1. INTRODUCTION

Currently, LiCoO$_2$ is widely used in commercial lithium-ion batteries as the cathode material, but its high cost, unsafety and toxicity prohibit it to be used in large-scale applications [1]. The increasing demand for electric vehicles promotes the development of advanced lithium-ion batteries with high safety, high energy density, long cycle life, etc. Since the demonstration of reversible electrochemical lithium insertion-extraction for LiFePO$_4$ in 1997 [2], lithium transition metal phosphates have attracted great interest as new promising cathode materials. Compared with LiCoO$_2$, the phosphates exhibit remarkable electrochemical and thermal stability.

Recently, the monoclinic lithium vanadium phosphate Li$_3$V$_2$(PO$_4$)$_3$ has been proposed as a cathode material for lithium-ion batteries [3–10]. It has the space group P21/n and crystallizes in a structure with corner-shared VO$_6$ octaheders and PO$_4$ tetraheders. At voltages higher than 3.0 V, Li is extracted from Li$_3$V$_2$(PO$_4$)$_3$ through four redox phenomena at about 3.59, 3.67, 4.06 and 4.55 V vs. Li, corresponding to a theoretical capacity of 197 mAh.g$^{-1}$. In addition, Li$_3$V$_2$(PO$_4$)$_3$ shows four reversible redox phenomena upon insertion of two Li$^+$ at 1.98, 1.88, 1.73 and 1.70 V vs. Li, corresponding to a theoretical capacity of 131 mAh.g$^{-1}$ at charge-discharge cut-off voltages of 1.5–3.0 V. In theory, five lithium ions can be reversibly inserted and extracted from the LixV$_2$(PO$_4$)$_3$ lattice, and the final products are Li$_5$V$_2$(PO$_4$)$_3$ and V$_2$(PO$_4$)$_3$, respectively. The valence of vanadium in different products can be +2, +3, +4 and +5. Therefore, over the whole range of charge-discharge voltages (1.5–4.8 V), the Li$_3$V$_2$(PO$_4$)$_3$ cathode material has the theoretical specific capacity of 328 mAh.g$^{-1}$, which is the highest energy density among the metal phosphates reported. It also possesses good Li$^+$-ion mobility, excellent stability, and satisfactory safety. These advantages suggest that Li$_3$V$_2$(PO$_4$)$_3$ can be a commercially useful positive electrode material.

As has been reported, the Li$_3$V$_2$(PO$_4$)$_3$ powders are usually prepared via conventional solid state reaction of mechanically mixed NH$_4$VO$_3$, LiOH·H$_2$O, H$_3$PO$_4$ and C$_{12}$H$_{22}$O$_{11}$ as the raw materials. The structure and morphology of the Li$_3$V$_2$(PO$_4$)$_3$ powders were characterized. The electrochemical property of the spherical Li$_3$V$_2$(PO$_4$)$_3$ cathode material was characterized by electrochemical measurements. At cut-off voltages of 3.0–4.3 V, 3.0–4.8 V and 1.5–4.8 V with current density of 0.2 mA·cm$^{-2}$, the cathode material showed initial discharge capacity of 124.7 mAh.g$^{-1}$, 157.3 mAh.g$^{-1}$, 270.2 mAh.g$^{-1}$ and capacity retention of 98.4%, 83.1% and 84.0% after 50 cycles, respectively. The charge-discharge performance tested at different current densities of 0.04 mA·cm$^{-2}$, 0.08 mA·cm$^{-2}$, 0.2 mA·cm$^{-2}$, 0.4 mA·cm$^{-2}$, 0.8 mA·cm$^{-2}$ and 2 mA·cm$^{-2}$ also showed the good rate capability.
bothermal reduction method and microwave carbothermal reduction method, using LiOH·H₂O, V₂O₅, H₃PO₄ and sucrose (C₁₂H₂₂O₁₁) as raw materials [11,12]. Monoclinic Li₃V₂(PO₄)₃ was also synthesized by a sol-gel method. Compared with a solid state reaction method, sol-gel method can mix the starting ingredients at molecular level. It has enormous advantages such as lower calcination temperature, shorter sintering time and smaller particle size of the resulting powder [13-19]. Thus, sol-gel method is a novel concept for the synthesis of an improved Li₃V₂(PO₄)₃.

In this work, we synthesized spherical Li₃V₂(PO₄)₃ powders via quenching of molten V₂O₅ followed by spray drying and carbothermal reduction processes, using NH₄VO₃, LiOH·H₂O, H₃PO₄ and C₁₂H₂₂O₁₁ as the raw materials. The structure, morphology, and electrochemical performance of the spherical Li₃V₂(PO₄)₃ cathode material have been investigated in detail.

