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# A novel synthesis and characterization of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C as a cathode material for lithium-ion battery

Cui Miao<sup>a</sup>, Peifeng Bai<sup>a</sup>, Qianqian Jiang<sup>b</sup>, Shuqing Sun<sup>a</sup>, Xingyao Wang<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, School of Sciences, Tianjin University, Tianjin 300072, China <sup>b</sup> Department of Applied Chemistry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

#### HIGHLIGHTS

• LiFePO<sub>4</sub> is synthesized for the first time by a hydrothermal stripping route.

• Hydrothermal stripping is an effective, simple and green route to synthesize material.

• Coating carbon effectively improves the electrochemical performance of LiFePO<sub>4</sub>.

• LiFePO<sub>4</sub>/C has an excellent electrochemical performance for lithium ion batteries.

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#### ABSTRACT

A novel hydrothermal stripping technique is developed to synthesize pure LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C cathode materials. The pure sample is directly synthesized by the cation exchange between the organic phase which is prepared with FeSO<sub>4</sub>·7H<sub>2</sub>O and naphthenic acid, and aqueous phase prepared with H<sub>3</sub>PO<sub>4</sub> and LiOH. SEM exhibits that the primary sizes of the well-distributed LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C particles are about 150 nm and 100 nm in diameter, respectively. TEM indicates the LiFePO<sub>4</sub>/C is uniformly coated with a carbon layer about 2.7 nm in size. The as-prepared LiFePO<sub>4</sub> exhibits a high initial discharge capacity of 135.5 mAh g<sup>-1</sup> at 0.1 C, and the LiFePO<sub>4</sub>/C composite sintered at 650 °C for 4 h exhibits the best electrode properties with discharge capacities of 151.7, 154.8, 149.8 and 139.1 mAh g<sup>-1</sup> at 0.1 C, 0.2 C, 0.5 C and 1.0 C rates, respectively. In addition, the LiFePO<sub>4</sub>/C also shows excellent capacity retention and cycle performances.

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#### 1. Introduction

Lithium-ion batteries, due to high energy density and working voltage, currently have better preference than other secondary battery systems [1]. Since the abundant raw materials, no toxicity, environmentally friendly and low cost [2], olivine LiFePO<sub>4</sub> has been considered as the most promising candidate electrode material for Li-ion batteries. Now, LiFePO<sub>4</sub> has been widely used in backup power systems and in electric and hybrid electric vehicles, as it presents a high theoretical capacity (170 mAh g<sup>-1</sup>) and thermal stability at high temperature [3,4]. However, LiFePO<sub>4</sub> has two obvious disadvantages: (1) low electronic conductivity leading to poor performance and actual specific capacity [5]. (2) Low tap density resulting in low volume specific capacity, which hinders the practical application of LiFePO<sub>4</sub> material used in small (portable

\* Corresponding author. E-mail address: wxyghw@tju.edu.cn (X. Wang). electronics) and large (heavy and light duty vehicles) applications [6]. Hence, some attempts have been made to improve the rate performance of LiFePO<sub>4</sub>, such as doping metal ions [7,8], coating an electronically conductive phase [9,10], minimizing the particle size [11], and developing new synthesis methods.

LiFePO<sub>4</sub> has been synthesized by many different techniques. In current, many researchers still adopt the traditional solid-state reaction synthesis method [12,13]. However, the severely grinding and long-time sintering cycles usually lead to the formation of larger particles with lower electrochemical performance. In contrast, the liquid-phase method, such as the sol–gel method [14], the coprecipitation method [15] and the hydrothermal method [16], usually can prepare pure materials with small particle size. This can reduce the diffusion distance of lithium ion in cathode materials and accelerate extrusion speed to improve the electrochemical performance. Ni et al. synthesized LiFePO<sub>4</sub> in a short time via hydrothermal process in the presence of organic acid, e.g. citric acid or ascorbic acid, and their discharge capacity of pure LiFePO<sub>4</sub> is 128 mAh g<sup>-1</sup>







