



# Synthesis of porous nano/micro structured $\text{LiFePO}_4/\text{C}$ cathode materials for lithium-ion batteries by spray-drying method


Xiao-mei GUAN<sup>1,2</sup>, Guo-jun LI<sup>1,2</sup>, Chun-yang LI<sup>1</sup>, Rui-ming REN<sup>1</sup>

1. Liaoning Key Laboratory for New Energy Battery, Dalian Jiaotong University, Dalian 116028, China;

2. School of Materials Science and Engineering, Dalian Jiaotong University, Dalian 116028, China

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**Abstract:** In order to enhance electrochemical properties of  $\text{LiFePO}_4$  (LFP) cathode materials, spherical porous nano/micro structured LFP/C cathode materials were synthesized by spray drying, followed by calcination. The results show that the spherical precursors with the sizes of 0.5–5  $\mu\text{m}$  can be completely converted to LFP/C when the calcination temperature is higher than 500  $^\circ\text{C}$ . The LFP/C microspheres obtained at calcination temperature of 700  $^\circ\text{C}$  are composed of numerous particles with sizes of  $\sim 20$  nm, and have well-developed interconnected pore structure and large specific surface area of 28.77  $\text{m}^2/\text{g}$ . The specific discharge capacities of the LFP/C obtained at 700  $^\circ\text{C}$  are 162.43, 154.35 and 144.03  $\text{mA}\cdot\text{h/g}$  at 0.5C, 1C and 2C, respectively. Meanwhile, the capacity retentions can reach up to 100% after 50 cycles. The improved electrochemical properties of the materials are ascribed to a small  $\text{Li}^+$  diffusion resistance and special structure of LFP/C microspheres.

**Key words:**  $\text{LiFePO}_4/\text{C}$  cathode; nano/micro structure; porous material; spray drying; electrochemical properties

## 1 Introduction

Olivine-structure lithium iron phosphate (LFP) has elicited much attention since its discovery in 1997 [1] because of its low cost, high energy density, safety, structure stability and environmental benignity [2,3]. However, two intrinsic drawbacks of LFP, namely, poor electronic conductivity ( $\sim 10^{-11}$  S/cm) and lithium ion diffusion coefficient ( $\sim 1.8 \times 10^{-14}$   $\text{cm}^2/\text{s}$ ) at room temperature [4], limit its commercial application. Considerable measures, such as conductive-layer coating [4,5], supervalent cation doping [6,7] and size reduction [8,9] have been implemented to overcome these drawbacks. Well-dispersed carbon can provide pathways for the transport of electrons, and reductive carbon can avoid the formation of  $\text{Fe}^{3+}$  [4,10]. Nanoparticles can provide an increased number of surface reaction sites for lithium ions and shorten the diffusion length of lithium ions [11]. However, nano-sized particles aggregate and absorb moisture from air. Technically, micro-sized spherical particles containing clusters of nanoparticles can address the drawbacks of nanoparticles, and spherical particles have better fluidity and higher packing density than the irregular-shaped

powders [12]. Simultaneously, porous strategy allows for the efficient percolation of electrolytes through the electrode, enhancing the diffusion of  $\text{Li}^+$  between the active materials [4]. Based on the above facts, LFP/C microspheres composed of interconnected pores and nanoparticles with a homogeneous carbon coating are believed to be an optimized structure and are expected to possess excellent electrochemical properties.

In this work, the spray drying method was employed to prepare spherical precursor as this method is a facile and scalable technique to fabricate micro-sized spherical materials. It was reported that the spherical LFP materials were synthesized by spray drying method in many researches [13–15]. Final LFP/C composites consisting of nanoparticles and interconnected pores were obtained by calcining precursor at different temperatures for 4 h. The structure, morphology and electrochemical performance of LFP/C materials were characterized and tested.

## 2 Experimental

### 2.1 Synthesis

A mixture of the as-synthesized  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{LiOH} \cdot \text{H}_2\text{O}$  (AR), citric acid (AR), oxalic acid (AR) and

de-ionized water was ball-milled for 15 h to obtain a precursor slurry. The molar ratios of both  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  to  $\text{LiOH} \cdot \text{H}_2\text{O}$  and citric acid to oxalic acid were 1:1. Citric acid and oxalic acid were used as chelating agent, reductant and carbon source. To obtain spray-dried solution, the slurry was placed in an air-circulating oven at 45 °C for 48 h and then diluted to a solution with a mass fraction of 10%. After being stirred at room temperature for 3 h by magnetic stirrers, the solution was spray-dried at 140 °C and 70 °C (inlet and outlet temperatures, respectively) at a feed rate of 450 mL/h to obtain the precursor (light yellow precipitate). During the spray drying step, the feeding spray solution was pumped to a tank reactor with a stream of hot air and sprayed into aerosol. The precursor powder formed as the moisture evaporated rapidly. The dry powder was finally separated from moist air in a centrifugal atomizer and was collected in a vial. Lastly, the precursor was calcined at different temperatures in pure Ar atmosphere. LFP/C composites were obtained as the temperature decreased.

