Short communication

Li$_3$V$_2$(PO$_4$)$_3$/C cathode material prepared via a sol–gel method based on composite chelating reagents

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ABSTRACT

Li$_3$V$_2$(PO$_4$)$_3$/C composite material has been firstly synthesized via a sol–gel method based on the composite chelating reagents of glycine and beta-cyclodextrin. The product is investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), high-resolution transmission electron microscopy (HR-TEM) and electrochemical method. In the range of 3.0–4.3 V, the LVP/C electrode presents excellent cyclic performance at high discharge rates. The largest capacities of 87.1, 89.9 and 74.5 mAh g^{-1} are delivered at 0.9C charge and 35C discharge rates, 0.7C charge and 40C discharge rates, 0.6C charge and 50C discharge rates, respectively. 86.8%, 89.7% and 90.8% of the largest values are retained for the LVP/C electrode at the three discharge rates in the 500th, 300th and 250th cycles, respectively. The unexceptionable high-rate and cyclic performance is attributed to the existence of the composite carbon sources and the small particle size of the Li$_3$V$_2$(PO$_4$)$_3$/C.

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1. Introduction

Rechargeable lithium ion batteries have been regarded as promising power sources for hybrid electric vehicles (HEVs) and electric vehicles (EVs) due to their high specific capacity and power density, high safety and environmental friendliness. Safety is one of the paramount factors in large-format lithium ion batteries applications [1]. Polyanion-type materials have been discovered as potential cathode candidates for lithium ion batteries for their high safety. Among these materials, monoclinic Li$_3$V$_2$(PO$_4$)$_3$ (LVP) is the most appealing because of its high ionic diffusion coefficient, capacity, discharge voltage and energy density, good cyclic performance and remarkable thermal stability.

In the monoclinic LVP, all three lithium ions can be completely extracted from the lattice in the range of 3.0–4.8 V. Nevertheless, the extraction of the third lithium ion at 4.55 V is kinetically the most difficult and coupled with a significant overvoltage [2–5]. Therefore, LVP is usually cycled in the range of 3.0–4.3 V, giving rise to a theoretical capacity of 133 mAh g^{-1}.

However, the intrinsic low electronic conductivity limits the practical implementation of the LVP material. Moreover, it is still necessary to further improve the rate capability of the LVP elec-

trode. Carbon coating on the surface of the LVP particles, reducing particle size and doping with guest atoms have been applied to solve these problems [6–11]. Conductive carbon can not only greatly improve the electronic conductivity of the LVP but also effectively inhibit the particle growth in the sintering process. Further reducing the particle size is beneficial to the rate capability of the LVP owing to the decrease of lithium ions diffusion and electrons transportation distances [12]. Sol–gel method is an effective solution route to synthesize the LVP material with small particle size. Hence, various carbon sources [7,12–17] have been used to form LVP/C composite materials, and sol–gel methods based on different chelating reagents [7,12,13,18] have also been developed to synthesize LVP/C.

Glycine with carboxylate and aliphatic amine groups has often been used as chelating reagent to synthesize inorganic materials with nano-sized particles. Beta-cyclodextrin with hydroxyl groups and special ring structure can form complexes and inclusions with metal ions. Additionally, glycine and beta-cyclodextrin can convert to carbon in the pyrolysis process in an inert atmosphere. However, no studies have yet been reported about the synthesis of the LVP/C via a sol–gel method using beta-cyclodextrin as a chelating reagent and carbon source.

In the work, we firstly synthesize the LVP/C composite material via a sol–gel method based on the composite chelating reagents of glycine and beta-cyclodextrin. The electrochemical performance, especially the cyclic performance at high discharge rates, has been studied for the LVP/C composite material.

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2. Experimental

The LVP/C composite material was synthesized by a sol–gel method based on composite chelating reagents, using $LiOH·H_2O$ (A.R.), NH_4VO_3 (A.R.), $NH_4H_2PO_4$ (A.R.), $C_2H_2O_4·2H_2O$ (oxalic acid, A.R.), $C_2H_5NO_2$ (glycine, A.R.) and beta-cyclodextrin as raw materials. Oxalic acid was employed as a reducing reagent. Glycine and beta-cyclodextrin were used both as composite chelating reagents and composite carbon sources. In the first step, NH_4VO_3 and oxalic acid in a stoichiometric ratio of 1:3 were dissolved into deionized water under mechanical stirring at room temperature for 0.5 h. Second, a mixture of $LiOH·H_2O$, $NH_4H_2PO_4$ and beta-cyclodextrin was added into the solution above with stirring at room temperature for 0.5 h to form a brownish yellow solution. Third, the brownish yellow solution was heated to 80 °C, and then the aqueous solution of glycine was added into it with violently stirring. The mass ratio of glycine and beta-cyclodextrin was 3:10. The mixture was heated at 80 °C until a gel was formed. Finally, the gel was dried at 80 °C for 6 h in vacuum, pre-heated at 350 °C for 4 h, and subsequently calcined at 800 °C for 8 h in N_2 atmosphere to yield the LVP/C composite material.