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[17]. Yu et al. reported that the LiFePO<sub>4</sub>/C was synthesized via carbothermal method by using different carbon sources, and the results of discharge capacity are unsatisfactory [18]. The hydrothermal technique initially used by Whittingham [19,20] for one-pot synthesis of LiFePO<sub>4</sub>, is an efficient method for preparing small LiFePO<sub>4</sub> particles. The conventional hydrothermal technique mostly used FeSO<sub>4</sub>·7H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub> and LiOH·H<sub>2</sub>O as the starting materials without any preprocessing process. In this work, a hydrothermal stripping technique [21,22] is developed for high-performance applications of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C. It is known that the naphthenic acid is a feasible efficiently metal extractant which is used in our synthesis route. Comparing to the conventional methods, the hydrothermal stripping synthesis can avoid other ions to poison the product, because the ferrous ion can be stripped and precipitated directly from the iron (II)-loaded organic phase by naphthenic acid. And when the stripping process is controlled properly, the pure LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C with small particle size can be produced. So we prepared the precursor via the stripping technique and described a new method based on hydrothermal stripping technique according to coupling principle to synthesize LiFePO<sub>4</sub>. The hydrothermal stripping is a facile, fast, one step synthesis, low consumption of drugs, effectively reaction control and green synthesis (organic and water phases could be recycled) method which is more suitable for industrial production. Therefore, the hydrothermal stripping technique which can be used to synthesize the pure materials with small particle size will be a promising method to synthesis LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C as cathode materials with excellent electrochemical performance for lithium ion batteries.

#### 2. Experimental

#### 2.1. Synthesis of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C

The hydrothermal stripping synthesis was started with an aqueous solution and an organic phase. The preparation of the aqueous solution: a certain amount of H<sub>3</sub>PO<sub>4</sub> solution and LiOH (the molar ratio of the Li:P was 1.2:1) was transferred to a beaker, and ascorbic, used as a reducing agent was added into the solution. The preparation of the organic phase: the iron (II)-loaded naphthenic acid was prepared immediately prior to each hydrothermal stripping experiment by mixing naphthenic acid and isooctyl alcohol, saponifying by 1:1 (v/v) ammonia, and adding FeSO<sub>4</sub>·7H<sub>2</sub>O. The solution was stirred for 0.5 h, the organic phase and aqueous phase were separated and the organic phase was washed with deionized water. In hydrothermal stripping experiment, first transfer the aqueous phase and organic phase into a stainless steel autoclave and heat to 250 °C for 3 h with vigorously stirring. After being cooled to 80 °C, maintain the temperature for 5 h, and the precipitate obtained was washed several times with deionized water and alcohol. At last, the product was dried at 80 °C for 12 h. Then mixed with a measured amount of glucose, the mixture was sintered at different temperatures for 4 h in a tubular furnace under an argon atmosphere.

#### 2.2. Characterization of samples

The crystal structures and phases of the LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C samples were identified by X-ray diffraction (XRD) (Rigaku D/max 2500v/pc made in Japan), and the local structure identified by a fourier transform infrared spectroscopy (FTIR) (NEXUS 470 FTIR Spectrometer made by Thermo). The lattice parameters of the lithium iron phosphate were refined by Rietveld analysis. The crystal morphology, particle size and carbon-coating layer of the samples were recorded by a transmission electron microscope (TEM, 100CX-II made by JOEL, Tokyo, Japan) and a scanning electron

microscopy (SEM, S-4800 made by Japan). Raman spectrum was recorded using a multi-wavelength micro-Raman spectroscope (JY HR800) utilizing 532.05 nm incident radiation and a 50 × aperture. Thermogravimetric analysis (NETZSCH STA 449 F3 Jupiter) measurement was performed from room temperature to 800 °C with the heating rate of 10 °C min<sup>-1</sup> in air atmosphere. The surface area of LiFePO<sub>4</sub>/C was measured by the Brunauer–Emmett–Teller (BET) (NOVA2200e, USA).

