一种新的流变相法制备锂离子电池纳米-LiVOPO₄ 正极材料

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摘要：   采用新型流变相法制备锂离子电池正极材料纳米-LiVOPO₄. 采用 X 射线衍射、扫描电子显微镜以及电化学测试等手段对 LiVOPO₄ 的微观结构、表面形貌和电化学性能进行了表征. 结果表明, 采用流变相法制备的 LiVOPO₄ 由粒径大约在 10−60 nm 的小颗粒组成. 首次放电容量, 首次充电容量以及库仑效率分别为 135.7 mAh·g⁻¹, 145.8 mAh·g⁻¹ 和 93.0%. 0.1C (1C=160 mA·g⁻¹)放电时, 60 次循环后, 放电容量保持在 134.2 mAh·g⁻¹, 为首次放电容量的 98.9%, 平均每次循环的容量损失仅为 0.018%. 而 1.0C 和 2.0C 放电时的放电容量达到 0.1C 放电容量的 96.5% 和 91.6%. 随着放电次数的增加, 电荷转移阻抗增加, 而锂离子在电极中的扩散系数达到 10⁻¹¹ cm²·s⁻¹ 数量级. 实验结果显示采用流变相法制备的 LiVOPO₄ 是一种容量高、循环性能好、倍率性能好的锂离子电池正极材料.

关键词：   锂离子电池；   流变相法；   LiVOPO₄；   倍率性能；   扩散系数
中图分类号：   O646

A New Rheological Phase Route to Synthesize Nano-LiVOPO₄ Cathode Material for Lithium Ion Batteries

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Abstract：   A novel lithium-ion battery cathode material, nano-LiVOPO₄, was synthesized by a new rheological phase method. The microstructure, surface morphology, and electrochemical properties were characterized by various electrochemical methods in combination with X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results show that the orthorhombic LiVOPO₄, obtained by this rheological phase method, is made up of 10−60 nm particles. The first discharge capacity, charge capacity, and columbic efficiency of LiVOPO₄ were found to be 135.7 mAh·g⁻¹, 145.8 mAh·g⁻¹, and 93.0%, respectively. After 60 cycles, the discharge capacity remained 134.2 mAh·g⁻¹, at 98.9% of the first discharge capacity, and the capacity loss per cycle was only 0.018% at 0.1C (1C=160 mA·g⁻¹). More than 96.5% and 91.6% of the discharge capacity at 0.1C were maintained at 1.0C and 2.0C, respectively. The charge transfer resistance increased with the increase of the cycle number and the diffusion coefficient of lithium ion in the nano-LiVOPO₄ was in the order of 10⁻¹¹ cm²·s⁻¹. Experimental results suggest that the rheological phase method is a good route for the synthesis of LiVOPO₄ cathode material of high capacity, good cycling performance, and good current rate capability for lithium ion batteries.

Key Words：   Lithium ion battery；   Rheological phase method；   LiVOPO₄；   Current rate capability；   Diffusion coefficient

Recently, performance of mobile electronic devices, such as mobile phone or laptop computer, is drastically improving and so, the demands for battery become more severe. Due to its large power density and cycle stability, lithium ion battery is now widely used for the electric source of mobile equipment. The current most important requirement for lithium ion rechargeable battery is to decrease cost and increase the power density. In the current battery, $LiCoO_2$ and graphitic carbon are commonly used for cathode and anode, respectively. However, natural abundance of Co is limited and this element is expensive. Therefore, development of cathode material without containing Co is strongly required. At present, great attentions are paid for transition metal phosphates, such as $LiMPO_4$ (M=Fe, Mn, Co)[1−4], $Li_3V_2(PO_4)_3$[5−10], and $LiVPO_4F$[11−12], as a new class of cathode materials for lithium ion batteries. These materials contain both mobile lithium ions and redox-active transition metals within a rigid phosphate network, and display remarkable electrochemical, and thermal stabilities as well as comparable energy density. Among these materials, $LiFePO_4$ is of great interest for the replacement of $LiCoO_2$ in Li ion batteries due to its low cost, nontoxicity and good electrochemical properties since 1997[1,13−17]. However, compared with $LiFePO_4$, $LiVOPO_4$ has an advantage of higher potential (4.0 and 3.7 V (*versus* Li/Li^+)) for charge and discharge, and this phosphate is highly interesting from the viewpoint of the alternative cathode[18−21]. Kerr *et al.*[22] presented that the triclinic phase $LiVOPO_4$ synthesized from ε-$VOPO_4$ showed the capacity of 100 mAh·g^{-1} up to 100 cycles at C/10 of current rate. Azmi *et al.*[19,23] reported that orthorhombic phase of $LiVOPO_4$ could be synthesized by impregnation method and exhibited fairly good cycle stability for Li de-intercalation and intercalation.

