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Comparison of electrochemical performances of $LiFePO_4$/C composite materials by two preparation routes

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ABSTRACT

This study reports on the preparation of $LiFePO_4$/C composite materials prepared by the hydrothermal and sol–gel processes for comparison. The synthesis condition on the hydrothermal process was performed at 170 °C for 19 h. The polystyrene (PS) polymer was used as a carbon source; the PS was added at a range of 0–5 wt.%. The temperature of the post-thermal process was set at 750–850 °C. The citric acid (denoted as CA) was used as the reducing agent and the carbon source in the sol–gel process. The temperatures of the sintering process were set at a range of 650–850 °C. The optimal sintering temperature was at 850 °C for 12 h in the hydrothermal process; the optimal carbon residue content was approximately 3.20 wt.%. It was revealed that the highest discharge capacity of $LiFePO_4$/C composites by the hydrothermal process at 0.1 C is 163 mAh g^{-1}. The optimal sintering temperature was found to be at 750 °C for the sol–gel process. The highest carbon content was approximately 11.94 wt.% as the molar ratio of CA is 1.0. The highest discharge capacity of $LiFePO_4$/C composites by the sol–gel process at 0.1 C was approximately 130.35 mAh g^{-1}.

1. Introduction

Lithium-ion batteries, due to their relatively high specific capacity, are considered for electric vehicle (EV), cell phones, laptop computers, digital cameras, renewable energy storage, and smart grid applications. The $LiFePO_4$ cathode material proposed by Padhi et al. [1] has attracted extensive attention for application in the next generation of rechargeable lithium-ion batteries due to its low cost, environmental benignancy, excellent safety characteristics, high capacity (theoretical capacity ~ 170 mAh g^{-1}), and excellent cycling performance. However, its poor conductivity, for electron and ion transfer, is the major barrier for commercial applications. The electron conductivity of $LiFePO_4$ is only 10^{-9} S cm^{-1} [2] and its lithium ion diffusivity is 10^{-14}–10^{-16} cm^2 s^{-1} [3]. There are three methods to improve the electronic conductivity, which include the following: (1) carbon coating; (2) doping with supervalent cations and (3) decreasing the particle size. The carbon coating is the most effective among these methods, and is a facile way to improve the conductivity of $LiFePO_4$ materials. The $LiFePO_4$ cathode materials can usually be prepared via a solid-state reaction [4,5], sol–gel process [6,7], and hydrothermal process [8–13]. Whittingham [8] revealed that the high-quality crystalline $LiFePO_4$ platelets can be obtained by a low temperature hydrothermal process.

In this work, we prepared the $LiFePO_4$/C composite materials by a hydrothermal process (using expensive Fe^{2+} salts, $FeSO_4$) and a post-sintering process, at temperatures of 750, 800 and 850 °C. The polystyrene polymer, which is with aromatic structure, was used as a carbon source. For comparison, we also prepared the $LiFePO_4$/C composites by a common soft chemistry route, i.e., a sol–gel process. The citric acid was used as the reducing agent and the carbon source in the sol–gel process (using cheap Fe^{3+} salts, $Fe(NO_3)_3$). The characteristic properties of $LiFePO_4$/C composite materials were examined by X-ray diffraction (XRD), micro-Raman spectroscopy, scanning electron microscopy (SEM), high-resolution transmission microscopy (HR-TEM), elemental analysis (EA), and micro-Raman spectroscopy. The electrochemical performances of the $LiFePO_4$/Li battery were examined by a galvanostatic charge/discharge method and a cyclic voltammetry method.

