

# Controlled Preparation and Surface Structure Characterization of Carbon-Coated Lithium Iron Phosphate and Electrochemical Studies as Cathode Materials for Lithium Ion Battery

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**Abstract** Amorphous carbon-coated lithium iron phosphate (C-LiFePO<sub>4</sub>) particles have been mass synthesized at the commercial scale by a controlled solid-state reaction method. Particles morphologies, olivine-type phase structures and the carbon coating features were investigated in details by various techniques as X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) imaging, and transmission electron microscopy (TEM, HRTEM) imaging, selected-area electron diffraction (SAED), X-ray energy dispersive spectroscopy microanalysis (XEDS), and X-ray photoelectron spectroscopy (XPS). Single-crystal nature of the olivine type LiFePO<sub>4</sub> structures was revealed by XRD and SAED analyses. TEM imaging showed rough nanoparticles spherical features with average size range of 50-200 nm. Homogenous coating features of carbon layers on the particles surface and olivine-LiFePO<sub>4</sub> phase are clearly observed in HR-TEM imaging and confirmed by the corresponding SAED pattern. Elemental binding energy from XPS analysis also confirmed that an amorphous sp<sup>2</sup> carbon coating layer and olivine type LiFePO<sub>4</sub> structures. It is indicated that the characteristics of sp<sup>2</sup> type conducting-coating layer on the particles surfaces gave rise to improved electrical conductivity by reducing the diffusion path of the electron and lithium ions, as directly evidenced from our charge-discharge cycling testing as the cathode in the Lithium ion battery cell.

**Keywords** Lithium Iron Phosphate, Olivine-Type Phase, X-Ray Diffraction, Transmission Electron Microscopy, X-Ray Photoelectron Spectroscopy, Electrochemical Capacity

## 1. Introduction

Extensive attention has been devoted to the development and characterizations of the phospho-olivine type lithium iron phosphate (LiFePO<sub>4</sub>) as an attractive cathode candidate in the lithium ion battery market, which was first reported by John Goodenough in 1997 as a promising cathode electrode for the rechargeable lithium-ion batteries[1]. Olivine-type LiFePO<sub>4</sub> exhibits various unique advantages such as low toxicity, low cost, high thermal and chemical stability, and good electrochemical performance in the fully charged state, and it also has a higher theoretical specific capacity (170 mAh g<sup>-1</sup>) and a flat charge-discharge profile at intermediate voltage (3.45 V vs Li/Li<sup>+</sup>), and reasonable cycle life[2-3]. However, LiFePO<sub>4</sub> has inherently low electrical conductivity, which results in its poor rate capability due to the poor

kinetics of lithium intercalation/deintercalation process [2-15]. This causes a bigger challenge for power-demanding applications such as hybrid electric vehicles and electric vehicles[2-6]. Nowadays many approaches have been successfully adopted to improve its electrical conductivity, such as metal cation doping and carbon-coating or addition[7-12], decreasing the particle size and producing nanoparticles [13-18]. It has been reported that carbon-coating would increase the surface electrical conductivity and smaller size of LiFePO<sub>4</sub> could shorten the diffusion length of Li-ion during lithium intercalation/deintercalation process[3, 6, 20]. Particularly, it is apparent that carbon coating has been reported to be very effective in the enhancement of capacity and rate capability on LiFePO<sub>4</sub> cathode[6-20, 24-33].

In the present work, we report large-scale commercial synthesis and structural morphologies of carbon coated lithium iron phosphate (C-LiFePO<sub>4</sub>) particles prepared using home-made amorphous micro-FePO<sub>4</sub> as the iron source and conducting black as carbon source. Furthermore, we examined the electrochemical performance of the

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C-LiFePO<sub>4</sub> particles as a cathode for the lithium-ion battery.

## 2. Experiments

### 2.1. Sample Preparation

First of all, in order to produce the homogenous carbon-coated LiFePO<sub>4</sub> products, the choice of suitable chemical precursors and starting reagents is very essential. Meanwhile, the appropriate temperature and pressure must be carefully selected to prevent the undesirable particle growth and the presence of impurity phase. Otherwise, undesired impurities, such as Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>P, can be contained in the final products.

Here, micro-FePO<sub>4</sub> powders were firstly synthesized via the solid-state reaction (i.e. pre-calcination), which was typically conducted by heating the mixture of the relatively cheap precursors of FeSO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (e.g. FeSO<sub>4</sub>:NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>=1:2) at up to 300°C. Consequently, the appropriate stoichiometric amount (e.g. 2:1) of amorphous micro-FePO<sub>4</sub> powders and Li<sub>2</sub>CO<sub>3</sub> powders were deeply calcinated under the high-temperature carbonization with presence of the conductive carbon source (i.e. acetylene black) in an industrial-type furnace. All the reagents used in the experiment are of analytical purity.

