

以 $\text{Fe}_2\text{P}_2\text{O}_7$ 为前驱体制备 LiFePO_4 及其电化学性能

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摘要: 以磷铁废渣($\text{Fe}_{1.5}\text{P}$)和温室效应气体 CO_2 为原料, 以磷酸为补充磷源合成磷酸铁锂(LiFePO_4)的前驱体 $\text{Fe}_2\text{P}_2\text{O}_7$, 并研究了其合成过程对 LiFePO_4 正极材料储能性能的影响。采用 SEM 观察了 LiFePO_4 的表面形貌, 采用 XRD 分析了 LiFePO_4 和 $\text{Fe}_2\text{P}_2\text{O}_7$ 的晶体结构。进一步对该方法进行优化, 发现 $\text{Fe}_{1.5}\text{P}$ 与磷酸混合物 ($n_{\text{Fe}_{1.5}\text{P}}:n_{\text{H}_3\text{PO}_4}=1:1$) 在 800 °C 热处理 6 h 合成的 $\text{Fe}_2\text{P}_2\text{O}_7$ 对应的 LiFePO_4/C 电化学性能最好, 在 0.1C, 0.2C, 0.5C 和 1C 倍率下的容量分别可达 130, 126, 117 和 108 $\text{mAh}\cdot\text{g}^{-1}$ 。

关键词: $\text{Fe}_2\text{P}_2\text{O}_7$; 磷铁废渣; CO_2 ; LiFePO_4 ; 锂离子电池

中图分类号: TB34

文献标识码: A

文章编号: 1001-4861(2018)02-0263-07

DOI: 10.11862/CJIC.2018.044

Synthesis of LiFePO_4/C Composites Using $\text{Fe}_2\text{P}_2\text{O}_7$ as Precursor by a Two-Setp Solid-State Method

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Abstract: $\text{Fe}_2\text{P}_2\text{O}_7$ was prepared from Fe-P waste slag and CO_2 using a solid-state method, and it was furtherly used as precursor of LiFePO_4 . The compositions and microstructures of the as-synthesized $\text{Fe}_2\text{P}_2\text{O}_7$ and LiFePO_4 were characterized by TG/DSC, XRD and SEM. It is found that $\text{Fe}_{1.5}\text{P}$ can be oxidized to $\text{Fe}_2\text{P}_2\text{O}_7$ over 700 °C in CO_2 atmosphere. The optimized synthesis of $\text{Fe}_2\text{P}_2\text{O}_7$ is described as: mixture of $\text{Fe}_{1.5}\text{P}$ and H_3PO_4 (extra P source) is calcined at 800 °C for 6 h, which gives the highest specific capacity of LiFePO_4 . The discharge capacity of the as-synthesized LiFePO_4 can reach as high as 130, 126, 117, and 108 $\text{mAh}\cdot\text{g}^{-1}$ with C-rates of 0.1C, 0.2C, 0.5C and 1C, respectively.

Keywords: $\text{Fe}_2\text{P}_2\text{O}_7$; Fe-P slag; CO_2 ; LiFePO_4/C ; Li-ion battery

In recent years, more and more concerns have been paid to environmental protection and energy conservation, therefore, the development of new energy

technology are speeding up. With the advantages of low cost, environmental friendliness, high safety, good cycle stability and high specific capacity (170 $\text{mAh}\cdot\text{g}^{-1}$),

