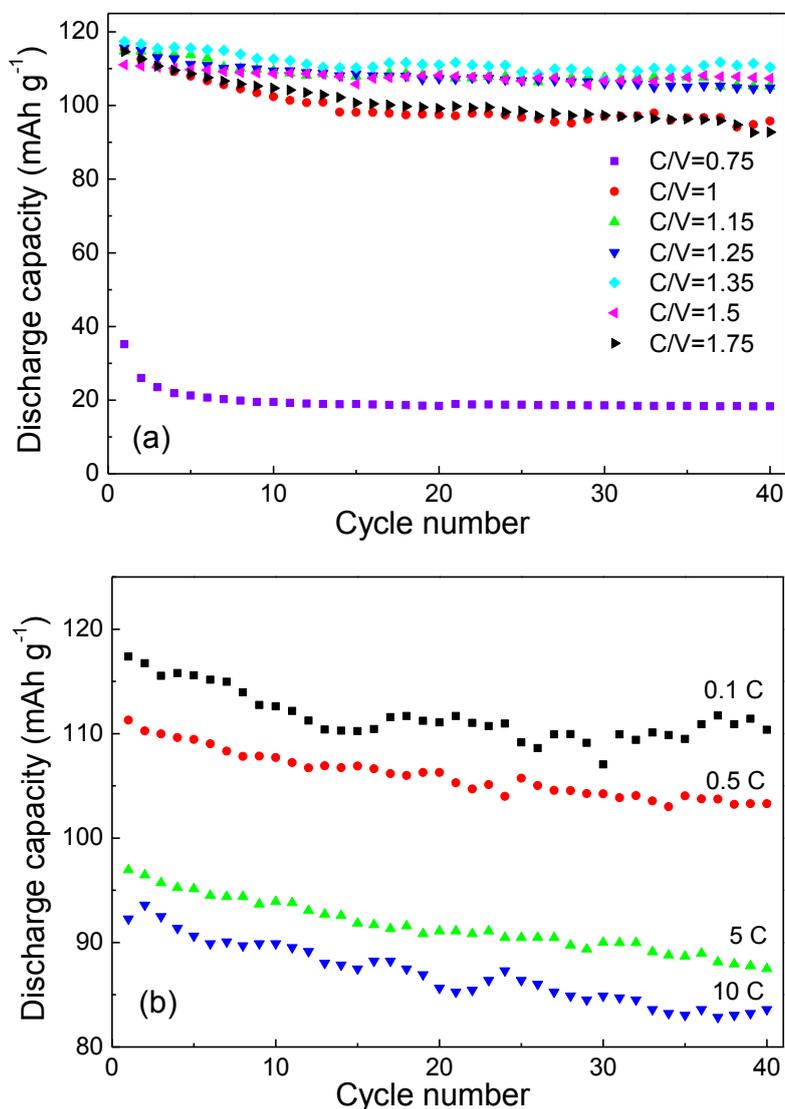


Figure 6. Effect of C: V ratios on cyclic (a) and rate performance (b) of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials synthesized from carbon nanotubes

These results were compared in Fig. 5(a) and (b). As expected, carbon content in cathode materials rises monotonically with the mass of carbon nanotubes used. Particle size decreases dramatically with C: V ratio at first, then levels off and starts to gradually increase. The smallest particle size was obtained at the ratio of 1.5. More importantly, when the ratio of C: V is above 1.15,

an obvious improvement in electron conductivity was observed. Since the density of carbon is lower than that of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, as expected, increasing carbon leads to a low tap density.

After determining the effect of C:V ratio on the physical properties of carbon nanotubes-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials, the discharge specific capacity and cyclic performance of each cathode material were compared at charge and discharge rates of $0.1C$, as shown in Fig. 6(a). The maximum specific capacity was observed with the C:V ratio of around 1.5. At this ratio, the smallest particle size and reasonable electron conductivity were observed. On the other hand, too much doped carbon in cathode material would have a negative effect, reducing the amount of active substances [27]. At the same time, using the optimized cathode material, the rate performance was determined at various charge-discharge rates as shown in Fig 6(b). Initial discharge capacity at $0.1C$ is around 117 mAh g^{-1} , but it drops to 110 mAh g^{-1} after only 40 cycles. When the charge-discharge rates increase to $10C$, the capacity dramatically declines to 83 mAh g^{-1} . It looks like the high-rate performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material synthesized carbon nanotube is not promising.

