Electrochimica Acta 56 (2011) 5667–5672

Contents lists available at ScienceDirect

Electrochimica Acta

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

Enhanced performance of $LiFePO_4$ through hydrothermal synthesis coupled with carbon coating and cupric ion doping

Bo Pei[a,b,1], Qiang Wang[a,b,1], Weixin Zhang[a,b,*], Zeheng Yang[a,b], Min Chen[a,b]

[a] School of Chemical Engineering, Heifei University of Technology, Hefei, Anhui 230009, PR China
[b] Anhui Key Laboratory of Controllable Chemical Reaction & Material Chemical Engineering, Hefei, Anhui 230009, PR China

ARTICLE INFO

Article history:
Received 16 August 2010
Received in revised form 8 April 2011
Accepted 9 April 2011
Available online 22 April 2011

Keywords:
Lithium ion batteries
Lithium iron phosphate
Hydrothermal synthesis
Modification
Post-heat treatment

ABSTRACT

A hydrothermal reaction has been adopted to synthesize pure $LiFePO_4$ first, which was then modified with carbon coating and cupric ion (Cu^{2+}) doping simultaneously through a post-heat treatment. X-ray diffraction patterns, transmission electron microscopy and scanning electron microscopy images along with energy dispersive spectroscopy mappings have verified the homogeneous existence of coated carbon and doped Cu^{2+} in $LiFePO_4$ particles with phospho-olivine structure and an average size of 400 nm. The electrochemical performances of the material have been studied by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge–discharge measurements. The carbon-coated and Cu^{2+}-doped $LiFePO_4$ sample (LFCu5/C) exhibited an enhanced electronic conductivity of 2.05×10^{-3} S cm^{-1}, a specific discharge capacity of 158 mAh g^{-1} at 50 mA g^{-1}, a capacity retention of 96.4% after 50 cycles, a decreased charge transfer resistance of 79.4 Ω and superior electrode reaction reversibility. The present synthesis route is promising in making the hydrothermal method more practical for preparation of the $LiFePO_4$ material and enhancement of electrochemical properties.

1. Introduction

Over the last decade, there has been an increasing demand for higher performance and cheaper rechargeable batteries in different electronic devices. Since phospho-olivines were first reported as cathode materials for rechargeable lithium batteries in 1997 [1], extensive studies have focused on $LiFePO_4$ material with olivine structure owing to its low cost, nontoxicity, environment benignity, cycling stability [2], high theoretical capacity (170 mAh g^{-1}) [3] and charge–discharge potential (3.45 V versus Li^+/Li). Moreover, $LiFePO_4$ has a good structural stability during charge–discharge cycles, which can improve safety at high temperatures compared with conventional cathode materials such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$.

However, a separation of FeO_6 octahedra by $PO_4{}^{3-}$ in the $LiFePO_4$ structure reduces its electronic conductivity, and a slightly distorted hexagonal close-packed oxygen array provides limited channels for lithium ion diffusion [1]. Thus when used as cathode materials for rechargeable lithium batteries, $LiFePO_4$ has drawbacks such as low electronic conductivity and slow lithium-ion diffusion across the $LiFePO_4/FePO_4$ boundary due to its intrinsic characteristics. Much effort has been made to eliminate these defects. Carbon coating from inorganic carbon black [4], organics [5,6] or polymers [3] has been used to improve the contact of C–$LiFePO_4$ and thereafter the efficiency of the electronic transfer to the material [7]. On the other hand, cation defects resulted from cation doping into the olivine structure can be beneficial to the diffusion of Li^+ in solid phase and increase electronic conductivity within the crystal, resulting in improved charge–discharge characteristics of the material [8–10].

Solid state reaction is commonly used to prepare carbon-coated and cation-doped $LiFePO_4$. However, due to inhomogeneous mixing of reagents in micro-scale, the nucleation rate and growth rate of the crystallites cannot always be consistent and it is difficult to prepare the product with a narrow particle size distribution. In this case, the regions in and near the center of big $LiFePO_4$ particles or agglomerates contribute very little to the electrochemical reaction, especially after many cycles of charge and discharge [11], since the lithium ions have to diffuse over a great distance between the surface and center of particles during lithium insertion or extraction. Besides, some impurities such as Li_3PO_4 [12], trivalent Fe_2O_3 and $Li_3Fe_2(PO_4)_3$ [13] cannot be avoided in the final product due to inhomogeneity of the reagents in solid state reaction, and they can reduce the energy density of $LiFePO_4$ [14] as inactive components. Due to these shortcomings, normally, it is difficult to produce $LiFePO_4$ materials with good electrochemical performances by solid state reaction. For example, Lee et al. [15] used a conventional

---

[*] Corresponding author at: School of Chemical Engineering, Heifei University of Technology, Tunxi Road 193#, Hefei, Anhui 230009, PR China.
Tel.: +86 551 2901450; fax: +86 551 2901450.
E-mail address: wxzhang@hfut.edu.cn (W. Zhang).

