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Glucose assisted synthesis of hollow spindle $LiMnPO_4/C$ nanocomposites for high performance Li-ion batteries

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ABSTRACT

Nano-sized hollow spindle $LiMnPO_4$ with a well-developed olivine-type structure was synthesized with the assistance of glucose in dimethyl sulfoxide (DMSO)/H_2O under ambient pressure and 108 °C. The scanning electron microscopy (SEM) and transmission electron microscope (TEM) images show that the $LiMnPO_4$ particles consist of hollow spindles with a mean width of 200 nm, length of 500-700 nm, and wall thickness of about 30-60 nm. The $LiMnPO_4/C$ nanocomposite was obtained by sintering nano-sized $LiMnPO_4$ with glucose at 650 °C under an inert atmosphere for 4 h. With a coated carbon thickness of about 10 nm, the obtained composite maintained the morphology and size of the hollow spindle. The electrochemical tests show the specific capacity of $LiMnPO_4/C$ nanocomposite is 161.8 mAh g^{-1} at 0.05C, 137.7 mAh g^{-1} at 0.1C and 110.8 mAh g^{-1} at 0.2 C. The retention of discharge capacity maintains 92% after 100 cycles at 0.2 C. After different rate cycles the high capacity of the $LiMnPO_4/C$ nanocomposite can be recovered. This high performance is attributed to the composite material's hollow spindle structure, which facilitates the electrolyte infiltration, resulting in an increased solid-liquid interface. The carbon layer covering the hollow spindle also contributes to the high performance of the $LiMnPO_4/C$ material as the carbon layer improves its electronic conductivity and the nano-scaled wall thickness decreases the paths of Li deintercalation.

1. Introduction

Since Goodenough and his co-workers reported that $LiFePO_4$ has the functions of Li^+ de/insertion in 1997, olivine-type polyanionic compounds, $LiMPO_4$ (M= Fe, Mn, Ni and Co), have been intensively studied as powerful cathode materials for lithium ion batteries due to their high structure and chemical stabilities [1,2]. $LiFePO_4$ presents a theoretical capacity of approximately 170 mAh g^{-1} and redox potential of 3.4 V vs. Li/Li^+. However, the theoretical energy density of $LiFePO_4$ is low, which limits its further development in terms of applications for electric cars. $LiNiPO_4$ and $LiCoPO_4$ present much higher redox potentials of 4.8 V and 5.1 V versus Li/Li^+, respectively, beyond what the electrolyte can bear. In comparison, $LiMnPO_4$ has almost the same theoretical capacity as $LiFePO_4$. The redox potential of $LiMnPO_4$ is 4.1 V vs. Li/Li^+, 0.7 V higher than that of $LiFePO_4$, fortunately, still within the stable electrochemical window of currently used liquid electrolytes. $LiMnPO_4$ also has a much higher theoretical energy density (701Wh kg^{-1}=171mAh g^{-1}×4.1 V), than that of $LiFePO_4$ (586Wh kg^{-1}=170mAh g^{-1}×3.45V). This feature plays an important role in increasing the cruising distance of an electric vehicle. Moreover, because of its rich raw materials, low cost, low environmental footprint, good structural stability, wide chemical compatibility, and safety, $LiMnPO_4$ is considered the most promising cathode material for Li batteries [3–7].

Compared to $LiFePO_4$, $LiMnPO_4$ is poor in electronic conductivity and low in Li^+ diffusion coefficient. These disadvantages consequently lead to poor performance, low reversibility, and limited rate capability [8,9]. Yamada et al. [10] have proved that $LiFePO_4$ is a semiconductor with ca. 0.3eV band gap, while $LiMnPO_4$ is almost an insulator with ca. 2eV band gap by the first principle. Therefore, the electronic conductivity of $LiMnPO_4$ is poor. Also, it is very difficult to synthesize the $LiMnPO_4$ material which can be reversibly charged and discharged. This is, so far, the main cause that the material has not been commercialized.

