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Research paper

Synthesis and electrochemical properties of nonstoichiometric composition $Li_{2.7}Ti_2(PO_4)_3/C$ with orthorhombic structure

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ABSTRACT

Carbon-coated $Li_{2.7}Ti_2(PO_4)_3$, a new mixed-valence titanium(III/IV) phosphate, is synthesized by the microwave-assisted sol-gel method using citric acid as both a chelating reagent and carbon source for the cathode material in lithium-ion batteries. The contents of Li, Ti and P are analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) and ion chromatography (IC). The microstructure, composition, and electrochemical performance of $Li_{2.7}Ti_2(PO_4)_3/C$ samples are characterized by X-ray Diffraction (XRD), X-ray photoelectron spectroscopy(XPS), scanning electron microscope (SEM) and cyclic voltammetry (CV). The $Li_{2.7}Ti_2(PO_4)_3/C$ sample exhibits a high initial discharge capacity of 123.6 mA h g^{-1} at 0.1C and outstanding cycling ability.

1. Introduction

Lithium-ion batteries (LIBs) have been considered to have great potential as power sources for the increasing energy demand. In previous reports, some positive electrode materials crystallized in an orthorhombic structure were prepared for LIBs, such as $LiFeO_2$ [1] and o-$LiMnO_2$ [2]. Recently, NASICON-type $LiTi_2(PO_4)_3$ has aroused the attention of researchers, because of the highly reversible redox couple(Ti^{4+}/Ti^{3+}) and relatively low redox potential (around 0.5 V), which is used as an anode material for Li-ion rechargeable battery. However, the electrochemical performance of $LiTi_2(PO_4)_3$ materials was restricted by inferior rate capability and fast capacity reduction [3]. There have been no reports on a new mixed-valence titanium (III/IV) phosphate, $Li_{2.7}Ti_2(PO_4)_3$, which was synthesized for use as a cathode material for LIBs. The preparation of a mixed valence of Ti^{3+} and Ti^{4+} is not easy, leading to difficulties during the synthesis process [4]. $Li_{2.7}Ti_2(PO_4)_3$ has many advantages including stable cycling ability, a low cost, and safety.

Carbon coating is a powerful method used to effectively improve the electrical conductivity of materials [5]. Moreover, it also can reduce the particles size by suppressing the growth of particles to lower the lithium-ion diffusion length [6]. Thus, citric acid is employed as a carbon source and chelating reagent to prepare $Li_{2.7}Ti_2(PO_4)_3$ by the sol-gel method [7]. In order to decrease the reaction time originating from a traditional sol-gel process, a microwave synthesis method may be employed to aid the material synthesis. The final products can be quickly obtained because the microwave energy is directly absorbed by the samples [8]. In this study, $Li_{2.7}Ti_2(PO_4)_3/C$ cathode material has been synthesized by the microwave-assisted sol-gel method. Furthermore, the preparation and electrochemical properties of $Li_{2.7}Ti_2(PO_4)_3/C$ are described in detail.

2. Experimental

2.1. Preparation of $Li_{2.7}Ti_2(PO_4)_3/C$

Appropriate amounts of the raw materials-LiCl, $TiCl_3$ (16 wt%, purple solution), $(NH_4)_3PO_4$, and carbon (citric acid as the carbon source)-were prepared to fabricate $Li_{2.7}Ti_2(PO_4)_3$ samples by the microwave-assisted sol-gel method. First, LiCl and $(NH_4)_3PO_4$ were dissolved in deionized water with magnetic stirring to form solution A. Then, citric acid was dissolved in the $TiCl_3$ purple solution with magnetic stirring to form solution B. Afterwards, solution A was added to solution B at a uniform speed while stirring for 1 h. The resulting solution was heated at 70 °C to form a gel and dried in a vacuum oven at 110 °C for 12 h to eliminate water. Finally, the resulting powder was pressed into pellets, placed into a crucible filled with activated carbon, and transferred to a 600-W microwave oven for 15 min. $Li_{2.7}Ti_2(PO_4)_3/C$ materials can be successfully synthesized.