收稿日期: 2017-08-22。收修改稿日期: 2017-11-14。

国家自然科学基金(No.21576170)和材料腐蚀与防护四川省重点实验室开放基金(No.2017CL19)资助项目。

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lithium iron phosphate (LiFePO_4) has established itself as a potent competitor of cathode material for Lithium ion battery (Li-ion battery) since the olivine-type LiFePO_4 was reported by Padhi et al. in 1997^[1-6]. In recent years, LiFePO_4 has been applied on the electric vehicle, especially on electric bus due to its relatively stable nature. However, relatively high cost of LiFePO_4 still prevents it from super extensive application. Recently, Hu et al. reported LiFePO_4 cathode materials using a precursor $\text{Fe}_2\text{P}_2\text{O}_7$ in Li-ion batteries^[7]. To furtherly cut down the cost, our group developed a method of synthesizing LiFePO_4 using Fe-P waste slag as Fe and P source. Fe-P waste slag used in this method comes from the by-product of yellow phosphorus industry, which is composed of iron and phosphor. Fe-P waste slag is plentiful, cheap and commonly used as building materials. The compositional formula of the Fe-P slag used throughout this work was determined as $\text{Fe}_{1.5}\text{P}$ ^[8]. This method proposed in this work can be able to dramatically cut back the cost of LiFePO_4 and promote its extensive application^[9-12].

Generally, some iron compound such as FeC_2O_4 , Fe_2O_3 and even expensive FePO_4 have been commonly used as raw materials to synthesize LiFePO_4 ^[11-18]. Recently, $\text{Fe}_2\text{P}_2\text{O}_7$ was demonstrated as a novel precursor for LiFePO_4 . Compared with FePO_4 and other precursors, $\text{Fe}_2\text{P}_2\text{O}_7$ has the following advantages: the same ratio of $n_{\text{Fe}}:n_{\text{P}}$, the same Fe and P chemical valence and similar crystal structure with LiFePO_4 ^[19-20]. In the synthesis of LiFePO_4 using $\text{Fe}_2\text{P}_2\text{O}_7$ as precursor, only lithium source is required, which give this method a simplified property.

Carbon dioxide (CO_2), which is the main greenhouse gas, is drawing more and more attention due to its effect on global warming. The CO_2 capture and utilization are one of the most promising strategies to reduce the CO_2 concentration in the atmosphere. In this work, CO_2 is utilized as oxidizing agent for preparing $\text{Fe}_2\text{P}_2\text{O}_7$. Also, Fe-P slag, which is a waste sourced from yellow phosphorus industry, is used as Fe and P source in this work. Both of them give the method proposed in this work an environmental-friendly properties.

In the work, a one-step solid-phase method was developed for synthesis $\text{Fe}_2\text{P}_2\text{O}_7$ using Fe-P waste slag and CO_2 , which can be furtherly used as precursor for LiFePO_4 preparation. Also, the as-synthesized LiFePO_4 was characterized as cathode of Li-ion battery. The synthesis method for $\text{Fe}_2\text{P}_2\text{O}_7$ is optimized and its influence on the properties of LiFePO_4 is investigated. In addition, the compositions and microstructures of the as-synthesized $\text{Fe}_2\text{P}_2\text{O}_7$ and LiFePO_4 samples are characterized by TG/DSC, XRD and SEM.

1 Experimental

1.1 Preparation

In this work, LiFePO_4/C composites were prepared from $\text{Fe}_2\text{P}_2\text{O}_7$, which was synthesized by solid-state reaction from $\text{Fe}_{1.5}\text{P}$ slag and phosphoric acid, as shown in Fig.1. $\text{Fe}_{1.5}\text{P}$ slag, which is a kind of Fe-P alloy, is a byproduct from the electrothermal reduction process for manufacturing yellow phosphorus. $\text{Fe}_{1.5}\text{P}$ slag used as Fe and P source in this method, which was pulverized and ground finely simultaneously before use.

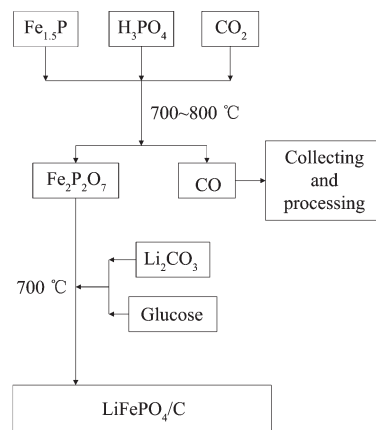


Fig.1 Flow chart for synthesis of LiFePO_4/C using $\text{Fe}_2\text{P}_2\text{O}_7$ as precursor

