

Synthesis of Carbon-coated LiFePO₄ Composites as a Cathode Material for Improved Electrochemical Performance

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In this work, the C@LiFePO₄ composite was successfully synthesized by a simple pyrolysis process, using ascorbic acid as the carbon source. The morphology and microstructure of the C@LiFePO₄ composite were examined by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The electrochemical properties were evaluated by the cyclic voltammetry and electrochemical impedance spectroscopy and the rate performance. The uniform carbon coating layer could effectively improve the electrical conductivity and the reversibility of lithium-ion de-intercalation and intercalation in the LiFePO₄ particles. Compared to the pristine LiFePO₄, the C@LiFePO₄ composite displayed much better rate capability and cycling stability. The enhanced rate performance and cycling stability of the C@LiFePO₄ composite could be attributed to the better crystallinity, the improved electrical conductivity as well as the protective effect of carbon layer on LiFePO₄ structure within the crystal structure of the composite.

Keywords: Olivine LiFePO₄; Carbon coating; Pyrolysis process; Cathode materials; Electrochemical performance

1. INTRODUCTION

With the heavy consumption of non-renewable energy such as oil and natural gas and the continuous deterioration of the environment, human society is facing severe challenges. Under such circumstances, lithium ion battery (LIB) has been paid more and more attention for its environmental friendliness and superior performance. Olivine structure LiFePO₄, as a phosphate cathode material, due to its safety, environmental friendliness, low price, relatively high theoretical capacity and working voltage as well as good cycling performance, has become a new generation of cathode materials for

LIBs especially for power supply batteries [1]. However, the electrochemical properties of LiFePO_4 are deteriorated by its slow kinetics of lithium-ion diffusion coefficient (10^{-14} to 10^{-16} $\text{cm}^2 \text{s}^{-1}$) and poor electrical conductivity ($<10^{-9}$ S cm^{-1}) [2-4], which greatly restricts the application of LiFePO_4 cathode material in the field of LIBs. Thus, effective strategies are needed to improve the battery performance of lithium iron phosphate.

Surface coating of carbon material has been regarded as one of the most common and effective modification methods to improve the electrochemical properties of LiFePO_4 [5, 6]. Generally, carbon material coated on the surface of LiFePO_4 can on one hand serve as a conductive agent to improve the electrical conductivity [7], and on the other hand increase the material porosity in which the solid-state diffusion distances are significantly shortened thus to enhance the ionic conductivity [8]. Moreover, the coating of carbon materials can inhibit the growth of LiFePO_4 particles to a certain extent and maintain a smaller size, which would also benefit the ionic conductivity of LiFePO_4 [9, 10].

Herein, carbon-coated LiFePO_4 (C@LiFePO_4) composite particles were prepared by using ascorbic acid as carbon source through a simple pyrolysis approach, and their electrochemical performances as cathode materials were also investigated. It was found that the C@LiFePO_4 nanocomposites exhibited significantly enhanced cathode performances in comparison with the pristine LiFePO_4 cathode. This work further demonstrates the feasibility of carbon coating to improve the electrochemical properties of LiFePO_4 cathode in LIBs with great potential for practical applications.

2. EXPERIMENTAL

2.1 Synthesis of C@LiFePO_4 nanocomposites

Unless otherwise specified, all chemical reagents involved were of analytical grade and obtained commercially from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used as received without further purification. Milli-Q purified water (the resistivity ≥ 18 $\text{M}\Omega \text{ cm}$) was used during the experimental process. The experiments for materials synthesis were carried out at room temperature and humidity.

LiFePO_4 particles were firstly synthesized through a simple polyol process. Typically, iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and lithium dihydrogen phosphate (LiH_2PO_4) were dissolved in diethylene glycol (DEG) in a stoichiometric molar ratio of 1:1. The solution was then transferred to a round bottom flask assembled with a refluxing condenser, and heated at 320 $^\circ\text{C}$ for 12 h. After reflux reaction, the precipitates were carefully collected by filtration and washing with deionized water and acetone for several times, followed by drying at 120 $^\circ\text{C}$ for 12 h under vacuum. The product of LiFePO_4 particles was thus obtained.