2. Experimental

2.1. Preparation of composite $LiFePO_4$/C materials

The $LiFePO_4$/C composite materials were prepared by a hydrothermal process and a post-sintering process. The appropriate quantities of $FeSO_4 \cdot 7H_2O$, $LiOH \cdot H_2O$, and $NH_4H_2PO_4$ (Aldrich) as the starting materials were dissolved in 200 mL deionized water. The molar ratio of Li:Fe:P was 2:1:1. The polystyrene (PS, MW 35,000,

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Aldrich) polymer was dissolved in acetone to form a 5 wt.% PS stock solution. Approximately 50 mL of 5 wt.% PS stock solution was added drop by drop into the above mixture solution while stirring. The added carbon source in the $LiFePO_4$ materials was maintained at 0–5 wt.% PS. The mixed solution was transferred into a 600 mL Teflon-lined stainless steel autoclave, which was heated at 170 °C for 19 h. After the solution cooled down to room temperature, the precipitate composite powder was cleaned and dried at 60 °C for 12 h under vacuum oven, followed by post-sintering at 750, 800, and 850 °C for 9 h under an Ar/H_2 (95:5, v/v) atmosphere. By contrast, the $LiFePO_4$/C composite materials were also prepared by a sol–gel process. $LiNO_3$, $Fe(NO_3)_3$, $NH_4H_2PO_4$ (Aldrich), and citric acid (CA) were used as the starting materials to prepare $LiFePO_4$/C composite materials. $LiNO_3$, $Fe(NO_3)_3$ and $NH_4H_2PO_4$ were dissolved in D.I. water, and mixed together to form a homogeneous mixture solution. The appropriate quantities of citric acid solution were slowly added into the resulting mixture solution. The molar ratio of Li:Fe:P:citric acid in the precursor solution was maintained at 1:1:1:0.5–1.0. After complete mixing, the sol was dried at 60 °C for 12 h. The wet gel was subsequently dried in a vacuum oven at 120 °C for 10 h. After thorough grinding with a mortar and pestle, the dry gel was sintered at 650, 750, and 850 °C for 12 h under an Ar/H_2 (95:5, v/v) atmosphere.

2.2. Material characterization

The crystal structure of $LiFePO_4$/C composite samples was examined by an X-ray diffraction (XRD) spectrometer (Philip, X'pert Pro System). The surface morphology was conducted by a scanning electron microscope (SEM, Hitachi). The residue carbon morphology was observed by a high-resolution transmission electron microscopy (HR-TEM, JEOL 2010F). The micro-Raman spectra were recorded on a confocal micro-Renishaw with a 632 nm He–Ne laser excitation. The residual carbon content in the sample was analyzed using Elemental Analyzer (Perkin Elmer 2400). The electron conductivity of the composite samples was measured by AC impedance method.

2.3. Electrochemical measurements

The electrochemical performances of the Li/$LiFePO_4$ composite battery were measured by using a two-electrode system (CR 2032 coin cell assembled in an argon-filled glove box). The $LiFePO_4$/C composite electrodes were prepared by mixing active $LiFePO_4$/C materials, Super P, and poly(vinyl fluoride) (PVDF) binder in a weight ratio of 90:5:5, pasted on an aluminum foil (Aldrich), and then dried in a vacuum oven at 120 °C for 12 h. The lithium foil (Aldrich) was used as the counter and reference electrode. A micro-porous PE film was used as the separator. The electrolyte was 1 M $LiPF_6$ in a mixture of EC and DEC (1:1, v/v, Merck). The $LiFePO_4$/Li composite batteries were charged by a constant current + a constant voltage profile (CC–CV) and discharged by a constant current profile, over a potential range of 2.0–3.8 V (vs. Li/Li^+) at varied C rates with an Autolab PGSTAT302N potentiostat. The second CV charge step of 3.80 V was terminated when the charged current was below 0.1 C current. The cyclic voltammetry (CV) was conducted by using an Autolab instrument at a scanning rate of 0.1 mV s^{-1} between 2.5 and 4.2 V.