In the first step, phosphoric acid (~85%) was used as the extra P source and mixed with $\text{Fe}_{1.5}\text{P}$ to keep $n_{\text{Fe}}:n_{\text{P}}=(2\sim1):1$. The mixture was thoroughly ground with ethanol in an agate mortar, and then dried in an oven at 70 °C. After that, the mixture was heat treated at 700~800 °C in a quartz tube furnace flushed by a CO_2 flow ($100\text{ mL}\cdot\text{min}^{-1}$) to start the reaction, and finally $\text{Fe}_2\text{P}_2\text{O}_7$ was collected. In the second step,

$\text{Fe}_2\text{P}_2\text{O}_7$, stoichiometric Li_2CO_3 and glucose were mixed thoroughly with ethanol in an agate mortar. After being dried, the mixture was calcined at $700\text{ }^\circ\text{C}$ in a quartz tube furnace in argon flow ($100\text{ mL}\cdot\text{min}^{-1}$), and finally LiFePO_4 sample was generated.

1.2 Material characterization

Thermogravimetric and differential scanning calorimetric analyses (TG/DSC) were carried out on a NETZSCH STA 499F3 instrument, where the sample was examined by heating from ambient to $850\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in a CO_2 atmosphere. The phase structures were analyzed by X-ray diffraction (XRD, Philips X'Pert Pro, Holland, $\text{Cu K}\alpha$ radiation, $\lambda=0.154\text{ 06 nm}$) with a step of $0.04^\circ\cdot\text{s}^{-1}$ from 10° to 70° at the power of 35 kV and 25 mA . The samples were examined and photographed with scanning electron microscope (SEM, Hitachi S-4800, Japan) operating 15 kV .

1.3 Electrochemical measurements

2025 type coin cells using the as-prepared LiFePO_4/C as cathode were assembled in a glovebox filled with argon ($\geq 99.99\%$). The cathode was prepared by mixing $83\%(w/w)$ LiFePO_4 powder with $10\%(w/w)$ of conductive acetylene black and $7\%(w/w)$ of commercial available LA-132 binder (Chengdu Indigo Power Sources Co. Ltd., China) to form rheological phase slurry, which was coated onto aluminum foil current collector with a loading density of $(1.04\pm 0.32)\text{ mg}\cdot\text{cm}^{-2}$. After being dried at $100\text{ }^\circ\text{C}$ under vacuum for 10 h , it was cut into round wafers (about 1.2 cm^2) as working electrodes. Lithium metal was applied as both the counter electrode and the reference electrode and Celgard 2300 film was used as the separator. $1.0\text{ mol}\cdot\text{L}^{-1}$ solution of LiPF_6 in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) ($1:1:1, V/V/V$, Shenzhen Capchem Chemicals Co. Ltd., China) was used as electrolyte. Galvanostatic chargedischarge measurements were conducted on a Neware battery-testing instrument (Shenzhen Neware Technology Ltd., China) in the voltage range of $2.4\sim 4.2\text{ V}$ vs Li^+/Li at room temperature. Electrochemical impedance spectroscopic (EIS) characterization was carried out on an electrochemical workstation con-

rolled by the Powersuit software (Princeton Applied Research, United States).

2 Results and discussion

XRD and TG/DSC measurements were performed to understand the reaction between $\text{Fe}_{1.5}\text{P}$ and H_3PO_4 under CO_2 atmosphere, and its results were presented in Fig.2. In this research, $\text{Fe}_{1.5}\text{P}$ and H_3PO_4 mixture was calcined at 700 and $800\text{ }^\circ\text{C}$ for 6 h in a CO_2 atmosphere. The as-synthesized sample powder was collected for XRD analysis, and its XRD patterns were presented in Fig.2a. There are obvious peaks of $\text{Fe}_2\text{P}_2\text{O}_7$ (PDF No.76-1762) in all the samples. Therefore, it's reasonable to conclude that $\text{Fe}_2\text{P}_2\text{O}_7$ was generated in the calcination of $\text{Fe}_{1.5}\text{P}$ and H_3PO_4 mixture at $800\text{ }^\circ\text{C}$ in a CO_2 atmosphere. However, there are still some Fe-P alloy remain in the sample due to its incomplete reaction. Comparing the XRD patterns, it is found that the sample fabricated at $800\text{ }^\circ\text{C}$ shows a more intense peak, indicating a relatively higher temperature can enhance the generation reaction of $\text{Fe}_2\text{P}_2\text{O}_7$. Based on this analysis, the possible reaction in the this process was described in reaction (1).

