Journal of Alloys and Compounds 488 (2009) L26–L29

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

Preparation and electrochemical studies of $Li_3V_2(PO_4)_3$/Cu composite cathode material for lithium ion batteries

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ARTICLE INFO

Article history:
Received 8 July 2009
Received in revised form 25 August 2009
Accepted 27 August 2009
Available online 1 September 2009

Keywords:
Lithium ion battery
Cathode material
Composite material
Electronic conductivity
Electrochemical kinetics

ABSTRACT

$Li_3V_2(PO_4)_3$/Cu composite cathode material was prepared via sol–gel method by adding of 1.8 wt% Cu powder into the precursor solution. The structural and physical properties, as well as the electrochemical performance of the material were compared with those of Cu-free $Li_3V_2(PO_4)_3$. X-ray diffraction showed that Cu did not enter the crystal structure of $Li_3V_2(PO_4)_3$. The $Li_3V_2(PO_4)_3$/Cu composite material had a higher electronic conductivity comparing with that of Cu-free $Li_3V_2(PO_4)_3$. Electrochemical impedance spectroscopy showed that the adding of Cu decreased the charge transfer resistance of the electrode. In addition, the lithium diffusion coefficient was prominently enhanced from 1.3×10^{-9} to 2.8×10^{-8} cm^2 s^{-1}. Based on the these advantages, the $Li_3V_2(PO_4)_3$/Cu composite material exhibited much better cycling performance than the Cu-free $Li_3V_2(PO_4)_3$.

1. Introduction

Polyanion materials such as $LiFePO_4$ [1–3], $LiCoPO_4$ [4], $LiMnPO_4$ [5] and $Li_3V_2(PO_4)_3$ [6–9] have been intensively studied as cathode materials for lithium ion batteries. The framework of these polyanion materials is constructed by a rigid $[PO_4]^{3-}$ network, which helps to stabilize the crystal structure of the materials. The oxygen atoms are fixed in the $[PO_4]^{3-}$ structure. This limits the likelihood of oxygen liberation, which leads to good thermal stability. On the other hand, incorporation of the $[PO_4]^{3-}$ groups also raises the charge–discharge potentials of the materials by the "inductive effect" [10].

Among these polyanion materials, $Li_3V_2(PO_4)_3$ has the largest theoretical capacity, which is 197 mAh g^{-1} based on three Li^+ ions are extracted from the material lattice. $Li_3V_2(PO_4)_3$ exists in two forms: a rhombohedra phase and a monoclinic phase. The latter has a close packing structure and shows better electrochemical properties. Monoclinic $Li_3V_2(PO_4)_3$ has a NASICON-type structure which is different from that of olivine $LiFePO_4$. This NASICON-type structure has the ability to facile faster Li^+ diffusion. However, as most of polyanion materials, the separated $[VO_6]$ octahedral in $Li_3V_2(PO_4)_3$ reduces the electronic conductivity of the material, which is an intrinsic drawback to its electrochemical performance. In order to increase the electronic conductivity of $Li_3V_2(PO_4)_3$, it is a common practice to prepare carbon coated materials [11,12]. Recently, some other researches showed that the electronic conductivity of $Li_3V_2(PO_4)_3$ could be improved by cation or anion substitution [13–15].

Another simple approach to enhance the electronic conductivity of cathode materials is mixing the precursor with some conductive metal powders. For instance, Croce et al., increased the specific capacity of $LiFePO_4$ from 110 to 140 mAh g^{-1} by adding of 1.0 wt% metal powder (Ag or Cu) into the precursor solution [16]. This approach was also successfully adapted to some other cathode materials such as $LiCoO_2$ [17], $LiMn_2O_4$ [18] and $LiNi_{1/3}Co_{13}Mn_{1/3}O_2$ [19]. However, up to now this approach has never been proposed for improving the electrochemical performance of $Li_3V_2(PO_4)_3$. Herein, in this work, we prepared $Li_3V_2(PO_4)_3$/Cu composite cathode material using sol–gel method. The electrochemical performance of the material was compared with that of Cu-free $Li_3V_2(PO_4)_3$. Based on this, the effects of Cu additive on the electrochemical performance of $Li_3V_2(PO_4)_3$ was studied and discussed.

