Electrochimica Acta 186 (2015) 117–124

Contents lists available at ScienceDirect

Electrochimica Acta

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

Electrochemical properties of self-assembled porous micro-spherical $LiFePO_4$/PAS composite prepared by spray-drying method

Zhaoyong Chen*, Qunfang Zhao, Ming Xu, Lingjun Li, Junfei Duan, Huali Zhu

School of Physics and Elctronic Science, Changsha University of Science and Technology, Changsha 410004, Hunan Province, China

ARTICLE INFO

Article history:
Received 23 August 2015
Received in revised form 13 October 2015
Accepted 22 October 2015
Available online 29 October 2015

Keywords:
Lithium iron phosphate
Cathode materials
Porous structure
Self-assembled micro-spherical particles
Spray drying

ABSTRACT

Polyacene (PAS) coated self-assembled porous micro-spherical $LiFePO_4$ cathode material is successfully synthesized by spray drying method. The crystal structure of the sample is examined by X-ray diffraction (XRD). The micro-spherical morphology with porous structure is observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrochemical properties are investigated via galvanostatic charge-discharge experiments and electrochemical impedance spectroscopy (EIS) analysis. The material exhibits a high lithium ion diffusion coefficient about $10^{-12}\,cm^2\,S^{-1}$, excellent electrochemical properties and good cyclability. The initial discharge capacity is as high as 168 mAh/g at 0.1 C rate, and the capacity retention is approximately 100% after 100 cycles at 1 C rate, almost no capacity fading. All demonstrate that self-assembled micro-spherical particles with nano primary particles and porous structure are benefit to improve the electrochemical performance of cathode materials.

1. Introduction

Due to the growing shortage of natural energy, the flourish of electronics and information industry and rapid development of electric vehicles (EV) in recent years, lithium-ion battery has attracted extensive studies of researchers. Since $LiFePO_4$ was first reported in 1997 by Padhi et al., olivine $LiFePO_4$ has been investigated intensively as one of the most promising cathode materials for rechargeable lithium-ion batteries [1–3].

$LiFePO_4$ has attracted remarkable attention due to its high theoretical capacity of 170 mAh/g, stable voltage plateau (vs. Li/Li^+), environmental friendly, low cost raw material, excellent thermal stability and good cycle performance. But it has two main shortcomings: (1) the low intrinsic electronic conductivity; (2) the slow diffusion coefficient of Li^+ ions [4,5]. In order to overcome these drawbacks, many efforts have been made by researchers, such as coating conductive carbon and conductive polymers, metal particles or metal oxides, doping other element into the crystal lattice, reducing the particle size and controlling the morphology, and selecting suitable synthesis methods [6–12]. To increase the diffusion coefficient of Li^+ ions, more attention has been put on nanoparticles owing to the short diffusion path of the lithium ion [13,14]. Nevertheless, the larger specific surface area of the nanopowders requires more polyvinylidene fluoride (PVDF) during the course of electrode preparation, resulting in increased resistance of the cell. Similarly, the contact between the particles and electrolyte is increased, which may increase the dissolution of the iron [1–18]. Furthermore, the nanoparticles result in low volume energy density [19]. So, nano lithium iron phosphate particles have not only obvious advantages, but also tiresome drawback. Studies have shown that spherical particles have better fluidity with less contact interface than irregular particles, which move easily and occupy the available vacancies, leading to higher volume energy density [20]. Therefore, larger and regular spherical particles self-assembled with nano primary particles have been prepared here.

So far, there are many synthesis routes for the preparation of $LiFePO_4$, such as solid-state reaction [21], hydrothermal route [22], sol-gel method [23], carbothermal reduction method [24], spray-drying method [25,26]. The solid-state route is traditional and simple for preparing $LiFePO_4$. But prepared particles are sub-micro and irregular [27]. The hydrothermal route is applied to synthesize fine and sheet particles [28]. In addition, the high quality $LiFePO_4$/C nanomaterials with ideal structure are synthesized by ion exchange approach [29]. In this work, spray-drying method was applied to prepare self-assembled porous micro-spherical $LiFePO_4$ coated with polyacene (PAS) as conductive polymer by pyrolysis of the phenolic resin, which delivered good cyclability. Thereinto, the large particles with size of 6-10 μm are self-assembled with nano primary particles (about 100 nm). The electrochemical

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* Corresponding author.
E-mail address: chenzhaoyongcioc@126.com (Z. Chen).

http://dx.doi.org/10.1016/j.electacta.2015.10.143
0013-4686/

performance of $LiFePO_4$ by spray-drying method was investigated. As a comparison, polyacene coated $LiFePO_4$ was synthesized by solid-state method.

2. Experimental

2.1. material preparation and characterization

$LiFePO_4$/PAS composite was synthesized via spray-drying method. Stoichimetric quantities of Li_2CO_3 (99.5%), $FeC_2O_4 \cdot 2H_2O$ (99.7%), $(NH_4)H_2PO_4$ (99.25%) and phenolic resin were mixed together well by ball-milling for 4 h in ethanol, and then spray-dried. The powder was calcined at 400 °C for 6 h and then 750 °C for 12 h under N_2. Eventually the self-assembled porous micro-spherical $LiFePO_4$/PAS composite (SALFP) was synthesized successfully, with 1.9 wt.% PAS in the sample.