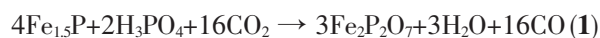


Fig.2b shows the TG and DSC curves of $\text{Fe}_{1.5}\text{P}$ and H_3PO_4 mixture in a CO_2 atmosphere. The weight loss of the mixture below $600\text{ }^\circ\text{C}$ is nearly $9.4\%(w/w)$ as labeled in the TG curve. As for the DSC pattern, there is one remarkable exothermic peak at $\sim 140\text{ }^\circ\text{C}$ and two remarkable endothermic peaks located at ~ 100 and $\sim 176\text{ }^\circ\text{C}$ respectively. The endothermic peaks located at ~ 100 and $\sim 176\text{ }^\circ\text{C}$ can be assigned to the evaporation of residual water and solvents in the mixture. It is noticed that there is another exothermic peak located at $627\text{ }^\circ\text{C}$, while the weight stop decreasing and starts increasing after the temperature goes up to $700\text{ }^\circ\text{C}$. In the reaction showed in equation (1), the mixture of $\text{Fe}_{1.5}\text{P}$ and H_3PO_4 react with CO_2 along with a mass increasing due to the participation of CO_2 and only CO generated. From this analysis, it is confirmed that the reaction of $\text{Fe}_{1.5}\text{P}$, H_3PO_4 and CO_2 can be started above $700\text{ }^\circ\text{C}$.

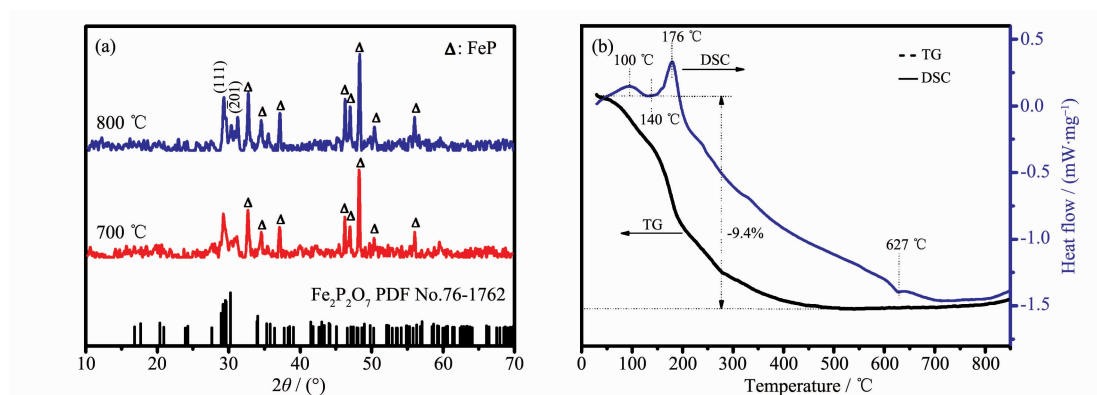


Fig.2 (a) XRD patterns of Fe_{15}P and H_3PO_4 mixture calcined in CO_2 at different temperatures; (b) Thermal analysis of mixture Fe_{15}P and H_3PO_4 heated in CO_2

To optimize the method of synthesizing $\text{Fe}_2\text{P}_2\text{O}_7$, different raw material ratio ($n_{\text{Fe}_{15}\text{P}}:n_{\text{H}_3\text{PO}_4}=1:1, 1.5:1, 2:1$) was applied in the preparation of $\text{Fe}_2\text{P}_2\text{O}_7$. The XRD patterns of the as-prepared samples are showed in Fig.3a. It can be found that the main phase of all the samples can be identified as $\text{Fe}_2\text{P}_2\text{O}_7$ (PDF No.76-1762)^[9]. Comparison with these samples, the sample with $n_{\text{Fe}_{15}\text{P}}:n_{\text{H}_3\text{PO}_4}=1:1$ has the most intense $\text{Fe}_2\text{P}_2\text{O}_7$

peaks, indicating it's the most suitable starting material ratio for $\text{Fe}_2\text{P}_2\text{O}_7$ preparation in this research.

