



## Effect of symbiotic compound $\text{Fe}_2\text{P}_2\text{O}_7$ on electrochemical performance of $\text{LiFePO}_4/\text{C}$ cathode materials



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### ABSTRACT

In order to study the effect of symbiotic compound  $\text{Fe}_2\text{P}_2\text{O}_7$  on electrochemical performance of  $\text{LiFePO}_4/\text{C}$  cathode materials, the  $\text{LiFePO}_4/\text{Fe}_2\text{P}_2\text{O}_7/\text{C}$  cathode materials were synthesized by in-situ synthesis method. The phase compositions and microstructures of the products were characterized by X-ray powder diffraction (XRD) and field emission scanning electron microscope (FESEM). Results indicate that the existence of  $\text{Fe}_2\text{P}_2\text{O}_7$  does not alter  $\text{LiFePO}_4$  crystal structure and the existence of  $\text{Fe}_2\text{P}_2\text{O}_7$  decreases the particles size of  $\text{LiFePO}_4$ . The electrochemical behavior of cathode materials was analyzed using galvanostatic measurement and cyclic voltammetry (CV). The results show that the existence of  $\text{Fe}_2\text{P}_2\text{O}_7$  improves electrochemical performance of  $\text{LiFePO}_4$  cathode materials in specific capability and lithium ion diffusion rate. The charge–discharge specific capacity and apparent lithium ion diffusion coefficient increase with  $\text{Fe}_2\text{P}_2\text{O}_7$  content and maximizes around the  $\text{Fe}_2\text{P}_2\text{O}_7$  content is 5 wt%. It has been had further proved that the  $\text{Fe}_2\text{P}_2\text{O}_7$  adding enhances the lithium ion transport to improve the electrochemical performance of  $\text{LiFePO}_4$  cathode materials. However, excessive  $\text{Fe}_2\text{P}_2\text{O}_7$  will block the electron transfer pathway and affect the electrochemical performances of  $\text{LiFePO}_4$  directly.

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## 1. Introduction

Lithium iron phosphate ( $\text{LiFePO}_4$ ) becomes a promising cathode materials due to the high theoretical capacity ( $170 \text{ mAh g}^{-1}$ ), low cost, low toxicity, environmental greenness and excellent stability [1–3] since the olivine-type lithium iron phosphate ( $\text{LiFePO}_4$ ) was reported by Padhi et al., in 1997 [4]. However, the low electronic conductivity ( $\sim 10^{-9} \text{ S cm}^{-1}$ ) and low ionic diffusion coefficient ( $\sim 1.8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ ) [5] can provide to operate at high power applications [6,7]. Therefore,  $\text{LiFePO}_4$  has been attracted attentions to solve this problem. Most of the efforts focused on the coating with conducting polymers [8] and carbon [9] or silver [10], doping cation [11–15] and minimizing particle size [16–18]. The carbon-coating and particles size minimization can improve the electrochemical performances of  $\text{LiFePO}_4$  due to the increase electronic conductivity and the short diffusion length of lithium ions, respectively, but, the addition of carbon and small particles will reduce the tap density and energy density [19].

The stoichiometric  $\text{LiFePO}_4$  cannot be controlled accurately in the synthesizing process. So, some symbiotic compounds would be formed in  $\text{LiFePO}_4$  cathode materials including  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_4\text{P}_2\text{O}_7$  and  $\text{Fe}_2\text{P}_2\text{O}_7$ , and so on. Zhanqiang Liu et al. [20] reported that the  $\text{Li}_3\text{PO}_4/\text{LiFePO}_4/\text{C}$  cathode materials based on  $\text{LiFePO}_4$  for lithium battery were prepared by a solid state reaction method, the results indicated that  $\text{Li}_3\text{PO}_4$  as lithium ion conductor can improve the electrochemical property of  $\text{LiFePO}_4$ . Recently, Gwang-Hee Lee [21] reported for the first time the utilization of  $\text{Fe}_2\text{P}_2\text{O}_7$  as an anode material in li-ion batteries. The  $\text{Fe}_2\text{P}_2\text{O}_7$  electrode as a new anode showed higher specific capacities ( $490 \text{ mAh g}^{-1}$  after 10 cycles at a rate of  $100 \text{ mA g}^{-1}$ ) and better cyclic performances than  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ . These results indicated that the  $\text{Fe}_2\text{P}_2\text{O}_7$  possesses high ionic diffusion rate. Therefore, an appropriate amount of coexisting  $\text{Fe}_2\text{P}_2\text{O}_7$  can be used as a lithium ion conductive material to effectively ameliorate the electrochemical performances of  $\text{LiFePO}_4$ , and  $\text{Fe}_2\text{P}_2\text{O}_7$  can partly replace carbon to improve the tap density of  $\text{LiFePO}_4$ . Therefore, it is interesting to investigate the effect of symbiotic compound  $\text{Fe}_2\text{P}_2\text{O}_7$  on electrochemical performance of  $\text{LiFePO}_4/\text{C}$  cathode materials. In this study, we report for the first time on  $\text{Fe}_2\text{P}_2\text{O}_7$  modified  $\text{LiFePO}_4/\text{C}$  composites synthesized by in-situ synthesis method, the structural properties and the