3. Results and discussion

The XRD patterns of pure $LiFePO_4$ materials prepared by the hydrothermal and the sol–gel processes are shown in Fig. 1(a) and (b), respectively. The XRD diffraction patterns revealed that both the pure $LiFePO_4$ and the $LiFePO_4$/C composite materials (XRD data not shown here) are all single phase materials with an olivine-type

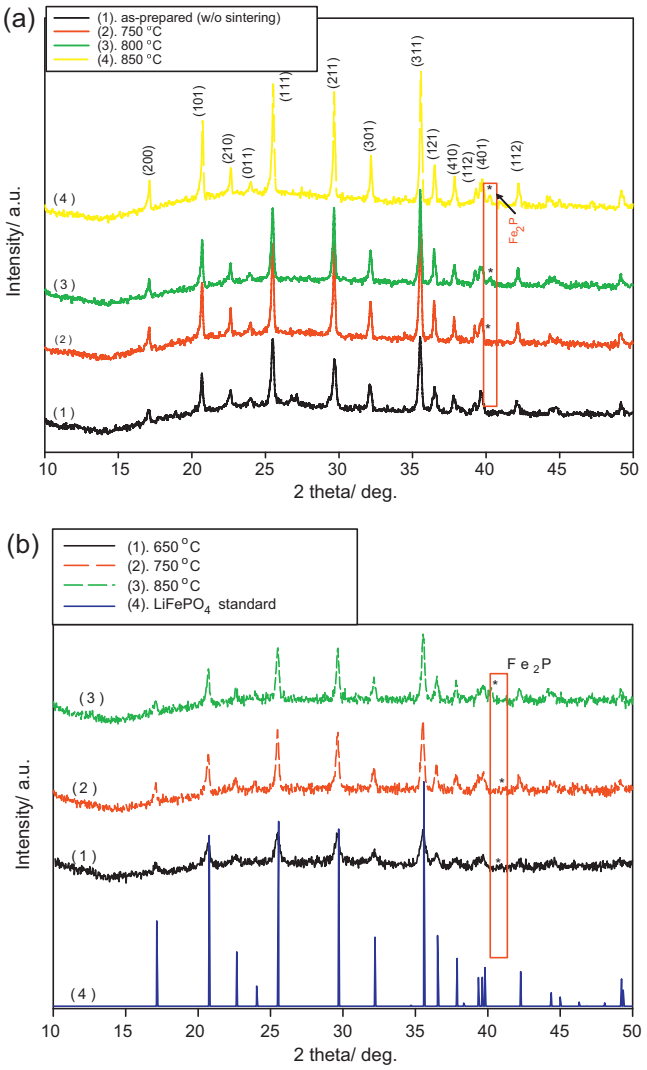

Fig. 1. XRD patterns for $LiFePO_4$/C by: (a) hydrothermal process and (b) sol–gel process.

structure indexed to the orthorhombic *Pnma* space group. A number of small Fe_2P peaks ($2\theta = 40.28°$, 44.20°, 47.29°) were found in the XRD pattern which can be ascribed to the reduction of phosphate and iron in the precursor by the presence of any reductive atmosphere. Nazar et al. [14,15] reported that metal phosphates (Fe_2P) exhibit a high electron conductivity of approximately 0.1 S cm^{-1}. No other impurity peaks were found, which indicates the high purity of the as-prepared $LiFePO_4$/C composite samples. Due to the high conductivity of Fe_2P phase, the electron conductivity of the $LiFePO_4$/C composite materials with Fe_2P and carbon may effectively enhance the electron conductivity of composite materials. The diffraction peak of the residual carbon cannot be found in the pattern; and may be their low content or amorphous state. The lattice parameters of the as-prepared pure $LiFePO_4$ sample and composite $LiFePO_4$/C sample were calculated based on the XRD patterns and are listed in Table 1. It was found that that the lattice parameters of all $LiFePO_4$ and $LiFePO_4$/C materials by the hydrothermal and sol–gel processes are the same as the standard $LiFePO_4$ (JCPDS card number 81-1173, a = 10.33 Å, b = 6.010 Å, c = 4.692 Å). The carbon source of PS or citric acid has no observable influence on the structure of $LiFePO_4$ composite materials.

The SEM image of the $LiFePO_4$/C composite (5 wt.% PS in oven bath) sample by the hydrothermal process is shown in Fig. 2(a).