Carbon wrapped hierarchical \( \text{Li}_3\text{V}_2(\text{PO}_4)_3 \) microspheres for high performance lithium ion batteries

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Nanomaterials are extensively studied in electrochemical energy storage and conversion systems because of their structural advantages. However, their volumetric energy density still needs improvement due to the high surface area, especially the carbon based nanocomposites. Constructing hierarchical micro-scaled materials from closely stacked subunits is proposed as an effective way to solve the problem. In this work, \( \text{Li}_3\text{V}_2(\text{PO}_4)_3 \)@carbon hierarchical microspheres are prepared by a solvothermal reaction and subsequent annealing. Hierarchical \( \text{Li}_3\text{V}_2(\text{PO}_4)_3 \) structures with different subunits are obtained with the aid of polyvinyl pyrrolidone (PVP). Moreover, excessive PVP interconnect and form PVP-based hydrogels, which later convert into conductive carbon layer on the surface of \( \text{Li}_3\text{V}_2(\text{PO}_4)_3 \) microspheres during the annealing process. As a cathode material for lithium ion batteries, the 3D carbon wrapped \( \text{Li}_3\text{V}_2(\text{PO}_4)_3 \) hierarchical microspheres exhibit high rate capability and excellent cycling stability. The electrode has the capacity retention of 80% after 5000 cycles even at 50C.
outstanding rate capability. However, the volumetric energy density of most reported lithium transition metal phosphate electrodes needs to be improved\(^{41-43}\). In this work, carbon wrapped \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) hierarchical microspheres from close stacked nanosheets are prepared by the facile solvothermal process with the aid of PVP. PVP plays a vital role in the formation of hierarchical microspheres and serves as the starting reagent for PVP-based hydrogels, which is carbonized to form the wrapping carbon layer on \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) microspheres. As cathode materials for lithium ion batteries, the hierarchical \(\text{Li}_3\text{V}_2(\text{PO}_4)_3@\text{carbon}\) microspheres exhibit excellent rate capability and cycling stability.

Materials and Methods

Materials Synthesis. In a typical synthesis, \(\text{V}_2\text{O}_5\) (144 mg) and oxalic acid in a molar ratio of 1:3 were dissolved into 12 mL of deionized water at 70 °C to form the \(\text{VOC}_2\text{O}_4\) solution, which was later poured into a 100 mL Teflon container. Then, stoichiometric amount of \(\text{NH}_4\text{H}_2\text{PO}_4\), \(\text{Li}_2\text{CO}_3\) and 2.5 g of polyvinyl pyrrolidone (PVP, molecular weight: 58,000) were added into the solution under magnetic stirring for 30 minutes. After that, 60 mL of isobutanol was added and stirred for another 1 h. The container was sealed in an autoclave and kept at 180 °C for 24 h. After cooling down to room temperature naturally, brown colored precipitate was collected and dried before annealing at 800 °C for 8 h in \(\text{H}_2\) /\(\text{Ar}\) (5:95, v/v) atmosphere to obtain carbon wrapped hierarchical \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) microspheres. In order to study the formation process of the hierarchical structures, different amount of water (8, 10, and 12 mL) and PVP (0, 1.5 and 2 g) were used during the solvothermal fabrication process. Moreover, the time-dependent experiments (2, 6, 24 and 48 h) were carried out to study the structure evolution.

Differential Scanning Calorimetry (DSC)/Thermogravimetric Analysis (TGA) instrument (Netzsch STA449C, Germany) was used to study the reactions during the annealing process and measure the carbon content in \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) microspheres. A combined X-ray diffraction (XRD, Rigaku D/max2500) with Cu K\(\alpha\) (\(\lambda = 1.5406 \, \text{Å}\) ) radiation. The morphologies of the samples were examined by field-emission scanning electron microscopy (SEM, FEI Nova NanoSEM 230) and transmission electron microscopy (TEM; JEOL-JEM-2100F transmission electron microscope). A combined Differential Scanning Calorimetry (DSC)/Thermogravimetric Analysis (TGA) instrument (Netzsch STA449C, Germany) was used to study the reactions during the annealing process and measure the carbon content in \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) microspheres. In order to study the formation process of the hierarchical structures, different amount of water (8, 10, and 12 mL) and PVP (0, 1.5 and 2 g) were used during the solvothermal fabrication process. Moreover, the time-dependent experiments (2, 6, 24 and 48 h) were carried out to study the structure evolution.

Electrochemical Measurements. The working cathode slurry was dispersed by dispersing the \(\text{CW}-\text{LVP}\) acetylene black and poly-(vinylidene fluoride) (PVDF) binder in the N-methylpyrrolidone solution with a weight ratio of 70:20:10. The slurry was painted on the aluminum foil and dried in a vacuum oven at 110 °C for 12 h. The half-cell assembly was carried out in a glove box filled with ultrahigh pure Argon using lithium foil as the anode, and 1.0 M LiPF\(_6\) in ethyl carbonate/dimethyl carbonate (1:1 v/v ratio) as the electrolyte. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (CHI604E, China). The galvanostatic charge/discharge performances of the electrodes were measured at room temperature using a Land Battery Tester (Land CT 2001A, China).