2. Experimental

For the preparation of $Li_3V_2(PO_4)_3$/Cu (hereby named as LVP-Cu) composite material, a NH_4VO_3 and LiH_2PO_4 mixture was firstly added into a glucose solution. The molar ratio of Li:V:P:glucose in the solution was adjusted as 3:2:3:0.3. Then 1.8 wt% of Cu powder was dispersed in the solution and a gel was obtained by heating and stirring the solution at 80 °C. This solution was then dried at 120 °C to get a precursor. The precursor was pressed into a pellet and pre-treated at 320 °C for 4 h in nitrogen flow until the decomposition reaction was completed. The resultant mixture was grounded and pressed into a pellet again, followed by heat treating at

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doi:10.1016/j.jallcom.2009.08.134

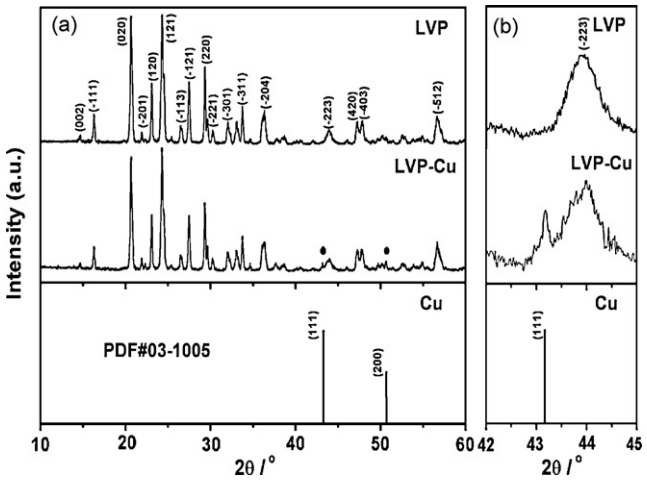

Fig. 1. (a and b) X-ray diffraction patterns of the LVP and LVP-Cu samples, together with that of Cu metal (PDF#03-1005) as a reference.

750 °C for 5 h in nitrogen flow. The preparation of Cu-free $Li_3V_2(PO_4)_3$ (named as LVP) followed the same procedure as described above but without adding of copper powder.

X-ray diffraction was performed on a Rigaku AXS D8 diffractometer with Cu Kα radiation. The diffraction data were recorded in the 2θ range of 10–60° with a scan rate of 3° min^{-1}. The cell parameters were calculated by the Celref3.0 Package. The morphological features of the materials were studied by scanning electron microscope (JSM-6700F). The existence of copper in the composite was confirmed by energy dispersive spectrometer (EX-84055BE). The electronic conductivity of the materials was measured on a Keithley2400 Source Meter by the van der Pauw method.

Electrochemical experiment was carried out using a two-electrode coin battery cell. A metallic lithium foil served as the anode electrode. The cathode electrode was composed of a mixture of $Li_3V_2(PO_4)_3$ active material (75 wt%), carbon black conductive additive (10 wt%) and poly-vinylidenefluoride binder (PVDF, 15 wt%). The slurry cathode mixture was pasted on an Al foil and dried in vacuum oven. The cathode and anode electrodes were separated by Celgard 2400 membranes. The electrolyte was a 1 mol L^{-1} lithium hexafluorophosphate ($LiPF_6$) solution dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1, by v/v ratio). Galvanostatic charge–discharge cycling was performed on a Land® (Wuhan, China) battery tester. Electrochemical impedance spectroscopy was collected on a ZAHNER®-IM6e electrochemical workstation. The impedance spectra were recorded by applying an *ac* voltage of 5 mV in the frequency range from 1 MHz to 1 mHz.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the LVP and LVP-Cu samples, together with the vertical lines those stand for the typical diffractions of Cu metal (PDF#03-1005) as a reference. It is seen from the figure that both the characteristic peaks of Cu (1 1 1) and (2 0 0) could be detected in the LVP-Cu composite. But the peaks are very weak due of the small amount of copper. Except for the diffractions of cooper, all of the peaks could be indexed to the monoclinic $Li_3V_2(PO_4)_3$ structure with space group of $P2_1/n$. Since the radius of copper cations (0.91 and 0.86 Å for Cu^+ and Cu^{2+}, respectively) are much bigger than that of V^{3+} (0.74 Å), if Cu was doped in the lattice of $Li_3V_2(PO_4)_3$, it would lead to an increase in the lattice parameters of the sample. For this reason, the lattice parameters of the samples were calculated from the XRD results. The (a, b, c, β) parameters of LVP-Cu are (8.608 Å, 8.593 Å, 12.047 Å, 90.2°), which are in concordant with those of LVP, i.e. (8.607 Å, 8.595 Å, 12.046 Å, 90.1°). This suggests that Cu did not enter the crystal structure of $Li_3V_2(PO_4)_3$ and the $Li_3V_2(PO_4)_3$/Cu composite was a mixture of Cu metal and $Li_3V_2(PO_4)_3$. The mean coherent domain size of the materials were calculated by the Scherer formula, which are 37 nm and 47 nm for $Li_3V_2(PO_4)_3$ and $Li_3V_2(PO_4)_3$/Cu, respectively.