Furtherly, the as-prepared $\text{Fe}_2\text{P}_2\text{O}_7$ was used for preparing LiFePO_4/C composite. Also, Li_2CO_3 and glucose were used as lithium source and carbon source respectively. In this research, LiFePO_4/C was synthesized by annealing $\text{Fe}_2\text{P}_2\text{O}_7$ and Li_2CO_3 mixture at 700 °C in an argon atmosphere for 6, 8, 10 h,

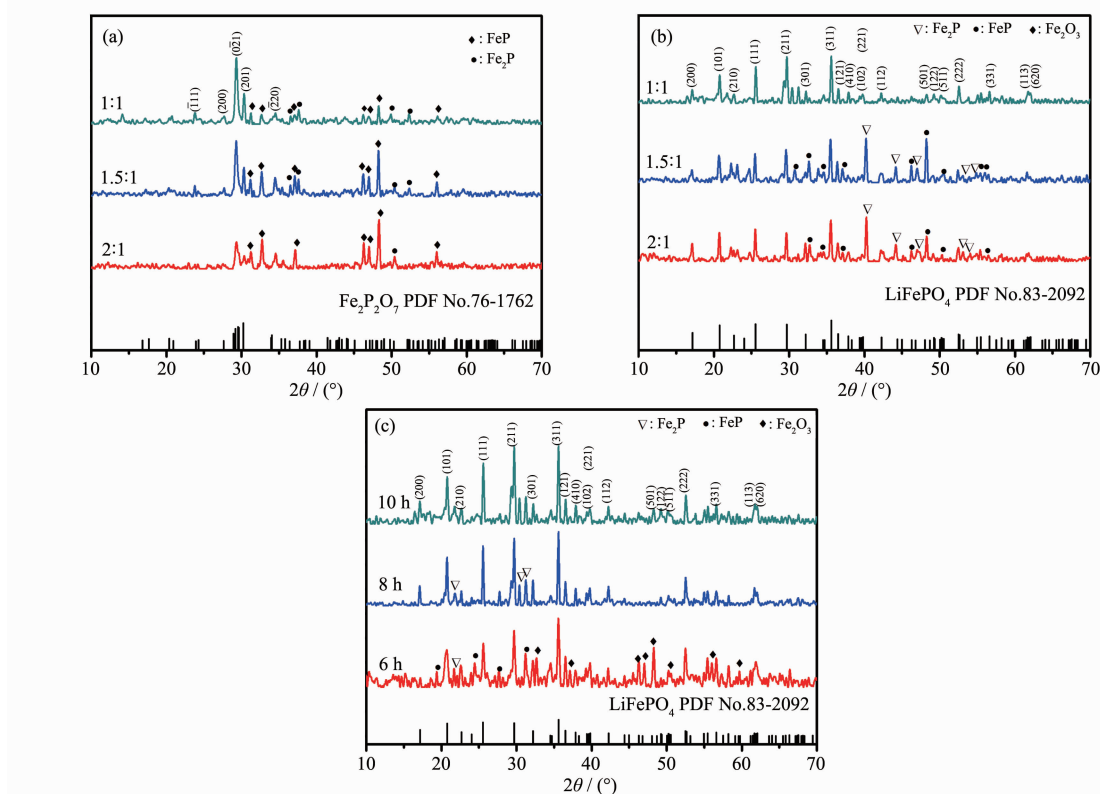


Fig.3 XRD patterns: (a) As-prepared $\text{Fe}_2\text{P}_2\text{O}_7$ with different molar ratios of Fe_{15}P and H_3PO_4 ; (b) LiFePO_4/C composites from $\text{Fe}_2\text{P}_2\text{O}_7$ synthesized with different molar ratios of Fe_{15}P and H_3PO_4 ; (c) LiFePO_4/C samples for different calcinating times