The carbon content was determined by the methodology previously reported [19], and the carbon amount of the LVP/C composite material is 7.5%.

X-ray diffraction pattern was obtained using a Rigaku D/max-III X-ray Diffractometer with Cu Kα radiation and recorded in the 2θ range from 15 to 60° with a scanning speed of 4° min^{-1}. The morphology of the sample was observed by a scanning electron microscope (SEM) (Philips XL30ESEM). The nanoscale microstructure was examined by a high-resolution transmission electron microscope (HR-TEM) (Tecnai F30).

The electrochemical measurements were performed using CR2032 coin-type cells. For the fabrication of the cathode electrodes, 85 wt% active material was mixed with 10 wt% acetylene black and 5 wt% polyvinylidene difluoride (PVDF) in an appropriate amount of N-methyl-2-pyrrolidine for 1 h to form slurry. The slurry was pasted onto the aluminum current collectors. Then the electrodes were dried at 120 °C in vacuum for 12 h. The coin-type cells were assembled in a glove box filled with high purity nitrogen. The lithium metal foil was served as the counter and reference electrode, Celgard2300 as the separator, and 1 M $LiPF_6$ dissolved into a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volumetric ratio of 1:1 as the electrolyte. The active material loading was about 4.3 mg cm^{-2}. The charge–discharge measurements were conducted on a multi-channel battery test system (HANTEST HT045) in the range of 3.0–4.3 V under different current densities.

3. Results and discussion

The XRD pattern of the LVP/C composite material is shown in Fig. 1a. All the diffraction peaks can be attributed to the single-phase LVP and well indexed as monoclinic structure with the space group $P2_1/n$. The sharp diffraction peaks indicate the good crystallinity of the material.

SEM image is used to analyze the morphology of the LVP/C material and shown in Fig. 1b. It can be seen that the LVP/C particles show good uniformity and have no coalescence. In order to further clarify the nanoscale microstructure of the sample, TEM investigation was also conducted and the TEM images are displayed in Fig. 1c. It is clear that nano-sized particles are presented and a uniform carbon layer about 5 nm in thickness is coated on the LVP particles. The existence of the carbon not only improves the electronic conductivity of the LVP but also inhibits the growth of the LVP particles.
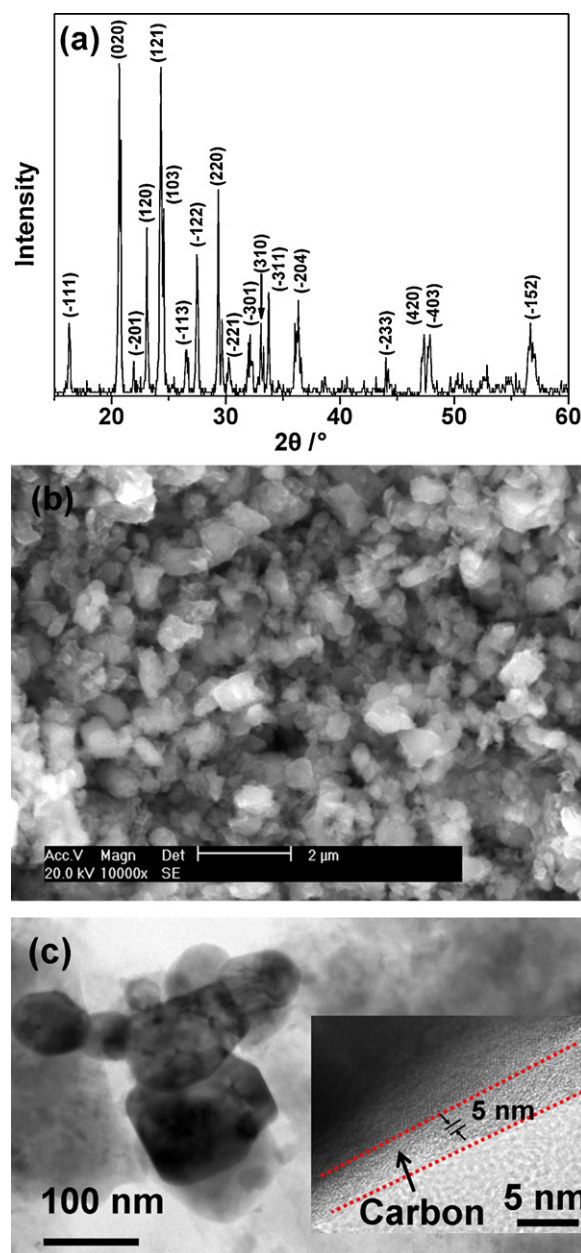

Fig. 1. (a) X-ray diffraction pattern, (b) SEM image, and (c) TEM images of the as-prepared $Li_3V_2(PO_4)_3$/C composite material.