2.2. Characterization

The structure and morphology of the $Li_{2.7}Ti_2(PO_4)_3/C$ materials were characterized by X-ray diffraction (XRD, Bruker D2) with Cu

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Kα radiation from 10° to 70° with a step size of 0.02°, infrared (IR) spectroscopy (Shimadzu IRAffinity-1) in the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}, scanning electron microscopy (SEM, Zeiss LEO 1430VP), and transmission electron microscopy (TEM, JEM-2010FEF). Elemental analyses for Li and Ti were carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS Advantage), and the content of the P was measured by ion chromatography (IC, ICS-2100) to determine the chemical compositions of the samples. The valences of Ti in the $Li_{2.7}Ti_2(PO_4)_3$/C materials were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi).

For the electrochemical tests, the cathode was prepared by mixing the active material, acetylene black, and polytetrafluoroethylene (PTFE) with a weight ratio of 80:10:10 in deionized water. The resulting slurry was spread onto an aluminum foil, cut into small wafers with a diameter of 10 mm, and dried in a vacuum oven at 110 °C for 12 h. Electrochemical cells were fabricated in an argon-filled glove box using Li metal as the counter electrode and $LiPF_6$ (1 mol L^{-1}), including ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) with a volume ratio of 1:1:1, as the electrolyte. In addition, Celgard 2400 was used as the separator.

The charge-discharge performance of the cells was characterized at room temperature by a battery testing system (LAND CT-2001A) within the voltage range of 2.0–3.5 V. Cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) measurements were carried out at room temperature using an electrochemical workstation (Chenhua CHI 650D) in the potential range of 2.0–3.5 V at a scan rate of 0.1 mV s^{-1} and with frequencies ranging from 0.01 Hz to 0.1 MHz, respectively.

3. Results and discussion

According to the analysis of chemical compositions of materials by ICP-AES and IC, the contents of Li, Ti, and P are 4.72, 24.01, and 71.27 wt%, respectively, demonstrating the chemical formula of the materials is nonstoichiometric $Li_{2.7}Ti_2(PO_4)_3$. Fig. 1a shows the XRD patterns of a $Li_{2.7}Ti_2(PO_4)_3$/C sample. All of the diffraction peaks can be indexed as orthorhombic $Li_{2.7}Ti_2(PO_4)_3$ (space group *Pbcn*) with the cell parameters a = 12.063(8) Å, b = 8.662(9) Å, and c = 8.710(8) Å (JCPDS: 80-2457), which coincides with previous reports [9]. There are no impurity phases detected from the XRD patterns, implying that single-phase $Li_{2.7}Ti_2(PO_4)_3$ can be prepared by this method and activated carbon plays an important role in the protective atmosphere. In addition, no obvious carbon peaks appeared in the XRD patterns, which suggests that the residual carbon has an amorphous structure and does not influence the crystal structure [10–12]. Furthermore, the carbon content in the final products was tested by an elemental analysis, and the result is merely 3.90 wt%, which contributes to the electrochemical performance. Fig. 1b shows the structure of NASICON-type $Li_{2.7}Ti_2(PO_4)_3$ observed along the c axis, and we can clearly see that each corner of the TiO_6 octahedra is linked to a PO_4 tetrahedron. Two Li atoms (Li1, Li2) appear at every asymmetric unit, and their sites are partially occupied in a channel structure that is approximately pentagonal, which is the main reason for the fast ionic conductivity [9].