For all functional materials, their properties were greatly influenced by the synthesis methods. Many preparation methods have been investigated with an aim to achieve high capacity $LiVOPO_4$, however, the capacity of the products ever reported is usually unsatisfactory in particular when discharged at a high current rate. To meet high power demands of lithium ion batteries in new applications, the rate capability of $LiVOPO_4$ has to be sig-nificantly improved. There are two main frequently employed strategies: one is to increase the intrinsic electronic conductivity by microstructure controlling, the other is to enhance lithium ion transport by reducing the bulk diffusion length, which can be achieved by utilization of nanostructured materials.

The rheological phase method is the process of preparing compounds or materials from a solid-liquid rheological mixture. That is, the solid reactants are fully mixed in a proper molar ratio, and made up by a proper amount of water or other solvents to form a Bingham body in which the solid particles and liquid substance are uniformly distributed, so that the product can be obtained under suitable experiment conditions[24]. Because of its low temperature, short calcination time, and products with small particle with uniform distribution, rheological method has been used to synthesize cathode and anode materials for lithium ion batteries[25−26]. In the present study, rheological technique is used to synthesize nano-$LiVOPO_4$. The microstructure and electrochemical properties of $LiVOPO_4$ as cathode material for lithium ion batteries were studied.

1 Experimental

Analytical grade powders of $LiOH\cdot2H_2O$ (AR), NH_4VO_3 (AR), $(NH_4)_2HPO_4$ (AR) and citric acid (AR) with equal amount of substance were mixed uniformly to get a mixture. Then 1.5 mL distilled water per gram mixture was added to the mixture under magnetic force stirring to obtain a mash. The mash was dried in vacuum at 80 ℃ for 4 h to form the precursor. The precursor was calcined in Ar atmosphere at 650 ℃ for 6 h to obtain blue $LiVOPO_4$ powders.

Phase identification and surface morphology studies of the samples were carried out by an X-ray diffractometer (XRD; D/MAX-gA, Rigaku Corporation, Japan) with Cu K_α radiation and scanning electron microscope (SEM; JSM 5600LV, JEOL Ltd., Japan, accelerating voltage of 20 kV). Elemental analyses for lithium, vanadium, and phosphorus were determined by atomic absorption spectroscopy (AAS; SP-3530AA) and inductively coupled plasma-atomic emission spectrometer (ICP; TY9900).

A slurry containing 80% (mass fraction, similarly hereinafter) $LiVOPO_4$, 10% acetylene black, and 10% PVDF (polyvinylidene fluoride) was made using *N*-methylprrolidinone (NMP) as the solvent. The electrodes with an area of 1 cm^2 were prepared by coating the slurry (about 100 μm in thickness) on aluminum foils followed by drying in vacuum at 60 ℃ for 12 h. Electrochemical tests were performed using a conventional cointype cell, employing lithium foil as a counter electrode and 1.0 mol·L^{-1} $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) (with EC and DMC volume ratio of 1:1) as the electrolyte. The assembly was carried out in an Ar-filled glove box. The electrochemical tests were carried out with an electrochemical work station (CHI660B, CHI Instruments Inc., Shanghai, China).

