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Preparation of porous-structured $LiFePO_4$/C composite by vacuum sintering for lithium-ion battery

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ABSTRACT

The $LiFePO_4$/C (LFP/C) composite as a cathode material for lithium-ion battery was synthesized by solid-state reaction under vacuum sintering condition (20–5 Pa). The effects of vacuum sintering temperature and time on the phase composition, morphological structure, and electrochemical performance of LFP/C composite were investigated by X-ray diffraction, scanning electron microscopy, galvanostatic charge–discharge cycling test, and electrochemical impedance spectroscopy. The synthetic LFP/C composite possessed uniform particle-size distribution with porous architecture upon sintering at 650 °C for 12 h and thus exhibited the highest discharge capacity and best cycle performance. The complete decomposition of citric acid at a suitable temperature under vacuum condition resulted in the formation of porous structure. Compared with atmospheric argon sintering, vacuum sintering method led to the formation of porous architecture, the porous sample showed excellent cycle performance with less than 2% capacity loss after 80 cycles at 0.2 C, and reached the discharge specific capacity of 87.6 mAh g^{-1} at 10 C rate, these are better than that of atmospheric argon sintering. The LFP/C composite prepared under vacuum sintering also reduced the optimum sintering temperature by nearly 100 °C compared with that prepared under atmospheric argon sintering.

1. Introduction

Lithium-ion batteries have been commercialized since 1991 and initially used in mobile devices, such as cell phones and laptops [1]. Currently, this technology is currently gaining considerable attention in the performance improvement of these batteries [2–4].

As one of the most promising active cathode materials for lithium-ion batteries, $LiFePO_4$ (LFP) is attracting considerable attention because of its various advantages, such as being low cost and nontoxic, as well as having a high theoretical capacity of 170 mAh g^{-1}, environmental benefits [5–8], and an approximately flat voltage plateau of around 3.4–3.5 V versus lithium. Usually, LFP is synthesized by solid-state reaction [9–13], carbothermal reduction [14–16], hydrothermal processing [17–19], or sol–gel methods [20,21]. Among them, solid-state reaction is the most common way of synthesizing LFP material. However, an extra inert reductive atmosphere is necessary to prevent Fe^{2+} oxidation during sintering [22]. Residual Fe^{3+} with serious particle agglomeration can easily exist [23–25], thereby affecting the consistency and electrochemical performances of LFP samples.

Vacuum sintering can enable the preparation of materials in medium (1333–1.33×10^{-1} Pa), high (1.33×10^{-1}–10^{-6} Pa), or even ultra-high vacuum ($< 10^{-6}$ Pa) conditions. Given that the vacuum condition is nearly free of oxygen, nitrogen, and hydrogen, the iron oxidation state (II) is effectively maintained during LFP sintering with good electrochemical performance. Gao et al. [26] first reported the synthesis of LFP by vacuum calcination. They found that compared with traditional Ar/N_2 atmosphere with constant pressure, LFP prepared under vacuum condition with a pressure of −0.1 MPa had a pure olive-type with small and uniform particle size and thus exhibited higher charge–discharge capacity. Zhang et al. [27] also studied the effect of carbon coating on $LiFePO_4$/C (LFP/C) prepared by vacuum thermal decomposition,

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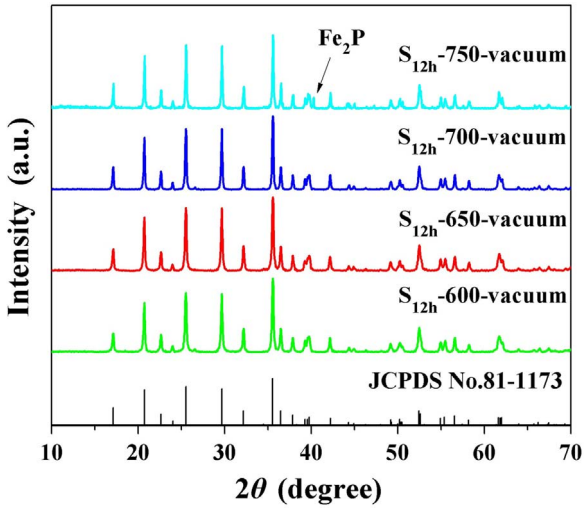

Fig. 1. XRD patterns of the LFP/C composites at different sintering temperatures under vacuum condition.

which delivered better cycle and rate performances than LFP/C by conventional sintering. Moreover, vacuum sintering can accelerate decomposition rate and reduce reaction temperature [28,29]. In this case, vacuum sintering is an energy-effective method for the synthesis of LFP/C owing to low input power consumption and the absence of inert protection atmosphere cost, especially for large-scale production.

