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Cycling stability of Li_3V_2 $(PO_4)_3$/C cathode in a broad electrochemical window

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ABSTRACT

In this paper, $Li_3V_2(PO_4)_3$/C was synthesized using the carbon thermal reduction method. The electrochemical performance of $Li_3V_2(PO_4)_3$/C in a broad electrochemical window was studied. The fine structure of $Li_3V_2(PO_4)_3$/C after cycling in different charge and discharge ranges was investigated by X-ray powder diffraction (XRD) refinement, X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The results show that the cycling stability of this material decreases with the increase of charge cut-off voltages. After cycling, the unit cell volume of $Li_3V_2(PO_4)_3$/C expanded irreversibly, in which the lengths of the Li(3)–O and V–O bonds became longer while those of Li(2)–O and Li(1)–O bonds became shorter. In the meantime, the amount of V^{5+} in the material increased and the carbon layer coated on the surface of the material was destroyed as the charge cut-off voltage was increased from 4.3 to 4.8 V. It is therefore reasonable to infer that the changes in the crystal structure of $Li_3V_2(PO_4)_3$/C cause the poor cycling performance of $Li_3V_2(PO_4)_3$/C. This result provides a research idea for improving the cyclic performance of $Li_3V_2(PO_4)_3$/C in the future.

1. Introduction

A great deal of effort has been made to determine new cathode materials for secondary batteries [1–3]. Lithium vanadium phosphate ($Li_3V_2(PO_4)_3$/C) based on anionic polymerization can produce a relatively high oxidation-reduction potential [4–7], which leads to better electrochemical and thermal stability [8]. The large lithium ion diffusion channels of $Li_3V_2(PO_4)_3$/C facilitate lithium ions being embedded in and extracted from it. $Li_3V_2(PO_4)_3$/C [9] has excellent rate performance and a high ion diffusion coefficient. Many researchers have been focusing on developing new types of cathode materials for lithium ion (Li-ion) batteries [10–13] by using theoretical calculations [14,15]. $Li_3V_2(PO_4)_3$/C has good safety performance [16,17], a high working voltage, great charging and discharging performance, and good reversibility. In the case of Li ions completely being removed, the theoretical specific capacity of $Li_3V_2(PO_4)_3$/C can reach 197 $mAh \cdot g^{-1}$ [18,19]. $Li_3V_2(PO_4)_3$/C displays two Li ion deintercalation processes in a range of 3.0–4.3 V and the theoretical specific capacity is 133 $mAh \cdot g^{-1}$. In addition, $Li_3V_2(PO_4)_3$/C has excellent low-temperature properties. Because of the above-mentioned advantages, $Li_3V_2(PO_4)_3$/C has attracted much attention [20,21].

$Li_3V_2(PO_4)_3$/C can exist in both orthorhombic and monoclinic crystal structures, both of which have the same cage structural unit $V_2(PO_4)_3$. $Li_3V_2(PO_4)_3$/C with a monoclinic crystal system has better lithium ion deintercalation performance [15,18,22], resulting in better electrical performance. Therefore, more researchers focus on $Li_3V_2(PO_4)_3$/C with a monoclinic structure. Monoclinic $Li_3V_2(PO_4)_3$/C belongs to a $P2_1/n$ space group. In this structure, the VO_6 octahedra and the PO_4 tetrahedra share oxygen atoms, where each VO_6 octahedron is surrounded by six PO_4 tetrahedra and each PO_4 tetrahedron is surrounded by four vanadium octahedra. Lithium atoms are in the cavity of this three-dimensional structure.

Previous studies [23,24] have found that the cycle stability of $Li_3V_2(PO_4)_3$/C decreased with the increase of the charge cut-off voltage. To our best knowledge, the cause for this decrease in the cycle stability of this material has not been investigated. Therefore, our focus of this work is to propose the cause of the decrease in the cycle stability of $Li_3V_2(PO_4)_3$/C.