[1] These authors contributed equally to this work.

0013-4686/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2011.04.024

solid-state method to prepare $Li_{1.05}Fe_{0.997}Cu_{0.003}PO_4$, which had an initial discharge capacity of 145 mAh g^{-1} at a discharge current density of 0.1 mA cm^{-2} and a retention rate over 90% after 30 cycles. Peña et al. [16] also used solid state method to obtain $LiFePO_4$ and mixed it manually with micrometric copper in a 5:95 weight ratio to prepare Cu_{mic5}–$LiFePO_4$, which had a first discharge capacity of about 110 mAh g^{-1} at 17 mA g^{-1}.

Hydrothermal reaction has been a promising way for preparing nanomaterials with homogeneous crystal structure and morphology at a low cost of energy. Gerbaldi et al. [17] chose hydrothermal reaction and post-heat treatment to prepare carbon-coated $LiFePO_4$ with hexadecyltrimethylammonium bromide (CTAB) as carbon source, which had a specific discharge capacity of ~140 mAh g^{-1} at 34 mA g^{-1} and the capacity is higher than that (<60 mAh g^{-1}) of pure $LiFePO_4$. Zhao et al. [18] adopted a one-pot hydrothermal method to prepare $LiFePO_4$ with M (M = La, Ce, Nd, Mn, Co, Ni) doping and then used the post-heat treatment for carbon coating. Although the conductivity of the products was increased to some extent, the discharge capacity and electronic conductivity were not improved significantly. Similarly, Ou et al. [19] synthesized $LiFePO_4$ hydrothermally with simultaneous magnesium doping and then with subsequent calcination for carbon coating to prepare $Li_{0.98}Mg_{0.02}FePO_4/C$. For comparison, $LiFePO_4/C$ was also prepared under the same conditions but without magnesium doping. The obtained results demonstrated that there was little doping effect in terms of discharge capacity and electronic conductivity. These results show that the one-pot hydrothermal method for $LiFePO_4$ synthesis and cation doping is not adequate to obtain the $LiFePO_4$ material with desirable electrochemical performances. This is probably due to the mild hydrothermal condition adopted, which cannot achieve effective cation doping in $LiFePO_4$ crystals.

In this study, hydrothermal reaction was adopted to synthesize pure $LiFePO_4$ particles with a narrow size distribution, which was then modified with carbon coating and cupric cation (Cu^{2+}) doping simultaneously by a subsequent heat treatment. The post-heat treatment was chosen to make the final product form a solid solution steadily, with the aim to improve its electrochemical properties. It is noted that in order to get homogeneous modification, sucrose and $Cu(Ac)_2$ as carbon and Cu^{2+} sources have been mixed with the pre-prepared pure $LiFePO_4$ in aqueous solution before the post-heat treatment. In comparison with the $LiFePO_4$ composite prepared by a conventional solid-state method [15,16] or by one-pot hydrothermal method followed by a heat treatment for carbon coating [18], the present carbon-coated and Cu^{2+}-doped $LiFePO_4$ material demonstrates higher electronic conductivity and better rate capability.

2. Experimental

2.1. Preparation of $LiFePO_4$ samples

The samples were synthesized by a hydrothermal method, followed by modification through heat treatment. Starting materials were $LiOH·H_2O$, $FeSO_4·7H_2O$ and $NH_4H_2PO_4$ (Shanghai Chemical Reagents Corporation, China) in a stoichiometric ratio 3:1:1. Firstly, $FeSO_4$ (1.5 mol L^{-1}) and $NH_4H_2PO_4$ (1.5 mol L^{-1}) aqueous solutions were mixed together and then LiOH aqueous solution (4 mol L^{-1}) was added to the mixture under vigorous stirring, which was then transferred to an autoclave made of stainless steel (Model WZF-1L, Weihai Automatic Control Reaction Kettle Corporation, China) and heated at 200 °C for 24 h. After the hydrothermal reaction, the autoclave was cooled to room temperature and the resulted precipitate was filtered, washed and dried at 60 °C for 12 h.