Results and Discussion

Figure 1 schematically illustrates the fabrication process of carbon wrapped \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) (\(\text{CW}-\text{LVP}\)) microspheres. Firstly, the \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) precursor colloids were synthesized using \(\text{VOC}_2\text{O}_4\), \(\text{Li}_2\text{CO}_3\), \(\text{NH}_4\text{H}_2\text{PO}_4\) and PVP. Then isobutanol was added into the colloids to form a two phase solution, where the PVP viscous polymers wrapped on the surface of the colloids. After solvothermal treatment, the hierarchical \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) precursor microspheres were fabricated. Meanwhile, the PVP viscous polymers that attached tightly to the surface of the \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) precursor particles convert into PVP-based hydrogels. The picture of the solvothermal product is shown in Supplementary Figure S1. Large amount of PVP-based hydrogels are clearly presented in brown color. These PVP-based hydrogels wrapped \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) precursor microspheres were annealed to form carbon wrapped \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) microspheres. Supplementary Figure S2 compares the TG and DSC results of the \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) surrounded by PVP-based hydrogels and pure \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) precursor. The weight loss of the composite precursor is 40% percent more than pure \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) precursor. The extra weight loss is attributed to the decomposition of dried PVP-based hydrogels at about 436 °C.

Figure 2 shows the structural characterization results of the carbon wrapped hierarchical \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) spheres. According to the XRD pattern (Fig. 2a), the obtained material can be assigned to monoclinic \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) with a space group \(P2_1/n\) (ICPDS No. 01-072-7074)\(^{44}\). No other phase is detected, suggesting the high purity of \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) samples. The SEM images (Fig. 2b,c) reveal the spherical morphology of the fabricated \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\), which has an average diameter of 3–4 \(\mu\)m. Moreover, the surface of \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) microspheres is coated by a smooth layer (Fig. 2c). Figure 2d shows two broad bands at 1350 and 1590 cm\(^{-1}\) on the Raman spectrum of the \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) microsphere, which corresponds to the typical D and G bands of carbon. The result indicates the existence of carbon in the composite. Two broad bands at 997 and 1135 cm\(^{-1}\) corresponding to the \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) phase are also shown in Figure S3. After removing \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) in the microspheres by HCl acid leaching, a hollow-structured microsphere is observed (Fig. 2e), which indicates the surface coating layer is composed of carbon. The TEM image (see supplementary information, Figure S4) confirms the existence of carbon layer on the surface of \(\text{Li}_3\text{V}_2(\text{PO}_4)_3\) microspheres, which is about 30 nm in thickness. The carbon is derived from the PVP-based hydrogels in the calcination process in Argon. According to the thermogravimetric (TG) analysis (Figure S5, supplementary information), the carbon content in the \(\text{CW}-\text{LVP}\) microspheres is 24.6 wt%.
assembled from close stacked nanosheets in parallel (Fig. 2f), which is believed to be helpful to improving the volumetric energy densities of the electrode.

Nitrogen adsorption-desorption measurement is carried out to further study the carbon wrapped Li$_3$V$_2$(PO$_4$)$_3$ microspheres and the results are shown in Fig. 3. The isothermal curve exhibits a typical IV-type hysteresis, indicating the mesoporous feature of the CW-LVP microspheres. According to Brunauer-Emmett-Teller (BET) method, the surface area of the CW-LVP microspheres is 35.1 m$^2$/g. Figure 3b shows the pore size distribution of the CW-LVP by Barret-Joyner-Halenda (BJH) method. The majority of pores are less than 10 nm. It is believed that the pores are largely produced from the surface carbon shell. The porous structure provides easier paths for electrolyte penetration and the reasonable BET surface area gives the sufficient surface contact area between electrode materials and electrolyte.

In order to study the formation of hierarchical microspheres, the solvothermal process is carefully studied, including the addition amount of PVP, isopropanol, and the solvothermal treatment time. The PVP based hydrogels are removed after solvothermal treatment to study the structural evolution of the Li$_3$V$_2$(PO$_4$)$_3$ precursor microspheres. The amount of PVP added has a great effect on the morphologies of the solvothermal prepared Li$_3$V$_2$(PO$_4$)$_3$ microstructures and the results are shown in Figure S6. No microspheres are formed without PVP in the solvothermal solution. The obtained aggregates are of microscale and have irregular shapes. However, nanosheet assembled microspheres are obtained when 1 g PVP is added. By increasing the PVP addition amount to 1.5 g, the nanosheets are closer stacked and form the hierarchical microspheres. Moreover, the usage of isobutanol is vital to build the nanosheet-assembled hierarchical structures. Only microspheres with smooth surface are obtained when no isobutanol is used (see Supplementary Figure S7).