The obtained LiFePO_4 particles were subsequently dispersed in 5 wt.% of ascorbic acid ethanol solution under magnetic stirring overnight, and allowed it to be gelatinized. The gelatinized particles were dried in vacuum oven at 80 $^\circ\text{C}$, and then precalcined at 350 $^\circ\text{C}$ for 4 h and further calcined at 700 $^\circ\text{C}$ for 10 h under Ar atmosphere. After cooling to room temperature, the calcined powder was

fully grinded to obtain the C@LiFePO₄ composite particles.

2.2 Materials Characterizations

The morphological features of the samples were characterized by using a field-emission scanning electron microscope (FESEM, HITACHI SU8010) and a transmission electron microscope (TEM, JEOL JEM-2100). The crystal structures of the samples were identified on a X-ray diffraction (XRD) (ARL, X'TRA) using Cu K α radiation ($\lambda = 0.15406$ nm), in which the measured 2θ values were ranged from 10° to 80° at room temperature. To determine the content of carbon in the C@LiFePO₄ sample, the thermogravimetric (TG) analysis was carried out using a thermogravimetric analyzer (SMP/PF7548/MET/600W, Mettler, Switzerland) with a heating rate of 10 °C min⁻¹ in air.

2.3 Electrochemical measurements

The electrochemical properties of the prepared samples were examined using coin cells. The uncoated and carbon-coated LiFePO₄ electrodes were fabricated by casting the slurry consisting of 80 wt% of active material (the prepared LiFePO₄ particles or C@LiFePO₄ composite particles), 10 wt% of conductive Super P carbon (Taiyuan lithium power technology center, China), and 10 wt% of poly(vinylidene fluoride) (PVDF, J&K Scientific Ltd.) in *N*-methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd., China) onto an aluminum foil. The fabricated electrode sheets were then dried at 120 °C under vacuum overnight and roll pressed, and further punched into circular discs for coin cells. The coin cell (CR2032) was fabricated using the circular disc as cathode and lithium metal (Taiyuan lithium power technology center, China) as a counter electrode separated by the polypropylene separator (Celgard 2400). The electrolyte used in the cells was a solution of 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) (Beijing Institute of Chemical Reagents, China). These cells were assembled in an argon-filled glovebox (Super 1220/750, MIKROUNA) and galvanostatically cycled between 2.5 V and 4.2 V (*vs.* Li/Li⁺) on a multi-channel battery cycler (Land Battery Test System). The electrochemical impedance spectra (EIS) were measured on an electrochemical workstation (CHI660E, Shanghai Chenhua Co., China), with the frequency range from 100 kHz to 10 mHz by applying an AC voltage of 5 mV amplitude, respectively. The cyclic voltammogram (CV) measurements were carried out at room temperature on the same electrochemical workstation (CHI660E, Shanghai Chenhua Co.) over the potential range 2.0~4.2 V *vs.* Li/Li⁺ at the scan rate of 0.1 mV s⁻¹.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the prepared pristine LiFePO₄ and C@LiFePO₄ composite cathode materials. As seen, the XRD pattern of C@LiFePO₄ composite material was identical to that of LiFePO₄ material, and all the XRD characteristic diffraction peaks were well consistent with the JCPDS file (no. 40-1499) for a pristine orthorhombic phase of LiFePO₄ [11]. This means that the

surface coating of carbon would not destroy the inherent olivine-crystal structure of LiFePO_4 . Meanwhile, the XRD peak intensities of the C@LiFePO_4 composite were relatively stronger than those of the pristine LiFePO_4 , indicating that the pyrolysis process for carbon coating would improve the crystallinity degree of the C@LiFePO_4 composite. The higher crystallinity of C@LiFePO_4 generally indicates fewer intrinsic defects, which would be more favorable for the transmission and migration of lithium ions [12, 13], thus probably leading to better electrochemical properties.