The electrochemical performance was evaluated in CR2032 coin-type cells. The cathode was prepared by mixing the active materials with acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 dissolved in N-methyl-2-pyrrolidinone (NMP) to form slurry with the assistance of ultrasound. The slurry was pasted onto an aluminum current collector and dried at 120 °C for 12 h under a vacuum atmosphere. The electrolyte 1 M LiPF<sub>6</sub> was dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ methyl-ethyl carbonate (EMC) (1:1:1, v/v). Celgard 2400 was used as the separator, while Li foil served as the counter electrode. The assembly was carried out in a pure argon-filled glove box (Etelux, Lab 2000/MB 200G) with the content of H<sub>2</sub>O and O<sub>2</sub> less than 1 ppm. The galvanostatic charge-discharge experiment was conducted using a battery testing system (LAND, CT2001A made by China) from 2.5 to 4.2 V at room temperature. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) curves were performed on an electrochemical analyzer (Gamry, PC14-750 made by USA).

#### 3. Results and discussions

#### 3.1. Structure analysis of the LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C powders

Hydrothermal synthesis is a powerful method to form a wide range of olivine-structured and well-crystalline materials with particle size generally in the micron size. Moreover, the temperature of the synthesis must exceed 175 °C to minimize iron disorder and to obtain material with the correct lattice parameters and volume [23–25]. In addition, citric acid or glucose was found to be an effective agent to minimize oxidation of ferrous to ferric in the aqueous solution used and to restrain the particle growth, and enhancing the electronic conductivity of the active material [20,26].

Fig. 1 shows the XRD patterns of the synthesized LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C powder. All the intense peaks in the spectrum clearly show a single phase formation of an olivine structure, which indicates that all three samples are well indexed to an orthorhombic, *Pnmb* space group (JCPDS Card NO.40-1499) without any impurity phase. However, the peaks of the LiFePO<sub>4</sub> (Fig. 1b) and LiFePO<sub>4</sub>/C



Fig. 1. XRD patterns of LiFePO<sub>4</sub> obtained without post-heat treatment (a), LiFePO<sub>4</sub> (b) and LiFePO<sub>4</sub>/C (c) obtained after post-heat treatment.

(Fig. 1c) with the post-heat treatment at 650 °C for 4 h are more narrow and sharp, which present a good crystalline degree compared with pure LiFePO<sub>4</sub> (Fig. 1a) without post-heat treatment. The calculated lattice constants of the as-synthesized samples are listed in Table 1. The lattice parameters of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C obtained after post-heat treatment changed little compared with those of LiFePO<sub>4</sub> without post-heat treatment, indicating that the well crystalline of the samples. Simultaneity, no obvious peaks corresponding to graphite are found in the XRD pattern, meaning that the carbon in the sample is not well crystallized and the coated carbon layers can only influence the surface of LiFePO<sub>4</sub> particles, and have almost no effect on the bulk.

The Fourier transform infrared spectroscopy (FTIR) is known to be a good method for investigating the structure of the sample at a local scale. The FTIR absorption spectrum of the carbon-coated LiFePO<sub>4</sub> (650 °C for 4 h) sample was shown in Fig. 2. The label shows that only the bands intrinsic to LiFePO<sub>4</sub> are observed, this indicates that no impurity phase poisons the material [27,28]. The FTIR absorption spectrum is a probe of the bulk properties. Individual absorbance maxima of the stretching modes are in the range 982–1136 cm<sup>-1</sup>. This corresponds to the stretching modes of PO<sub>4</sub><sup>3-</sup> unit and the bands in the spectra range  $400-550 \text{ cm}^{-1}$  are sensitive to the local lithium environment. The FTIR spectrum displays no absorption at 424 cm<sup>-1</sup> which is the vibrational signature of Li<sub>3</sub>PO<sub>4</sub> [29]. The FTIR absorption spectrums of LiFePO<sub>4</sub> and carbon-coated LiFePO<sub>4</sub> have no obvious difference, indicating that the amount of carbon in the sample cannot influence the basic framework of the sample. The FTIR exhibits the position of the peaks intrinsic to the material, which reveals that the sample produced via the hydrothermal stripping technique, is without impure matter to poison the crystalline structure, and this corresponds well to the spectrum of XRD (Fig.1c).