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effect of  $\text{Fe}_2\text{P}_2\text{O}_7$  on electrochemical performance of  $\text{LiFePO}_4/\text{C}$  cathode materials are investigated.

## 2. Experimental

### 2.1. Synthesis

The  $\text{LiFePO}_4/\text{Fe}_2\text{P}_2\text{O}_7/\text{C}$  cathode materials were prepared by in-situ synthesis method. The starting materials were ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ , A.R.), iron oxalate dehydrate ( $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , A.R.), lithium carbonate ( $\text{Li}_2\text{CO}_3$ , A.R.), and glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ , AR, 5 wt% of starting materials). Firstly, all the starting materials were dispersed into ethanol and then ball milled for 4 h. The mixture was initially dried at  $85^\circ\text{C}$ , hand grinded with an agate mortar, and treated at  $350^\circ\text{C}$  for 6 h, then calcined at  $700^\circ\text{C}$  for 24 h in a tube furnace under flow purified  $\text{N}_2$  atmosphere with the heating rate of  $5^\circ\text{C min}^{-1}$ . After the tube furnace is cooled to room temperature, The  $\text{LiFePO}_4/\text{Fe}_2\text{P}_2\text{O}_7/\text{C}$  cathode materials ( $\text{Fe}_2\text{P}_2\text{O}_7$  content is 1 wt%, 2 wt%, 3 wt%, 5 wt% and 7 wt%, respectively) were obtained. The obtained products were defined as sample A, B, C, D and E, respectively. The carbon content of samples is about 0.5 wt%.

### 2.2. Characterization and electrochemical measurements

Structural analysis was carried out using X-ray diffraction (XRD, X'Pert PRO,  $\text{CuK}\alpha$  radiation). The morphology and micro-structure of  $\text{LiFePO}_4/\text{Fe}_2\text{P}_2\text{O}_7/\text{C}$  cathode materials were observed with a field emission scanning electron microscope (SEM, FEI Quanta 200F).

Coin cells of the 2430 configuration were assembled in an argon-filled glove box. The cathode was prepared by mixing 80 wt%  $\text{LiFePO}_4/\text{Fe}_2\text{P}_2\text{O}_7/\text{C}$  powder with 10 wt% conductive carbon black and 10 wt% polyvinylidene fluoride (PVDF) in a *n*-methyl-2-pyrrolidone (NMP) solution, which was then coated onto aluminum foil current collector and dried at  $115^\circ\text{C}$  for 12 h in a vacuum drying oven. Lithium metal was used as the anode and a 1 M solution of  $\text{LiPF}_6$  in EC: DEC (1: 1, v/v) was used as the electrolyte with a microporous polypropylene sheet (Celgard 2320) as the separator. The charge–discharge tests were conducted on a battery test system (Land, C2001A) with cut-off voltages of 2.5 V and 4.2 V, the cyclic voltammetry (CV) was conducted on a CHI660E electrochemical workstation in the voltage range of 2.5–4.2 V.

## 3. Results and discussion

### 3.1. Phase composition and morphology

Fig. 1 shows the XRD patterns of  $\text{LiFePO}_4/\text{Fe}_2\text{P}_2\text{O}_7/\text{C}$  cathode materials. It can be seen that the main phase of these samples (A, B, C, D and E) can be identified as  $\text{LiFePO}_4$  with an ordered olivine structure indexed to orthorhombic *Pnma* (PDF card number: 81-1173), and there is no evidence of diffraction peaks for  $\text{Fe}_2\text{P}_2\text{O}_7$  and carbon due to their amorphous structure and/or low content in samples (Fig. 1a). To explain the existence of  $\text{Fe}_2\text{P}_2\text{O}_7$  in cathode materials further, the  $\text{LiFePO}_4/\text{Fe}_2\text{P}_2\text{O}_7/\text{C}$  cathode material with 20 wt%  $\text{Fe}_2\text{P}_2\text{O}_7$  was synthesized. Fig. 1b shows the XRD patterns of cathode material with 20 wt%  $\text{Fe}_2\text{P}_2\text{O}_7$ . It can be seen that a new set of diffraction peaks appear in XRD of  $\text{LiFePO}_4$  and it can be clearly identified as  $\text{Fe}_2\text{P}_2\text{O}_7$ . The possible reaction mechanism is  $2\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + 2\text{NH}_4\text{H}_2\text{PO}_4 \rightarrow \text{Fe}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 \uparrow + 2\text{CO} \uparrow + 2\text{CO}_2 \uparrow + 7\text{H}_2\text{O} \uparrow$ .  $\text{Fe}_2\text{P}_2\text{O}_7$  is believed to be present in samples A, B, C, D and E because the sensitivity of XRD analysis is finite. In addition, no impurities such as  $\text{Li}_4\text{P}_2\text{O}_7$ ,  $\text{Li}_3\text{PO}_4$  and others are observed. All diffraction peaks are narrow, indicating that the  $\text{LiFePO}_4$  grains are high crystallinity.

