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Phase-change enabled 2D $Li_3V_2(PO_4)_3/C$ submicron sheets for advanced lithium-ion batteries

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HIGHLIGHTS

- $Li_3V_2(PO_4)_3/C$ submicron sheets were synthesized via a phase-change method.
- $Li_3V_2(PO_4)_3/C$ cathode materials presents excellent rate and cycle performances.
- $Li_3V_2(PO_4)_3/C$ cathode materials delivers excellent low-temperature performances.

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ABSTRACT

The exploration of cathode materials with high capacity and power, fast charge/discharge rate, long lifespan and broad temperature adaptability is a challenge for the practical application of lithium ion batteries. Here, submicro-sheet $Li_3V_2(PO_4)_3/C$ (LVP/C) cathode materials have been successfully synthesized via a simple and universal phase-change method. This designed melting process increases the crystallinity and decreases the Li^+ diffusion distance, which effectively enhances the cycling stability and rate performances of the LVP/C cathode materials. The LVP/C cathode materials exhibit high discharge specific capacity of 130 mAh g^{-1} in the first cycle. The capacity retention is almost 100% after 100 cycles. In addition, at 10 C, more than 80% of initial discharge capacity is retained after 800 cycles, indicating excellent cycle performance at high rate. Moreover, the synthesized LVP/C materials perform excellent low-temperature properties. At -20 °C, the specific capacity can reach 105 mAh g^{-1} at 0.5 C. This study provides a novel template-free synthesis method for nano/micro materials.

1. Introduction

Lithium-ion batteries (LIBs) have emerged as the overwhelming choice for portable power sources in the modern world, due to their high energy density and sustainable chemical architecture after long-term repeated use [1–11]. However, as more demand emerges for electrical vehicles and hybrid electric vehicles, as well as emphasis shifts to the large-scale power grid [12], LIBs have been heavily restricted by the poor performances and high cost of the cathode materials. LIBs cathode materials mainly include $LiCoO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiFePO_4$. $LiCoO_2$ is the first commercial cathode for LIBs. However the structure tends to be unstable at high levels of delithiation [13]. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ suffers the same electrochemical issues as $LiCoO_2$ with rapid capacity loss during cycling [14]. $LiFePO_4$ delivers high thermal and structure stability but its redox potential is relatively low [15].

As alternative materials, phosphate cathode materials, such as $LiMnPO_4$, $LiCoPO_4$ and $Li_3M_2(PO_4)_3$ (M = V, Fe) have attracted considerable interests for their high operating voltages, high structure stability, low cost and environmental benignity [16–18]. Among these phosphates, monoclinic $Li_3V_2(PO_4)_3$ (LVP) is one of the most attractive cathodes for practical application. Monoclinic LVP has the largest theoretical capacity, 197 mAh g^{-1}, on the basis of three Li^+ extractions from the material lattice [19,20]. LVP presents

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the NASICON structure, which has the ability to facilitate Li^+ diffusion. LVP shows much faster Li^+ diffusion rate than the traditional cathode materials, such as $LiCoO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiFePO_4$, resulting in the excellent rate performance and low temperature performance [21–23]. In addition, LVP also has the advantages of high safety and high structure stability [24–27].

However, the practical application of LVP cathode materials for LIBs is impeded by several critical issues. Firstly, similar to other phosphates, the electronic conductivity of LVP is poor, which has to be enhanced by carbon coating [28–31], particle size reduction [32–34] and doping with other ions [35–38]. More critical problem is the complicated synthesis process of high-performance materials. The LVP prepared by a simple solid state method usually presents disordered morphology and poor electrochemical performances [25,26,39]. In order to prepare LVP samples with homogeneous particle size, regular morphology and excellent electrochemical performances, various methods have been explored, such as sol-gel method, hydrothermal method, spray pyrolysis method, freeze-drying method, electro-spinning method and so on, which usually need high-cost templates or complexing agents. The high-cost complexing agents and complicated synthesis process make these methods difficult to be applied in practical production [40–42]. Thus, it is urgent to find an easy and low-cost synthesis method to prepare high-performance LVP.

In those synthesis methods mentioned above, the templates and complexing agents work as a stabilizer to support the precursors. In the synthesis process, they can react with the raw materials to form amorphous phase or liquid precursors, which can control the crystal growth process and the morphology of the final products. However, the high-cost templates and complexing agents can be discarded when the precursors are stable in the pre-reaction stage. For example, if the precursors are crystalized in the pre-reaction stage, the destruction and reconstruction of the crystal structure between the precursors and the final products can generate homogeneous nano/micro scale particles with regular morphology without any templates and complexing agents.

Here, highly crystalline submicro-sheet LVP/C with homogeneous size and ordered morphology was prepared by a novel phase-change method. The LVP/C cathode has excellent structure stability, which improves the cycle performances. In addition, the thin sheet structure shortens the Li^+ diffusion distance and enhances the rate performances at room temperature and low temperature. The morphology controlling mechanism in the phase-change process and the electrochemical performances of LVP/C will be discussed in detail.

