

低温固相反应合成 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 正极材料及其性能

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摘要: 利用 $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ 湿凝胶, $\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ 和 C 等作原料, 通过低温固相还原反应在 550 °C 焙烧 12 h 制备出 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 正极材料。采用 XRD, SEM 和电化学测试对 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 样品性能进行研究。XRD 研究表明本法所合成的 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 同传统的高温固相反应法所合成的 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ 一样同属于单斜晶系结构。SEM 测试表明所合成的样品平均粒径大小约为 0.5 μm 且粒径分布较窄。电化学测试表明以 0.2 C 的倍率放电时, 样品的首次放电容量为 130 $\text{mAh} \cdot \text{g}^{-1}$, 室温下循环 30 次后其比容量为 124 $\text{mAh} \cdot \text{g}^{-1}$ 。

关键词: 锂离子电池; 正极材料; $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; 低温固相还原反应; 循环伏安法

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Cathode Material $\text{Li}_3\text{V}_2(\text{PO}_4)_3$: Low Temperature Solid-state Reaction Synthesis and Performance

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Abstract: $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material was prepared by low temperature solid-state reaction. $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydrogel, $\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and C were used as starting materials to prepare the precursor, and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was obtained by sintering the precursor at 550 °C for 12 h. The property of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical measurement. XRD studies show that the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample obtained has the same monoclinic structure as that synthesized by conventional solid-state reaction. SEM image exhibits that the particle size is about 0.5 μm with narrow size distribution. Electrochemical test shows that the initial discharge capacity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powder is 130 $\text{mAh} \cdot \text{g}^{-1}$ at the rate of 0.2 C, and the capacity retains 124 $\text{mAh} \cdot \text{g}^{-1}$ after 30 cycles at room temperature.

Key words: lithium ion batteries; cathode material; $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; low temperature solid-state reaction; cyclic voltammetry (CV)

Currently, LiCoO_2 is the most widely used cathode materials for lithium-ion batteries. However it is relatively expensive, especially for large-scale applications such as backup power systems and hybrid

electric vehicles. Many people are working on a cheap and effective replacement for LiCoO_2 ^[1~7]. Since the demonstration of reversible electrochemical lithium insertion-extraction for LiFePO_4 in 1997^[8], lithium

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transition metal phosphates have attracted much interest as promising new cathode materials for lithium-ion batteries^[9-13]. Recently, it has been shown that Li could be extracted from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with a theoretical capacity of $197 \text{ mAh} \cdot \text{g}^{-1}$ ^[14]. Considering the very good stability of this material and the voltage range of operation, the compound could make commercially useful as a positive electrode material. Usually, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is synthesized by a conventional solid-state reaction^[15], involved with high sintering temperature and long sintering time, and it is difficult to obtain small and homogenous $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles, which is crucial to its electrochemical performance, especially the cyclic stability. In this work, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was synthesized by low temperature solid-state reaction, and its electrochemical performance was evaluated.

1 Experimental

$\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gel was prepared as follows: 250 mL of 10% (V/V) H_2O_2 solution was slowly added to 0.06 mol V_2O_5 and was vigorously stirred at room temperature for 6 h. The dark red homogenous $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gel was obtained after aging for 4 days. Stoichiometric $\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and 25wt% excess C were added to the above $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gel. The mixture was strongly stirred for 8 h at room temperature, dried under vacuum at 80°C , and finally ground to obtain the precursor. The precursor was calcined at 300°C for 4 h, then heated to 550°C for 12 h under an inert atmosphere. The subsequent thermal treatment in this work is lower than the conventional solid-state reaction method, which is usually at $800\sim 900^\circ\text{C}$ for 16~36 h^[10,16].

The powder X-ray diffraction (XRD, Rint-2000, Rigaku) measurement using $\text{Cu K}\alpha$ radiation ($\lambda=0.15406 \text{ nm}$, 40 kV) was employed to identify the crystalline phase of the synthesized materials. The lattice parameters were calculated by the least square method using the internal Si reference. The particle size and morphology of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders were observed by scanning electron microscope (JEOL, JSM-5600LV) with an accelerating voltage of 20 kV.

Charge/discharge tests were performed using

CR2025 coin-type cell. For positive electrode fabrication, the prepared powder was mixed with 10wt% of carbon black and 10wt% of polyvinylidene fluoride in N-methyl pyrrolidinone until slurry being obtained. And then, the blended slurry was pasted onto an aluminum current collector, and the electrode was dried at 120°C for 10 h in vacuum. The test cell was consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, and $1 \text{ mol} \cdot \text{L}^{-1} \text{ LiPF}_6$ in $\text{EC}:\text{EMC}:\text{DMC}=1:1:1$ (in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged over a voltage range of 3.0 V to 4.2 V vs Li/Li^+ electrode at room temperature. Cyclic voltammogram was tested at a scanning rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$ in the voltage range of 3.0~4.4 V.