Usually, the high temperature solid state calcination was systematically carried out under controlled temperature ranges (700°C-800°C) and certain pressure for over 5-10 h. By controlling the calcination temperature and atmosphere pressures, the LiFePO<sub>4</sub> powders products could be produced maximum at 5kg/day. The yield purity of the as-prepared LiFePO<sub>4</sub> powders was up to 95% that collected in the bag filter regardless of the conducting carbon sources.

### 2.2. Sample Characterization

The phase purity and microstructure were characterized and recorded by XRD using a D/max-2000 Rigaku diffractometry with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) operated at 40 kV and 30 mA with in the scanning angle ( $2\theta$ ) ranging from 20° to 70°, and a step of 0.01°.

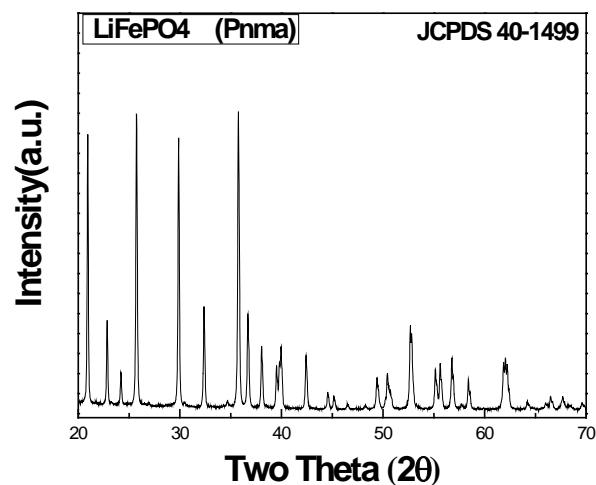
The morphologies of as-prepared particles were examined using a scanning electron microscopy (Carl Zeiss, InLens, WD= 9.6, 15Kv). The dispersed particles supported on a 200 mesh holy carbon film coated Cu grids were characterized at nanoscale by a conventional transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM), and selected area electron diffraction (SAED) techniques using a JEOL 3010 microscopy equipped with XEDX system at 300 kV. Surface chemical elements characterizations of particles were determined and recorded by X-ray photoelectron spectrometer (XPS) using a Kratos ULTRA DLD XPS with a mono-chromated Al source that gives an energy resolution better than 0.5 eV at a pass energy smaller than 20eV. Both survey scans (with a pass energy of 160 eV and a scan step of 1eV) and core scans (with a pass energy of 20 eV and a scan step of 0.1eV) were collected. The spectra were

calibrated by setting the C 1s peak as 285 eV.

Electrochemical properties were measured on electrodes prepared by using the mixtures of comprising 85 wt% active materials, 10 wt% acetylene black, and 5 wt% polyvinylidene fluorides (PVDF) binder. The LiFePO<sub>4</sub> electrode films were fabricated by doctor blade technique on aluminum foil. The cells consisted of the electrode, a lithium metal counter electrode and the electrolyte of a 1 M solution of LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1). The cells were assembled and handled in an Ar-filled glove box and were evaluated using coin-type cells. Galvanostatic discharge/charge tests were carried out using a program-controlled LAND Celltest-2001A system between 2.5 V and 4.2 V versus the Lithium counter electrode at room temperature.

## 3. Results and Discussion

The powder X-ray diffraction pattern (XRD) taken from the as-prepared particles is shown in Fig.1. It clearly revealed that the C-LiFePO<sub>4</sub> particles were indexed well to a pure orthorhombic system of **olive-type** structure (P<sub>nma</sub>, JCPDS: 40-1499). No any impurities phase such as transition metal compounds Li<sub>3</sub>PO<sub>4</sub> and FePO<sub>4</sub> were detected by XRD. Carbon phase was not found apparently from the XRD pattern, which indicates it may exist in amorphous form.



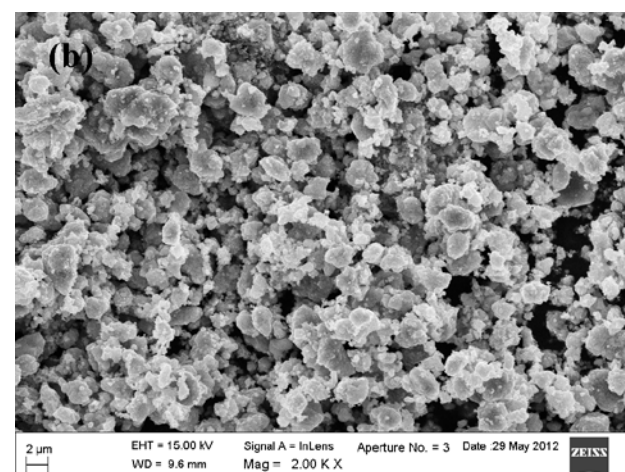
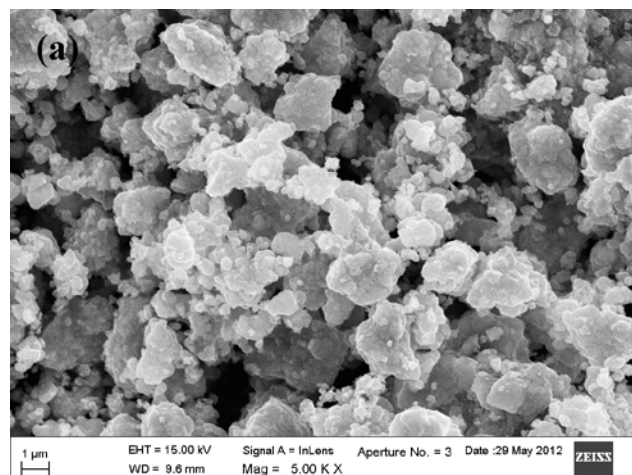
Powder XRD pattern of the C-LiFePO<sub>4</sub> particles