To study the carbon state of LiFePO<sub>4</sub>/C composite, the corresponding Raman spectrum has been presented in Fig. 3. The Raman spectrum of LiFePO<sub>4</sub>/C contains two peaks, one is at 1343 cm<sup>-1</sup>, which is attributed to the D-band and the other is at 1596  $\,\,{\rm cm^{-1}}$ which is assigned to the G-band. The G-peak corresponds to graphite in-plane vibrations with E<sub>2g</sub> symmetry, and the D-peak is generally associated with a double-resonance effect [30]. The value  $I_D/I_G$  can be used to evaluate the degree of disorder for the pyrolytic carbon. The low peak intensity ratio of  $I_D/I_G$  ( $I_D/I_G = 1.41$ ) as well as the G-band position gives a measure of the quality of the carbon coating, indicating the carbon is mainly in amorphous state [31,32]. There is also a low peak at 960 cm<sup>-1</sup> associated with the intramolecular stretching mode of  $PO_4^{3-}$  unit which shows blue iridescence dominated by the two bands characteristic of carbon [33]. The nitrogen ad/desorption isotherm was measured to determine the Brunauer-Emmett-Teller (BET) surface area of LiFePO<sub>4</sub>/C composite as shown in Fig. 4, and the surface area of LiFePO<sub>4</sub>/C is 6.534 m<sup>2</sup> g<sup>-1</sup>.

## 3.2. The morphology and particle size of the LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C powders

Fig. 5 shows SEM images of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C composite samples. Rodlike and small size particles with minimal agglomeration

#### Table 1

Structural lattice parameters of LiFePO<sub>4</sub> without post-heat treatment, LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C obtained after post-heat treatment.

Sample	LiFePO4 without post-heat treatment	LiFePO <sub>4</sub> obtained after post-heat treatment	LiFePO <sub>4</sub> /C
a (Å <sup>3</sup> )	10.348	10.332	10.339
b (Å <sup>3</sup> )	6.007	6.004	6.011
c (Å <sup>3</sup> )	4.703	4.691	4.700
v (Å <sup>3</sup> )	292.36	291.06	292.14



**Fig. 2.** Fourier transform infrared spectroscopy (FTIR) spectrum of pure LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C samples.

are obtained for both LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C. The primary particles of the LiFePO<sub>4</sub> sample obtained at a sintering temperature of 650 °C for 4 h (a) are about 200–300 nm in length and 150 nm in diameter. Compared with LiFePO<sub>4</sub> (a), the LiFePO<sub>4</sub>/C (c) particles sintered at the same temperature and time are smaller due to the inhibition of crystal growth to a great extent, by the presence of carbon in the reaction mixture [34]. The particle sizes of the LiFePO<sub>4</sub>/C samples (b-f) increase as sintering temperature increases. At a low temperature of  $600 \,^{\circ}C(b)$ , the sizes of the particles are more unequal in size with a broad size distribution. By increasing the temperature to  $650 \degree C(c)$ , the major grains of LiFePO<sub>4</sub>/C sample were of a size about 100–150 nm in length and 100 nm in diameter. Along with the temperature increasing (d: 700 °C, e: 750 °C), the particle size of the LiFePO<sub>4</sub>/C samples is remarkable different. There are a greater number of agglomerated micro-sized sticks that are most likely grown on the account of small grains. At 800 °C (f), the particles agglomerated greatly with the growth of the primary particles which is comparable to the theoretically calculated growth morphology of LiFePO<sub>4</sub> [35]. Reducing the sintering temperature is favorable for preventing particle growth but unfavorable for crystalline. Therefore the better feasible sintering temperature is 650 °C.

#### 3.3. TEM and TG analysis of LiFePO<sub>4</sub>/C

Fig. 6 shows the TEM images of LiFePO<sub>4</sub>/C composite. It is clearly seen that the crystal lattice of LiFePO<sub>4</sub> and the surface of particles are coated and connected by carbon derived from glucose. The



Fig. 3. Raman spectroscopy of LiFePO<sub>4</sub>/C composite.