The post-heat treatment was used to modify the prepared $LiFePO_4$ with carbon coating and cation doping. Sucrose (Shanghai Chemical Reagents Corporation, China) in 10:100 weight ratio to $LiFePO_4$ powders, and $Cu(CH_3COO)_2$ (Shanghai Chemical Reagents Corporation, China) in 0:100, 3:100, 5:100 and 7:100 molar ratio to $LiFePO_4$, respectively, were firstly dissolved in distilled water to form a transparent solution, with a liquid–solid ratio of 2:1 (mL:g), then mixed with $LiFePO_4$ powders at room temperature using an ultrasonic device operated at 250 W and 40 kHz (KQ3200E, Kunshan Ultrasonic Instruments Corporation, China) for 20 min to form a uniform slurry. The slurry samples were dried at 90 °C for 12 h to remove the excess water, and the final precursors were obtained. The precursors were first calcinated at 350 °C for 4 h (heating rate: 4.0 °C min^{-1}) and then at 650 °C for 9 h (2.0 °C min^{-1}) in a tube furnace with N_2 atmosphere.

The pure $LiFePO_4$ with subsequent heat treatment but without carbon coating and Cu^{2+} doping was also prepared and named as LFP. The material coated with carbon and doped with 0%, 3%, 5% and 7% Cu^{2+} were named as LFP/C, LFCu3/C, LFCu5/C and LFCu7/C, respectively.

2.2. Characterization of the samples

The composition and phase purity of the prepared samples were examined by X-ray diffraction (XRD) based on a D/max-γB X-ray diffractometer (Shimadzu International Trading Corporation, Japan) with a Cu Kα radiation source ($\lambda = 0.154106$ nm) operated at 40 kV and 80 mA. Lattice parameters for the lithium iron phosphate were refined by Jade 5.0 software. Transmission electron microscopy (TEM) images of the samples were taken with a H-800 transmission electron microscope (Hitachi Limited Corporation, Japan), operated at an accelerating voltage of 200 kV. The samples were also examined by JEOL-7500B and JSM-6490LV scanning electron microscopes (JEOL Limited Corporation, Japan) and energy dispersive spectroscopy (EDS), operated at an accelerating voltage of 20 kV after they were dispersed on a silicon substrate in alcohol and then coated with gold. The carbon content in the samples was tested using a Perkin-Elmer Series II CHNS/O (USA) elemental analyzer.

2.3. Electrochemical measurements

The cathode was prepared by mixing 80 wt% active material, 15 wt% acetylene black (Beijing Chemical Reagents Corporation, China) and 5 wt% polyvinylidene fluoride (PVDF, Shanghai Chemical Reagents Corporation, China) as a binder in a solvent of *N*-methyl-2-pyrrolidone (NMP, Shanghai Chemical Reagents Corporation, China) to form a homogeneous slurry. Then the mixed slurry was cast onto aluminum foil with the slurry thickness controlled. After the evaporation of the solvent at 60 °C for 2 h in air, the cathode was roll-pressed and cut into pellets of required size for coin-cell fabrication, then the pellets were further dried under high vacuum at 120 °C for 5 h. Lithium foil (Energy Lithium Limited Corporation, China) was used as the anode. The liquid electrolyte used was 1 mol L^{-1} $LiPF_6$ in a 1:1 (volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), and the separator was a polypropylene membrane with micro-pores (Celgard 2400). The coin-type cells (CR2032) were assembled in an Ar-filled dry glove box. The galvanostatic charge–discharge experiment was conducted using a battery testing system (BTS-5 V/10 mA, Neware Technology Limited Corporation, China) from 2.5 to 4.2 V (versus Li^+/Li) at a specific current of 50–500 mA g^{-1} and room temperature. Cyclic voltammetry (CV) was performed at a scan rate of 0.05 mV s^{-1} from 2.5 to 4.2 V (versus Li^+/Li) on an electrochemical workstation (CHI-660B, Shanghai Chenhua Instrument Limited Corporation, China). In electrochemical impedance spectroscopic (EIS) measurements, the excitation potential applied to the cells was 5 mV and the frequency ranged from 100 kHz to 10 mHz.