## 2.2 Characterization

TG–DSC measurement was carried out with a STA904 apparatus from room temperature to 800 °C in Ar atmosphere at a heating rate of 1/6 °C/min. X-ray diffraction (XRD, D/Max-Ultima<sup>+</sup>) was performed with an Empyrean X-ray diffractometer with  $\text{Cu K}_\alpha$  radiation ( $V=40$  kV,  $I=40$  mA) to identify the crystalline phase of all samples. The scanning range was from 10° to 90° with a step size of 0.02°. The micro-morphology and particle size of the samples were investigated through scanning electron microscopy (SEM, JEOL/JSM–6360LV). Field emission SEM (FE-SEM, SUPRA 55) was applied to obtaining cross-sectional images of the microspheres. Nitrogen adsorption–desorption isotherm was measured at 77 K after degassing the samples at 125 °C for 4 h, and the tests were conducted with a specific-surface-area analyzer (3SI-MP–11) through Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods.

## 2.3 Electrochemical measurements

The electrochemical properties of the as-prepared LFP/C powders as active cathode materials were evaluated by using a two-electrode coin-type cell (CR2032) of  $\text{Li}|\text{LiPF}_6|\text{LFP/C}$  ( $V(\text{EC}):V(\text{EMC}):V(\text{DMC})=1:1:1$ ). The separator was a polypropylene membrane (Celgard 2400), and the lithium metal served as the counter and reference electrode. The working cathode slurry was fabricated by mixing the active material (LFP/C), super P II and polyvinylidene fluoride (PVDF) at a mass ratio of 80:7:13 in *N*-methyl pyrrolidinone (NMP). The slurry was prepared as follows: PVDF (13%, mass fraction) was dissolved in NMP to obtain a uniform,

transparent and viscous liquid. Then, the LFP/C (80%, mass fraction) and super P II (7%, mass fraction) were added into the solution in turn. The suspension was stirred for 6–8 h to obtain uniform slurry. The slurry was pasted onto an Al foil with a thickness of 50  $\mu\text{m}$  and dried at 70 °C for 4 h in an oven and 110 °C for 12 h in vacuum. After cooling to room temperature, the Al foil with active material was punched into disks with 10 mm in diameter. LFP/C was approximately 4.0 mg in each disk.

The cells were assembled in a glove box (Unilab, MB–20–G) filled with dry and high-purity Ar gas. Galvanostatic charge–discharge tests at different current densities with voltages ranging from 2.0 to 4.2 V were performed on a Neware battery tester. A cyclic voltammetry (CV) test was conducted on an electrochemical workstation (CHI660B, CH Instruments) in a voltage range of 2.5 to 4.2 V and at a scan rate of 0.1 mV/s. Electrochemical impedance spectroscopy (EIS) was also conducted on an electrochemical workstation (AUTOLAB, PGSTAT302N) in a frequency range of 100000–0.01 Hz. All tests were performed at room temperature.

## 3 Results and discussion

### 3.1 Phase composition

Figure 1 shows the TG and DSC curves of the precursor. The TG curve presents several mass losses and the DSC curve displays the corresponding endothermic or exothermic peaks. The first mass loss (about 13%) from room temperature to 170 °C is caused by the release of physically absorbed water and crystal water of citrate [16]. The second mass loss corresponding to the endothermic peaks at approximately 180 °C results from the dehydration of oxalate [17]. The next mass loss accompanied by the endothermic peak from 225 to 300 °C is attributed to the decomposition of citrate [16]. The weak endothermic peak between 300 and 400 °C is due to the decomposition of oxalate into amorphous

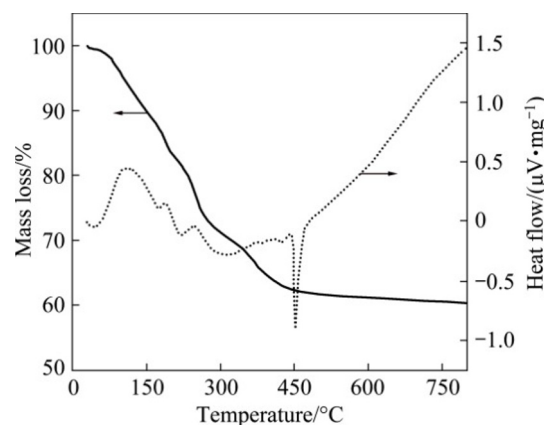


Fig. 1 TG–DSC curves of precursor

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