Fig. 4. Nitrogen adsorption/desorption isotherms of the LiFePO<sub>4</sub>/C composite.

suitable carbon layer is a primary decisive factor on the improvement of electrochemical performance of LiFePO<sub>4</sub>. The surface of LiFePO<sub>4</sub> coated with a carbon layer can inhibit the particle growth and help obtain a smaller particle [20,25]. Moreover, the thinner carbon layer is not adequate to form a continuous conductive layer to enhance the electronic conductivity, while the thicker carbon layer would reduce the tap density of the sample [36]. It can be clearly seen from the high resolution TEM image (Fig. 6b), that there is a ~2.7 nm thick amorphous carbon layer evenly coating the LiFePO<sub>4</sub> particles.

The carbon content of the LiFePO<sub>4</sub>/C sample was measured by the thermogravimetric (TG) method in air as shown in Fig. 7. TG result showed the sample started to lose weight below 350 °C, attributed to the physisorbed water molecules and the chemisorbed polyol species. At higher temperature, the LiFePO<sub>4</sub>/C sample began to be oxidized to Li<sub>3</sub>Fe<sub>2</sub> (PO<sub>4</sub>)<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> with the mass of the sample starting to grow. At about 650 °C, the LiFePO<sub>4</sub>/C sample finished the oxidizing reactions in air and the mass of the sample contained constant. The total weight gain in the TG is about 2.61%, and then the carbon content is calculated to be 2.46 wt% (5.07%– 2.61%) [33,37,38]. In additional, the tap density of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C samples is measured by tap density instrument (FZS4-4B, China), and the tap density of the samples is 0.87 and 0.83 g cm<sup>-3</sup>, respectively.

### 3.4. Effects of carbon content on the discharge and cycling performance of LiFePO<sub>4</sub>/C

Fig. 8 presents that the carbon content influence the potential application of LiFePO<sub>4</sub> in lithium-ion battery, and its electrochemical performance with respect to a Li intercalation/deintercalation is investigated in the voltage range of 2.5-4.2 V. The active material loading on the composite electrode is between 2.4 and 2.64 g, the thickness of the electrode is 150  $\mu$ m and a rate of 1.0 C corresponded to a current density of 170 mA  $g^{-1}$ . As shown in Fig. 8(A), all the samples are prepared at 650 °C for 4 h in an Ar atmosphere. The initial discharge capacity of the LiFePO<sub>4</sub> is 132.0 mAh  $g^{-1}$  at 0.2 C, which is higher than the previous report [17,39,40]. Compared with the bare LiFePO<sub>4</sub>, the initial specific capacity of LiFePO<sub>4</sub>/C is 154.8 mAh  $g^{-1}$  at 0.2 C, and there is a distinct capacity skip phenomenon. Fig. 8(B) shows the charge-discharge curves, for various currents, of LiFePO<sub>4</sub>/C sample. The discharge capacities are 151.7 mAh  $g^{-1}$ , 154.8 mAh  $g^{-1}$  and 149.8 mAh  $g^{-1}$  at a rate of 0.1 C. 0.2 C and 0.5 C. respectively. Even at the high rate of 1.0 C, the cathode delivers a high discharge capacity of 139.1 mAh  $g^{-1}$  with a stable flat discharge voltage plateau above 3.0 V upon increasing current.

The cycling performances of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C are showed in Fig. 8(C). The first specific discharge capacity of the LiFePO<sub>4</sub> is 135.5 mAh g<sup>-1</sup> at 0.1 C, and the specific capacity is 136.5 mAh g<sup>-1</sup> after 10 cycles. Compared to 0.1 C, the specific capacity is 132.0 mAh g<sup>-1</sup>, 115.2 mAh g<sup>-1</sup>, 90.4 mAh g<sup>-1</sup>, and their capacity retention is 99.1%, 96.4%, 93.6% at 0.2 C, 0.5 C and 1.0 C after 10 cycles, respectively. The figures show that the pure LiFePO<sub>4</sub> samples display inferior rate performances attributing to its poor electronic conductivity, especially the high rate performance. Whereas the LiFePO<sub>4</sub>/C samples showed a faster increase in capacity than pure LiFePO<sub>4</sub>, its specific capacity is 156.1 mAh g<sup>-1</sup> at 0.1 C. This behavior



Fig. 5. SEM images of pure LiFePO<sub>4</sub> ((a) 650 °C 4 h) and LiFePO<sub>4</sub>/C powders obtained at (b) 600, (c) 650, (d) 700, (e) 750 and (f) 800 °C for 4 h.