Fig. 2 shows the SEM images of sample A (Fig. 2a), sample C (Fig. 2b), sample D (Fig. 2c), and sample E (Fig. 2d). The SEM images show that the samples are uniform in particle size and no agglomeration, the particles size of cathode materials decreases gradually with increase of  $\text{Fe}_2\text{P}_2\text{O}_7$  content. Sample A with 1 wt%  $\text{Fe}_2\text{P}_2\text{O}_7$  and sample C with 3 wt%  $\text{Fe}_2\text{P}_2\text{O}_7$  are about  $1\ \mu\text{m}$ , and sample D with 5 wt%  $\text{Fe}_2\text{P}_2\text{O}_7$  and sample E with 7 wt%  $\text{Fe}_2\text{P}_2\text{O}_7$  are about 300 nm. The existence of  $\text{Fe}_2\text{P}_2\text{O}_7$  inhibits grain growth of  $\text{LiFePO}_4$  effectively and improves the particles dispersion. Meanwhile, we find that the surface of particles turn from smooth to rough with the increase of  $\text{Fe}_2\text{P}_2\text{O}_7$ , and  $\text{Fe}_2\text{P}_2\text{O}_7$  and carbon coat on the surface of  $\text{LiFePO}_4$  particles and fill the interspaces between  $\text{LiFePO}_4$  particles. The existence of  $\text{Fe}_2\text{P}_2\text{O}_7$  helps to improve the electrochemical performances of cathode materials: (1)  $\text{Fe}_2\text{P}_2\text{O}_7$  possesses high ionic diffusion rate, so existence of  $\text{Fe}_2\text{P}_2\text{O}_7$  can improve electrochemical performances of cathode materials; (2) The decreasing of particles size because of  $\text{Fe}_2\text{P}_2\text{O}_7$  adding can shorten diffusion length of lithium ions to improve electrochemical performances of cathode materials.

### 3.2. Electrochemical performance

Fig. 3a shows the charge–discharge curves at 0.1C at room temperature for all samples. The charge–discharge specific

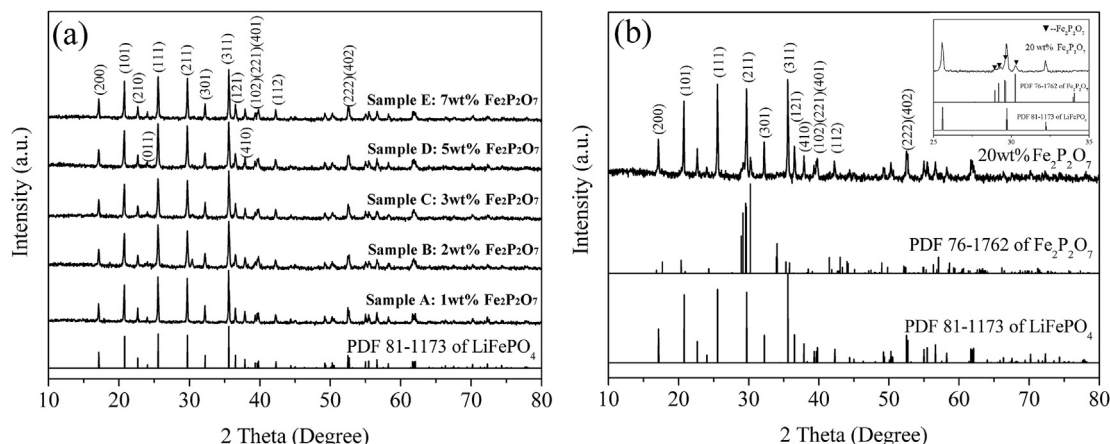


Fig. 1. XRD patterns of the  $\text{LiFePO}_4/\text{Fe}_2\text{P}_2\text{O}_7/\text{C}$  cathode materials.

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