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SHORT COMMUNICATION

Synthesis of graphene-supported $LiFePO_4$/C materials via solid-state method using $LiFePO_4(OH)$ as precursors

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Abstract

The solid-state method is a mainly adopted large-scale preparation of $LiFePO_4$ cathode materials for Li-ion batteries but suffers from a challenge of irregular morphology and particle agglomeration. Herein, a graphene-supported $LiFePO_4$/C@G composite with uniform morphology and electronic conducting network was synthesized via a freeze-drying assisted solid-state method without ball milling using the integrated $LiFePO_4(OH)$ as precursor. The integrated $LiFePO_4(OH)$ as precursor may avoid segregation of element caused by inhomogeneous mixing of raw materials in the process of solid-state preparation. The as-prepared graphene-coated $LiFePO_4$/C@G shows excellent electrochemical properties with a specific capacity of 156, 154, 150, 145, 139, 132 mA h g^{-1} at 0.1, 0.2, 0.5, 1, 2, 5 C and a capacity retention of around 97.0% for 200 cycles at 2 C. This can be attributed to uniform element distribution and continuous electronic conducting network. The freeze-drying assisted solid-phase method using $LiFePO_4(OH)$ precursor and graphene is a promising route for production of $LiFePO_4$/C materials with excellent performances.

Keywords $LiFePO_4$ · $LiFePO_4(OH)$ · Graphene · Cathode materials · Lithium-ion batteries

Introduction

Lithium ferrous phosphate ($LiFePO_4$) cathode material is considered to be one of the most promising cathode materials for lithium-ion power batteries due to the abundant raw materials, high safety, environmental friendliness. However, low electron conductivity and ion diffusion limit the electrochemical properties of $LiFePO_4$ materials, hindering the commercialization process [1]. Effective strategy to improve the conductivity of $LiFePO_4$ is proven to be carbon coating along with preferential nanocrystallization [2–6] and ion doping [7–9], which can make the electrochemical performances of $LiFePO_4$ materials reach a level of commercial application. At present, the cost and stability of its preparation process are still a bottleneck of limiting its large-scale application compared to conventional lead-acid and nickel-hydrogen batteries [10, 11]. Therefore, it is essential for a wide industrial application to develop an inexpensive and facile solid-state method to produce a uniform $LiFePO_4$ material without particle agglomeration.

Although many researchers have reported many procedures of synthesizing $LiFePO_4$, such as spray pyrolysis [12], combination of spray pyrolysis and ball-milling [13], spray drying [14], sol–gel [15], coprecipitation [16] and conventional solid-state reaction method [17], the synthesis method of $LiFePO_4$ materials can be generally divided into solid state reaction and solution method. Solution method usually is accompanied with complex preparation process, leading to the high cost of preparation [10]. Accordingly, the large-scale preparation mainly adopts solid state method, although the solid state method encountered some application issues such as particle agglomeration with irregular morphology [5, 18]. In a conventional solid-state process of preparation, an iron source, phosphorus source

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and Li source are used as starting materials for synthesizing $LiFePO_4$ materials. Before it is decomposed at a temperature ranging from 600 to 700 °C for 8–15 h, a precursor is usually obtained via mixing the starting materials through ball milling. The ball milling can help both homogeneity and reduction of the particle size. However, the ball milling often brings about irregular morphology and particle agglomeration, resulting in unstable electrochemical performances [19]. In addition, ball milling also increases the cost of material preparation. To reduce irregular morphology and the particle agglomeration of $LiFePO_4$ materials in conventional solid-state method, the introduction of integrated materials containing the Li, Fe, P elements as raw materials, such as $LiFePO_4(OH)$, is very necessary. The $LiFePO_4(OH)$ was first reported by Whittingham to be formed through the reaction of $FePO_4{\cdot}H_2O$ and CH_3COOLi in hydrothermal process [20]. Subsequently it was found that nano-sized $LiFePO_4$ reacts with H_2O to form $LiFePO_4(OH)$ in a wet environment [21, 22], and the $LiFePO_4(OH)$ could still be reverse-reacted to $LiFePO_4$ after high-temperature heat treatment [22]. Next, $LiFePO_4(OH)$ or $LiFe(PO_4)(OH)_xF_{1-x}$ was synthesized by solvothermal method [23–25]. After mixing it with carbon, the $LiFePO_4(OH)$ was electrochemically active, with a specific capacity of 130 mA h g^{-1} at 0.1C. Another research on $LiFePO_4(OH)$ has suggested that it can also be obtained by $FePO_4$ H_2O through H^+/Li^+ exchange [26]. In addition, the effective strategy to relieve the sluggish kinetics of $LiFePO_4$ is to integrate $LiFePO_4$ and graphitized carbonaceous materials with large contact area such as graphene and carbon nanotubes [27–29], which is widely applied for synthesizing high-rate hybrid electrodes with the least carbon content. For instance, the graphene-modified $LiFePO_4$ materials were fabricated and promoted the improvement of its overall electrochemical performance [28, 30]. To the best of our knowledge, no research on using the integrated $LiFePO_4(OH)$ as a precursor for synthesizing $LiFePO_4$ material has been reported. Based on the above considerations, we applied the integrated $LiFePO_4(OH)$ compound containing Li, Fe, P elements as precursor, so that a morphology-inherited $LiFePO_4$ material with uniform element distribution can be obtained without ball milling.