2 Results and discussion

Fig.1 shows the XRD pattern of $LiVOPO_4$ derived from rheological phase method. As shown in Fig.1(a), All the reflections from the $LiVOPO_4$ could be indexed reliably using a standard structural refinement program. XRD peaks in Fig.1 agree well with those of the standard JCPDS card No.72-2253. The $LiVOPO_4$ compound possesses an orthorhombic symmetry, space group *Pnma*, characterized by the unit cell parameters a=0.7446(4) nm, b=0.6278(4) nm, and c=0.7165(4) nm. Except for peaks corresponding to $LiVOPO_4$, no other peaks can be found, suggesting that the rheologically synthsized $LiVOPO_4$ is very pure. The $LiVOPO_4$ framework structure is closely related to that found in $VOPO_4$ and comprises infinite chains of corner-shared VO_6 octahedra, cross-linked by corner-sharing PO_4 tetrahedron[27−28]. The cell parameters for the rheologically prepared material compare favorably with literature values reported by Lii *et al.*[28] for a
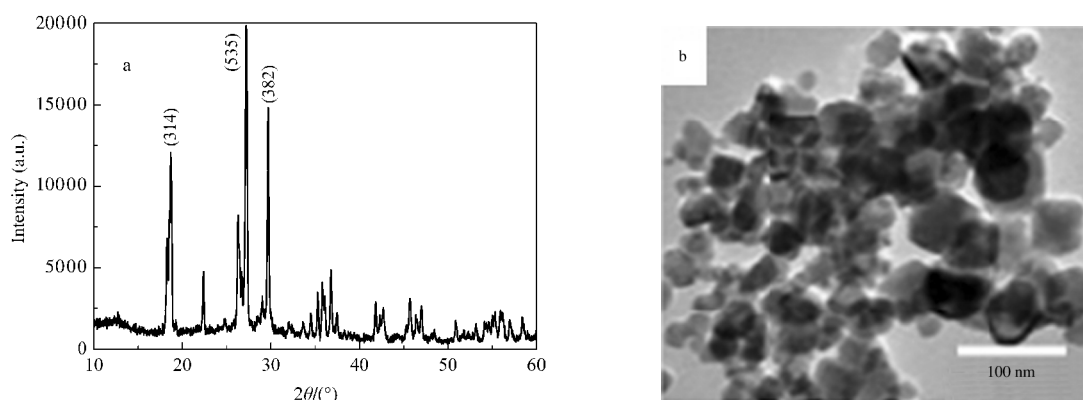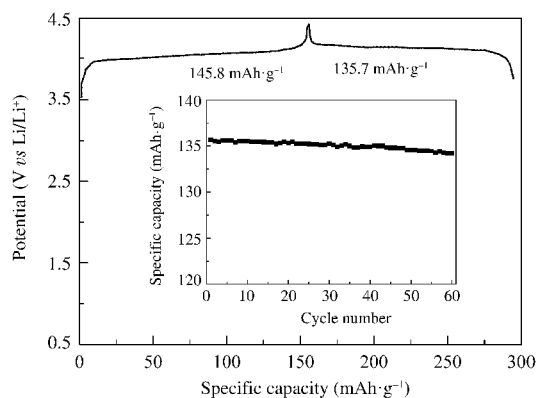
Fig.1   XRD pattern (a) and SEM image (b) of LiVOPO₄

hydrothermally prepared sample, i.e., a=0.7446(3) nm, b=0.6292(2) nm, and c=0.7177(2) nm. Elemental analysis results confirmed the expected stoichiometry of LiVOPO₄.

As seen from Fig.1(b), the scanning electron microscopy (SEM) examination indicated that the rheologically synthsized LiVOPO₄ consists of particles with average primary size in the range of 10−60 nm, which agrees well with the average crystal size of around 35 nm calculated from the XRD profile. They also showed the presence of considerable material agglomeration. The agglomerates averaged around 50 nm in size.

The lithium extraction/insertion behavior for the LiVOPO₄ active material relies on the reversibility of the V^{4+}/V^{5+} redox couple:

$$LiVOPO_4 \Leftrightarrow VOPO_4 + Li^+ + e^-$$

Fig.2 shows the initial charge-discharge curve of the rheologically synthesized LiVOPO₄ material. These data were collected at 25 ℃ at an approximate $0.1C$ (16 mA·g⁻¹) rate using voltage limits of 3.0 and 4.3 V (vs Li/Li⁺). As shown in Fig.2, at low current density, orthorhombic LiVOPO₄ prepared by rheological phase method is highly attractive as the alternative cathode for lithium ion rechargeable battery. This is because LiVOPO₄ exhibits high discharge potential of 3.85 V and reasonably large capacity. The initial oxidation process equates to a material spe-
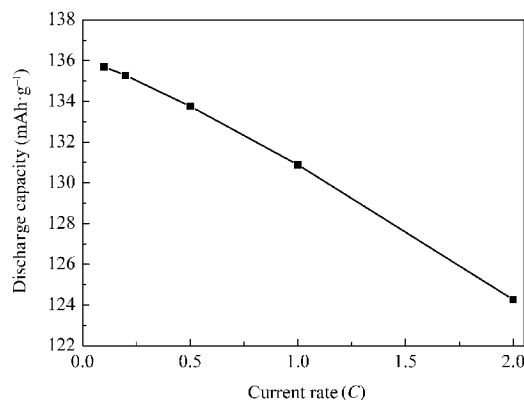
cific capacity of 145.8 mAh·g⁻¹ during this lithium extraction. Based on a theoretical specific capacity for LiVOPO₄ of 166 mAh·g⁻¹[20] and assuming no side reactions, the fully charged material corresponds to Li₀.₁₂VOPO₄. Excursions to higher oxidation potentials (ultimately up to 5.0 V (vs Li/Li⁺)) resulted in the increased irreversibility as well as active material degradation evidenced by electrolyte discoloration. The reinsertion process amounts to 135.7 mAh·g⁻¹, indicating a higher first-cycle charge reversibility of 93% than the literature value (85%) reported by Barker et $al.$[29].

The cycling performance was tested at $0.1C$ (16 mA·g⁻¹) in the range of 3.0−4.3 V as shown in the insert figure in Fig.2. After cycling 60 times, the discharge capacity of LiVOPO₄ is sustained at 134.2 mAh·g⁻¹, which is 98.9% of the initial capacity, and the capacity loss per cycle is only 0.018%, suggesting LiVOPO₄ derived by rheological phase method is promising as alternative cathode material for lithium ion batteries with high capacity and good cycling performance.

Fig.3 shows the discharge capacity of LiVOPO₄ as a function of current rate. As shown in Fig.3, discharge capacity of LiVOPO₄ drastically decreased with increasing current rate due to the increase of the polarization of electrode. The discharge capacity of LiVOPO₄ at $0.1C$ (16 mA·g⁻¹), $1.0C$ (160 mA·g⁻¹),

Fig.2   Electrochemical performance data for a typical Li/ LiVOPO₄ cell cycled between 3.0 and 4.3 V at approximate $0.1C$ (16 mA·g⁻¹) rate for charge and discharge

The inset figure in Fig.2 is the cycling performance curve.

Fig.3   Discharge capacity of LiVOPO₄ as a function of current rate

potential window: 3.0−4.3 V (vs Li/Li⁺); $1C$=160 mA·g⁻¹

and 2.0C (320 mA·g^{-1}) is 135.7, 130.9, and 124.3 mAh·g^{-1}, respectively. More than 96.5% and 91.6% of the discharge capacity at 0.1C are sustained at 1.0C and 2.0C, respectively. This result is better than that of the LiVOPO$_4$ reported by Azmi *et al.*[19], indicating good current rate capability of LiVOPO$_4$ synthesized by rheological phase method. The good current rate capability may result mainly from the small particle size and large surface area of LiVOPO$_4$ nanoparticles. The smaller the particle size, the larger the surface area and the lower the current density, which results in less polarization of electrode and better current rate capability of LiVOPO$_4$. Further work is underway to find out if there are any other reasons leading to good current rate capability of LiVOPO$_4$.

The chemical diffusion coefficient was measured with the potential step technique. In this method, the current generated due to an applied voltage step, is measured as a function of time. The measured current decays as the lithium ion diffuses through the electrode. The step ends when the current becomes less than 1% of the maximum current at the onset of the applied potential. The $i-t$ and $i-t^{-1/2}$ curves for the two powders at the applied potential step of 0.1 V (*vs* Li/Li$^+$) (3.94→4.04 V) are shown in Fig. 4. By assuming that the semi-finite diffusion of lithium ion in the electrode is the rate-determining procedure, the diffusion coefficient (D) of lithium ion in the electrode can be determined by the following Cottrell equation[30]:

$$i=nFD^{1/2}c_0\pi^{-1/2}t^{-1/2}$$

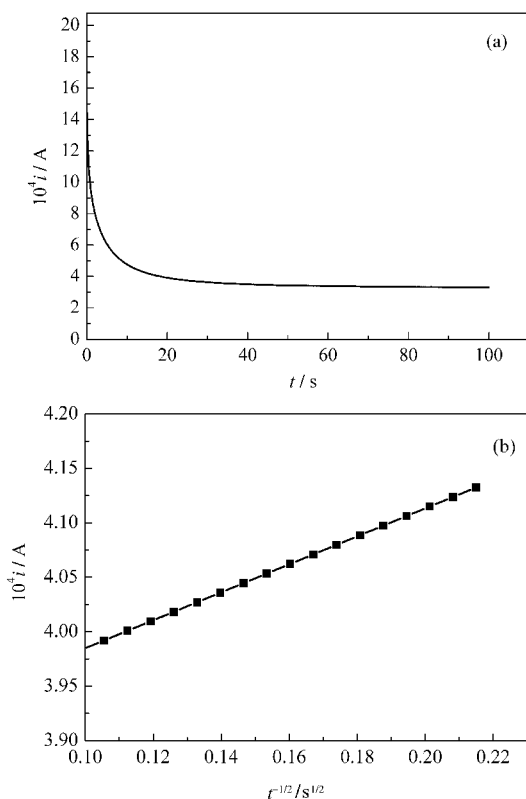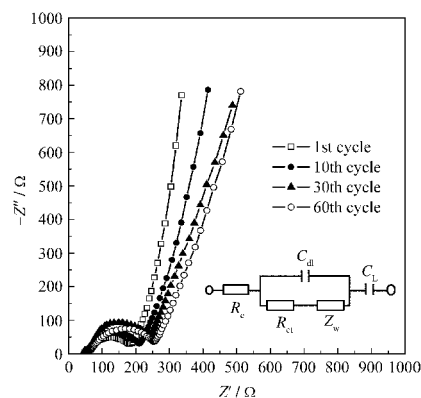where, n is the number of the redox reactions, F is the Faraday

Fig.5 Electrochemical impedance spectroscopy of nano-LiVOPO$_4$ electrode at various cycling times

In the equivalent circuit, R_e is the electrolyte resistance, R_{ct} is the charge-transfer resistance, C_{dl} is the double layer capacitance, Z_w is the Warburg impedance, and C_L is the intercalation capacitance.

constant, and c_0 is the lithium ion concentration in the solid electrode, which can be calculated from the open circuit voltage. According to Fig.4 and Cottrell equation, the diffusion coefficient of lithium ion in the electrode can be calculated to be 5.52×10^{-11} cm^2·s^{-1}, which is as same magnitude again as the value (2.79×10^{-11} cm^2·s^{-1}) reported by Ren *et al.*[20]. The experiment results show that the current rate capability of LiVOPO$_4$ by rheological phase method is better than that reported by Azmi *et al.*[19], while the diffusion coefficient of lithium ion in the electrode is in the same order. This may be due to the difference in preparation methods of materials and testing means of diffusion coefficient.

The electrochemical impedance spectroscopy of nano-LiVOPO$_4$ and the equivalent circuit are displayed in Fig.5.

All the spectra show a semicircle in the high frequency range and an inclined line in the low frequency range. The semicircle in the high frequency range is associated with the "charge transfer reactions" at the interface of electrolyte/oxide electrode, which corresponds to the charge transfer resistance. The inclined line in the low frequency range is attributable to "Warburg impedance" that is associated with lithium ion diffusion through the oxide electrode. The semicircle increases with the increase of cycle number. This indicates that the "charge transfer" resistance becomes larger with the increase of cycle number. The figure also shows that the slope of the inclined line varies with the cycle number. The slope of the inclined line at the first cycle is the biggest and after cycling 10 times it gets smaller. However, when the cycle number reaches 60, the slope of the inclined line becomes stable.

3 Conclusions

(1) Orthorhombic nano-LiVOPO$_4$ with particle size in the range of 10–60 nm was synthesized by a new rheological phase method.

(2) The first discharge of LiVOPO$_4$ is 135.7 mAh·g^{-1} and 98.9% of that is kept after 60 cycles. More than 96.5% and

Fig.4 $i-t$ (a) and $i-t^{-1/2}$ (b) curves of nano-LiVOPO$_4$ electrode

91.6% of the discharge capacity at $0.1C$ are sustained at $1.0C$ and $2.0C$, respectively. The chemical diffusion coefficient of lithium ion in the nano-LiVOPO₄ was measured with the potential step technique and the value is in the order of 10^{-11} $cm^2 \cdot s^{-1}$.

(3) Rheological phase method is a good route to synthesize LiVOPO₄ cathode material with high capacity, good cycling performance, and good current rate capability for lithium ion batteries.

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