Fig. 6. TEM images of LiFePO<sub>4</sub>/C sample.

can be explained by the existence of carbon coating, which enhances the electronic conductivity of bare  $LiFePO_4$  and provides inter-grain connectivity to the hybrid electrode. There is only a small amount of fading observed in the figures. Obviously, the small carbon content cannot form a continuous carbon conducting layer and the large amount of carbon content can lead to a long lithium diffusion length. This all can influence the deintercalation—intercalation of the lithium ions and restrict the cycling stability performance and capacity. Therefore, the cycling performance and specific capacity were enhanced by the carbon coating layer which can avoid the core material direct contact with the acidic electrolyte, in order to improving the electronic conductivity of LiFePO<sub>4</sub> sample [23,26].

### 3.5. Effects of sintering temperature on the discharge and cycling performance of LiFePO<sub>4</sub>/C

Fig. 9 shows the temperature of intermedium on the electrochemical properties of the LiFePO<sub>4</sub>/C composite. The various calcining temperatures of LiFePO<sub>4</sub>/C were used for comparison. As shown in Fig. 9(A), when the temperatures are 600 and 700 °C, the discharge capacities are 126.3 mAh g<sup>-1</sup> and 127.6 mAh g<sup>-1</sup> at 0.2 C, respectively. Additionally, there is no tremendous heterogeneity in specific capacity and flat voltage plateau. However, when the temperature is 650 °C, the specific discharge capacity is 154.8 mAh g<sup>-1</sup> which is higher than others. There is also a longer flat voltage plateau, attributing to the low temperature (600 °C) which cannot make the sample crystallize well to form microsize particles and the high temperature (700 °C) may lead to the particles agglomerating greatly with the growth of the primary particles which is consistent with the SEM observation in Fig. 5.



Fig. 7. TG curve of the LiFePO<sub>4</sub>/C sample.

In order to investigate the temperature in the process of calcination of LiFePO<sub>4</sub>/C composite on the rate performance, the cycling performances of LiFePO<sub>4</sub>/C samples are shown in Fig. 9(B). From the curves, the sample (b) sintered at 650 °C exhibits excellent rate performance compared with the others. The specific discharge capacity is 139.1 mAh  $g^{-1}$  at 1.0 C and shows a similar value during the following nine cycles. This indicates the temperature can influence the morphology structure of the particle which is controlled by the size and crystallinity of the sample. However, the discharge capacity decreases while the temperature is lower or higher than 650 °C. This is caused by the supply of electrons from the interface electrochemical reaction becoming problematic and the particles cannot be crystallized well or agglomerate into a mass which restricts the particles contact with electrolyte and the lithium ion diffusion. On the other hand, when the lower current density was applied, the electrode was able to retrieve its capacity. The specific capacity is 161.9 mAh  $g^{-1}$  which is higher than the starting discharge capacity, indicating that the high rate cycle cannot destroy the interior structure of the sample and make it activate any further. This retention of LiFePO<sub>4</sub>/C on extended cycling shows that the LiFePO<sub>4</sub>/C possesses an excellent rate capability and good cycle life. Those results convince us that the glucose is 10% as that of LiFePO<sub>4</sub> (carbon content is 2.46%) and the sintering temperature is 650 °C for 4 h can optimize the preparation of the LiFePO<sub>4</sub>/C material which can facilitate the intercalation and deinterca lation of lithium ions.

#### 3.6. CV and EIS analysis of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C

Cvclic voltammetry (CV) was carried out in order to investigate the effect of carbon coating in the electrochemical properties of LiFePO<sub>4</sub>. Fig. 10 illustrates the CV profiles of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C in the voltage range of 2.5–4.2 V at a scan rate of 0.1 mV s<sup>-1</sup>. As for cyclic voltammogram, the separation potential between anodic peak and cathodic peak is an important parameter to value the electrochemical reaction reversibility. Both the samples show that similar CV curves with only one pair of redox peaks respond to the intercalation/deintercalation of lithium ions into/from the bulk. It should be noticed that the LiFePO<sub>4</sub>/C sample shows more symmetrical and spiculate shape of the peak profile. The profile of LiFePO<sub>4</sub>/C presents a polarization with a potential separation of 0.29 V which is smaller than 0.49 V presented by LiFePO<sub>4</sub> between the anodic and the cathodic peaks. This attributes to the morphology surface of the LiFePO<sub>4</sub> decorated by a carbon layer which can enhance the conductivity and reversibility of the particle.