Fig. 2 shows the SEM images of the samples. It is seen that both the LVP and LVP-Cu particles are in micrometer scale. But the particle size of LVP-Cu is a little bit bigger than that of LVP. Under a higher

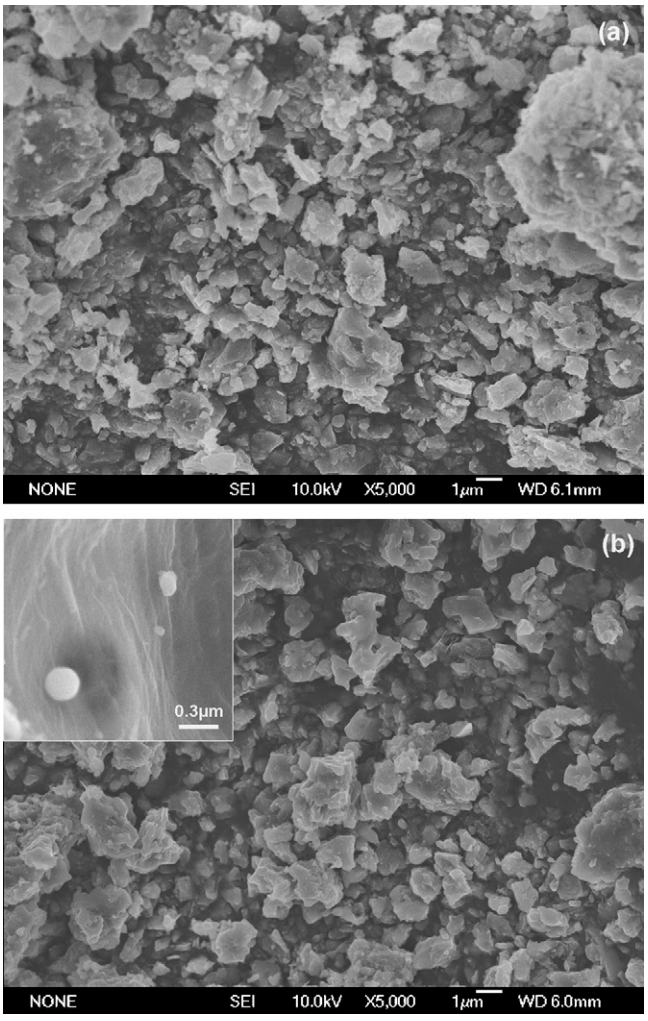

Fig. 2. SEM images of the LVP (a) and LVP-Cu (b) samples.

magnification (insert of Fig. 2b), some white-colored small particles can be observed on the particle surface of LVP-Cu. Energy dispersive spectroscopy (Fig. 3) confirms that they are the Cu particles in the composite.

The electronic conductivity of LVP was measured to be 1.1×10^{-4} S cm^{-1}, which is much higher than that of pristine $Li_3V_2(PO_4)_3$, i.e. 9×10^{-8} S cm^{-1} [20]. This is due to the residual

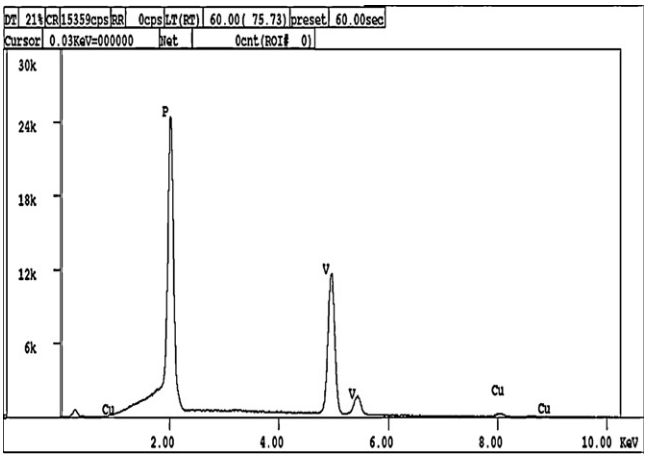

Fig. 3. Energy dispersive spectroscopy of the LVP-Cu sample.