To understand the chemical bonding and molecular structure of the $Li_{2.7}Ti_2(PO_4)_3$/C sample, the IR spectrum is shown in Fig. 2a. The absorption peak at 447 cm^{-1} is ascribed to Ti—O—Ti bands, and the absorption peaks around 598 and 627 cm^{-1} could be connected with the stretching vibration of Ti—O bands. Further, the absorption peak at 867 cm^{-1} could be attributed to symmetric P—O bands, and the absorption peaks near 999, 1037, and 1196 cm^{-1} may be related to P—O—P bridge vibrations, which are the characteristic absorptions of P—O—P linkers. Finally, the absorption peaks around 1437 and 1503 cm^{-1} are due to Fermi resonance peaks of P—O—P bridge vibrations. All of these assignments are consistent with those reported earlier [13–18]. To confirm the presence of the mixed Ti^{3+}/Ti^{4+} valence in the $Li_{2.7}Ti_2(PO_4)_3$/C sample, the Ti 2p spectrum was recorded by XPS and is shown in Fig. 2b. The Ti 2p spectrum is generally made up of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ peaks. Ti^{3+} for the Ti $2p_{1/2}$ and $2p_{3/2}$ peaks is located at 463.9 and 458.4 eV, respectively. Further, Ti^{4+} for the Ti $2p_{1/2}$ and $2p_{3/2}$ peaks is located at 464.3 and 459.9 eV, respectively, which is consistent with previous reports [19]. According to the careful peak separation of Ti^{3+} and Ti^{4+}, it was found that $Li_{2.7}Ti_2(PO_4)_3$ consists of both Ti^{3+} (86%) and Ti^{4+} (14%), indicating that the average valence of Ti is 3.14. Additionally, we can clearly determine that the content of Li is deficient (2.7 mol) on the basis of the above analyses. Therefore, the chemical composition of the obtained materials is nonstoichiometric $Li_{2.7}Ti_2(PO_4)_3$ in nature. These results are similar with the above element analyses.

The morphology of the $Li_{2.7}Ti_2(PO_4)_3$/C samples is shown in Fig. 3. The SEM image in Fig. 3a shows that the particles have a granular shape that is approximately 0.2–2 μm in diameter. To check the carbon coating on the $Li_{2.7}Ti_2(PO_4)_3$ particles, a TEM analysis of the sample was carried out. Fig. 3b shows a lattice spacing of 0.337 nm, corresponding to the (3 1 1) plane of orthorhombic $Li_{2.7}Ti_2(PO_4)_3$. It is clearly seen that about 9-nm-thick carbon layer is not uniform. The present carbon layer does prevent an increase in the particles size, which contributes to improving the electronic conductivity of $Li_{2.7}Ti_2(PO_4)_3$, thereby enhancing the electrochemical properties [20].

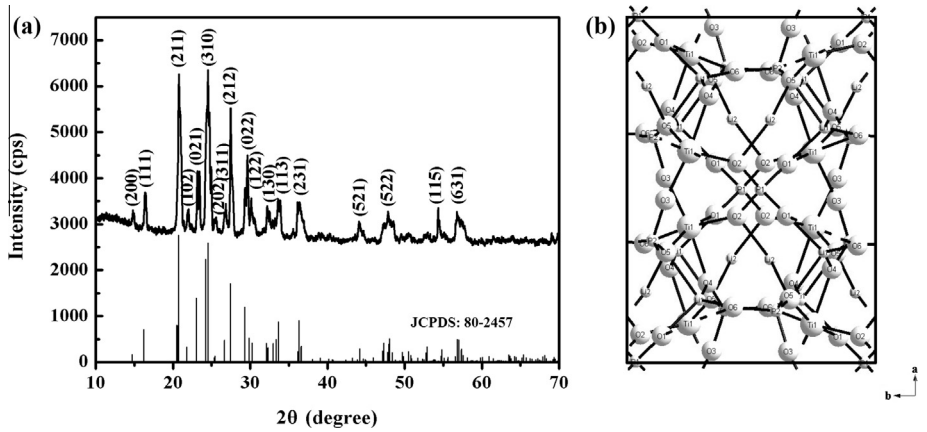

Fig. 1. (a) XRD patterns of a $Li_{2.7}Ti_2(PO_4)_3$/C powder; (b) structure of the projected unit cell of $Li_{2.7}Ti_2(PO_4)_3$ viewed along the c axis.