2. Experiments

2.1. Materials synthesis

The LVP/C samples were prepared by a phase-change method using LiOH, V_2O_5, and $NH_4H_2PO_4$ as raw materials with the molar ratio of 3:1:3. Firstly, the raw materials were grounded with mortar to form uniform powder and were put into the Al_2O_3 crucible. Then the mixtures were put into the high-temperature muffle furnace for 30 min at 800 °C. Next, the mixtures were removed out quickly and cooled to the room temperature to obtain the precursor. The precursor was mixed with 20 wt% glucose by ball-milling for 4 h and then the mixtures were calcinated at 750 °C for 10 h in Ar atmosphere to obtain a crystalline LVP/C-1 sample.

For comparison, LVP/C was also prepared by solid state method assisted with ball-milling pretreatment. LiOH, V_2O_5, $NH_4H_2PO_4$ and 20 wt% glucose were mixed by ball-milling for 4 h. After drying in the air oven at 80 °C, the precursor was calcinated for 10 h at 750 °C in Ar atmosphere to obtain the crystalline LVP/C-2 sample.

2.2. Materials characterization

The crystalline structures of the synthesized samples were characterized by X-ray diffraction (XRD) with a powder X-ray diffractometer (DX-2700) with Cu Kα radiation at $\lambda = 1.54$ Å in the 2θ range of 10°–70°.

The Fourier transforms infrared (FT-IR) absorption spectra measured by a JASCOFTIR 4100 spectrometer were used to determine the bonding nature of the samples. Each spectrum was recorded at the average rate of 48 scans with a resolution of 4 cm^{-1} collected from 600 cm^{-1} to 1600 cm^{-1} in reflection mode.

In situ diffuse reflectance IR spectroscopic (DRIFTS) was measured by Nicolet iS50 Fourier transforms infrared spectrometer. The DRIFTS was studied in the temperature from 25 °C to 750 °C at heating rate of 10 °C min^{-1}.

^7Li MAS NMR experiments were performed on a Varian Infinityplus-400 spectrometer with the ^7Li Larmor frequency of 155.36 MHz. The samples were spun up to 25 kHz using a 2.5 mm rotor. The chemical shift were referenced to 1 M LiCl aqueous solution ($\delta = 0$ ppm). All the spectra were acquired using a single pulse with the 90 pulse length of 1.3 μs and a recycle delay of 10 ms. The spectra baselines were adjusted by the Dmfit program.

The morphologies of the samples were characterized by the scanning electron microscope (SEM, JEOL 4800) and transmission electron microscope (TEM, JEM-2100). Thermogravimetric analysis (TGA) of the composites was conducted in air at a heating rate of 10 °C min^{-1} from 50 °C to 850 °C using a thermal analyzer (PYRIS Diamond TG-DTA, High Temp 115).

2.3. Electrochemical measurements

Electrochemical properties of the samples were studied with CR2016 coin cells using metallic lithium as the anode. The cathode was made from the prepared samples, Super P and Polyvinylidene Fluoride (PVdF) in a weight ratio of 8:1:1. The active mass loading of the electrodes ranged from 1.3 to 1.6 mg cm^{-2}. The obtained slurry was uniformly pasted on an Al foil and dried in vacuum at 120 °C. CR2016 coin-type cells were assembled in an argon-filled glove box using a Celgard 2325 membrane as a separator, 1 M $LiPF_6$ in ethylene carbonate, diethyl carbonate and ethylmethyl carbonate (EC/DMC/EMC, 1:1:1 vol) as electrolyte. Galvanostatic charge-discharge was performed in the voltage window of 3.0–4.3 V vs. Li^+/Li on a Land automatic battery tester (Wuhan, China). The electrochemical tests at low temperature of −20 °C were performed in high-low temperature test chamber with a Land automatic battery tester.

Cyclic voltammetry (CV) curves were recorded between 3.0 and 4.3 V vs. Li^+/Li by CHI 660C electrochemical work station at 25 °C. Electrochemical impedance spectroscopy (EIS) of the battery was measured in a frequency range of 100 KHz to 0.1 Hz using a Salarton 1287 test system with perturbation amplitude of 10 mV under open circuit potential conditions.

3. Results and discussion

Fig. 1a shows the XRD patterns of the precursors. The precursor of LVP/C-1 mainly contains $LiVOPO_4$ (PDF-01-085-2438), indicating that the V^{5+} has been reduced into V^{4+} during the high-temperature melting process. However, the precursor of LVP/C-2 is just mainly comprised of $NH_4VO(O_2)_2NH_3$ (PDF-711619) with V^{5+} and Li_3PO_4 (PDF-711528). In addition, the XRD patterns of final products in Fig. 1b show that both LVP/C-1 and LVP/C-2 are monoclinic LVP with a space group of $P2_1/n$, which is consistent with previous reports [15,43]. However, there are some impurities such as Li_3PO_4 in the final sample of LVP/C-2 as shown in Fig. 1b,