Solid State Ionics 298 (2016) 44–50

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Investigation on high performance $LiFePO_4$ nanoplates with the {010} face prominent for lithium battery cathode materials

Haiyang Guo, Yan Liu *, Yukun Xi, Chun Xu, Qing Lv

School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 200235, PR China

ARTICLE INFO

Article history:
Received 29 June 2016
Received in revised form 26 October 2016
Accepted 27 October 2016
Available online xxxx

Keywords:
B-axis orientation
Aqueous electrolyte
Cyclic voltammetry
$LiFePO_4$
Li-ion battery

ABSTRACT

$LiFePO_4$ nanoplates were synthesized by using ethylene glycol (EG) as a solvent. The morphologies and sizes of the $LiFePO_4$ particles were strongly dependent on synthetic parameters such as concentrations and mole ratio of reactants. $LiFePO_4$ particles are nanoplates with the {010} face prominent, namely, with a short b-axis and the samples are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) test analysis. Fourier transform infrared spectroscopy (FTIR) analysis implied that the defect concentrations of the $Fe^{\bullet}_{Li}$ antisite in $LiFePO_4$ nanoplates were very low. The electrochemical behaviors were investigated by cyclic voltammetry measurements in the Li_2SO_4 aqueous electrolyte. It was shown that all samples could undergo lithium-ion deintercalation and intercalation upon oxidation and reduction at a scan rate range of 5–20 mV/s. Only the sample (formed in a $FeSO_4 \cdot 7H_2O$ to H_3PO_4 and $LiOH \cdot H_2O$ ratio of 1:1.5:2.7 with appropriate concentration) could undergo lithium-ion deintercalation and intercalation at a large scan rate even at 280 mV/s and showed excellent rapid charge and discharge performance. This provided a facile way to prepare high performance $LiFePO_4$ nanoplate cathode material for lithium ion batteries.

1. Introduction

The olivine lithium iron (II) phosphate ($LiFePO_4$) is a promising cathode material for use in lithium-ion batteries because of its high operating voltage (~3.4 V vs Li/Li^+), large theoretical capacity (~170 mAh g^{-1}), and thermal stability, as well as being inexpensive, nontoxic, and environmentally benign [1]. Although $LiFePO_4$ has been applied to practical uses, there is still a long way to go such as the severe safety problems, the economic and environmental problem. The flammable organic electrolytes used in lithium-ion batteries may cause the production of intense smoke or fire in the case of improper use such as overcharge or short-circuit [2–3]. Furthermore, the lithium battery is comparatively expensive owing to strict control of the assembling environment and the use of costly organic electrolytes [4].

To tackle these problems at their root, the aqueous rechargeable lithium battery (ARLB) was first proposed in 1994, and it has drawn significant attention in recent years [5–6]. Using an aqueous electrolyte has many advantages, such as safety, low cost, and high ionic conductivity, which make the ARLB quite attractive, especially as a power source for Electric Vehicles (EVs) [7]. In 1994, J. Dahn et al. reported a $VO_2/LiMn_2O_4$ rechargeable aqueous battery [8]. For the first time, $LiFePO_4$ was considered as a cathode material in ARLB's by Manickam et al. in 2006 [9]. He et al. [10], in an aqueous 0.5 M Li_2SO_4 solution, found that $LiFePO_4$ displayed both a surprisingly high initial capacity of 140 mAh g^{-1} at 1 °C rate and recognizable voltage plateau at a rate as high as 20C, which was superior relative to the other electrode materials in ARLB's. Recently, the same authors reported the high capacity decay in aerated electrolyte solution, amounting to 37% after only 10 cycles [11]. In the same study, they demonstrated qualitatively by a brief cyclovoltammetric test, that a carbon layer deposited from a vapor phase over $LiFePO_4$ particle, suppressed the capacity fade [11]. Recently, Wu's group reported a coated Li metal issued as negative electrode for an ARLB. Due to the "cross-over" effect of Li^+ on the coating, the ARLB delivers an energy density which is about 80% higher than that of traditional lithium-ion battery [12].

At the present, the disadvantage of $LiFePO_4$ is its low electronic and ionic conductivity, which limits the electrochemical properties according to the charge-discharge rate [13]. For the latter obstacle, both the size and orientation control of $LiFePO_4$ are necessary because lithium-ion diffusion in $LiFePO_4$ can only occur along [010] direction [14–16].

* Corresponding author.
E-mail address: lyan@sit.edu.cn (Y. Liu).

http://dx.doi.org/10.1016/j.ssi.2016.10.015
0167-2738/

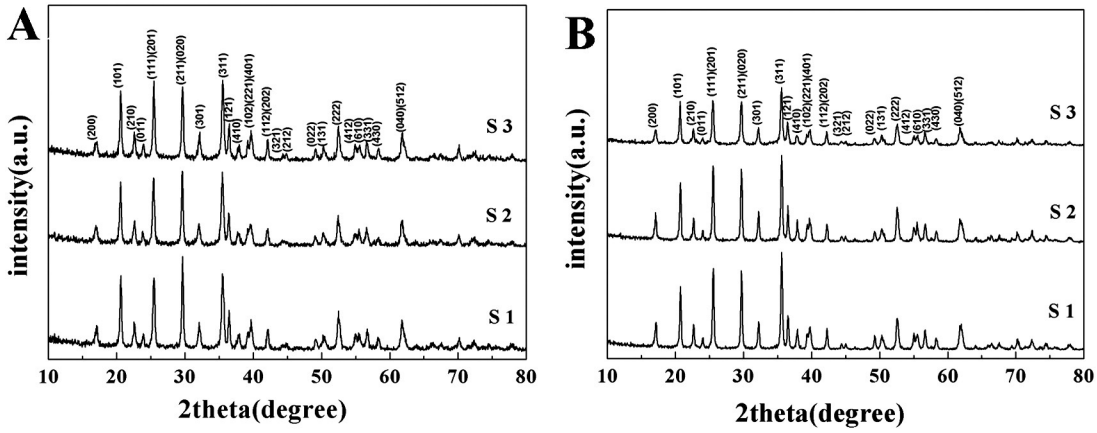

Fig. 1. XRD patterns of S 1, S 2 and S 3 Samples before (A) and after (B) carbon coating, respectively.