3.3 Sucrose as carbon source

When compared with carbon nanotubes, as a carbon source, sucrose is more easily available and low cost, which is crucial for commercial production. Importantly, sucrose can be carbonized to form graphitized carbon at elevated temperatures in a mixture with $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles, thereby enabling to enhance electron conductivity. Thus, it is useful to explore the possibility of using sucrose as a carbon source to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode materials. At first, the carbon utilization of sucrose was determined during the cathode material synthesis (the synthesis scheme is shown in Fig. 7). In order to mimic the actual procedures, 1.0 g sucrose was heat-treated at 300°C for 4 hours in Ar atmosphere, and then pyrolyzed at 800°C in Ar atmosphere once again for 24 hours. After the two stages of heat treatment, the remaining mass of carbon was 0.20 g. So the carbon utilization of sucrose during the cathode material synthesis was calculated around 48%.

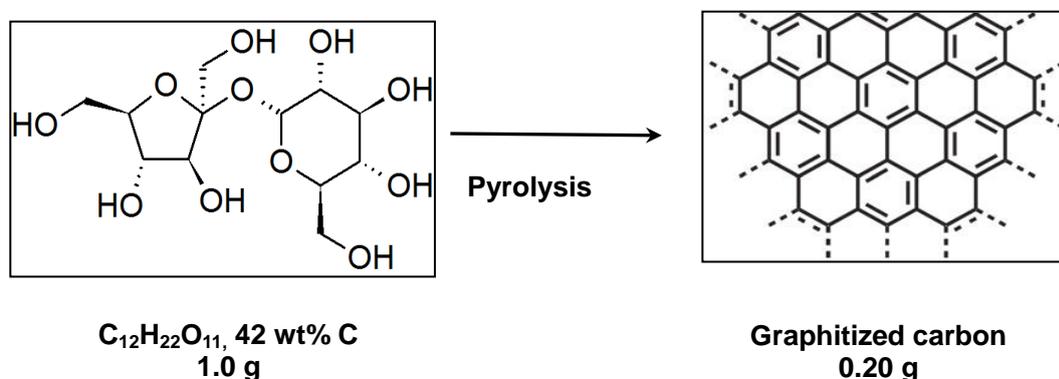


Figure 7. The scheme of the carbonization procedure of sucrose at the elevated temperatures

To optimize the amount of sucrose used in cathode material synthesis, various ratios of C: V ranging from 1.25 to 2.5 were employed to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials. The

correlation between these ratios and the physical properties of the cathode material including carbon content, particle size, electron conductivity and tap density was studied. The results are summarized in Fig 8. Carbon content in cathode material was found to be increasing with C: V ratio, with a large slope when the ratio is above 2.0. Particle size tends to decrease with C: V ratios showing a minimum between 2.0 and 2.25. As expected, a sharp increase in electron conductivity was measured with the sample synthesized from a C: V ratio of above 2.25. This means that, when the sucrose amount increase to this value, graphitized carbon layers are able to uniformly cover the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles, forming an electric conductive network.