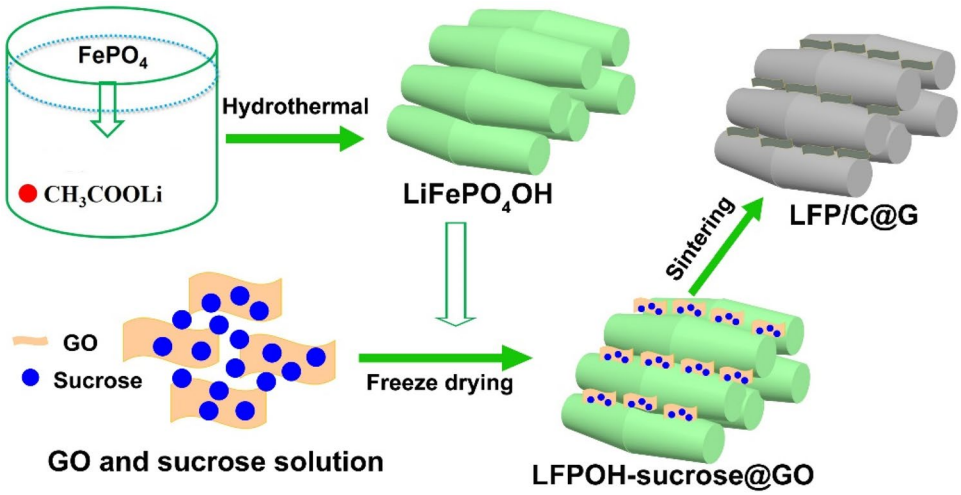
Herein, a graphene-supported $LiFePO_4$/C@G composite with uniform element distribution is successfully synthesized using the integrated $LiFePO_4(OH)$ and the sucrose in graphene oxide (GO) suspension as raw materials. The as-prepared $LiFePO_4$/C@G exhibits excellent electrochemical performances due to uniform particle and electronic conducting network formed with graphene and surface coating carbon layer. This provides a reference for large-scale preparation route of $LiFePO_4$/C materials.

Experimental

The $LiFePO_4OH$ precursor was prepared by hydrothermal method using $FePO_4{\cdot}2H_2O$ and CH_3COOLi as raw materials. Specifically, 0.006 mol of CH_3COOLi was dissolved in 120 ml of deionized water. Then, stoichiometric $FePO_4{\cdot}2H_2O$ (0.006 mol) was added into the above solution under continuous stirring for 30 min. Then, the total solution was transferred into a 200 ml of stainless-steel autoclave, sealed and heated at 180 °C for 72 h. The resultant product was washed with deionized water for several times and was dried in a vacuum at 80 °C, before the $LiFePO_4OH$ precursor was obtained. After it was mixed with 14 wt% of sucrose in 3 wt% graphene oxide (GO) suspension, the obtained mixture was freeze-dried and calcined at 700 °C for 10 h under N_2 atmosphere. Finally, the $LiFePO_4$/C@G composite was obtained. The $LiFePO_4$/C was synthesized via the same procedure except without adding GO for comparison.