2 Results and discussion

Fig.1 shows the XRD pattern collected for the prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powder. It is evident that all fundamental peaks can be indexed to the monoclinic structure (space group $P2_1/n$). The following crystallographic parameters, $a=0.8534 \text{ nm}$, $b=1.2026 \text{ nm}$, $c=0.8571 \text{ nm}$, $\beta=89.518^\circ$, and cell volume= 0.8796 nm^3 is in good accordance with the literature report^[16].

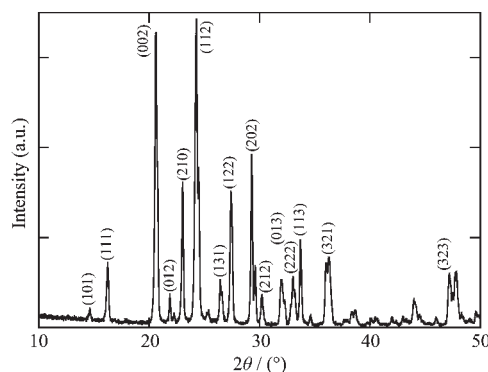
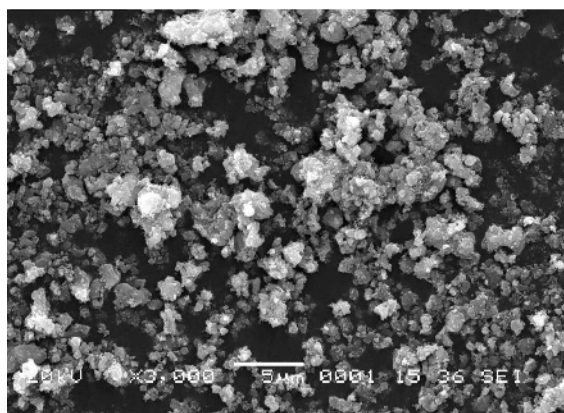
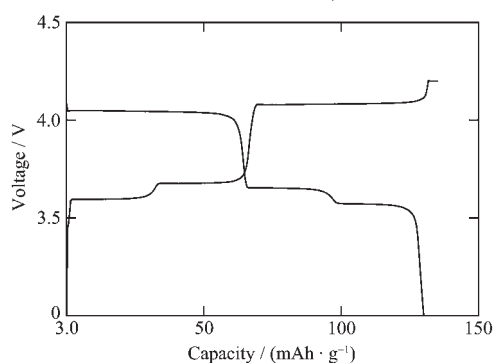


Fig.1 XRD pattern of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

The morphology of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample was examined by SEM, and is shown in Fig.2. Fine particles are observed, and the particle size is about $0.5 \mu\text{m}$ with narrow size distribution. The first charge-discharge curves of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cycled between 3.0 V and 4.2 V at the rate of 0.2 C are shown in Fig.3. Three reversible plateaus are clearly seen in the charge and discharge curves, corresponding to two Li^+

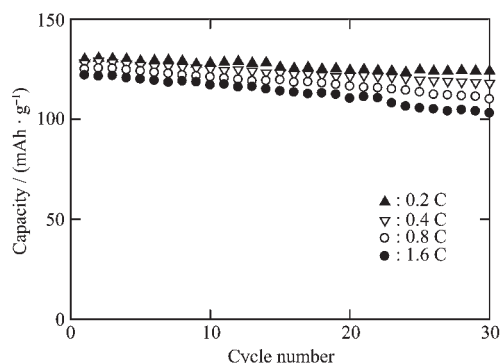
Fig.2 SEM image of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

reversibly extracted and intercalated in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The first lithium ion is extracted in two steps, i.e. at 3.60 V and 3.68 V plateaus versus Li/Li^+ , with a charge capacity of $30 \text{ mAh} \cdot \text{g}^{-1}$ and $37 \text{ mAh} \cdot \text{g}^{-1}$, respectively. The second lithium ion, however, is extracted in a single step, at 4.08 V plateau versus Li/Li^+ , with a charge capacity of $68 \text{ mAh} \cdot \text{g}^{-1}$. Therefore, the charge capacity can total up to $135 \text{ mAh} \cdot \text{g}^{-1}$. A reversible reaction upon re-insertion of two Li^+ in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was observed in the discharge process. The discharge curve is also composed of three plateaus with slight potential shift to 4.04, 3.62 and 3.58 V vs Li/Li^+ , delivering a total capacity of $130 \text{ mAh} \cdot \text{g}^{-1}$. Namely, the initial charge/discharge cycle of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample exhibits a high coulombic efficiency and a high electrode reaction reversibility.