Generally, the approaches to improve the electrochemical performance of $LiMnPO_4$ are the same as those for $LiFePO_4$. To

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improve electronic conductivities and Li^+ diffusion coefficient of $LiMnPO_4$, various methods have been developed, such as carbon or conductive material coating on the particle surface [6,11–15], bulk phase element doping [16–19], and reduction in crystallite size [20,21]. H.Tong et al. synthesized $LiMnPO_4.Li_3V_2(PO_4)_3/C$ nanoparticles with a diamiter of 100~200 nm by using $MnV_2O_6 \cdot 2H_2O$ as the precursor, which exhibit a high discharge capacity in the voltage range of 1.5 to 4.5 V [22]. For $LiMPO_4$ (M=Mn and Fe), it was reported that the size effect and particle morphology had great influence on the electrochemical activity [23–27]. So the reduction in $LiMnPO_4$ particle size and morphology control are the main means to increase its activity. Compared with the high temperature solid phase method, the hydrothermal, solvothermal, [4,11,28–30], and polyol methods [13–15,31] are more desirable to control the micro-nanostructure of $LiMnPO_4$ in a liquid phase environment. For example, Goodenough et al. [32] reported the synthesis of $LiMnPO_4$ nanoplates with a diameter of around 2 μm and a thickness of around 50 nm. The nanoplates were prepared by a simple solvothermal method at 200 °C for 12 h. The sample had a capacity of 107.5 mAh g^{-1} at 0.05 C. Using a novel polyol method, Wang et al. [33] synthesized well-dispersed $LiMnPO_4$ plates with a thickness of about 20-30 nm and a specific capacity of 144 mAh g^{-1} at 0.05 C. C. Delacourt et al. [34] first calculated the depositing condition of $LiMnPO_4$ in aqueous solution by thermodynamics. In this condition, the pure $LiMnPO_4$ particles with diameter of 100-200 nm were obtained by 4-days reflux reaction. The reversible discharge capacity was 70 mAh g^{-1} at 0.05C(between 2-5 V vs. Li/Li^+).

To control particle size and morphology, our team previously succeeded to synthesize sphere-like $LiFePO_4/C$ nanocomposites with particle sizes of about 100-300 nm via a solution-phase method. This was achieved using the dimethyl sulfoxide (DMSO)/H_2O system under ambient pressure and 108 °C. The synthesized $LiFePO_4/C$ sample showed excellent rate and cycle performances [35,36]. This method facilitated the direct synthesis of uniform micro/nano particles in a liquid phase, which did not need to operate under high pressure and high temperature.

In this paper, we attempt to take the advantage of the aforementioned method to synthesize nano $LiMnPO_4$ particles although $LiMnPO_4$ differs from $LiFePO_4$ in several ways. The resulting primary $LiMnPO_4$ samples are agglomerates composed of cubic nanoparticles, in an approximate range of 30-50 nm. To decrease agglomeration of the particles, we add a certain amount of glucose as a surfactant in the DMSO/H_2O system. The synthesized $LiMnPO_4$ particles turn out to have a hollow spindle structure, with uniform particle size distribution and no agglomeration. Both the primary and the glucose-assisted $LiMnPO_4$ materials show excellent electrochemical performances after coated with carbon with the latter taking the lead in performance.

2. Experimental

2.1. Preparation of $LiMnPO_4$

Deionized water and DMSO (V_{H2O}=V_{DMSO}=25ml) was mixed in a flask. 5% glucose was slowly added to the above solution. The DMSO-H_2O solution with glucose was vigorously stirred and heated to 108 °C for 2 h, then cooled to room temperature.

0.05 mol manganese acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$, 99%) and 3.42 ml phosphoric acid (H_3PO_4, 85%)was dissolved in sequence into the above solution under constant stirring for 60 min at 50 °C. Then, 6.3545 g lithium hydroxide ($LiOH \cdot H_2O$, 99%) was slowly added into the flask. The final concentration of lithium hydroxide was 1.5 mol L^{-1}. To obtain a mixture pH of 7, the molar ratio of Li: Mn: P was about 3:1:1. The mixture was then vigorously stirred and heated to 108 °C for 2 h in a nitrogen atmosphere. After cooled down to room temperature and stored overnight, the $LiMnPO_4$ material was separated by centrifugation and washed three times with deionized water and ethanol to remove the residual DMSO and organic remnants. As a final step the material was dried overnight in an oven at 60 °C and the resulting product was named as $LiMnPO_4$-A.

