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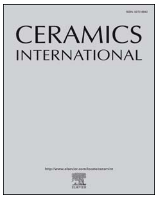

Formic acid as additive for the preparation of high-performance $FePO_4$ materials by spray drying method

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ABSTRACT

High-performance ferric phosphate ($FePO_4$), with well-defined ellipsoid morphology and uniform particle size distribution, is successfully fabricated via a green spray drying method with formic acid as additive. It is found that the added formic acid plays a crucial role for the formation of the well-distributed $FePO_4$ particles. Benefited by the outstanding structure and properties of ferric phosphate prepared above, a high performance of lithium iron phosphate ($LiFePO_4$) has been prepared. It exhibits high capacity, especially at high charging/discharging rate (158.4 mAh g^{-1} at 0.2 C and 107.3 mAh g^{-1} at 10 C), and excellent cycling stability (without capacity fading after cycling for 200cycles at 1 C). All these impressive electrochemical performance could be ascribed to the $FePO_4$ precursor, and further attributed to the addition of formic acid, which may play as a template, resulting in the well-defined morphology, uniform particles size distribution, hierarchical pore structure, and high surface area of the ferric phosphate.

1. Introduction

Lithium iron phosphate ($LiFePO_4$) was first reported by Goodenough and co-workers in 1997 [1]. Compared to other cathode material [2,3], $LiFePO_4$ holds good thermal stability and excellent cycle stability with a high theoretical capacity of 170 mAh g^{-1} and a flat charge/discharge voltage platform of 3.45 V [4,5]. Moreover, the low-cost and environmental friendly raw materials have further entitled $LiFePO_4$ to be a promising cathode material for lithium-ion batteries [5–8]. Recently, much effort has been devoted to synthesizing $LiFePO_4$ with high capacity and good cycling life. In fact, the excellent electrochemical performance of $LiFePO_4$ mainly relies on the texture and morphology of the precursor $FePO_4$. Therefore, a facile and green synthesis method to prepare $FePO_4$ with good textural properties becomes critical [9–11].

The commonly used method to prepare $FePO_4$ is precipitation in solution. Soluble ferric salts and phosphates are usually used as raw materials and alkali as precipitant during such progress [12–22]. Typically, the involvement of the washing process to remove impurity ions from the product highly consumes both time and water. To alleviate these issues, spray drying method has been employed as an alternative way to prepare $FePO_4$ in our group.

Generally, spray drying method uses the atomizer to disperse the precursor mixture solution containing Fe^{3+}, PO_4^{3-}, and additives, into tiny droplets and evaporates the solvent by the thermal drying medium. $FePO_4$ is finally obtained by subsequent calcination process. To facilitate the removal of impurity ions except for Fe^{3+} and PO_4^{3-} during calcination, thermolabile and soluble raw materials such as ferric nitrate ($Fe(NO_3)_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and ammonia ($NH_3 \cdot H_2O$) are often used in spray drying process. It is worth mentioning that the commonly used additive of ammonia usually results in the emission of flue gas and particle aggregated during the synthesis progress. Therefore, it becomes critical to find a substitute additive to supplement the process.

In this work, formic acid (HCOOH) was used as substitute additive of ammonia in the preparation of $FePO_4$ with spray drying method. Amazingly, it was found that formic acid not only helped to resolve the flue problem of toxic ammonia, but also produced the $FePO_4$ materials with well-defined ellipsoid morphology, uniform particle size distribution, high surface area, and hierarchical pore structures. With the materials as precursor, $LiFePO_4$ with outstanding electrochemical performance has been successfully prepared.

2. Experimental

2.1. The preparation of $FePO_4$ and $LiFePO_4$

Firstly, 0.4 mol L^{-1} ammonium dihydrogen phosphate ($NH_4H_2PO_4$,

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99.0%, Kermel Chemical Reagents Co., Tianjin) were added to 0.4 mol L^{-1} ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98.5%, Aladdin Chemical Reagents Co., Shanghai) with stirring for 30 min. Subsequently, formic acid (HCOOH, 88.0%, Kermel Chemical Reagents Co., Tianjin) with a certain molar ratio to Fe^{3+} (Fe^{3+} : HCOOH = 1:10, 1:15, 1:20 and 1:25) was added drop by drop into the mixed solution under vigorous stirring. The mixture was continuously stirred at 70 °C for a certain time (3, 12, 24, 30, 36 h, respectively). Then, the mixture went through a pneumatic nozzle spray dryer (Aina Precision Instrument Factory, Shanghai) with an inlet air temperature of 190 °C and a feeding rate of 600 ml h^{-1}. The obtained powders were calcinated under air flow at the rate of 10 °C min^{-1} from room temperature to 600 °C and maintained for 6 h in a muffle furnace (Shanghai Science and Technology Instruments Co., Shanghai), then naturally cooled down to room temperature. The sample was marked as FA-$FePO_4$. In order to understand the role of formic acid in the synthesis process, two intermediate samples were taken from the different stages of preparation process. Sample a-$FePO_4$ was filtered from the stage of mixed solution after being kept at 70 °C for 36 h. Sample b-$FePO_4$ was the evaporation mixture at the stage of spray drying process, which possibly consisted of $FePO_4$ and ammonium nitrate (NH_4NO_3). Sample FA-free-$FePO_4$ was the product using almost the same process as FA-$FePO_4$ preparation, but without formic acid (shown in Fig. 1).