The crystalline phases of the samples were identified by a PANalytical X'PertPro X-ray diffractometer (Cu Kα radiation, 40 kV). The particle morphologies of the samples were examined by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). X-ray photoelectron spectroscopy (XPS) data were collected by a PHI Quantera SXM spectrometer using the C 1 s peak with 284.8 eV, and the corresponding fitted spectra were carried out by using XPSPEAK 4.1 software. Thermogravimetric analysis (TGA) was measured using STA 449F3 analyzer (NETZSCH Co.) under air atmosphere to obtain carbon content of composites at a heating rate of 10 °C min^{-1}.

The electrochemical tests were investigated by assembling CR2016 coin-type cells. The cathode electrode was fabricated by coating aluminum foil with the slurry composed of 80 wt% of active material $LiFePO_4$/C, 10 wt% of polyvinylidene binder and 10 wt% of Super-P in *N*-methyl-2-pyrrolidone. After drying at 120 °C for 12 h in a vacuum, the electrode was punched into disc with the diameter of 14 mm as the cathode. Lithium foil served as the counter electrode, and Celgard 2400 membrane was used as the separator. The electrolyte is consisted of a solution of 1 M $LiPF_6$ in EC and DMC (volume ratio of 1:1). The buttoned batteries (CR2016) were assembled in a glove box filled with argon. After the assembled batteries were laid aside for 3 h, the electrical performance of batteries were tested on the batteries tester (Land CT 2001A, Land Co. China) under a voltage range of 2.0 ~ 4.5 V. Cyclic voltammetry and AC impedance spectroscopy measurements were performed at electrochemical workstation (CHI604E, Chenhua, China). The amplitude and frequency range of AC impedance are 5 mV and 0.1 ~ 100 kHz, respectively.



Scheme 1 Schematic illustration for synthesis of the LFP/C@G sample

Results and discussion

The preparation process is shown in Scheme 1. To solve component segregation of the raw materials and improve the consistency of the $LiFePO_4$ materials in mixing in solid-state preparation method of $LiFePO_4$ materials, a strategy was proposed that the reaction phases were reduced in the mixing of raw materials through using $LiFePO_4(OH)$ containing Li, Fe and P as precursor. $LiFePO_4(OH)$ precursor was prepared by hydrothermal method using $FePO_4$ and CH_3COOLi as raw materials, followed by thermal conversion of $LiFePO_4OH$ in the presence of sucrose in graphene oxide (GO) suspension as carbon sources for graphene-supported $LiFePO_4$/C composite.

Figure 1 presents XRD patterns of the $LiFePO_4(OH)$ precursor, LFP/C and LFP/C@G samples. As shown in Fig. 1, the diffraction peaks of the as-prepared LiFePO4(OH) samples match well with the standard diffraction peaks of $LiFePO_4(OH)$ (JCPDS No. 041–1376), indicating the high purity of the prepared $LiFePO_4(OH)$ sample. $2\theta = 17.82°$, 18.59°, 19.02°, 22.53°, 25.90°, 26.80°, 27.23°, 29.38° and