2. EXPERIMENTAL

First, we used the melt quenching method to prepare V₂O₅ sol. NH₄VO₃ was heated in air atmosphere at 800°C for 2 h. At high temperature, the NH₄VO₃ was decomposed into V₂O₅ and V₂O₅ was melted to obtain liquid V₂O₅. The liquid V₂O₅ was then quenched into deionized water. The mixture was stirred at room temperature for 4 h to obtain V₂O₅ sol. After carefully analyzing the concentration of V₂O₅ in the sol, we added analytically pure LiOH·H₂O, H₃PO₄ and sucrose (C₁₂H₂₂O₁₁) into the sol in a molar ratio of LiOH·H₂O:V₂O₅:H₃PO₄:C₁₂H₂₂O₁₁ = 3:1:3:0.2 and stirred again for 2 h, resulting in the homogeneously mixed sol. The spherical precursor powders containing LiOH·H₂O, V₂O₅, H₃PO₄ and C₁₂H₂₂O₁₁ were obtained from the mixed sol via a spray drying method. The spherical Li₃V₂(PO₄)₃ powders were synthesized by sintering the precursor powders at 800°C for 16 h in a nitrogen atmosphere. During the sintering process, the sucrose in the precursor would pyrolyse at high temperature and produce reductive atmosphere. The V⁵⁺ in the precursor would be reduced to V⁴⁺ and Li₃V₂(PO₄)₃ was obtained. The residual pyrolytic carbon (as electronic conducting agent) mixed within the Li₃V₂(PO₄)₃ particles to form the composite Li₃V₂(PO₄)₃/C. During the sintering, the reactions may be very complex. We assume the carbothermal reaction can be approximately written as the formula below.

\[
3\text{LiOH·H}_2\text{O} + \text{V}_2\text{O}_5 + 3\text{H}_3\text{PO}_4 + 0.2\text{C}_{12}\text{H}_{22}\text{O}_{11} = \text{Li}_3\text{V}_2(\text{PO}_4)_3 + \text{CO}_2 + 11.2\text{H}_2\text{O} + 1.4\text{C}
\]

According to the formula, the obtained composite will be Li₃V₂(PO₄)₃/1.4 C. The calculated residual carbon content is about 4 wt%.

Powder X-ray diffraction (XRD, D/max-rB) with CuKα radiation was used to identify the crystalline phase and crystal lattice parameters of the powders. The particle morphology, particle size and particle size distribution of the powders were observed using a scanning electron microscopy (SEM, JSM6301F). We also tested the actual carbon content of the Li₃V₂(PO₄)₃/C powders by dissolving the Li₃V₂(PO₄)₃/C in diluted HNO₃, filtering, drying and weighing the mass of the residual carbon.

Experimental test cells for electrochemical measurement used the cathode with the composition 80 wt% Li₃V₂(PO₄)₃/C, 10 wt% carbon black, and 10 wt% PTFE. The separator was a Celguard 2400 microporous polypropylene membrane. The electrolyte was 1M LiPF₆ EC+DEC (1:1 by vol.). A lithium metal anode was used in this study. The cells were assembled in a glove box filled with argon gas. The charge-discharge cycling was galvanostatically performed at 20 ºC and a current density of 0.04 mA·cm⁻², 0.08 mA·cm⁻², 0.2 mA·cm⁻², 0.4 mA·cm⁻², 0.8 mA·cm⁻² and 2 mA·cm⁻² with cut-off voltages of 3.0–4.3 V, 3.0–4.8 V and 1.5–4.8 V (vs Li/Li⁺).

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the spherical precursor and Li₃V₂(PO₄)₃/C powders. In the XRD pattern of the precursor powders, we can observe some weak diffraction peaks ascribing to V₂O₅. The strong and sharp peaks on the Li₃V₂(PO₄)₃/C powders’ XRD spectra indicate the product was well crystallized. The peaks can be indexed to the monoclinic structure (space group P2₁/n). There is no evidence of impurities’ peaks indicates the product is almost phase pure.
Preparation and Characterization of Spherical Li$_3$V$_2$(PO$_4$)$_3$/C Cathode Material for Lithium-ion Batteries

Fig. 2 shows the morphology of the precursor and Li$_3$V$_2$(PO$_4$)$_3$/C powders. The powders are both composed of well-dispersed spherical particles. The precursor powders have the particle size distribution of about 1–10 μm. The surface of the spherical precursor particle is smooth and the crystalline grains almost can not be observed.