For comparison, $LiMnPO_4$-B was produced via a similar method except that glucose was absent.

2.2. Preparation of $LiMnPO_4/C$

The **$LiMnPO_4/C$** composite was formed by milling $LiMnPO_4$-A or $LiMnPO_4$-B with a certain amount of glucose. The milled powder was collected and then heated at 650 °C for 4 h in an atmosphere of (N_2:H_2=95:5) at a heating and cooling rate of 6 °C min^{-1}. The resulting product was named as $LiMnPO_4$-A/C and $LiMnPO_4$-B/C, which the amount of carbon was determined to be ~2.9 and ~2.7 wt%, respectively.

2.3. Characterization and Electrochemical measurements

The electrodes containing the $LiMnPO_{4\text{-}A/C}$ or $LiMnPO_{4\text{-}B/C}$ were prepared using the following procedure: A mixture of $LiMnPO_4$-A/C or $LiMnPO_4$-B/C composite (70wt%), polyvinylidene fluoride (PVdF) (10wt%), carbon black (20wt%) was ground uniformly in an agate mortar. Next, N-methyl-2-pyrrolidone (NMP; Analytical grade) was added to the above mixture under continuous stirring for 30 min. The obtained slurry was then spread on a piece of weighed aluminum sheet with a width of 12 mm, dried at 60 °C for 4 h, then tabulated at 10 Mpa for 10 min, and dried again at 120 °C for 12 h under a vacuum (-0.1 Mpa) atmosphere.

The coin cells (CR2025) were assembled with Li as the negative electrode, polypropylene microporous membrane as the separator, 1 mol L^{-1} $LiPF_6$ (EC: DEC: DMC is 1: 1: 1, V/V/V) as the electrolyte in an Ar-filled ZKL glove box (Nanjing University Instrument Plant, China). The cells were tested using a land CT2001A battery tester (Wuhan Jinnuo Electronics Co. Ltd. China) at room temperature at rates of 0.05C, 0.1C, 0.2C, and 1C. In the electrochemical stability experiments, the cells were cycled between 2.50 V and 4.50 V vs. Li/Li^+. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on an electrochemical workstation (Shanghai Chenhua Instrument Company, China). The CV test scan rates were 0.2 mV s^{-1},0.5 mV s^{-1},0.8 mV s^{-1} and 1.0 mV s^{-1} over a cell voltage from 2.5 V to 4.8 V. For EIS, the scan frequency ranged from 0.05 Hz to10 kHz.

Phase analysis and cell parameter determination of all samples were performed by X-ray diffraction (XRD) using a D8 X diffractometer (Germany, Bruker) with Cu-Ka radiation. The scan data were collected in a 2θ range from 10-80° at a speed of 0.06°s^{-1}. The particle morphology of the synthesized materials was analyzed by the scanning electron microscopy (SEM) (FESEM, Hitachi S4300), transmission electron microscope (TEM) and high resolution transmission microscopy (HRTEM) (JEOL, JEM-2010).

3. Results and discussion

3.1. Structure and morphology characterization

XRD patterns of the $LiMnPO_{4\text{-}A}$ ($LiMnPO_{4\text{-}A/C}$) and $LiMnPO_{4\text{-}B}$ ($LiMnPO_{4\text{-}B/C}$) materials are shown in Fig. 1. The diffraction peaks show a characteristic pattern of $LiMnPO_4$ (PDF reference number 33-0804). As no other impurity peaks are detected, the samples have a pure olivine structure, with an orthogonal crystal system indexed in the Pnma group. Notice that our synthesis system is the DMSO/H_2O solution under ambient pressure and 108 °C. Under