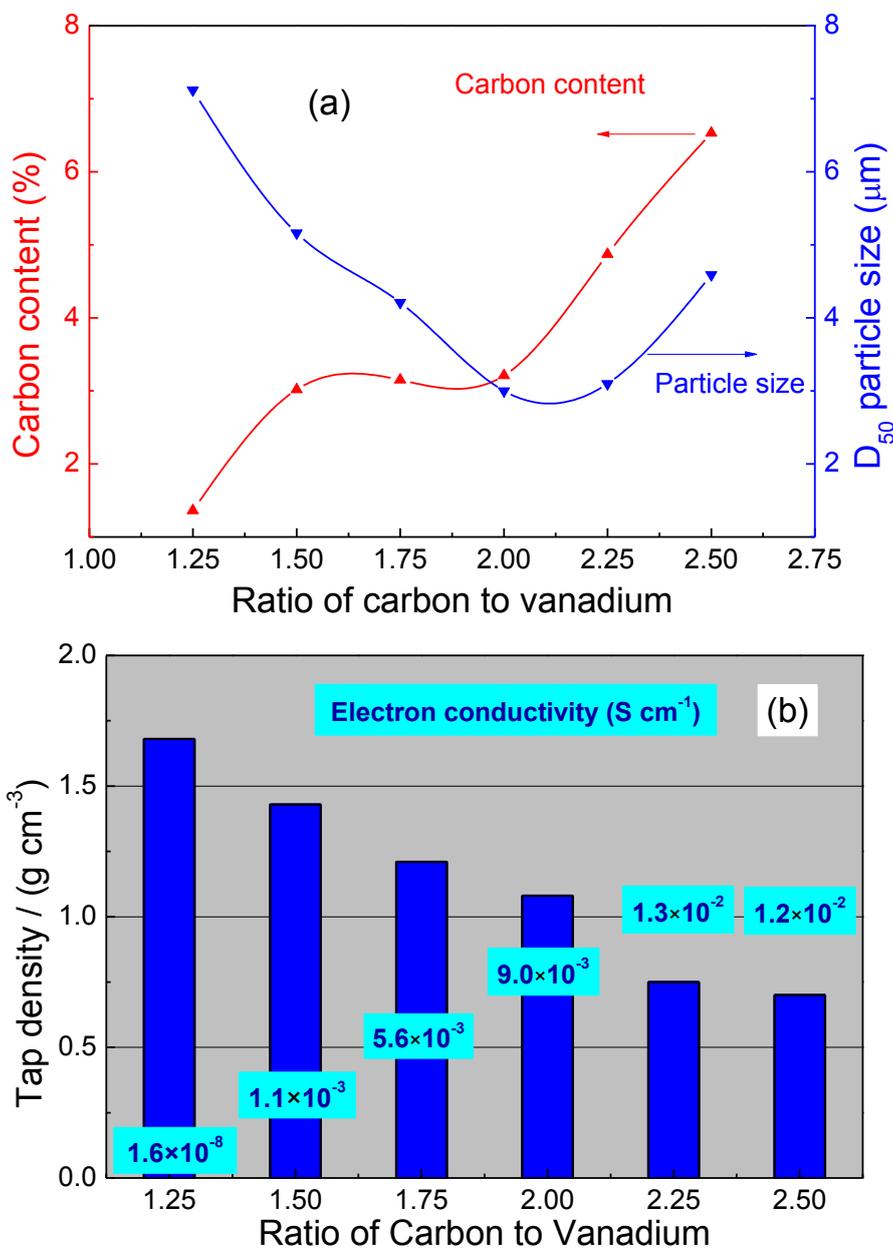


Figure 8. Effect of C:V ratios on (a) carbon content and particle size, and (b) electron conductivity and tap density of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ synthesized from sucrose

To study the effect of C: V ratios on the electrochemical performance of sucrose-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials, the charge and discharge cyclic performance in a voltage range of 3.0-4.3 V were tested in half cells as shown in Fig. 9. The maximum discharge capacity at 0.1C around 130 mAh g^{-1} was achieved at a C: V ratio of 1.75, also showing a good cycle performance with a capacity retention of 98% after 40 cycles. The smallest particle size and highest electron conductivity were obtained at this ratio, and these factors probably are responsible for the high performance. On the other hand, as expected, too high carbon content also would dilute the concentration of active $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, leading to a decline of specific capacity due to the electrochemical inactivity of carbon.