In this regard, it appears that controlling the crystal structure of $LiFePO_4$ with shortened lithium-ion diffusion pathways as well as oriented {010} facets can serve as an effective solution to improve ionic conductivity [17–18].

In the paper, we report a simple solvothermal method to fabricate $LiFePO_4$ nanoplates with a large (010) plane by controlling synthetic parameters such as concentrations and mole ratio of reactants. The sample can undergo lithium-ion deintercalation and intercalation normally at a large scan rate by cyclic voltammetry measurements in the Li_2SO_4 aqueous electrolyte and shows excellent rapid charge and discharge performance. This provides a facile way to prepare high performance $LiFePO_4$ nanoplate cathode material for lithium ion batteries.

2. Experimental

For the synthesis of $LiFePO_4$ Sample 1 (S 1), $FeSO_4 \cdot 7H_2O$, H_3PO_4, and $LiOH \cdot H_2O$ were applied as initial reactants in a molar ratio of 1:1.5:2.7 and ethylene glycol (EG) was used as a solvent. H_3PO_4 was slowly dropped into the LiOH solution under stirring. After a white suspension formed through the neutralization reaction, $FeSO_4$ solution was introduced to the suspension. The volume of ethylene glycol was 80 ml. After stirring for 40 min, the precursors were transferred into a sealed autoclave and were heated to 180 °C for 10 h. Then the autoclave was cooled down to room temperature. The obtained gray-green precipitates from the autoclave were washed with deionized water and ethanol, dried in a vacuum oven for 3 h at 80 °C. To achieve carbon coating, $LiFePO_4$ nanoplates were mixed with polypropylene and then carbonized at 650 °C for 3 h in Ar atmosphere. For the synthesis of $LiFePO_4$ Sample 2 (S 2), the procedures were kept unchanged except the concentration of precursors. The volume of ethylene glycol in S 2 was 130 ml. For the synthesis of $LiFePO_4$ Sample 3 (S 3), the procedures were kept unchanged except molar ratio of $FeSO_4 \cdot 7H_2O$, H_3PO_4, and $LiOH \cdot H_2O$ was 1:1:2.7 and the volume of ethylene glycol was 130 ml.

The phase purity of the sample was analyzed by X-ray diffraction (Bruker D8 advance, Germany). The particle morphologies of synthesized materials were characterized by a scanning electron microscopy (Quanta200). The crystal orientation was characterized by the transmission electron microscope (FEI, Tecnai G2F20). The antisite defects about synthesized materials were characterized by Fourier transform infrared spectroscopy.

To perform the cyclic voltammetric measurements, a standard three electrode cell was applied. The counter electrode and reference electrode were used a platinum gauze and a saturated calomel electrode, respectively. The working electrodes were made through a slurry coating procedure. The slurry consisted of 80 wt.% active material, 10 wt.% polyvinylidene fluoride (PVDF) and 10 wt.% active carbon dissolved in *N*-methyl pyrrolidinone (NMP), and was spread uniformly on Pt disk, and then were vacuum dried overnight at 100 °C. The electrolyte was 1 M Li_2SO_4, which were thoroughly deaerated with high-purified argon. All electrochemical measurements were performed on a CS310 electrochemical workstation.

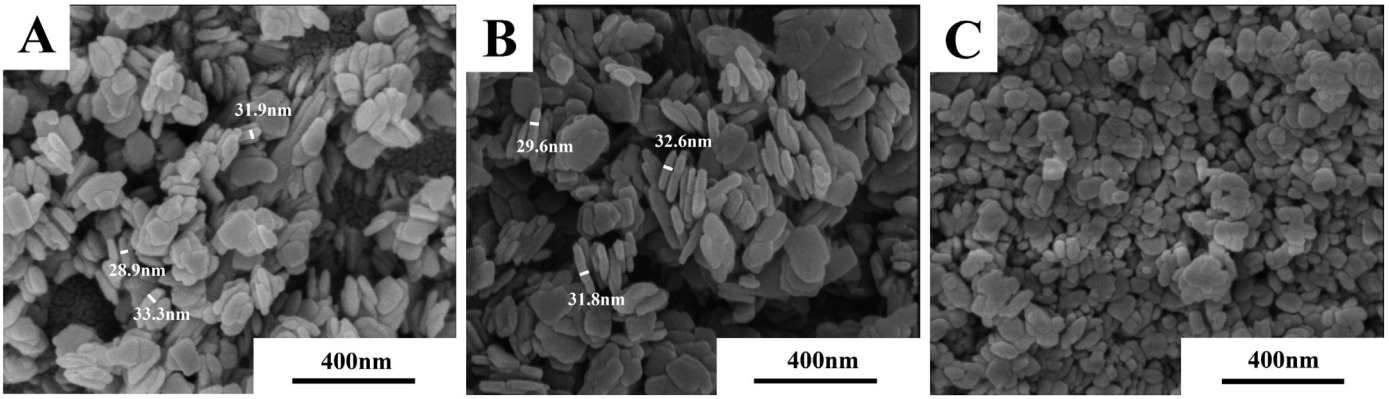

Fig. 2. SEM images of S 1(A), S 2(B) and S 3(C) before carbon coating, respectively.