2. Experimental

Lithium hydroxide (Beijing Xinhua chemical reagent factory, China; Analytical Grade), vanadium pentoxide (Tianjin Bodi Chemical Industry Co., Ltd., China, Analytical Grade), ammonium dihydrogen phosphate (Shantou Xilong Chemical Co., Ltd., Shantou city, Guangdong province, China;, Analytical Grade), and sucrose (Tianjin Dongli District Tianda Chemical Reagent Factory, Analytical Grade) with a molar ratio of 3:1:3:2/3 were ground in a ball mill by adding 15 ml of hydrogen peroxide (the mass fraction of hydrogen peroxide was 30%) to the ball milling dispersion agent. After it was pre-sintered for 4 h under 300 °C, the

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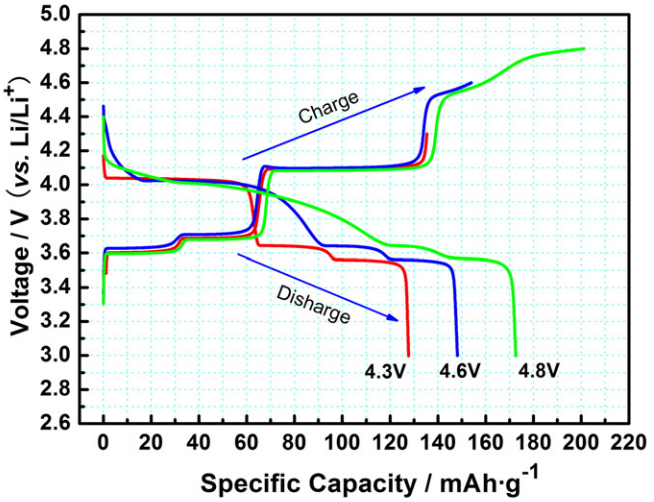

Fig. 1. Initial charge/discharge curves of $Li_3V_2(PO_4)_3/C$ at a 0.2 C rate in different electrochemical windows.

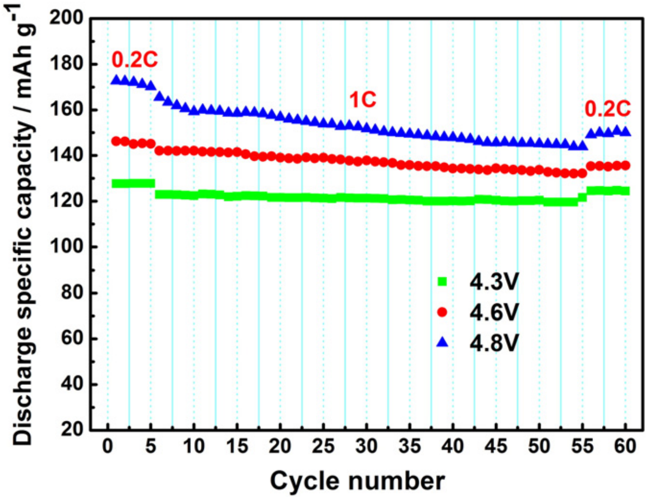

Fig. 2. Cycle performance of $Li_3V_2(PO_4)_3/C$ in different electrochemical windows.

sample was sintered at 800 °C for 6 h. Then the $Li_3V_2(PO_4)_3/C$ sample was fully ground to prepare for the characterization and electrochemical evaluation in next step.

The crystal structure of the synthesized material was characterized using X-ray diffraction (XRD) with a D/max–γβ X' pert diffractometer (Rigaku, Japan) with Cu Kα radiation at a voltage of 45 kV, a current of 50 mA, the scanning range of 5°–120° and step size 0.01°. The X-ray absorption near edge structure (XANES) spectra of the as-prepared samples were collected in the transmission mode at the U7C Beamline of the National Synchrotron Radiation Laboratory (NSRL, Hefei, China). The storage ring of the NSRL was operated at 0.8 GeV with a maximum current of 300 mA. The fixed-exit Si (111) flat double crystals were used as the monochromator. The X-ray photoelectron spectroscopy (XPS) analysis was performed using an energy spectrometer (PHI-5700 ESCA, American Physics Electron Company), in which Al Kα radiation was used as the stimulation source. Transmission electron microscopy (TEM) study was conducted by using a JEM-2100 transmission electron microscope (JEOL) and the accelerating voltage was set to 200 kV.

The as-synthesized $Li_3V_2(PO_4)_3/C$ material, polyvinylidene fluoride (Wuxi DE fluorine long anticorrosive equipment Co., LTD, Battery Grade), acetylene black (Shanghai HaoHua Chemical industry Co., Ltd), and *n*-methyl-2-pyrrolidone (Puyang City Maiqi Fine Chemical Co., Ltd., Analytical Grade) were mixed as a cathode slurry. The cathode electrode was compacted under a pressure of 5 Mpa and dried in vacuum at 120 °C for 12 h. The electrolyte used was 1 mol/L $LiPF_6$ with ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate as the solvents. Coin cells were assembled in a glove box. The electrochemical performance of the samples was tested by using a BTS-5 V/5 mA battery test system (Neware, China).