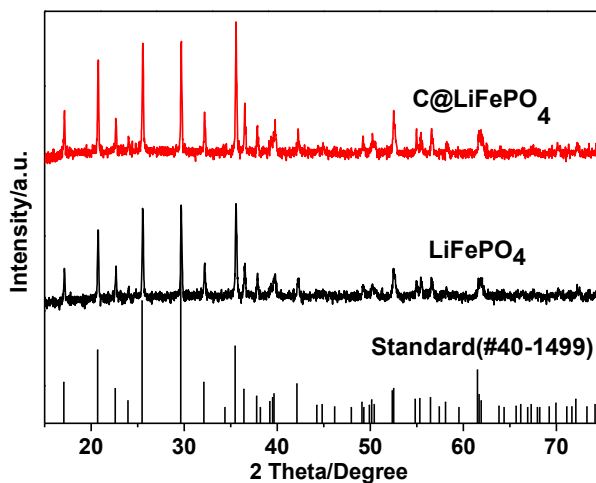


Figure 1. The XRD patterns of as-prepared LiFePO_4 and C@LiFePO_4 cathode materials.

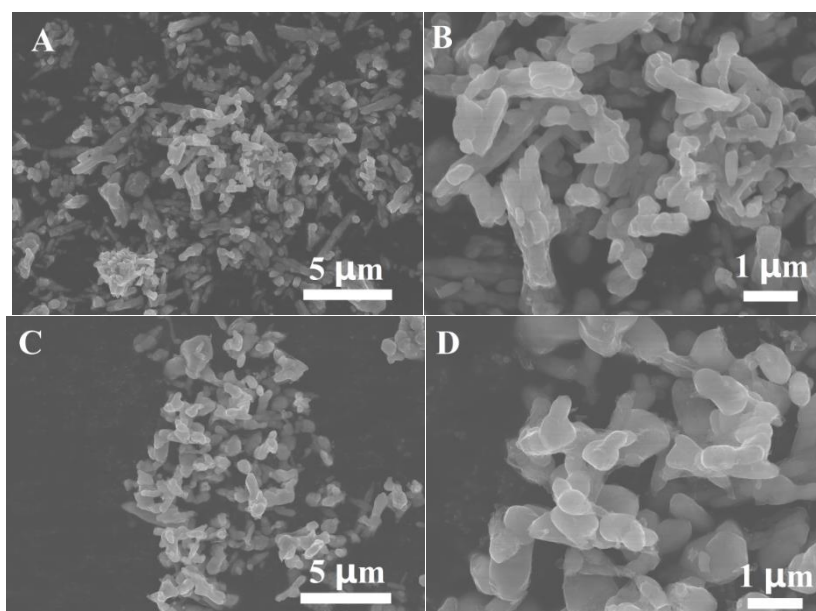


Figure 2. FESEM images of as-prepared LiFePO_4 (A, B) and C@LiFePO_4 (C, D) cathode materials at different magnifications.

Figure 2 presents the SEM images of the prepared pristine LiFePO_4 and C@LiFePO_4 composite cathode materials. Both pristine LiFePO_4 (Figure 2(A) and (B)) and C@LiFePO_4 (Figure

2(C) and (D)) composite materials were irregularly-shaped particles with an average particle size of about 1.5 μm , confirming that the surface coating of carbon did not significantly change the morphological feature of LiFePO_4 material. However, the surface coating of carbon could to some extent reduce the agglomeration degree of LiFePO_4 particles. To further investigate the effect of surface coating of carbon on the morphological features of LiFePO_4 particles, the prepared LiFePO_4 and C@LiFePO_4 composite particles were also examined by TEM technique. Figure 3 shows the TEM images of the pristine LiFePO_4 and C@LiFePO_4 composite materials at different magnifications. As shown, the irregular particle of LiFePO_4 was about 1.5 μm with a relatively smooth surface (Figure 3(A) and (B)), while the C@LiFePO_4 composite was composed of irregular particles covered with a rough surface (Figure 3(C) and (D)). Such a rough surface on the C@LiFePO_4 particles was probably due to the surface coating of carbon layer. Meanwhile, the surface coating of carbon would also slightly restrain the particles' aggregation, thus making the particles' size of C@LiFePO_4 smaller in comparison with the pristine LiFePO_4 .

