

Interface Synthesis of FePO₄ with Different Morphologies and Effect of Morphology on the Electrochemical Performance of LiFePO₄/C

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Abstract

In our work, interface synthesis method was put forward to prepare FePO₄ with different morphologies, and the effect of morphology on the preparation and electrochemical performance of LiFePO₄/C was investigated. The results showed that the morphology of FePO₄ was amorphous and monoclinic at the treatment temperatures of 30 °C and 80 °C, respectively. LiFePO₄/C prepared from two crystal precursors were both hemispherical hollow with an olivine crystal structure. LiFePO₄/C produced from the monoclinic structured precursor exhibited smaller-sized morphology and better electrochemical performance, and its discharge capacities were 155.9 mA h g⁻¹ and 141.8 mA h g⁻¹ at the rates of 0.1 C and 1 C, respectively. After 150 cycles, its capacity retention was about 97.8 % and 95.1 % at 0.1 C and 1 C, respectively.

Keywords

FePO₄, LiFePO₄/C, lithium-ion battery, composite materials, energy storage and conversion

Introduction

Since LiFePO₄ was reported as a cathode material for lithium-ion battery by Goodenough in the 1990s,¹ it has been considered as a promising cathode material for Li-ion battery due to its advantages, such as low cost, no toxicity, high thermal stability, a relatively high theoretical capacity of 170 mA h g⁻¹ and excellent cycling performance.^{2–5} LiFePO₄/C composite has been successfully put into practice by carbon coating, which is a good solution to enhance the conductivity of pristine LiFePO₄.^{6–8} Aiming to improve the electrochemical properties, different precursors, such as FePO₄, Fe₂O₃, FeC₂O₄ have been used as precursors to prepare LiFePO₄/C composite. Among them, FePO₄ has attracted much more attention as a good precursor, and different methods have been studied to synthesize FePO₄.^{9–13} These methods, however, commonly involve complicated synthetic routes and high synthetic costs. In addition, there are few reports about the effect of the crystal style of FePO₄ on the preparation and electrochemical performance of LiFePO₄/C composite.

Herein, we report an interface synthesis method to prepare FePO₄ with different crystal types, and the effect of crystal type on the electrochemical performance of LiFePO₄/C composite was investigated.

Experiment

FePO₄ precursor was prepared using low-cost FeSO₄ and H₃PO₄ as raw materials. 200 mL of a water solution of FeSO₄, $c(\text{FeSO}_4) = 0.13 \text{ mol L}^{-1}$, and 9 mL of H₃PO₄, $w(\text{H}_3\text{PO}_4) = 85 \%$, were mixed together in the reaction still, stirred for 1 h, then 200 mL of ethanol were added into the solution under vigorous stirring for 3 h. Subsequently, the temperature of the slurry was kept at 30 °C and 80 °C for 5 h, respectively, filtrated, washed and dried. The precursor prepared at 30 °C was labelled as S1, the precursor prepared at 80 °C was labelled as S2. Then, the as-prepared precursor and LiOH·H₂O were mixed in a mill. Simultaneously, a proper amount of glucose (C₆H₁₂O₆) was added into the mixture as carbon source. After drying treatment, the mixture was calcined at 650 °C for 12 h and cooled down under N₂ atmosphere. Finally, the LiFePO₄/C composite samples were obtained. They were labelled as L1 (prepared from S1), and L2 (prepared from S2), respectively.

The crystalline phases of synthesized FePO₄ precursor and LiFePO₄/C composite were identified with X-ray diffraction (XRD, X'Pert Pro MPD, Cu K α radiation, $\lambda = 1.54178 \text{ \AA}$). The particle morphologies and sizes of the samples were examined by field-emission scanning electron microscopy (FE-SEM, SIRION). The Brunauer–Emmett–Teller (BET) specific surface area of as-synthesized samples was determined by using an instrument of ASAP2020. The elemental result was analysed by X-ray fluorescence spectrometer (Axios).

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The electrochemical performances were investigated in CR2025 coin-type lithium half-cells. NMP was employed as the solvent, blended slurry consisting of active material, acetylene black and PVDF binder in a weight ratio of 75 : 15 : 10 were coated on Al sheet ($\phi = 12$ mm) and dried at 110 °C in a vacuum for 12 hours. Lithium foil served as the reference and counter electrode, and Celgard 2300 membrane was used as the separator. The electrolyte consisted of a solution of LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 1 by volume), $c(\text{LiPF}_6) = 1 \text{ mol L}^{-1}$. Coin cells were assembled in a dry glove-box filled with high-purity argon. The charge and discharge performance was determined by an automatic NEWARE battery cycler (Neware BTS-610) in a voltage range of 2.5–4.3 V at room temperature (25 ± 2 °C).