The $LiFePO_4$ coated carbon was prepared as following procedures: FA-$FePO_4$, Li_2CO_3 (97%, Guanghua Chemical reagents Co., Guangdong), glucose ($C_6H_{12}O_6$, 99.9%, Boao Biotechnology Co., Shanghai) and ethanol (CH_3CH_2OH, 99.7%, Chemical Reagents Co., Nanjing) were mixed thoroughly, and then underwent ball milling at 400 r min^{-1} for 12 h. The resultant sample was firstly heated from temperature to 350 °C with a heating rate of 5 °C min^{-1} and calcinated at 350 °C for 2 h in a tube furnace (Zhonghuan Electric Furnace Co., Tianjin). Then the sample was further heated up to 600 °C at the rate of 5 °C min^{-1} and maintained for 18 h before cooled down to room temperature. Nitrogen (N_2, 99.999%, Yuejia Gas Co, Guangzhou) is used to keep the atmosphere inert throughout the whole calcination process. The sample of $LiFePO_4$ coated carbon was then obtained, marked as FA-LFP/C. To facilitate the evaluation of electrochemical performance, commercial material was chosen as reference sample.

2.2. Characterization of $FePO_4$ and $LiFePO_4$

The crystalline phase of samples was characterized by powder X-ray diffraction (XRD, TD-3500, Tong-da, China) with Cu Kα radiation at 40 kV and 30 mA, scanning from 10° to 70° at 4.8° min^{-1}. The morphology and microstructure of samples were characterized by Merlin field emission scanning electron microscopy (SEM, Carl Zeiss, Germany) and JEM-2100HR microscope transmission electron microscope (TEM, JEOL, Japan). X-ray photoelectron spectra (XPS) were recorded on ESCALAB250 (Thermo-VG Scientific, USA). The thermo-degradation of the present samples was investigated by thermo-gravimetric analyzer (Q600SDT, USA). The local structure was identified by a Fourier transform infrared spectrometer (FTIR, TENSOR27, Bruker, Germany). Specific surface areas and pore size distribution were measured by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption at 77 K on a Tristar II 3020 gas adsorption analyzer (Micromeritics, USA).

2.3. Electrochemical performance test of $LiFePO_4$

The cathode materials consisted of $LiFePO_4$, carbon black and polyvinyllidene fluoride (PVDF, Acoma Group, France) with mass ratio of 8:1:1. The three compositions were mixed with N-methyl-pyrrolidone (NMP, 99%, Kermel Chemical Reagents Co., Tianjin), then stirred for 5 h to deploy uniform slurry. The as-prepared slurry was coated on 20 μm-thick aluminum foil (LEEDEN Energy Storage Materials and Technology Co., Suzhou) and dried at 80 °C for 12 h under vacuum. The assembly of the cells was carried out in a type of Lab-2000 glove box by using metallic lithium foil as anode, polypropylene micro-porous as separator, and 1 mol L^{-1} lithium hexafluorophosphate ($LiPF_6$) with a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) solution as the electrolyte (1 mol L^{-1} $LiPF_6$/EC/DMC, Newzhoubang Technology Co., Shenzhen). Then the cells were charged and discharged over a voltage of 2.5–4.2 V at different charge/discharge rate (0.2 C, 0.5 C, 1 C, 5 C, 10 C) by using a Neware battery testing system (Neware Electronics co., Shenzhen). All the tests were carried out at room temperature.

3. Results and discussion

3.1. The characterization of $FePO_4$

Fig. 2a shows a typical SEM image of the spherical morphology of the FA-free-$FePO_4$ sample with a size range of 1–5 μm. The magnified image in Fig. 2b further reveals that the FA-free-$FePO_4$ spheres are actually densely stacked by irregular spherical particles with a size range of 200–400 nm. Interestingly, from the SEM images of Fig. 2c and d, both b-$FePO_4$ and FA-$FePO_4$ consist of ellipsoid particles with size of about 200 nm and 100 nm, respectively. The particle size of FA-$FePO_4$

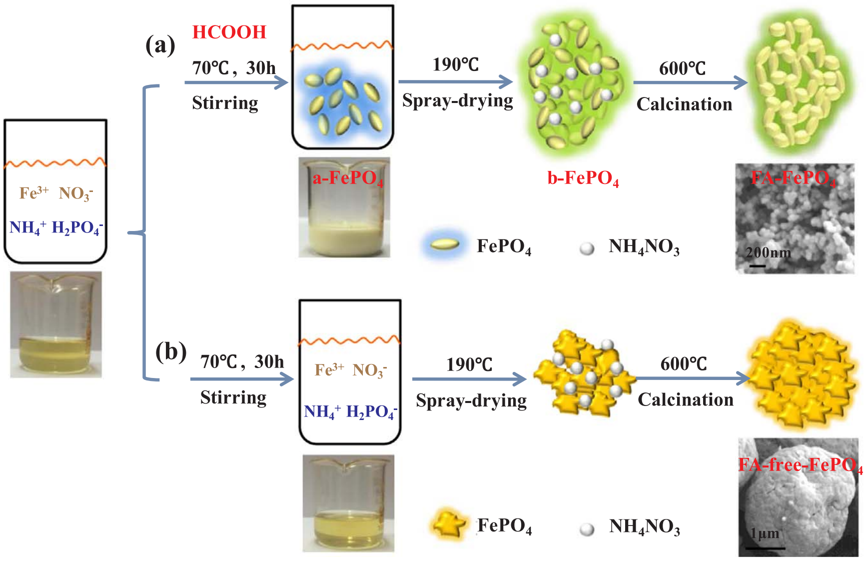

Fig. 1. The schematic synthesis process of $FePO_4$ with (a) and without (b) formic acid.