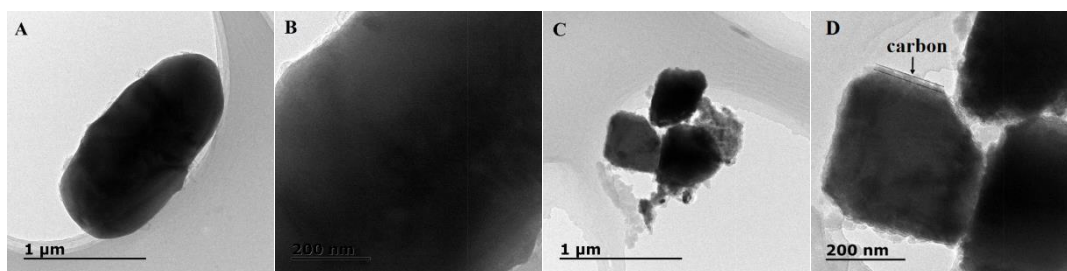


Figure 3. TEM images of the prepared (A) (B) LiFePO_4 and (C) (D) C@LiFePO_4 cathode materials.

In order to determine the exact amount of carbon in the C@LiFePO_4 composite material, the TG analysis was performed. Figure 4 shows the TG data of the prepared pristine LiFePO_4 and C@LiFePO_4 composite materials, which were tested under oxygen atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ with a temperature range from 50 $^{\circ}\text{C}$ to 900 $^{\circ}\text{C}$. It can be seen that the pristine LiFePO_4 sample gained a weight of 5.32% ranging from 50 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$, which could be attributed to the formation of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and Fe_2O_3 during oxidation [14, 15]. In contrary, the C@LiFePO_4 composite exhibited an initial weight gain of 4.9% within the temperature range of 50 $^{\circ}\text{C}$ to 470 $^{\circ}\text{C}$, followed by a weight loss to 100.92%. According to the previous report [16], the carbon content of the C@LiFePO_4 sample could be estimated from the difference between the TG curves of LiFePO_4 and C@LiFePO_4 . Thus, the carbon content of C@LiFePO_4 was found to be about 4.4%.

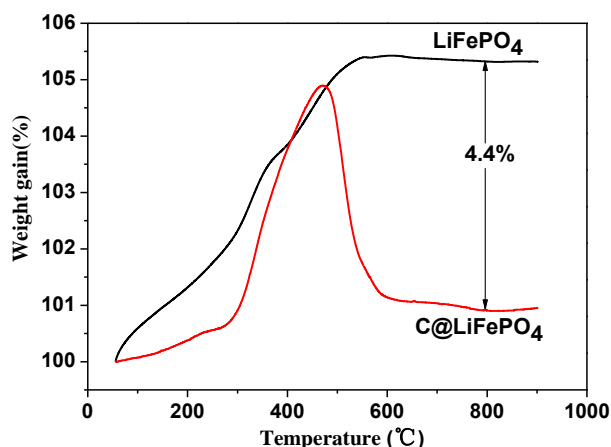


Figure 4. TG curves of as-prepared LiFePO₄ and C@LiFePO₄ cathode materials.