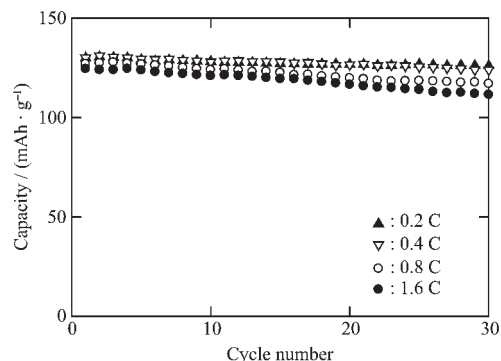
Fig.3 First charge-discharge curves of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at the rate of 0.2 C

The electrochemical cycling performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ compound was evaluated in the $\text{Li}/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cell configuration in the voltage range of 3.0~4.2 V at room temperature. Fig.4 shows the cyclic charge/discharge profiles for the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials at

different rate. As seen in Fig.4, after 30 cycles, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample exhibits a discharge capacity about $124 \text{ mAh} \cdot \text{g}^{-1}$, $118 \text{ mAh} \cdot \text{g}^{-1}$, $110 \text{ mAh} \cdot \text{g}^{-1}$ and $103 \text{ mAh} \cdot \text{g}^{-1}$ at the rate of 0.2 C, 0.4 C, 0.8 C and 1.6 C respectively. Namely, the capacity decreases continuously at a rate of 0.15% per cycle at 0.2 C, 0.26% per cycle at 0.4 C, 0.40% per cycle at 0.8 C, and 0.49% per cycle at 1.6 C. From above results, it can be concluded that the as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample has better cycling performance than those synthesized by conventional solid-state reaction reported by the literature^[16].

Fig.4 Electrochemical cycling performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at room temperature

The electrochemical cycling performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ compound was also tested at 55 °C in the voltage range of 3.0~4.2 V at different rate. As seen in Fig.5, after 30 cycles, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample exhibits a discharge capacity about $126 \text{ mAh} \cdot \text{g}^{-1}$, $124 \text{ mAh} \cdot \text{g}^{-1}$, $117 \text{ mAh} \cdot \text{g}^{-1}$ and $111 \text{ mAh} \cdot \text{g}^{-1}$ at the rate of 0.2 C, 0.4 C, 0.8 C and 1.6 C, respectively. Namely, the capacity decreases continuously at a rate of 0.10% per cycle at 0.2 C, 0.15% per cycle at 0.4 C, 0.26%

Fig.5 Electrochemical cycling performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at 55 °C

per cycle at 0.8 C, and 0.34% per cycle at 1.6 C. Obviously, the electrochemical cycling performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ tested at 55 °C is improved. The improved cycleability may be attributed to the increased diffusion of lithium ions at the elevated temperatures.

The cyclic voltammetry (CV) for the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ electrode in the first cycle at a scanning rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$ is shown in Fig.6. The cyclic voltammetry profile indicates the oxidation/reduction potential at which lithium ion is extracted from or inserted into the lattice. As shown in Fig.6, the electrode of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ exhibit three reversible redox peaks, which is in well agreement with the first charge-discharge results.

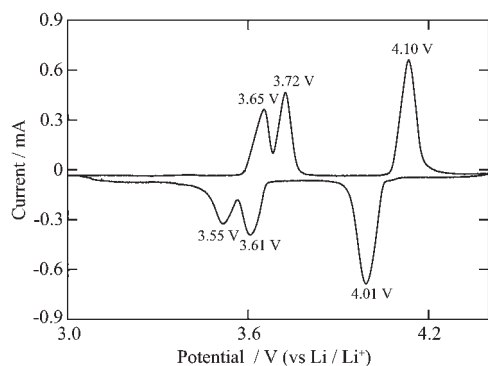


Fig.6 CV of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ electrode in the first cycle

3 Conclusions

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powder was prepared by low temperature solid-state reaction under an inert atmosphere. XRD patterns show that $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has monoclinic structure; SEM images show that the particle size is about $0.5 \mu\text{m}$ with narrow size distribution. An initial charge and discharge capacity is about $135 \text{ mAh} \cdot \text{g}^{-1}$ and $130 \text{ mAh} \cdot \text{g}^{-1}$, respectively. The discharge capaci-

ty retains $124 \text{ mAh} \cdot \text{g}^{-1}$ after 30 cycles at room temperature.

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