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Preparation of high performance carbon-coated $LiMnPO_4$ nanocomposite by an acetate-assisted antisolvent precipitation method

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HIGHLIGHTS

- ► A novel antisolvent precipitation method is developed to synthesize $LiMnPO_4$ material.
- ► The precursor is composed of $Mn_3(PO_4)_2$ and Li_3PO_4 nanoparticles.
- ► The carbon-coated $LiMnPO_4$ with the particle size of 60 nm is obtained.
- ► The C-$LiMnPO_4$ material exhibits excellent rate capability and stable cyclability.

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ABSTRACT

A novel acetate-assisted antisolvent precipitation method combined with ball milling and heat treatment is developed to synthesize nanosized carbon-coated $LiMnPO_4$ material. The precursor prepared by the precipitation process is composed of $Mn_3(PO_4)_2$ and Li_3PO_4 nanoparticles. After heat treatment of the ball-milled mixture of precursor and glucose, the carbon-coated $LiMnPO_4$ with the particle size of around 60 nm is obtained. The $LiMnPO_4$ nanocomposite synthesized at the optimized conditions delivers specific discharge capacities of 154, 134, 120, 90, and 61 mAh g^{-1} at the rates of 0.05, 0.2, 1, 5, and 10C, respectively, which are comparable to some of the best reported C-$LiMnPO_4$ materials prepared by other synthesis methods. This material further exhibits good cycling stability, especially at high discharge rates of 5C and 10C.

1. Introduction

Lithium-ion batteries as the front-runners in energy storage systems have attracted much attention due to the growing market demand for portable electronic devices and electric vehicles [1–3]. In 1997, Padhi et al. introduced olivine-type lithium transition metal phosphates $LiMPO_4$ (M = Fe, Mn, Co, Ni) as desirable cathode materials owing to their outstanding properties such as high stability, environmental benignity, and low cost [4]. Among them, $LiFePO_4$ has been extensively studied and successfully commercialized [5–8]. Given the great success of $LiFePO_4$, $LiMPO_4$ (M = Mn, Co, Ni) with a higher redox potential is favored in the recent research. The high voltages of $LiCoPO_4$ (4.9 V vs. Li^+/Li) and $LiNiPO_4$ (5.1 V vs. Li^+/Li) materials are beyond the stable electrochemical windows of present electrolytes, thus developing $LiMnPO_4$ (4.1 V vs. Li^+/Li) seems to be more promising.

However, the inherently low ionic and electronic conductivities of $LiMnPO_4$ render it difficult to achieve excellent electrochemical activity [9]. Inspired by the previous research on $LiFePO_4$, the strategies including carbon coating [10], ion-doping [11], and particle size reduction [12,13] have been adopted to overcome these limitations. Various methods such as sol–gel [12], polyol [14], hydrothermal [15], solvothermal [16], ultrasonic spray pyrolysis [17], and precipitation [18–22] have already been attempted to prepare nanosized carbon-coated $LiMnPO_4$ (referred to as C-$LiMnPO_4$ hereafter). Of the reported methods, the precipitation process is

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a commercially viable one due to its simplicity and low cost. Delacourt et al. synthesized ~100 nm $LiMnPO_4$ particles by a direct precipitation technique [18]. Liu et al. used the 100–300 nm thick plate-like $NH_4MnPO_4 \cdot H_2O$ as the precursor to prepare $LiMnPO_4$ which preserved the morphology of $NH_4MnPO_4 \cdot H_2O$ [19]. Kim et al. synthesized 70 × 150 nm–100 × 300 nm $LiMnPO_4$ particles through a sequential precipitation [20]. In spite of these efforts, the $LiMnPO_4$ materials prepared by precipitation methods only exhibit moderate specific capacity and limited rate capability. Therefore, it is a great challenge to develop a new precipitation method to further decrease the particle size of the $LiMnPO_4$ material for improving its capacity, especially at high rates.

Antisolvent precipitation is a robust and scalable method mainly used in the preparation of nanoscale pharmaceutical ingredients [23–26]. According to classical precipitation theory, the formation mechanism of precipitate involves generation of supersaturation, nucleation, and particle growth. The kinetics of the latter two processes would determine the final size of precipitated particles. In an antisolvent precipitation process, the antisolvent is used to lower the solubility of compounds in the liquid solvent. Adding the solution of compounds to the antisolvent would generate the high supersaturation, which enables formation of nuclei more favorable than particle growth, yielding the precipitate with small particle size [23,24]. To our knowledge, antisolvent precipitation has not been used to prepare cathode materials. In the current efforts, we aim at developing a novel method based on antisolvent precipitation to synthesize ultrafine C-$LiMnPO_4$ composite.

Herein, we present an acetate-assisted antisolvent precipitation method combined with ball milling and heat treatment to synthesize C-$LiMnPO_4$ nanocomposite. The aqueous solution containing Mn^{2+} and $PO_4{}^{3-}$ is added to the ethanol solution of lithium acetate for the preparation of the nanosized precipitate as the precursor. Ethanol serves as the antisolvent. Subsequently, the precursor is ball-milled with glucose and heat-treated to obtain C-$LiMnPO_4$. The compositions and morphologies of the precursor and $LiMnPO_4$ samples are studied by scanning electron microscopy, energy dispersive X-ray spectroscopy, and transmission electron microscopy. The synthetic conditions of C-$LiMnPO_4$ such as heating temperature, heating time, and glucose content are optimized. The C-$LiMnPO_4$ nanocomposite prepared by this method displays excellent rate capability and stable cycling performance.