respectively. The XRD patterns of the as-synthesized LiFePO_4/C composites with different $\text{Fe}_2\text{P}_2\text{O}_7$ and calcinating times are shown in Fig.3b and Fig.3c respectively. It is noted that all the samples exhibit pounced crystallographic control, and all the indexed peaks of 10 h sample matches well with the standard peaks of LiFePO_4 , indicating that LiFePO_4 was generated in the calcination process^[14]. However, there was some Fe-P alloy still remained in the products while the reacting time was 6 or 8 h, indicating that calcination for 10 h is necessary for synthesizing LiFePO_4 in this research.

Theoretically, $\text{Fe}_2\text{P}_2\text{O}_7$ has the same valence of Fe and P element with LiFePO_4 , also share the same ratio of $n_{\text{Fe}}:n_{\text{P}}$ with LiFePO_4 , which makes the second step to be a complex reaction. Its the main reason for using $\text{Fe}_2\text{P}_2\text{O}_7$ as an intermediate product for LiFePO_4 preparation in this work. Furtherly, Li_2CO_3 was introduced as lithium source to synthesize LiFePO_4 . Also, glucose was used as carbon source for improving the composites conductivity. Based on the XRD analysis, it was proved that LiFePO_4 was generated from the reaction between $\text{Fe}_2\text{P}_2\text{O}_7$ and Li_2CO_3 successfully. The possible reaction in this process was described in reaction (2).



The morphology of the as-prepared LiFePO_4/C

composites was performed by SEM in the same magnification. Fig.4 (a,b), (c,d), (e,f) show the SEM images of LiFePO_4/C composites with calcination time of 6, 8 and 10 h, respectively. The SEM images show that all the samples have a similar particle size of 2~5 μm , and there are some agglomeration especially for 6 and 10 h sample. However, it is obvious that the sample with 10 h calcination time show a smoother surface than that of 6 and 8 h calcination time. It indicating a better carbon coating surface gives an improved electrochemical properties to LiFePO_4/C composites.

To evaluate the electrochemical energy storage properties of the as-prepared LiFePO_4/C samples, coin-cell type Li-ion batteries was assembled with lithium metal counter electrode. Fig.5a shows the voltage profiles of LiFePO_4/C samples cycled at 0.1C. Obviously, all the voltage patterns exhibit flat plateaus, which correspond to the lithium ion's extraction and insertion in LiFePO_4/C cathode. For all the voltage patterns, their charge plateaus located at about 3.45 V and discharge plateaus located about 3.42 V. However, specific capacity of LiFePO_4/C samples with different calcining times is quite different. The discharge capacities of the LiFePO_4/C samples of 6, 8, and 10 h calcining time at 0.1C are 99, 98 and 130 $\text{mAh} \cdot \text{g}^{-1}$, while their coulombic