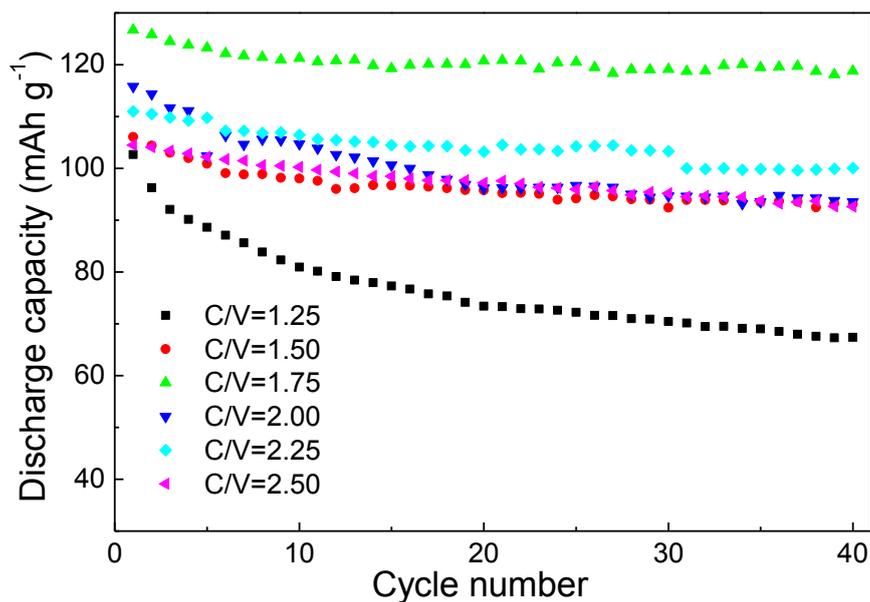


Figure 9. Effect of C:V ratios on cyclic and rate performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials synthesized from sucrose

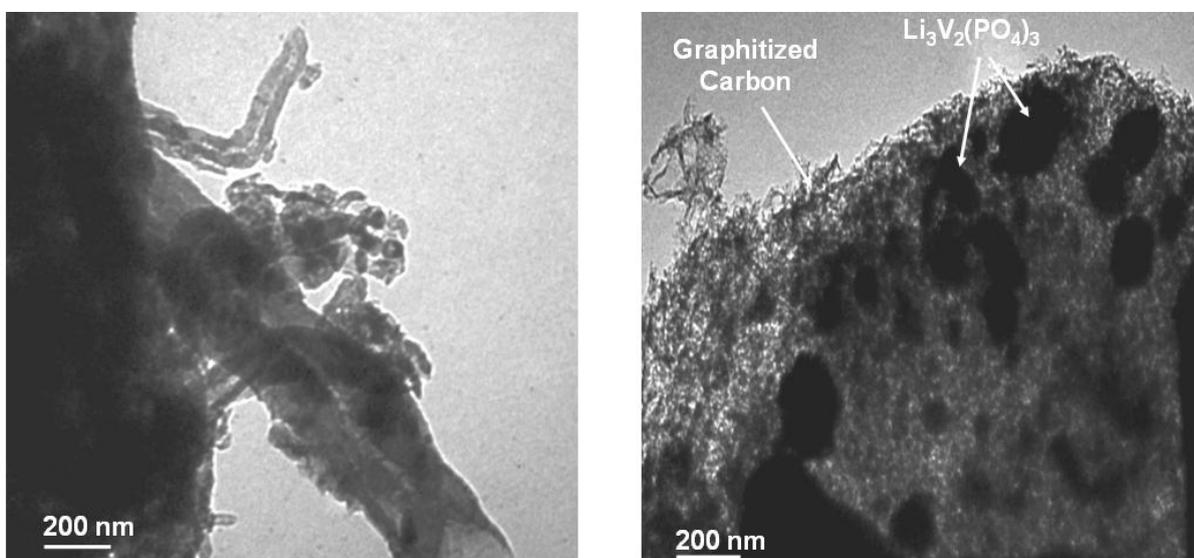


Figure 10. TEM images of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials synthesized from (a) carbon nanotubes and (b) sucrose