Results and Discussion

Table 1 shows the elemental analysis of FePO₄ prepared at different temperatures. For both samples, the mole ratio of P to Fe is 1.005, indicating the high purity of the prepared FePO₄.

Fig. 1 shows the XRD patterns of the as-prepared FePO₄ (Fig. 1a–b) and LiFePO₄ (Fig. 1c–d). The XRD patterns of FePO₄ indicate FePO₄ prepared at 30 °C (Fig. 1a), and 80 °C (Fig. 1b) was amorphous and monoclinic, respectively, indicating that treatment temperature had a significant effect on the crystal structure of the as-prepared samples. All the diffraction peaks of LiFePO₄ are consistent with the olivine structured LiFePO₄, which indicates that the morphology of FePO₄ has no significant effect on the structure of LiFePO₄.

The SEM images of the as-prepared FePO₄ (Fig. 2a–b) and LiFePO₄ (Fig. 2c–f) are presented in Fig. 2, from which we can see that the FePO₄ precursor prepared at 30 °C (Fig. 2a) and 80 °C (Fig. 2b) both show irregular shape, and the porous structure can be seen on their surface, different from the spherical and spheroidal shaped FePO₄ reported in literatures,¹⁴ which may be due to template role played by ethanol. In the ethanol system, ethanol is not only contributory to extraction and crystallization, but also acts as template agent to some extent. Thus, the iron phosphate crystal nuclei form, gradually grow and eventually develop into an irregular porous appearance with the cooperative

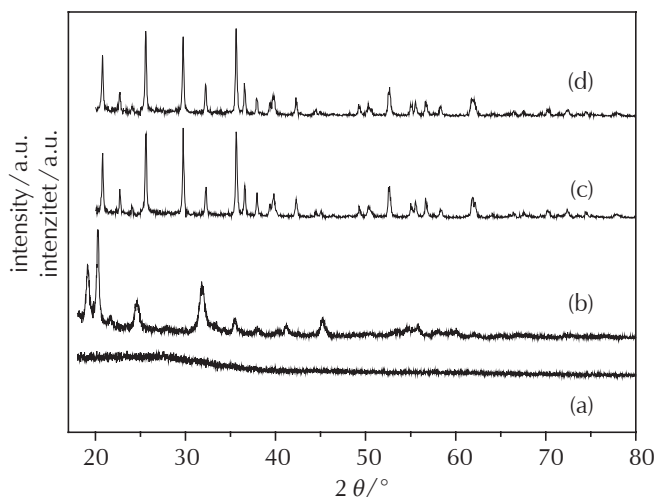


Fig. 1 – XRD spectra of S1 (FePO₄ precursor prepared at 30 °C) (a), S2 (FePO₄ precursor prepared at 80 °C) (b), L1 (prepared from S1) (c), and L2 (prepared from S2) (d)
Slika 1 – XRD-spektri S1 (prekursor FePO₄ pripravljen pri 30 °C) (a), S2 (prekursor FePO₄ pripravljen pri 80 °C) (b), L1 (pripravljen iz S1) (c) i L2 (pripravljen iz S2) (d)

effect of FePO₄ and CH₃–CH₂– group in ethanol molecules. With close observation, the particle size of FePO₄ precursor prepared at 80 °C is slightly smaller than that prepared at 30 °C. Such result can be explained by the formula of crystal nucleation rate proposed by A. E. Nielsen, and equation of crystal growth rate proposed by Dieksen, etc.^{15–16} According to their research, the crystal nucleation rate is faster at higher temperature, thus, the particle size of FePO₄ prepared at 80 °C is relatively smaller. BET analyses were performed to investigate the specific surface area of the samples. The specific surface area of S2 is 68 m² g⁻¹, larger than that of S1 (45 m² g⁻¹), which may have an effect on the morphology of the prepared LiFePO₄. Fig. 2 (c–d) and Fig. 2 (e–f) show the SEM images of L1 and L2, respectively. As shown in the images, they are all hemispherical hollow. It should be noted that such appearance was firstly synthesized to the best of our knowledge. Obviously, L2 is smaller than L1, the average particle size of L2 is about 1 μm, while the average particle size of L1 is about 20 μm, and the specific surface area of L2 (15 m² g⁻¹) is larger than that of L1 (10 m² g⁻¹), which may indicate the difference between their electrochemical performance.