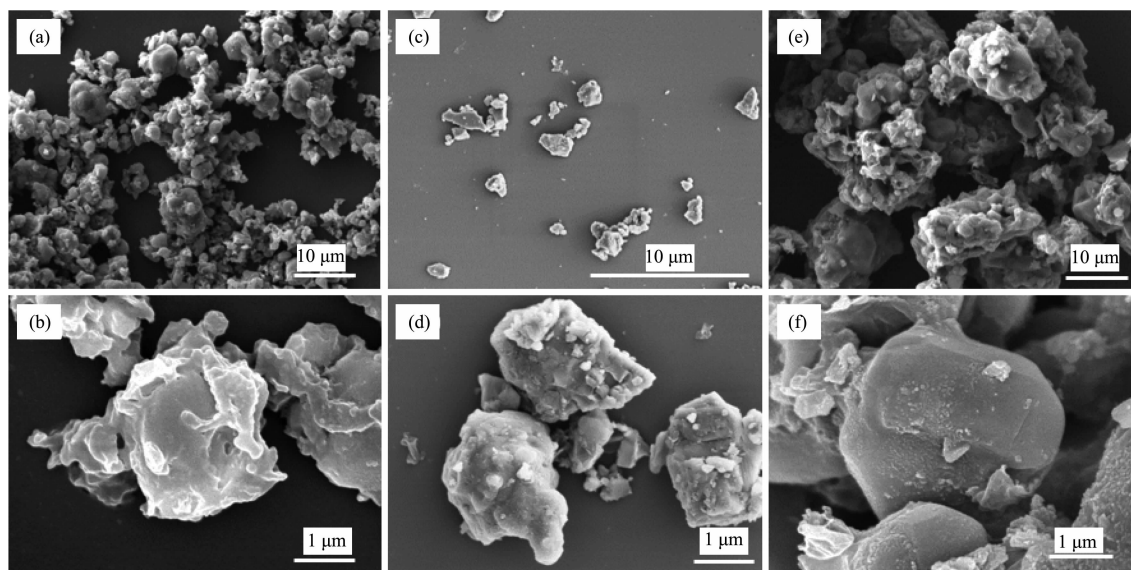


Fig.4 SEM images of the as-synthesized LiFePO_4/C materials with different calcinating times:

(a, b) 6 h; (c, d) 8 h; (e, f) 10 h

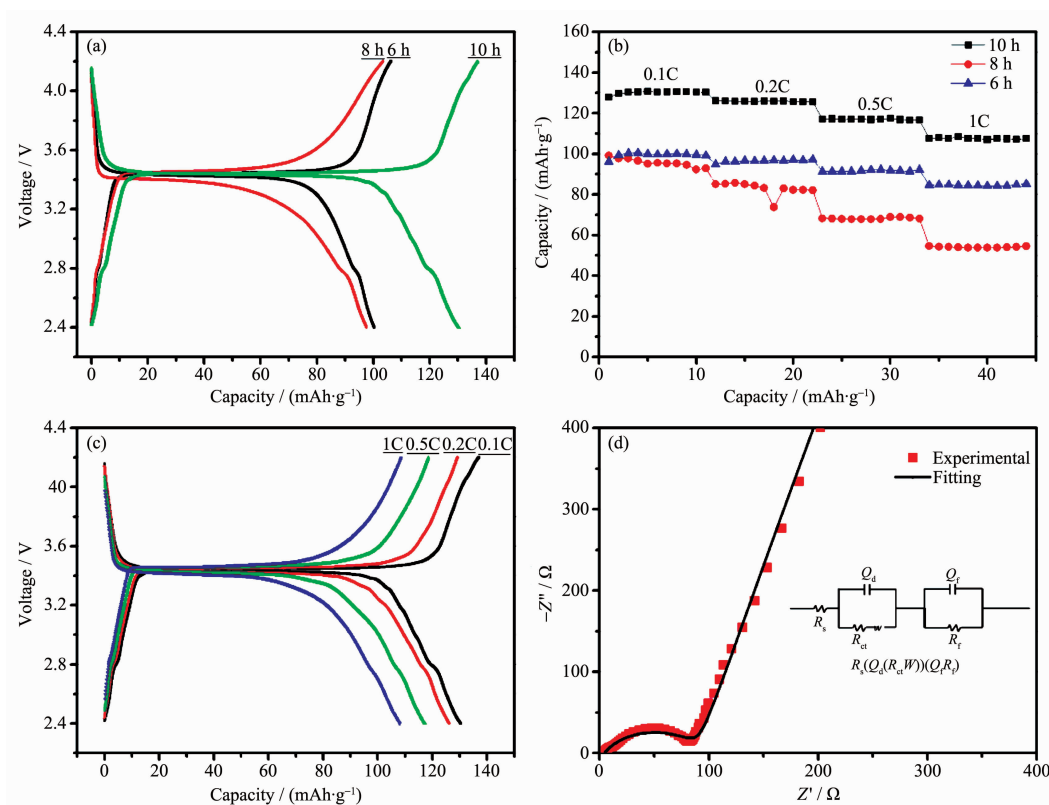


Fig.5 (a) Galvanostatic charge-discharge curves of the LiFePO₄/C composites synthesized with different calcining time; (b) Cycling performance of LiFePO₄/C composites at 0.1C, 0.2C, 0.5C, 1C; (c) Galvanostatic charge-discharge curves of LiFePO₄/C composites with different current rate; (d) EIS plots of LiFePO₄/C composites with 10 h calcining time and the inset is the corresponding equivalent circuit model