In the present study, the porous LFP/C composite was synthesized by one-step vacuum sintering method under relatively high vacuum degree (20–5 Pa). Sintering temperature and time were investigated to optimize the parameters for LFP/C composite preparation under vacuum condition. For comparison, LFP/C composite sintered under conventional argon atmosphere of 101325 Pa was also prepared. The phase composition, morphology, and electrochemical performance of LFP/C composites were detected by X-ray diffraction (XRD), scanning electron microscopy (SEM), charge–discharge test, and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. LFP/C preparation

The amount of Li_2CO_3 (AR), $FeC_2O_4 \cdot 2H_2O$ (AR), $NH_4H_2PO_4$ (AR), and citric acid (as carbon source) at a mole ratio of $n_{Li}:n_{Fe}:n_{P}:n_c$ = 1:2:2:0.4 were mixed and ball milled with the ethanol as disperser to obtain the LFP with a carbon content of around 3 wt%. After 6 h of being milled at a rotation speed of 300 rpm, the mixed slurry was oven dried at 50 °C, forming the precursor. The precursor was then sintered in a vacuum tube furnace (Zhonghuan Lab Furnace Co., Tianjin, China) using a quartz crucible at the heating rate of

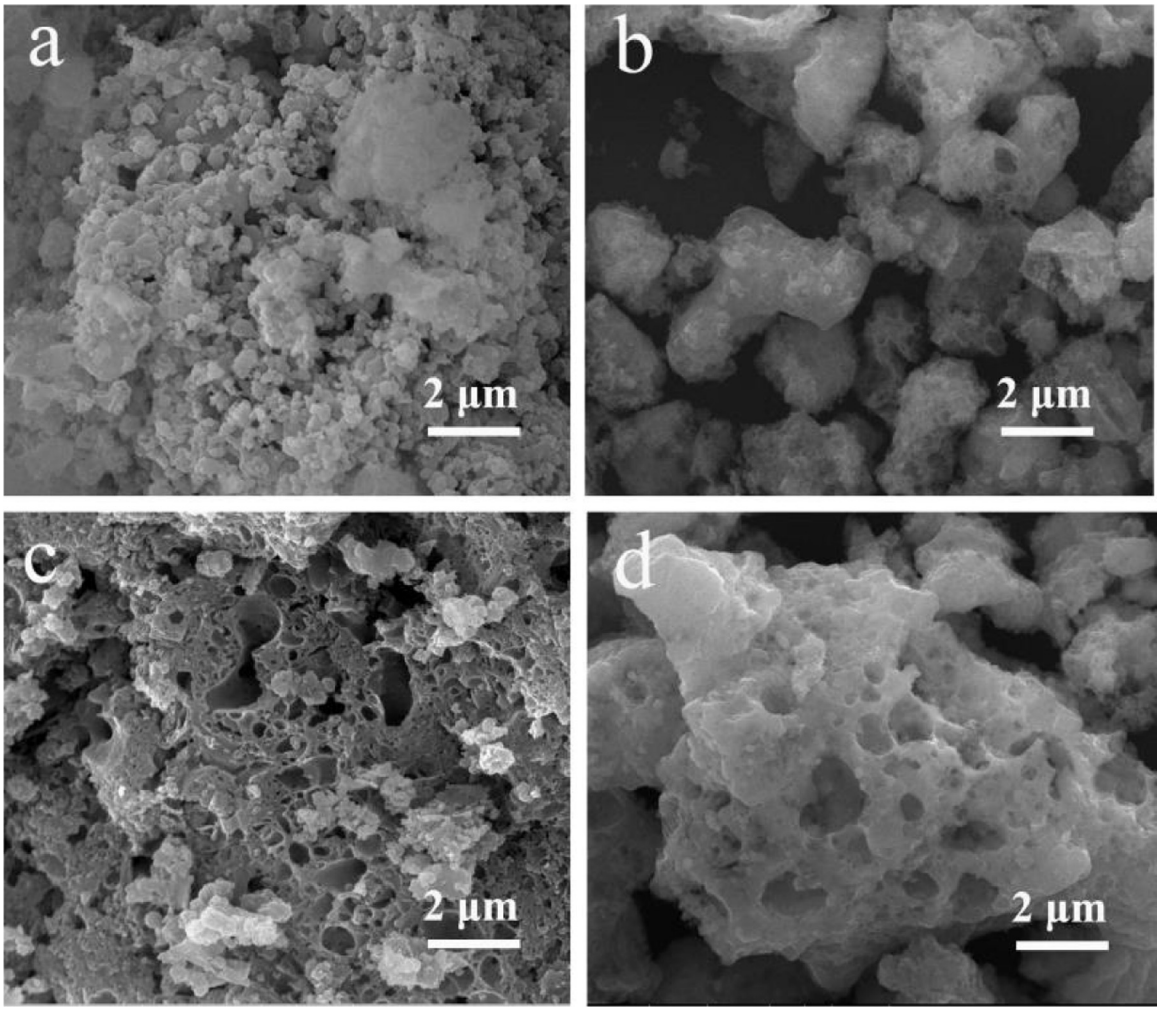

Fig. 2. SEM images of synthesized LFP/C composites for different vacuum sintering temperatures: (a) 600 °C, (b) 650 °C, (c) 700 °C, and (d) 750 °C.

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