Time-dependent experiment (2, 6, 24 and 48 h) is also carried out to study the structural evolution of the hierarchical precursor microspheres. As shown in Figure S8 (supplementary information), the microspheres with small nanosheet subunits are readily formed after 2 h solvothermal treatment. After 6 h solvothermal treatment, the nanosheets are more clearly detected. By extending the solvothermal time to 24 and 48 h, the nanosheets become larger and more separated. The thickness of the nanosheet is about 20 nm.

The volume ratio between isobutanol and water also affects the morphologies of the solvothermal products significantly. Figure 4 shows the SEM images of the Li$_3$V$_2$(PO$_4$)$_3$ microspheres prepared from the different volume ratio of isobutanol and water. When 8 mL water is combined with 60 mL isobutanol, the solvothermal products are mainly composed of nanoplates. The lengths of Li$_3$V$_2$(PO$_4$)$_3$ nanoplates can be 1–2 μm in width and about 50 nm in thickness (Fig. 4a,b). When the amount of water is increased to 10 mL, the precursor microflowers assembled from petal-like nanosheets are formed (Fig. 4c,d). When increasing the amount of water to 12 mL, hierarchical Li$_3$V$_2$(PO$_4$)$_3$ microspheres with close packed parallel nanosheets can be obtained (Fig. 4e,f).

The carbon wrapped Li$_3$V$_2$(PO$_4$)$_3$ hierarchical microspheres were assembled into coin cells to measure their electrochemical performances. The mass loading density of the CW-LVP electrode is about 1 mg cm$^{-2}$. Figure 5a shows the cyclic voltammograms (CVs) curves of the CW-LVP electrodes in the voltage range of 3.0–4.3 V vs. Li/Li$^+$ with different scanning rates. Three intensive pairs of redox peaks are detected on the CV curves at various scan rates, suggesting the good reversibility and stability of the CW-LVP electrode. The detection of multiple peaks at
3.63, 3.72 and 4.14 V during the anodic scan of 0.1 mV s⁻¹ show that the multi-step lithium extraction process and the phases change from Li₃V₂(PO₄)₃ to Li₂.₅V₂(PO₄)₃, Li₂V₂(PO₄)₃ and to LiV₂(PO₄)₃, respectively. And the three cathodic peaks at 3.99, 3.62, and 3.54 V are attributed to lithium insertion process, and the phases change in reverse, respectively. The small peak shift at high scan rates suggests the low polarization of the electrode materials.

Figure 5b shows the charge-discharge profiles of the CW-LVP electrodes at various rates (Here 1 C corresponds to 133 mA g⁻¹) in the voltage range of 3.0–4.3 V. The discharge plateaus at 3.99, 3.62 and 3.54 V and charge plateaus at 4.14, 3.72 and 3.63 V at 0.5 C are clearly observed, demonstrating the multi-step Li⁺ ions intercalation/de-intercalation process. Result match well with the CV curves. The discharge/charge profiles almost overlapped.
before 1 C rate. The main plateaus can be clearly presented even at 10, 20 and 50 C. The initial charge and dis-
charge capacities at 0.5 C are 130.7 mA h g\(^{-1}\) and 121.3 mA h g\(^{-1}\), respectively. And the corresponding initial cou-
lombic efficiency at 0.5 C is about 92.8%. The capacity loss may be attributed to the formation of SEI layer on the
surface of the electrode materials. Figure 5c shows the rate performance of the electrode materials. The CW-LVP
microspheres have specific capacities of 122, 120 and 115 mA h g\(^{-1}\) at 0.5, 1, and 20 C, respectively. After charging
at the rate of 20 C, a specific discharge capacity of 110 mA h g\(^{-1}\) can be achieved even at discharging rate of 50 C,
which is 90% of the capacity at 0.5 C. When the current is reset to 1 C, a capacity of 120 mA h g\(^{-1}\) can be restored.
Results demonstrate the excellent rate capability of the electrode materials. Figure 5d shows the cycling perfor-
mance of the CW-LVP electrode at 1 C. The initial specific discharge capacity of CW-LVP is 120.5 mA h g\(^{-1}\). After
200 cycles, it retains a capacity of 110.1 mA h g\(^{-1}\), giving a capacity retention of 91.4%. The long-term cycling
stability of the electrode at 50 C is also evaluated and the result is shown in Fig. 5e. The CW-LVP cathode exhibits
a high initial discharge capacity of 105.3 mA h g\(^{-1}\) and gradually increases to 112.8 mA h g\(^{-1}\) after 500 cycles. The
continuous capacity increase in the initial cycles can be attributed to the electrode wettability by the electrolyte,
particularly at high rates\(^{35}\). After 5000 cycles, the CW-LVP electrode still retains a stable capacity of 85 mA h g\(^{-1}\),
giving a capacity retention of 80.7%. The result demonstrates the superior cycling stability of the electrode. The
electrochemical impedance spectrum (Supplementary Figure S9) simulation result shows that the charge transfer
resistance of the CW-LVP electrode is only 85.5 Ohm, which is much lower than 500 Ohm of the LVP particle
electrode without using PVP in the fabrication process. The superior rate performance and cycling stability is
much better than the previously reported electrodes (see Supplementary Table S1)\(^{14,37–40,44,46–48}\). Although the
carbon content in CW-LVP is a little high for practical application, the bicontinuous carbon in the CW-LVP is
considered to be a better conducting material than the common discontinuous acetylene black for cathode. As
shown in Supplementary Figure S10, the carbon wrapped LVP microspheres exhibit higher capacity and much
better rate capability than the LVP microspheres without carbon layer on their surface. The result demonstrates
the significant contribution of the carbon wrapping layer on the electrochemical performance improvement.
Some similar structures with lower carbon content can be achieved by changing the amount of PVP or water
in the solvothermal process. When the amounts of PVP are decreased to 1.5 and 1.0 g, the carbon content of
carbon wrapped LVP microspheres is decreased to 12.6% and 2.8%, respectively (Supplementary Figure S11a).
When the amount of distilled water in solvent is decreased to 10 mL, the carbon content of carbon wrapped LVP
microflowers is decreased to 9.45% (Supplementary Figure S11b). The excellent electrochemical performance of
the CW-LVP electrodes can be attributed to the three dimensional carbon wrapped, nanosheet-assembled hier-
archical microspheres: (1) the porous carbon shell can improve the electron transportation and provide the elec-
trolyte penetration path; (2) the nanosheet subunits can reduce the Li\(^+\) ion diffusion and electron transportation