Stoichimetric amounts of Li_2CO_3 (99.5%), $FeC_2O_4 \cdot 2H_2O$ (99.7%), $(NH_4)H_2PO_4$ (99.25%) and phenolic resin were mixed thoroughly by ball-milling for 4 h in ethanol, the resulting slurry was dried at 35 °C for 24 h to evaporate the ethanol, subsequently ball-milled again for 30 min. Finally the as-prepared precursor was calcined at 400 °C for 6 h and then 750 °C for 12 h under N_2 to prepare the $LiFePO_4$/PAS composite (SLFP).

X-ray diffraction (XRD, Rigaku D/Max 200PC, Japan) with a graphite monochromator and Cu kα radiation ($\lambda = 0.154505$ nm), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to detect the crystal structure and morphology of $LiFePO_4$/C particles. The energy dispersive spectroscopy (EDS) was performed using OXFORD 7426 as the SEM attachment with the acceleration voltage of 20 kV.

2.2. Electrochemical measurements

The positive electrode consisted of 80 wt% as-prepared composites, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) as a binder, and metal Al foil was used as collector. Celgard 2400 was used as separator which was soaked in 1.0 mol L^{-1} $LiPF_6$/EC + DMC (EC: DMC = 1:1 in volume ratio) electrolyte. The SALFP loading and SLFP loading were about 4.00 mg cm^{-2}. Lithium metal foil was used as the counter electrode during electrochemical measurements. All cells were assembled in an argon-filled glove box. The constant current-constant voltage (cc-cv) charge and galvanostatic discharge tests were carried out in the voltage range of 2.5-4.1 V using a Land BT2001A automatic battery test system. The electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 10 mHz to 10^5 Hz on a CHI660B electrochemical working station (Chenhua, Shanghai, China), and the perturbation amplitude was controlled at ±5 mV.

3. Results and discussion

The synthetic flow chart in this paper is showed in Fig. 1. The synthetic process includes droplet generation, spray drying, carbonization. Firstly, The precursor solution was prepared by introducing Li_2CO_3, $FeC_2O_4 \cdot 2H_2O$, $(NH_4)H_2PO_4$ and phenolic resin into ethanol. Next, the mixed precursor solution was continuously stirred for dispersion and simultaneously transported to the spray reactor by the high-pressure pump. Then the droplets were formed by an atomization process of the precursor solution using a nebulizer. The droplets were dried as a result of contact with hot air in the drying tower, in which the ethanol evaporated and phenolic resin attached on the surfaces of raw materials. At the end of the drying procedure, the porous spherical precursors were generated [30]. Subsequently, these particles were heated in a tube furnace under N_2, and the $LiFePO_4$/PAS composites were synthsized successfully.

Fig. 2 presents the XRD patterns of SALFP and SLFP. All samples can be indexed to the olivine $LiFePO_4$ with orthorhombic crystal structure (JCPDS No. 83-2092, space group Pnma), which exhibit good crystallinity. Moreover, no impure peaks are found in the patterns of SALFP and SLFP, which illustrate the phase purity of the samples.

As shown in SEM images (Fig. 3), the porous micro-spherical particles self-assembled with nano primary particles were obtained successfully via spray-drying method (Fig. 3a-c) while the particles synthesized by solid-state method were irregular (Fig. 3d-f). Compared with irregular particles, the self-assembled micro-spherical particles are in favor of increasing the volume energy density of the materials owing to better fluidity of spherical particles with less contact interface than irregular particles, which move easily and occupy the available vacancies. In addition, these

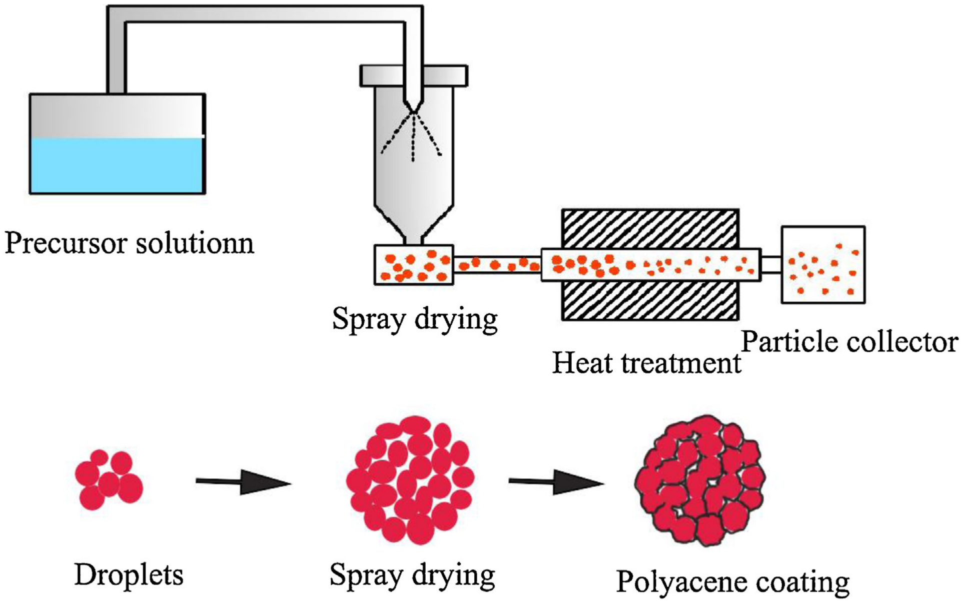

Fig. 1. A schematic diagram of spray drying method.