Nanostructures of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode materials were compared in Fig. 10 when carbon nanotubes and sucrose were used as carbon sources with optimized C: V ratios, respectively. The TEM images indicate that the carbon coating observed on a carbon nanotube-synthesized cathode material was non-uniform. On the other hand, a uniform coverage of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles was achieved in the graphitized carbon resulted from the carbonization of sucrose. This is the major reason that electron conductivity in the sucrose-synthesized cathode material is much higher than that in the carbon nanotube-synthesized one, leading to a higher cycle performance. Due to these advantages of using sucrose as a carbon source, we further electrochemically characterized the composite cathode material and determined its high-rate cyclic performance.

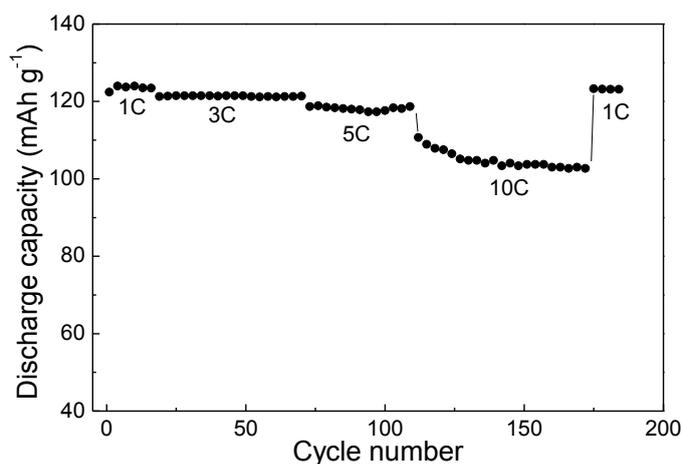


Figure 11. Rate performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material synthesized from sucrose

As shown in Fig. 11, the rate performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials was further studied at high charge-discharge rates in the potential range of 3.0-4.3 V corresponding to the first two Li^+ extraction/insertion [30]. At 1C charge and discharge rates, the discharge capacity is around 124 mAh g^{-1} . When the rates are increased to 3C and 5C, the discharge capacities remain at 121 and 118 mAh g^{-1} , respectively, without any degradation after 40 cycles. It is worth noting that the discharge capacity is as high as 109 mAh g^{-1} at 10C charge and discharge rates, with a retention of 94% after 60 cycles. When the charge and discharge rates reversibly change back to 1C, the discharge capacity of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material is 123 mAh g^{-1} , similar to the original capacity (124 mAh g^{-1}). These results indicate that an excellent high-rate charge and discharge performance is achieved for the sucrose-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode material, which is very important to the automotive applications [31].

4. CONCLUSIONS

Five different carbon sources (sucrose, graphite, carbon nanotubes, citric acid, and carbon black) were used to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite cathode materials via the carbothermal reduction method. Their electrochemical performance was found to be greatly dependent on the

physical properties of the cathode materials including particle size, carbon content, electron conductivity and the tap density, which are directly correlated to the employed carbon sources in synthesis. Even though the carbon nanotube-synthesized cathode material exhibited the reasonable specific capacity at low charge-discharge rates, its low electron conductivity leads to a poor high-rate performance because of the unsuccessful coating of carbon. When compared with carbon nanotubes, sucrose as a carbon source is more easily available and low cost, which is more suitable for scale-up production. Importantly, it has been theoretically and experimentally verified that sucrose can be carbonized to form graphitized carbon at elevated temperatures, which surrounds the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles and thereby enhances electron conductivity. This is the major reason that electron conductivity in sucrose-synthesized cathode material is much higher than that in the carbon nanotube-synthesized one. After further optimization of the ratio of C: V in sucrose-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials, the initial capacity at 1C charge and discharge rates is as high as 124 mAh g^{-1} . Importantly, an excellent high-rate performance was achieved; the capacity was 109 mAh g^{-1} at 10C charge and discharge rates with a retention of 94% after 60 cycles.

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