Fig. 2(c) shows after being sintered at 800 ºC, the obtained Li$_3$V$_2$(PO$_4$)$_3$/C powders are still spherical but shrank obviously, compared to the precursor. The particle size distribution of Li$_3$V$_2$(PO$_4$)$_3$/C is about 1–6 μm and mostly is around 2 μm. Each of the spherical particles is made up of a large number of sub-micrometer crystalline grains, as shown in Fig. 2(d). It is tested that the tap-density of the spherical Li$_3$V$_2$(PO$_4$)$_3$/C powders is as high as 1.1 g·cm$^{-3}$, which is higher than that of the irregular Li$_3$V$_2$(PO$_4$)$_3$/C powders we prepared before (usually lower than 1.0 g·cm$^{-3}$). As has been pointed out [20–25], electrode materials composed of spherical particles with appropriate particle size and particle size distribution are expected to have higher tap-density, higher energy density and better manufacturing performance, we believe the spherical Li$_3$V$_2$(PO$_4$)$_3$ should be one of the important directions of this material. By optimizing the melt quenching – spray drying – carbothermal reduction process, the powders’ tap-density can be further improved. We will report the results elsewhere.

The actual carbon content of the Li$_3$V$_2$(PO$_4$)$_3$/C powders is about 5 wt%, determined by the method described above. The experimental carbon content (5 wt%) is close to the calculated data (4 wt%), indicating the assumed carbothermal reduction equation mentioned in the experimental part is roughly correct.

Fig. 3 shows the initial charge-discharge curves of the Li$_3$V$_2$(PO$_4$)$_3$/C at current density of 0.2 mA·cm$^{-2}$ with cut-off voltages of 3.0–4.3 V. Both curves show three obvious charge-discharge voltage plateaus at around 3.6 V, 3.7 V and 4.1 V. According to Ref. [5], all plateaus correspond to lithium extraction and insertion associated with the V$^{3+}$/V$^{4+}$ redox couple as the first two lithiums of Li$_3$V$_2$(PO$_4$)$_3$ are extracted during charging. The small voltage difference between the charge and discharge plateaus in Fig. 3 shows its good kinetics. The small hysteresis implies high reversibility and a low overvoltage, which confirms the potential suitability of the Li$_3$V$_2$(PO$_4$)$_3$ as an active material for lithium-ion batteries. The cathode material has a first cycle charge capacity of 130.7 mAh/g followed by a discharge capacity of 124.7 mAh/g, giving the rather high initial charge-discharge efficiency of 95.4%. Fig. 4 shows the cycling performance of the Li$_3$V$_2$(PO$_4$)$_3$/C at 0.2 mA·cm$^{-2}$. After 50 cycles, the reversible discharge capacity is 122.7 mAh.g$^{-1}$, showing the retention of 98.4% of the capacity. Fig. 5 shows the initial charge-discharge curves of the Li$_3$V$_2$(PO$_4$)$_3$/C at current density of 0.2 mA·cm$^{-2}$ with cut-off voltages of 3.0–4.3 V at different currents. At currents density of 0.04 mA·cm$^{-2}$, 0.08 mA·cm$^{-2}$, 0.2 mA·cm$^{-2}$, 0.4 mA·cm$^{-2}$, 0.8 mA·cm$^{-2}$ and 2 mA·cm$^{-2}$, the cathode materials have the initial discharge capacity of 127.9 mAh.g$^{-1}$, 126.6 mAh.g$^{-1}$, 124.7 mAh.g$^{-1}$, 122.0 mAh.g$^{-1}$, 118.4 mAh.g$^{-2}$ and 117.4 mAh.g$^{-2}$, respectively. The excellent cycling performance and rate capability of the Li$_3$V$_2$(PO$_4$)$_3$/C cathode material show the material is promising for use in power lithium-ion batteries.