Table 1 – Elemental analysis of FePO₄ prepared at different temperatures (S1: 30 °C, S2: 80 °C)

Tablica 1 – Elementna analiza FePO₄ pripravljenog pri različitim temperaturama (S1: 30 °C, S2: 80 °C)

Sample Uzorak	w _{Fe} / %	w _P / %	w _S / %	w _{Ca} / %	w _{Mg} / %	w _{Si} / %	w _{Na} / %
S1	29.18	16.36	0.033	0	0.022	0	0.014
S2	29.30	16.34	0.041	0	0.019	0	0.023

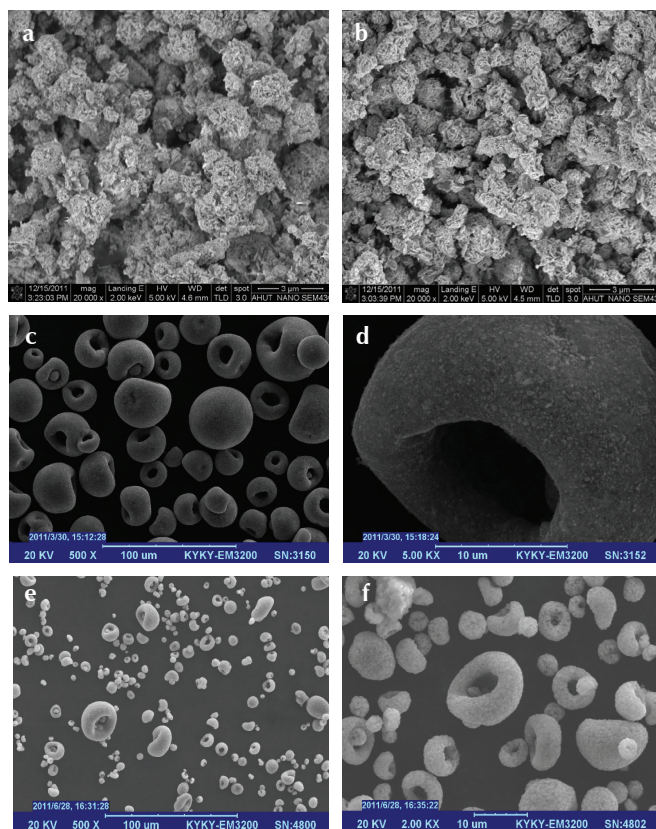


Fig. 2 – SEM images of S1 (FePO₄ precursor prepared at 30 °C) (a), S2 (FePO₄ precursor prepared at 80 °C) (b), L1 (prepared from S1) (c–d), and L2 (prepared from S2) (e–f)

Slika 2 – SEM slike S1 (prekursor FePO₄ pripravljen pri 30 °C) (a), S2 (prekursor FePO₄ pripravljen pri 80 °C) (b), L1 (pripravljen iz S1) (c–d) i L2 (pripravljen iz S2) (e–f)

Fig. 3 shows the charge and discharge curves and cycling performance of LiFePO₄/C composite at different rates. As displayed in Fig. 3(A), each charge–discharge curve exhibits a flat and long potential plateau around 3.4 V. The discharge capacities of L1 are 150.7 mA h g⁻¹ and 135.2 mA h g⁻¹ at the rates of 0.1 C and 1 C, respectively. The discharge capacities of L2 are 155.9 mA h g⁻¹ and 141.8 mA h g⁻¹ at the rates of 0.1 C and 1 C, respectively. Obviously, L2 exhibits better electrochemical performance. Additionally, L2 also demonstrates better cycle stability. After 150 cycles, the capacity retention of L2 is about 97.8 % and 95.1 % at 0.1 C and 1 C, respectively, and the capacity retention of L1 is about 94.6 % and 90.3 % at 0.1 C and 1 C, respectively, as illustrated in Fig. 3(B). The better electrochemical performance of L2 can be explained by its smaller particle size. The smaller the particle size is, the smaller is the diffusion resistance of Li ion. Thus, the utilization of the active materials improves, meanwhile, the volume change caused by the intercalation and extraction behaviour of Li ion is smaller, which benefits the structural stability, thus a slower capacity decline can be seen.