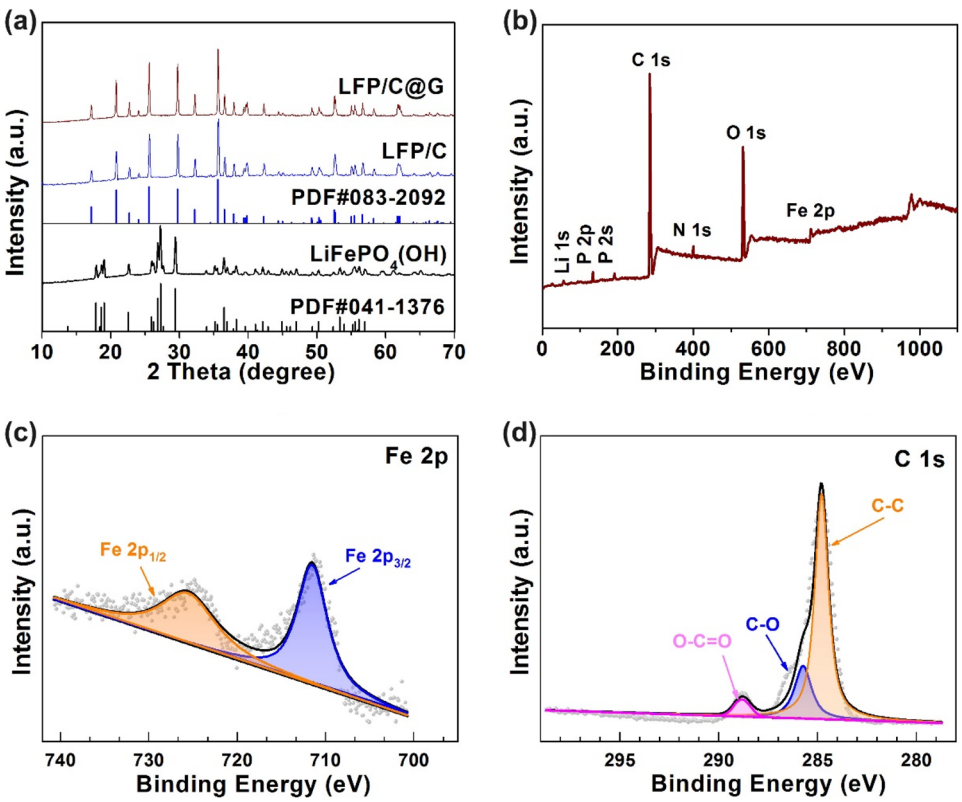


Fig. 1 XRD patterns for the as-prepared samples (**a**) as well as XPS survey (**b**) and high-resolution elemental of Fe 2p (**c**) and C 1 s (**d**) for the LFP/C@G

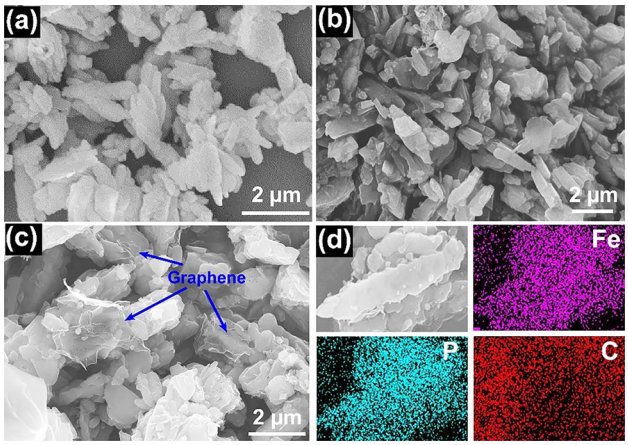


Fig. 2 SEM image of $LiFePO_4(OH)$ raw material (**a**), LFP/C (**b**) and LFP/C@G (**c**) as well as EDS images (**d**) of the LFP/C@G

36.47° positions correspond to the characteristic diffraction peaks of (100), (011), (001), (−101), (111), (021), (−120), (101) and (−201) crystal planes, respectively. In addition, the diffraction peaks of the obtained LFP/C and LFP/C@G samples from $LiFePO_4(OH)$ also are well indexed to olivine structured $LiFePO_4$ with space group Pnma (JCPSD 83–2092). This indicates that $LiFePO_4$/C composites with high purity can be synthesized using $LiFePO_4(OH)$ with Li, Fe and P elements as raw material. XPS spectrum was obtained to verify the elemental compositions and chemical states, shown in Fig. 1b–d. The XPS survey spectrums of the $LiFePO_4$/C@G sample show the typical peaks for Fe 2p, C 1 s, P 1 s and O 1 s, respectively. In the high-resolution spectrum of the Fe 2p, two peaks located at about 711 and 724 eV, matching to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, which may be ascribed to Fe (II) state [31]. In Fig. 1d, the peak for C 1 s at 284.7, 286.1 and 288.7 eV can be regarded as C–C band, C–O band and O–C = O band, which evidences the presence of the modified graphene [30].