3. Results and discussion

The constant-current charge/discharge test was carried out to evaluate changes in electrochemical performance of the samples in different electrochemical windows. As shown in Fig. 1, three plateaus in the charge-discharge curve are observed in a range of 3.0–4.3 V. During charge-discharge, Li ions were extracted and inserted as illustrated in the following:

$(Li_3V_2(PO_4)_3 \rightarrow Li_{2.5}\,V_2(PO_4)_3 \rightarrow Li_2V_2(PO_4)_3 \rightarrow Li_1V_2(PO_4)_3)$.

where the first lithium ion was extracted in two steps.

Four plateaus are observed in a range of 3.0–4.8 V, which correspond to the following extraction process of three lithium ions:

$(Li_3V_2(PO_4)_3 \rightarrow Li_{2.5}\,V_2(PO_4)_3 \rightarrow Li_2V_2(PO_4)_3 \rightarrow Li_1V_2(PO_4)_3 \rightarrow V_2(PO_4)_3)$.

When the $Li_3V_2(PO_4)_3/C$ was cycled in 3.0–4.3, 3.0–4.6 and 3.0–4.8 V ranges, the first discharge capacities of the samp were 127, 146 and 172 mAh g^{-1}, respectively. The charge/discharge mechanism of $Li_3V_2(PO_4)_3/C$ is a two phase transition mechanism in a 3.0–4.3 V range (as Reaction 1–3). During charge to 4.8 V, the process also contains a sequence of two-phase transition process; while for discharge to 3.0 V, it consists of a single-phase (solid-solution) process and two-phase transition process. That is, upon the re-intercalation of the first two Li^+, the Li concentration change uniformly from $V_2(PO_4)_3$ to $Li_2V_2(PO_4)_3$ without phase boundary; while regarding to the re-intercalation of the third Li^+, it follows the two-phase process of $Li_2V_2(PO_4)_3$–$Li_{2.5}V_2(PO_4)_3$–$Li_3V_2(PO_4)_3$.

$$Li_3V^{+3}V^{+3}(PO_4)_3 \rightarrow Li_{2.5}V^{+3}V^{+3.5}(PO_4)_3 + Li^+ + e^- \tag{1}$$

$$Li_{2.5}V^{+3}V^{+3.5}(PO_4)_3 \rightarrow Li_2V^{+3}V^{+4}(PO_4)_3 + Li^+ + e^- \tag{2}$$

$$Li_2V^{+3}V^{+4}(PO_4)_3 \rightarrow Li\,V^{+4}V^{+4}(PO_4)_3 + Li^+ + e^- \tag{3}$$

The cycling performance of the $Li_3V_2(PO_4)_3/C$ sample in different electrochemical windows was evaluated and the results are shown in Fig. 2. It can be seen that the $Li_3V_2(PO_4)_3/C$ sample has good cycle performance in the 3.0–4.3 V voltage range. However, the cycling performance of this material becomes worse with the increase in voltage. Compared to that in the 3.0–4.3 V voltage range, the discharge specific capacity attenuation is relatively quicker in 3.0–4.6 and 3.0–4.8 V voltage ranges, which is probably caused by the irreversible expansion of the crystal lattice. Moreover, the higher the charge cutoff voltage is, the more serious the lattice volume expansion is, and thereby the worse the cycle performance is.

To investigate the structure stability of $Li_3V_2(PO_4)_3/C$ in different electrochemical windows, the XRD of $Li_3V_2(PO_4)_3/C$ before cycling and ex-situ XRD of $Li_3V_2(PO_4)_3/C$ discharged to 3.0 V after 60 cycles (charge and discharge at 0.2 C rate and charge and discharge at 1 C rate) was conducted, and the Rietveld refinements are shown in Fig. 3a–d. The diffraction intensity data of all $Li_3V_2(PO_4)_3/C$ materials were refined by using the General Structure Analysis System program [25,26]. It can be seen that the observed and calculated patterns match very well. All diffraction peaks can be indexed to a pure monoclinic structure phase, which is chosen as the refinement model. The lattice parameters for the $Li_3V_2(PO_4)_3/C$ material before (pristine) and after cycles under different electron exchange conditions are compared in Table 1. The crystal lattice of the $Li_3V_2(PO_4)_3/C$ material expands irreversibly with the increase of charge cut-off voltage. The higher charge cut-off voltage is,