Fig. 8. Initial charge-discharge curves of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C at 0.2 C (A), the curves of LiFePO<sub>4</sub>/C at different rates (B) and cycling performance (C) of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C.

In order to study the effect of carbon layer on the kinetics process of the electrode materials, electrochemical impedance spectroscopy (EIS) measurement of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C was carried out at fully discharge state after the electrodes were activated three cycles at a rate of 0.1 C in the frequency range between 100 KHz and 10 mHz shown in Fig. 11. All profiles include semicircles which relates to charge-transfer resistance ( $R_{ct}$ ) for lithiation reaction at the interface of electrolyte and cathode in the high frequency region, and a sloping line in the low frequency region which relates to a diffusion rate of Li ion in the electrolyte to the bulk electrode material [41]. The size of the semicircle formed form the middle—high frequency region of the data exhibits a good correlation with capacity results in Fig. 8. The LiFePO<sub>4</sub>/C sample exhibited a smaller charge-transfer resistance

(234  $\Omega$ ) than that of the LiFePO<sub>4</sub> (346  $\Omega$ ) sample without carbon coated. A smaller diameter semicircle reflects low charge-transfer impendence with an electrode material. After carbon coating the LiFePO<sub>4</sub> particles, the transfer resistant between them may be improved. In the low frequency region, the sloping line of LiFePO<sub>4</sub>/C particles are more favorable for the intercalation/deintercalation of lithium ions into/from the bulk as the carbon layers which can enhance the electronic conductivity and restrict the particles growth compared to the bare LiFePO<sub>4</sub>. In addition, the smaller particle size is associated with the lower electronic or ionic resistance at the boundary of the crystallites within each polycrystalline particle of the active material, thus enhancing the reversible capacity of LiFePO<sub>4</sub>/C material [42,43].



Fig. 9. Initial charge-discharge curves of LiFePO<sub>4</sub>/C at 0.2 C (A), and cycling performance of LiFePO<sub>4</sub>/C (B) samples obtained with different temperatures: (a) 600 °C, (b) 650 °C, (c) 700 °C.



Fig. 10. CV curves of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C.



Fig. 11. Electrochemical impedance spectra of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C.

#### 4. Conclusion

We developed an effective, simple and green route to synthesize LiFePO<sub>4</sub> cathode material, and the LiFePO<sub>4</sub>/C composite was synthesized by the high-temperature treatment that followed. XRD and SEM demonstrated the well-crystallized and well-distributed LiFePO<sub>4</sub>/C particles that were sintered at the temperature of 650 °C for 4 h. TEM showed that LiFePO<sub>4</sub> material was uniformly coated with a carbon layer, with about 2.7 nm in thickness and the carbon content is 2.46%. The initial discharge capacity of LiFePO<sub>4</sub> is 135.5 mAh  $g^{-1}$  at 0.1 C, and the discharge capacity increased to 151.7 mAh g<sup>-1</sup>, 154.8 mAh g<sup>-1</sup>, 149.8 mAh g<sup>-1</sup> and 139.1 mAh g<sup>-1</sup> after being carbon coated at 0.1, 0.2, 0.5 and 1.0 C, respectively. These results demonstrate that the pure LiFePO<sub>4</sub> and LiFePO<sub>4</sub>/C, without poison to destroy the structures of the materials, attributing to the green process of the synthesis. But the product synthesis via hydrothermal stripping technique still has two questions: 1) the product has to be washed many times to obtain the pure sample as some organic phase cling on the product; 2) with a low productive rate ( $\sim 65\%$ wt). Therefore, the synthesis of LiFePO<sub>4</sub> particle which provides a novel facile method can be optimized for excellent electrochemical performance as a lithium ion battery cathode material.

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