efficiencies are 94.46%, 94.35%, and 95.13%, respectively. Consequently, the sample with 10 h calcining time exhibits the most excellent discharge capacity and coulombic efficiency.

The cycle performances of the LiFePO₄/C composites with different C-rates are present in Fig. 5b. The sample with 10 h calcining times has the a higher discharge capacity than other samples, which shows 130, 126, 117, and 108 mAh·g⁻¹ at 0.1C, 0.2C, 0.5C and 1C, respectively. The discharge specific capacities of the LiFePO₄/C samples at 0.1C keep increasing in the first few cycles due to cathode activation process. The galvanostatic charge/discharge curves of the LiFePO₄/C sample with 10 h calcining time at 0.1C, 0.2C, 0.5C, and 1C are illustrated in Fig. 5c. The coulombic efficiencies at the rate of 0.1C, 0.2C, 0.5C, and 1C are 95.13%, 97.64%, 99.13%, and 99.15%, respectively. Based on this analysis, it is proved that the as-prepared LiFePO₄/C sample with 10

h calcining time has great energy storage capacity as cathode for Li-ion battery.

To investigate the electrode reaction process and diffusion behavior, EIS measurement was conducted under the open-circuit potential of coin cells. The Nyquist plots of 10 h sample with the equivalent circuit is presented in Fig. 5d. The EIS plots is well fitted by the $R_s(Q_d(R_{ct}W))(Q_fR_f)$ equivalent circuit model using ZSimpWin software. In this equivalent circuit, R_s , R_{ct} , Q_d , and Q_f denote the solution resistance, charge-transfer resistance, constant phase element of the electrolyte film/electrode interface, and the constant phase element of the film, respectively^[14]. Herein, constant phase element (CPE) is used instead of capacitance because the electrode film is not continuous and the sizes of particles vary around an average. The simulated results show that the values of R_s and R_{ct} are 4.28 and 87.05 Ω respectively. The low and stable interface resistance of the LiFePO₄/C

cathode indicates that the as-prepared LiFePO_4/C composites has fast reaction kinetics.

3 Conclusions

A novel solid-state method was developed to synthesize $\text{Fe}_2\text{P}_2\text{O}_7$ using Fe-P waste slag and CO_2 as raw materials. Furtherly, the as-synthesized $\text{Fe}_2\text{P}_2\text{O}_7$ was used as precursor for synthesizing LiFePO_4 by adding Li_2CO_3 as lithium source. As for synthesis of $\text{Fe}_2\text{P}_2\text{O}_7$, the optimized synthesis procedure is $\text{Fe}_{1.5}\text{P}$ and H_3PO_4 mixture ($n_{\text{Fe}_{1.5}\text{P}}:n_{\text{H}_3\text{PO}_4}=1:1$) be heat treated at $800\text{ }^\circ\text{C}$ for 6 h. The as-prepared LiFePO_4 can get capacities of 130, 126, 117, and 108 $\text{mAh}\cdot\text{g}^{-1}$ at 0.1C, 0.2C, 0.5C and 1C, while the corresponding coulombic efficiencies are 95.13%, 97.64%, 99.13%, and 99.15%, respectively. Consequently, in this work, a novel simplified and environmentally friendly route is successfully developed to synthesize $\text{Fe}_2\text{P}_2\text{O}_7$ precursor for LiFePO_4 .

Acknowledgements: This work is financially supported by the National Science Foundation of China (Grant No. 21576170) and the Opening Project of Material Corrosion and Protection Key Laboratory of Sichuan province (Grant No. 2017CL19).

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