Fig. 6 shows the initial charge-discharge curves of the Li$_3$V$_2$(PO$_4$)$_3$/C at current density of 0.2 mA·cm$^{-2}$ at cut-off voltages of 3.0–4.8 V. On the charge curve, there are four obvious voltage plateaus around 3.6 V, 3.7 V, 4.1 V and 4.6 V. According to Ref. [5], the plateaus around 3.6 V, 3.7 V and 4.1 V correspond to...
to the extraction of the first two lithium ions (the first lithium ion was extracted in two steps). These plateaus are associated with the V$^{3+}$/V$^{4+}$ redox couple. The plateau around 4.6 V corresponds to the extraction of the third lithium ion. It is associated with the V$^{4+}$/V$^{5+}$ redox couple. The cathode material has a first cycle charge capacity of 174.8 mAh/g followed by a discharge capacity of 157.3 mAh/g, and the rather high initial charge-discharge efficiency of 90.0%. Fig. 4 shows the cycling performance of the Li$_3$V$_2$(PO$_4$)$_3$/C at 0.2 mA·cm$^{-2}$. After 50 cycles, the reversible discharge capacity is 130.7 mAh.g$^{-1}$, showing the retention of 83.1% of the capacity. Fig. 7 shows the initial discharge curves of the Li$_3$V$_2$(PO$_4$)$_3$/C at 0.2 mA·cm$^{-2}$. After 50 cycles, the reversible discharge capacity is 130.7 mAh.g$^{-1}$, showing the retention of 83.1% of the capacity. Fig. 7 shows the initial discharge curves of the Li$_3$V$_2$(PO$_4$)$_3$/C at 0.2 mA·cm$^{-2}$. At currents density of 0.04 mA·cm$^{-2}$, 0.08 mA·cm$^{-2}$, 0.2 mA·cm$^{-2}$, 0.4 mA·cm$^{-2}$, 0.8 mA·cm$^{-2}$, and 2 mA·cm$^{-2}$, the cathode materials have the initial discharge capacity of 164.5 mAh.g$^{-1}$, 160.6 mAh.g$^{-1}$, 157.3 mAh.g$^{-1}$, 155.3 mAh.g$^{-1}$, 151.5 mAh.g$^{-1}$, and 129.4 mAh.g$^{-1}$, respectively, indicating an excellent rate capability.

Fig. 8 shows the second charge-discharge curves of the Li$_3$V$_2$(PO$_4$)$_3$/C at current density of 0.2 mA·cm$^{-2}$ with cut-off voltages of 1.5–4.8 V. The cathode material has a second-cycle charge capacity of 272.3 mAh.g$^{-1}$ followed by a discharge capacity of 270.2 mAh.g$^{-1}$. Fig. 4 shows the cycling performance of the Li$_3$V$_2$(PO$_4$)$_3$/C at 0.2 mA·cm$^{-2}$. After 50 cycles, the reversible discharge capacity is 226.9 mAh.g$^{-1}$, showing a retention of 84.0% of the capacity. Fig. 9 shows the initial discharge curves of the Li$_3$V$_2$(PO$_4$)$_3$/C with cut-off voltages of 1.5–4.8 V at different currents. At currents density of 0.04 mA·cm$^{-2}$, 0.08 mA·cm$^{-2}$, 0.2 mA·cm$^{-2}$, 0.4 mA·cm$^{-2}$, 0.8 mA·cm$^{-2}$, and 2 mA·cm$^{-2}$, the cathode material has the initial discharge capacity of 284.9 mAh.g$^{-1}$, 277.6 mAh.g$^{-1}$, 254.9 mAh.g$^{-1}$, 218.7 mAh.g$^{-1}$, 204.2 mAh.g$^{-1}$, and 191.3 mAh.g$^{-1}$, respectively.

A lot of research work can be done to further improve the electrochemical performance of Li$_3$V$_2$(PO$_4$)$_3$ cathode materials. For example, the substitution of intercalated cations (Li$^+$), metal cations (V$^{3+}$), and anion units (PO$_4^{3-}$) are possible to solve the problem of overvoltage and hysteresis of Li$_3$V$_2$(PO$_4$)$_3$ at high voltage or to
smooth the charge-discharge curves. On the other hand, the tap-density of Li$_3$V$_2$(PO$_4$)$_3$/C cathode materials should also be improved.

4. CONCLUSION

Well-crystallized, phase-pure monoclinic lithium vanadium phosphate Li$_3$V$_2$(PO$_4$)$_3$/C powders composed of spherical particles have been synthesized via quenching of molten V$_2$O$_5$ followed by spray drying and carbothermal reduction processes, using NH$_4$VO$_3$, LiOH·H$_2$O, H$_3$PO$_4$ and C$_{12}$H$_{22}$O$_{11}$ as the raw materials. This polyanion-type cathode material has excellent electrochemical performance, including broad voltage range, high specific capacity, excellent cycling performance and satisfactory rate capability. Combined with the inherent advantages of phosphates, such as excellent stability and satisfactory safety, the Li$_3$V$_2$(PO$_4$)$_3$ cathode materials are viable candidates for high energy-density and power-demanding lithium-ion batteries.

The new preparation method proposed in this work is suitable to synthesize spherical Li$_3$V$_2$(PO$_4$)$_3$/C powders. We expect the new process can be optimized to further improve the cathode material’s tap-density and energy-density. Further studies in this field are very promising and significant.

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