**Figure 4.** SEM images of the LVP products prepared by adding different amount of water and removing the
PVP-based hydrogels. (a,b) 8 ml, (c,d) 10 ml, and (e,f) 12 ml (e,f), corresponding to the interior microspheres
in CW-LVP).
Conclusions

In summary, three-dimensional carbon wrapped Li$_3$V$_2$(PO$_4$)$_3$ hierarchical microspheres are successfully synthesized by the solvothermal method and subsequent annealing process. The formation of the hierarchical precursor microspheres during the solvothermal process is investigated. As a cathode material for lithium ion batteries, carbon wrapped Li$_3$V$_2$(PO$_4$)$_3$ microspheres show excellent long-term stability and rate capability. These superior electrochemical performances are attributed to the favorable carbon wrapped hierarchical structures, which ensure the fast lithium ion diffusion, high conductivity and great structural stability.
43. Sun, P. et al. Li$_3$V$_2$(PO$_4$)$_3$ encapsulated flexible free-standing nanofabric cathodes for fast charging and long life-cycle lithium-ion batteries. *Nanoscale* **8**, 7408–7415 (2016).
44. Rui, X., Yan, Q., Skyllas-Kazacos, M. & Lim, T. M. Li$_3$V$_2$(PO$_4$)$_3$ cathode materials for lithium-ion batteries: A review. *J. Power Sources* **258**, 19–38 (2014).
45. Liu, H. M. et al. Facile synthesis of NaV$_6$O$_{15}$ nanorods and its electrochemical behavior as cathode material in rechargeable lithium batteries. *J. Mater. Chem.* **19**, 7885–7891 (2009).
46. Liu, Q. et al. A simple diethylene glycol-assisted synthesis and high rate performance of Li$_3$V$_2$(PO$_4$)$_3$/C composites as cathode material for li-ion batteries. *Electrochimica Acta* **111**, 903–908 (2013).
47. Wang, L., Liu, H., Tang, Z., Ma, L. & Zhang, X. Li$_3$V$_2$(PO$_4$)$_3$/C cathode material prepared via a sol–gel method based on composite chelating reagents. *J. Power Sources* **204**, 197–199 (2012).
48. Zhang, L. et al. Li$_3$V$_2$(PO$_4$)$_3$@C/graphene composite with improved cycling performance as cathode material for lithium-ion batteries. *Electrochimica Acta* **91**, 108–113 (2013).

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Author Contributions

S.L., Q.T., A.P., W.X. and G.C. proposed the idea. S.L., A.P. and Q.T. performed the battery assembly and test. Q.T. and L.H. synthesized the materials. Y.T. and X.T. conducted characterization of materials. S.L., Q.T., A.P., W.X. and G.C. reviewed the clinical aspects and writing of manuscript. All authors read and approved the final manuscript.

Additional Information

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