The electrochemical properties of the prepared LiFePO₄ and C@LiFePO₄ composite samples were examined to investigate the influence of carbon coating on the electrochemical properties of LiFePO₄, including CV curves, electrochemical impedance spectra and rate performance. Figure 5 shows the CV curves of the prepared pristine LiFePO₄ and C@LiFePO₄ samples. Both samples displayed a pair of redox peaks with a relatively good symmetry, in association with the de-intercalation and intercalation of lithium ions. The oxidation and reduction peak of the pristine LiFePO₄ cathode materials were 3.7 V and 3.3 V, respectively, with a potential difference of 0.4 V, whereas the oxidation and reduction peak of the prepared C@LiFePO₄ composite located at 3.6 V and 3.3 V, respectively, with a relatively smaller potential difference of 0.3 V. Compared with the pristine LiFePO₄, the potential difference of C@LiFePO₄ composite was reduced by 0.1 V, indicating the improved reversibility of the de-intercalation and intercalation of lithium ions and the weakened polarization within the C@LiFePO₄ composite [17]. In addition, the current intensity of the redox peak of C@LiFePO₄ composite was also slightly higher than that of pristine LiFePO₄, arising from the improved electrical conductivity of the C@LiFePO₄ composite induced by carbon coating [18]. Figure 6 shows the typical EIS Nyquist plots of the prepared pristine LiFePO₄ and C@LiFePO₄ samples, consisting of a semicircle in the high frequency region and a straight line in the low frequency region. It was found that the charge transfer resistance (R_{ct}) of the prepared C@LiFePO₄ sample was only about 53.1 Ω , which was significantly less than that (~226.0 Ω) of the prepared pristine LiFePO₄. This confirms that the surface carbon coating would effectively improve the electrical conductivity of LiFePO₄ particles, thus further leading to the decreased charge transfer resistance of C@LiFePO₄.

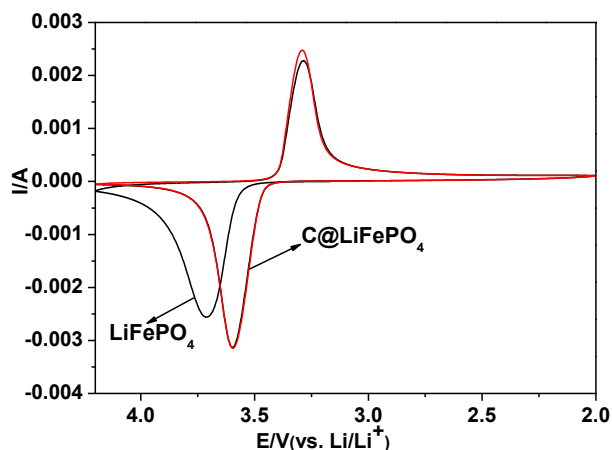


Figure 5. Cyclic voltammety curve of as-prepared LiFePO_4 and C@LiFePO_4 cathode materials in the range of 2.0~4.2 V.

Figure 7 shows the rate performance of the prepared pristine LiFePO_4 and C@LiFePO_4 composite materials, which were performed in the potential range of 2.5 V ~ 4.2 V at a rate of 0.1 C, 0.5 C and 1 C, respectively. As seen, all the specific discharge capacities of the prepared C@LiFePO_4 composite at different rates were much higher than those of the prepared pristine LiFePO_4 cathode. The specific discharge capacities of the prepared pristine LiFePO_4 cathode were 121.5, 79.2 and 53.4 mAh g^{-1} , respectively, and the specific discharge capacities of the prepared C@LiFePO_4 composite were improved to 147.0, 104.9 and 85.9 mAh g^{-1} at 0.1 C, 0.5 C and 1 C, respectively.

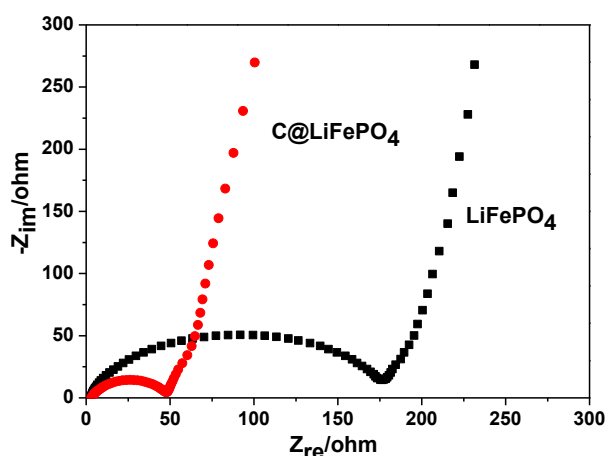


Figure 6. Electrochemical impedance spectra of as-prepared LiFePO_4 and C@LiFePO_4 cathode materials.