Figure 2 shows SEM images of the $LiFePO_4(OH)$ precursor and carbon-coated $LiFePO_4$/C material. As seen from Fig. 2a, $LiFePO_4(OH)$ precursor possesses uniform spindle-shaped morphology with 2 μm in length and 300 nm in width. There is a smooth surface with no other impurity phase on the material particles. In Fig. 2b, SEM images of the carbon-coated LFP/C sample shows little different morphology compared with the $LiFePO_4(OH)$ precursor. This indicates that the morphology of LFP/C materials can be regulated by $LiFePO_4(OH)$ precursor. In order to further improve the rate performance of LFP/C, GO was added to the LFP/C sample, and its SEM was shown in Fig. 2c. In Fig. 2c, graphene can be observed in the LFP/C@G sample, indicating that the graphene is successfully coated on the surface of LFP/C particles. The EDS results of LFP/C@G in Fig. 2d show that C, P and Fe are uniformly distributed in the LFP/C@G sample. Therefore, the $LiFePO_4(OH)$ precursor can be used as raw materials for synthesizing uniform $LiFePO_4$/C materials without the ball milling, which is beneficial for engineering application [32, 33].

Figure 3 shows rate capability and cycling performances of the LFP/C and LFP/C@G samples synthesized from $LiFePO_4(OH)$ precursor. In Fig. 3a, the LFP/C sample shows

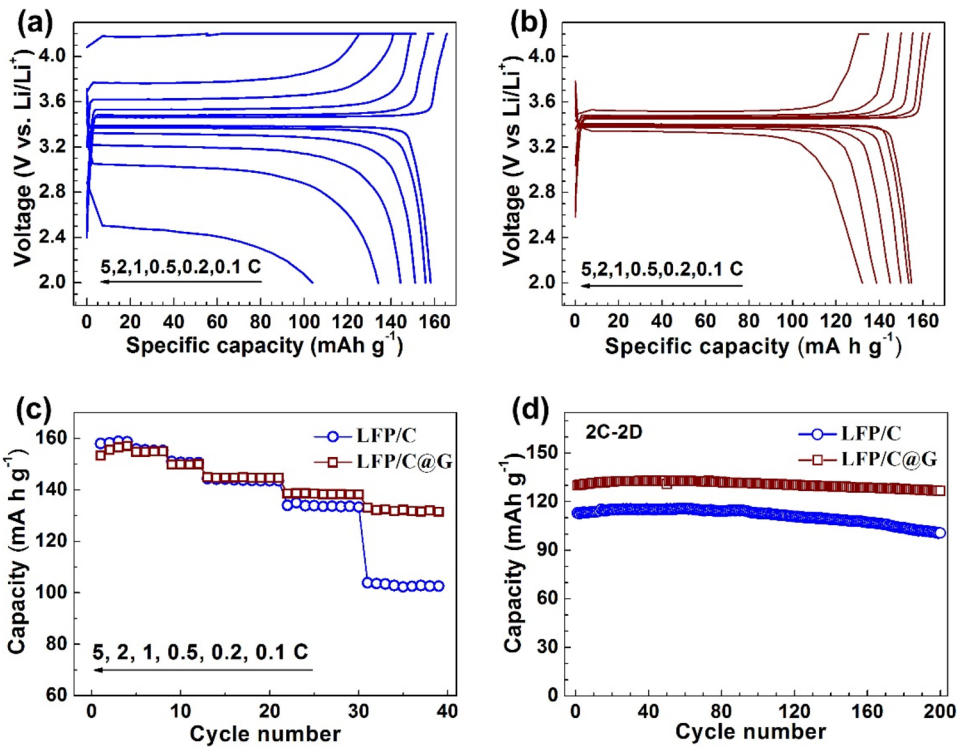


Fig. 3 Charge/discharge curves for LFP/C (**a**) and LFP/C@G (**b**) as well as their rate capability (**c**) and cycling performance (**d**)