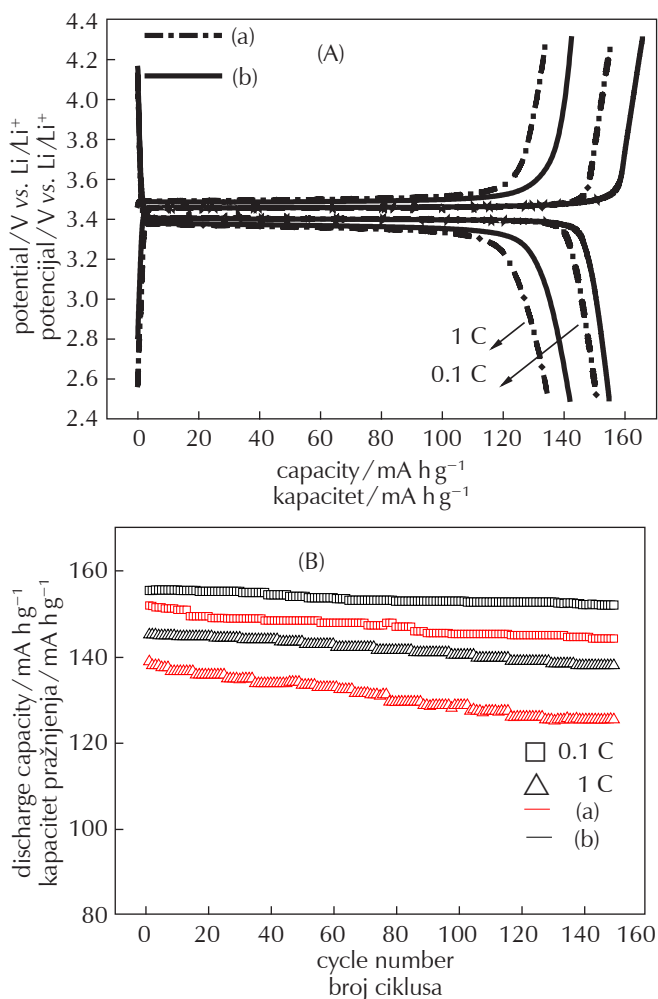


Fig. 3 – Charge–discharge curves of L1 (prepared from S1) (a) and L2 (prepared from S2) (b) at different current rates (A); cycling performances of L1 (prepared from S1) (a) and L2 (prepared from S2) (b) (B)

Slika 3 – Krivulje punjenja i pražnjenja za L1 (pripravljen iz S1) (a) i L2 (pripravljen iz S2) (b) pri različitim brzinama struje (A); ciklička svojstva L1 (pripravljenog iz S1) (a) i L2 (pripravljenog iz S2) (b) (B)

Conclusion

This work has prepared FePO₄ with amorphous and monoclinic crystal form via an interface synthesis method, and studied its effect on the electrochemical performance of LiFePO₄/C. The results showed that LiFePO₄/C prepared from two precursors were both hemispherical hollow with an olivine crystal structure. LiFePO₄/C produced from the monoclinic structured precursor exhibited smaller size and better electrochemical performance, and its discharge capacities were 155.9 mA h g⁻¹ and 141.8 mA h g⁻¹ at the rates of 0.1 C and 1 C, respectively. After 150 cycles, its capacity retention was about 97.8 % and 95.1 % at 0.1 C and 1 C, respectively.

List of abbreviations and symbols

Popis kratica i simbola

BET	– Brunauer–Emmett–Teller
C	– a charge or discharge current equal to the capacity of a battery divided by 1 h – struja punjenja ili pražnjenja jednaka kapacitetu baterije podijeljenom s 1 h
FE-SEM	– field-emission scanning electron microscopy – pretražna elektronska mikroskopija s emisijom polja
L1	– LiFePO ₄ /C composite prepared from S1 – kompozit LiFePO ₄ /C pripravljena iz S1
L2	– LiFePO ₄ /C composite prepared from S2 – kompozit LiFePO ₄ /C pripravljena iz S2
NMP	– N-methyl-2-pyrrolidone – N-metil-2-pirolidon
PVDF	– poly(vinylidene fluoride) – poli(viniliden-fluorid)
S1	– FePO ₄ precursor prepared at 30 °C – prekursor FePO ₄ pripremljen pri 30 °C
S2	– FePO ₄ precursor prepared at 80 °C – prekursor FePO ₄ pripremljen pri 80 °C
XRD	– X-ray diffraction – rendgenska difrakcija

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SAŽETAK

Međufazna sinteza FePO₄ različitih morfologija i utjecaj morfologije na elektrokemijska svojstva LiFePO₄/C

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U ovom je radu korištena metoda međufazne sinteze za pripravu FePO₄ različitih morfologija te je istraživana učinkovitost morfologije na pripravu i elektrokemijska svojstva LiFePO₄/C. Rezultati su pokazali da je FePO₄ pri temperaturi obrade 30 °C amorfno, a pri 80 °C monoklinsko. LiFePO₄/C je pripremljen iz dvaju prekursora oblika polukružne šupljine s kristalnom strukturom olivina. LiFePO₄/C proizveden iz monoklinski strukturiranog prekursora pokazao je sitniju morfologiju i bolja elektrokemijska svojstva, a njegovi kapaciteti pražnjenja naboja bili su 155,9 mA h g⁻¹ i 141,8 mA h g⁻¹ pri brzini od 0.1 C i 1 C. Nakon 150 ciklusa, njegov kapacitet zadržavanja je oko 97,8 % i 95,1 % pri 0.1 C i 1 C.

Ključne riječi

FePO₄, LiFePO₄/C, litij-ionska baterija, kompozitni materijali, energija pohrane i pretvorbe

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