Fig. 2a shows the initial charge and discharge curves of the LVP/C cathode at different current densities in the range of 3.0–4.3 V. For the 0.1C charge curve, three plateaus at 3.59, 3.67 and 4.08 V are observed, corresponding to the extraction of two lithium ions and the phase transitions of $Li_xV_2(PO_4)_3$ from x = 3.0 to 2.5, 2.0 and 1.0, respectively. The first lithium ion is extracted with two steps due to the existence of the ordered phase $Li_{2.5}V_2(PO_4)_3$. Then, the second lithium ion is removed via a single step, accompanied with the complete oxidation of V^{3+} to V^{4+}. Three discharge plateaus at 4.05, 3.65 and 3.58 V are assigned to the reinsertion of the two lithium ions, corresponding to the phase transitions of $Li_xV_2(PO_4)_3$ from x = 1.0 to 2.0, 2.5 and 3.0, respectively. The potential differences between each couple of charge and corresponding discharge plateaus are less than 0.04 V, indicating the transportation of electrons and the diffusion of lithium ions are easy in the carbon-coated LVP/C composite material. Compared with the theoretical capacity of 133 mAh g^{-1}, 130.5 mAh g^{-1} is delivered at 0.1C charge–discharge rate. The initial
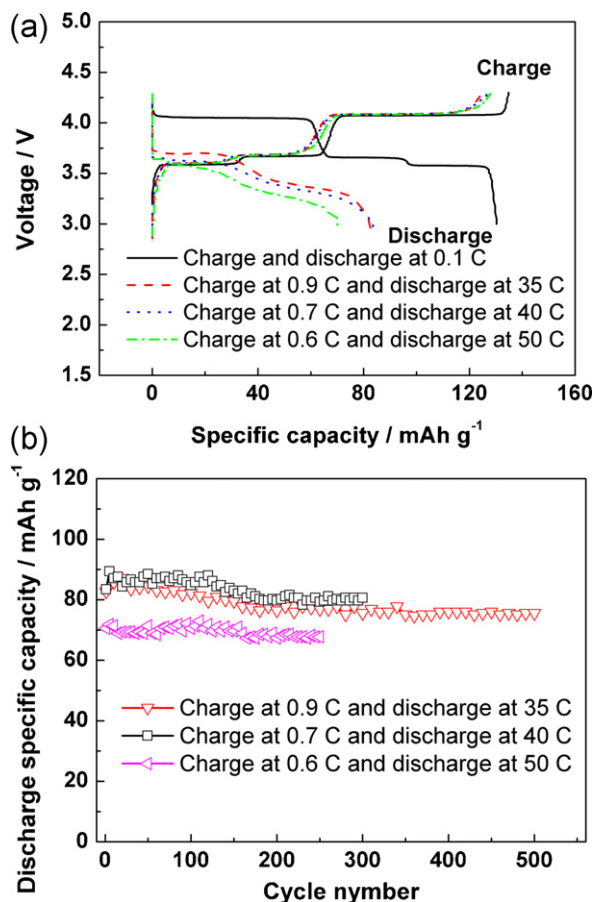
Fig. 2. (a) Charge–discharge curves and (b) cyclic performance of $Li_3V_2(PO_4)_3$/C composite material at various charge–discharge rates in the range of 3.0–4.3 V.

discharge capacities reach 82.7, 83.4 and 70 mAh g^{-1} at 0.9C charge and 35C discharge rates, 0.7C charge and 40C discharge rates, 0.6C charge and 50C discharge rates, respectively.

Fig. 2b shows the cyclic performance of the LVP/C composite material at different charge and discharge rates. Owing to the activation of the electrodes, the largest capacities of 87.1, 89.9 and 74.5 mAh g^{-1} are delivered at 0.9C charge and 35C discharge rates, 0.7C charge and 40C discharge rates, 0.6C charge and 50C discharge rates after several cycles, respectively. 86.8%, 89.7% and 90.8% of the largest values are retained for the LVP/C electrodes at discharge rates of 35, 40 and 50C in the 500th, 300th and 250th cycles, respectively. Unexceptionable capacity retentions are presented for the LVP/C electrodes at high discharge rates.

The excellent electrochemical performance of the product may be related to the existence of the composite chelating reagents in the synthetic process, the composite carbon sources and the small particle size. The composite chelating reagents, especially the beta-cyclodextrin with special ring structure, are beneficial to the homogeneous distribution of the metal ions. And then the high pure LVP could be easily obtained. Maybe the two kinds of carbon from glycine and beta-cyclodextrin are complementary, so the electronic conductivity of the LVP/C could be effectively improved and the growth of the LVP/C particles could be greatly inhibited. The high electronic conductivity and small particle size are advantageous to the rate capability and cyclic performance of the LVP/C composite material.

4. Conclusions

The LVP/C material, with unexceptionable cyclic performance at high discharge rates, has been firstly synthesized via a sol–gel method based on the composite chelating reagents of glycine and beta-cyclodextrin. The exciting results may be related to the existence of the composite chelating reagents in the synthetic process, the composite carbon sources and the reduced particle size.

Acknowledgments

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