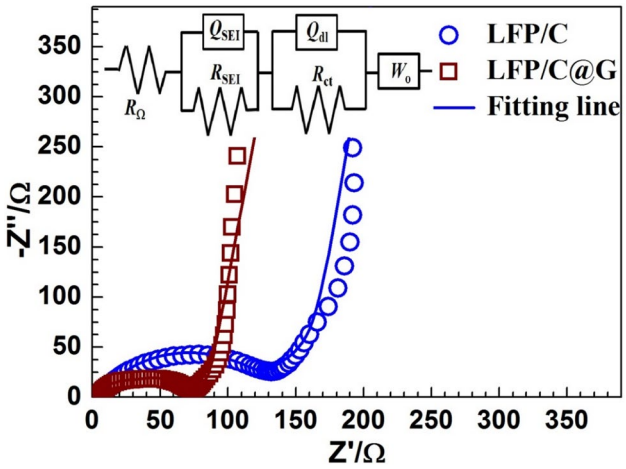


Fig. 4 EIS plots of LFP/C and LFP/C@G samples

an initial specific capacity of 158 mA h g^{-1} at rate of 0.1 C (close to theoretical capacity of 170 mA h g^{-1}), indicating a high purity of the as-prepared LFP/C sample, while the LFP/C sample just maintains a specific capacity of 135 and 106 mA h g^{-1} at a high rate of 2 and 5 C, respectively and shows a great polarization with merely a voltage platform of 2.5 V at 5 C, indicating that the rate performance of the LFP/C sample needs to be further improved. It is worthy of mentioning that the carbon content of the LFP/C and LFP/C@G samples is calculated to be 1.49 and 4.37 wt% from the thermogravimetric (TGA) curves (Fig. S1), respectively [34]. Therefore, the inferior rate performance of LFP/C sample may be mainly due to the low electronic conductivity resulting from less carbon content of only 1.49 wt%. To further improve the rate performance of the LFP/C sample, GO was added to the LFP/C sample for synthesizing the graphene-supported $LiFePO_4$/C composite (LFP/C@G). In Fig. 3b, the LFP/C@G delivers a specific capacity of 156, 154, 150, 145, 139, 132 mA h g^{-1} at 0.1, 0.2, 0.5, 1, 2 and 5 C with a higher voltage platform of 3.3 V at 5 C, showing excellent rate performance (Fig. 3c). As shown in Fig. 3d, the specific capacity of the LFP/C@G sample drops from 131 to 127 mA h g^{-1} in the 200 cycles at 2 C, showing a longer capacity retention of 97.0% compared with the LFP/C (capacity retention of 89.2%), indicating better cycling stability for LFP/C@G. The above electrochemical results demonstrate that a $LiFePO_4$ material with excellent electrochemical performances can be obtained using $LiFePO_4$(OH) as precursor combined with graphene modification.

Electrochemical impedance spectroscopy (EIS) of the as-prepared samples was performed in the fully discharged (lithiation) state, as shown in Fig. 4. The EIS profiles consist of a partially overlapped semicircle in the high-frequency region followed by a sloping line in the low-frequency region. The semicircle in the high- and middle-frequency regions is due to the charge-transfer resistance (R_{ct}). The sloping line in the lower frequency represents the Warburg impedance (W_s) associated with lithium-ion diffusion in the bulk of the electrode [35, 36]. By fitting data, the charge-transfer resistance of LFP/C and LFP/C@G samples was approximately 68 and 130 Ω, respectively, indicating better kinetic behavior of the LFP/C@G sample. The EIS result validates that the superior rate performance of LFP/C@G sample results from the improved electrochemical reaction kinetics.

Conclusion

In summary, we prepared a graphene-supported $LiFePO_4$/C@G composite with uniform morphology and electronic conducting network via a freeze-drying assisted solid-phase method using the integrated $LiFePO_4$(OH) as precursor. The as-prepared LFP/C samples show a similar spindle-shaped morphology as the $LiFePO_4$(OH) precursor, indicating a feasibility for regulation of the $LiFePO_4$/C morphology by $LiFePO_4$(OH). Moreover, the graphene-supported $LiFePO_4$/C@G shows better electrochemical properties with a specific capacity of 156, 154, 150, 145, 139, 132 mA h g^{-1} at 0.1, 0.2, 0.5, 1, 2, 5 C, which benefits from the synergetic effect of uniform $LiFePO_4$(OH) as precursor and continuous graphene electronic conducting network. The freeze-drying assisted solid-phase method using $LiFePO_4$(OH) as precursor without ball milling provides a new insight for solving the problem of particle agglomeration caused by ball milling in solid-state method. The strategy would apply to olivine materials with other transition metals (Mn, Co or Ni).

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