More importantly, after 25 cycles, the C@LiFePO_4 cathode retained the discharge capacity of 141.6 mAh g^{-1} (~96.3% of the initial capacity), 100.2 mAh g^{-1} (~95.5% of the initial capacity) and 81.3 mAh g^{-1} (~94.6% of the initial capacity) at a rate of 0.1 C, 0.5 C and 1 C, respectively, while the pristine LiFePO_4 cathode retained only 117.6 mAh g^{-1} (~96.8% of the initial capacity), 68.1 mAh g^{-1} (~86.0% of the initial capacity) and 45.1 mAh g^{-1} (~84.5% of the initial capacity), respectively.

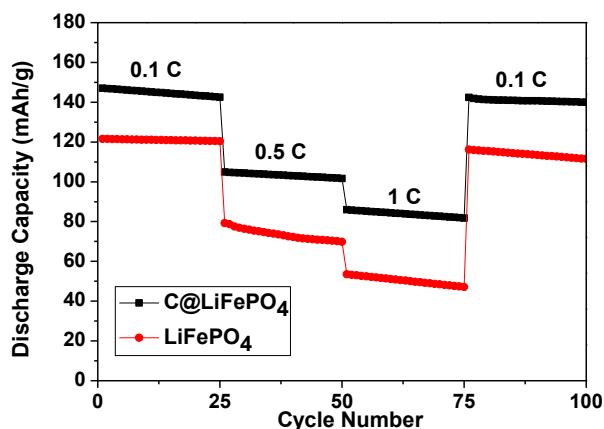


Figure 7. The rate performance of as-prepared LiFePO₄ and C@LiFePO₄ cathode materials.

This result demonstrates that the C@LiFePO₄ sample possessed much better cycling stability than the pristine LiFePO₄ sample. It should be noted that when the current density went back to 0.1 C, the prepared C@LiFePO₄ sample could exhibit a reversible capacity of 143.5 mAh g⁻¹, demonstrating its relatively good reversibility. The improved rate performance and cycling stability of the prepared C@LiFePO₄ composite cathode could be attributed to the following reasons. Firstly, the prepared C@LiFePO₄ composite cathode possessed a higher crystallinity with less intrinsic defects, which would be favorable for the transferring and migration of lithium ions within the crystal [19]. Secondly, the carbon layer coated on the surface of LiFePO₄ particles could improve the electrical conductivity and thus decrease the charge transfer resistance [20], which would further improve the rate performance. Lastly, the carbon layer coated on the surface of LiFePO₄ particles could also effectively alleviate the damage of LiFePO₄ structure from electrolyte corrosion during the delithiation-lithiation process of cycling [5, 21], thus achieving the excellent cycling stability of the C@LiFePO₄ composite at different current densities.

4. CONCLUSIONS

In summary, LiFePO₄ particles were successfully synthesized by a polyol method, and a layer of carbon was then uniformly coated on the surface of LiFePO₄ to obtain the C@LiFePO₄ composite particles through a simple pyrolysis process by using ascorbic acid as carbon source. The carbon coating would not destroy the inherent olivine-crystal structure of LiFePO₄, and had no remarkable influence on the morphological features of the LiFePO₄ particles. The carbon amount in the C@LiFePO₄ composite was determined to be about 4.4%. Compared to the pristine LiFePO₄, the C@LiFePO₄ composite materials exhibited much improved electrochemical properties, including the better reversibility of the de-intercalation and intercalation of lithium ions, the improved electrical conductivity, the decreased charge transfer resistance, as well as the improved rate performance and cycling stability. This work demonstrates that the as-prepared C@LiFePO₄ composite offers pretty good lithium storage capacity and rate capability, indicating its great potential as a cathode material for

high-performance lithium ion batteries.

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