2. Experimental

2.1. Reagents

Lithium acetate dihydrate ($LiAc \cdot 2H_2O$) and glucose were purchased from Beijing Yili Fine Chemical Company (Beijing, China). Manganese acetate tetrahydrate ($Mn(Ac)_2 \cdot 4H_2O$) was obtained from Xilong Chemical Limited Company (Shantou, China). H_3PO_4 (85 wt%), HCl (37 wt%), and anhydrous ethanol were purchased from Beijing Chemical Reagent Company (Beijing, China). All these reagents were of analytical grade and used as received without further purification.

2.2. Synthesis procedure

The aqueous solution was prepared by adding 14.7 g of $Mn(Ac)_2 \cdot 4H_2O$, 4.08 mL H_3PO_4, and 6 mL HCl to 50 mL deionized water. 600 mL ethanol acted as the antisolvent, in which 26.4 g of $LiAc \cdot 2H_2O$ was dissolved. The aqueous solution was dropped slowly to the ethanol solution at 70 °C under vigorous stirring, and then the mixture was kept at 70 °C for 3 h. The obtained white precipitate was washed several times with ethanol and dried in an oven at 60 °C for 4 h. Subsequently, the precipitate was ball-milled with or without glucose for 6 h and sintered at 550 °C for 5 h in N_2 atmosphere to prepare C-$LiMnPO_4$ and bare $LiMnPO_4$, respectively.

2.3. Characterization of morphology, structure, and composition

The crystal structures of bare $LiMnPO_4$ and C-$LiMnPO_4$ were identified by a D/max2400 power X-ray diffractometer (XRD) (Rigaka, Japan) with Cu-Kα radiation ($\lambda = 1.5405$ Å) in a 2θ range of 10°–70°. The morphologies of the prepared nanomaterials were observed with an S-4800 scanning electron microscope (SEM) (Hitachi, Tokyo, Japan) and a Tecnai G2 F20 transmission electron microscope (TEM) (FEI, Portland, USA). Energy dispersive X-ray spectroscope (EDS) was applied to analyze the elemental composition of the precipitate. Carbon contents of the composites were determined by a Vario EL III elemental analyzer (Elementar, Germany). An ASAP2010 apparatus (Micromeritics, USA) was employed to estimate the specific surface areas of bare $LiMnPO_4$ and C-$LiMnPO_4$ powders.

2.4. Electrochemical measurements

C-$LiMnPO_4$ (80 wt%), carbon black (10 wt%), and poly(vinylidene fluoride) binder (10 wt%) in *N*-methylpyrrolidone were stirred into a homogeneous slurry. The obtained mixture was casted on aluminum foil and dried under vacuum at 100 °C overnight. Round disks with a diameter of 12 mm were cut for electrochemical characterizations. The electrodes typically had an active material loading of 2.8 mg cm^{-2} and volumetric density of 1.1 g cm^{-3}. Coin-type cells were assembled in an argon-filled glove box ($O_2 \leq 50$ ppm, $H_2O \leq 0.1$ ppm). Lithium foil served as both anode and reference electrode. Mixture of ethylene carbonate and diethyl carbonate (1:1, *m*/*m*) containing 1 M $LiPF_6$ was used as the electrolyte. The cells were charged in a constant current and constant voltage mode (galvanostatically charged to 4.5 V at a rate of 0.05C, then potentiostatically charged at 4.5 V till current drops to 0.01C), and then discharged to 2.5 V at a specific rate (1C = 170 mAh g^{-1}) using a LAND battery test system. Cyclic voltammetry (CV) was operated on a CHI600D electrochemical workstation (Chenhua, Shanghai, China) between 2.5 V and 4.9 V at a scanning rate of 0.1 mV s^{-1}.

3. Results and discussion

3.1. Mechanism of the acetate-assisted antisolvent precipitation

The acetate-assisted antisolvent precipitation process for the preparation of the precursor is shown in Fig. 1. $Mn(Ac)_2$, H_3PO_4, and HCl are dissolved in deionized water to obtain a homogeneous aqueous solution. Then the aqueous solution is added to the ethanol solution of lithium acetate. Ethanol as the antisolvent induces the high supersaturation of Li_3PO_4 and $Mn_3(PO_4)_2$. Acetate in the ethanol as the proton acceptor further increases supersaturation while lithium ion acts as a precipitant to form Li_3PO_4. The high supersaturation created by acetate and antisolvent is supposed to lead a fast formation of nuclei and limited particle growth, yielding the precipitate with small particle size.

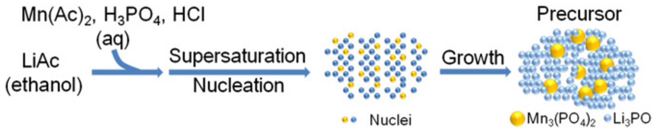

Fig. 1. Schematic illustration of the acetate-assisted antisolvent precipitation process.