Figure 1. Powder XRD pattern

From the SEM images shown in Fig.2a and Fig.2b, it is observed that the as-prepared LiFePO<sub>4</sub> particle assemblies exhibiting spherical or elliptical morphology with nano-aggregated surface features having a size distribution from 1–3  $\mu$ m. The typical bright-field magnified TEM images in Fig.3a shows that the LiFePO<sub>4</sub> particles assemblies are composed of densely aggregated nanoparticles showing rough spherical shapes with sizes in the range of 50-200 nm regardless of the types of carbon sources used. Further details are evidenced from the selected area electron diffraction (SAED) pattern showed in the Fig. 3b. The appearance of distinct and diffuse SAED rings

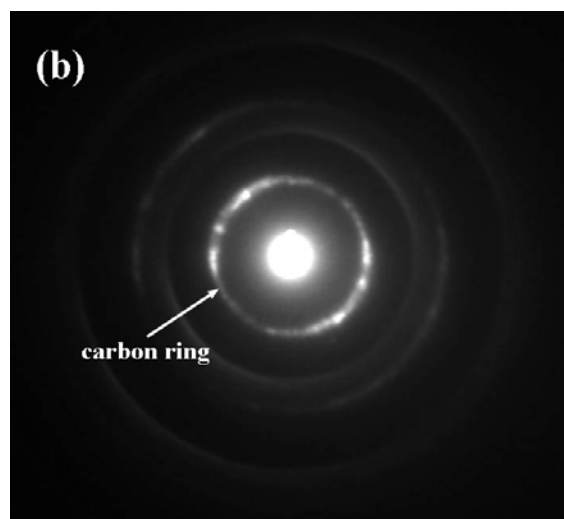
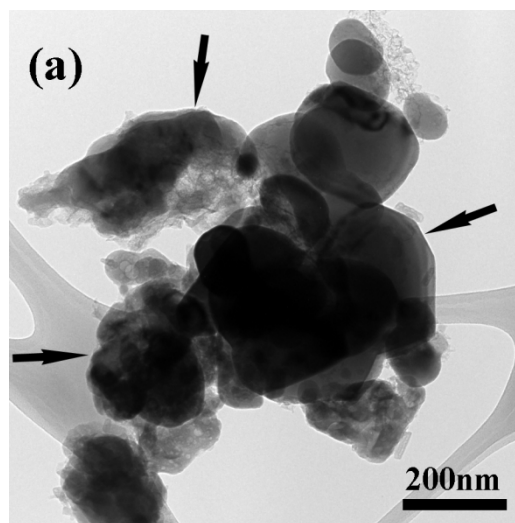
confirms the co-existence of an amorphous phase together with  $\text{LiFePO}_4$  crystal phase. Fig. 3c is a HR-TEM image that gives further insight of the morphology of C- $\text{LiFePO}_4$  particle, such a HR-TEM image view clearly indicated that an amorphous carbon layer covered the surface of the  $\text{LiFePO}_4$  particles with a thickness of 3-4 nm layer, and its corresponding SAED pattern shown in Fig. 3d can be indexed as the [100] direction of the olivine phase crystal. It has been reported that the formation of amorphous carbon in the surfaces of the particles owes to the nature of the carbon source during solid-reactions, and was indeed generated by carbonization of the conductive carbon source precursor [19, 20]. Meanwhile, it is observed that the coating layer was uniform and the thickness of carbon on the particle was in the range of several nanometers, suggesting that the carbon precursor played an important role in reducing the  $\text{LiFePO}_4$  particle size during the high temperature calcinations process. This result is obviously attributable to the amorphous carbon coating that inhibits grain growth as reported by several groups [19-21]. The well-resolved lattice fringes demonstrate the high crystalline and single-crystal features of the core- $\text{LiFePO}_4$  structures. The d-spacing of 0.47 nm as marked in Fig. 3c is consistent with spacing of the (001) plane of the orthorhombic  $\text{LiFePO}_4$  phase. The corresponding SAED pattern also clearly confirms the single-crystal and olivine-phase nature of the  $\text{LiFePO}_4$  particle. The index of the electron diffraction spots corresponding to the (020) and (002) planes of  $\text{LiFePO}_4$  crystals are labelled in Fig. 3d, further revealing the single-crystalline nature of the  $\text{LiFePO}_4$  particles during solid state reaction under higher temperature and pressures.

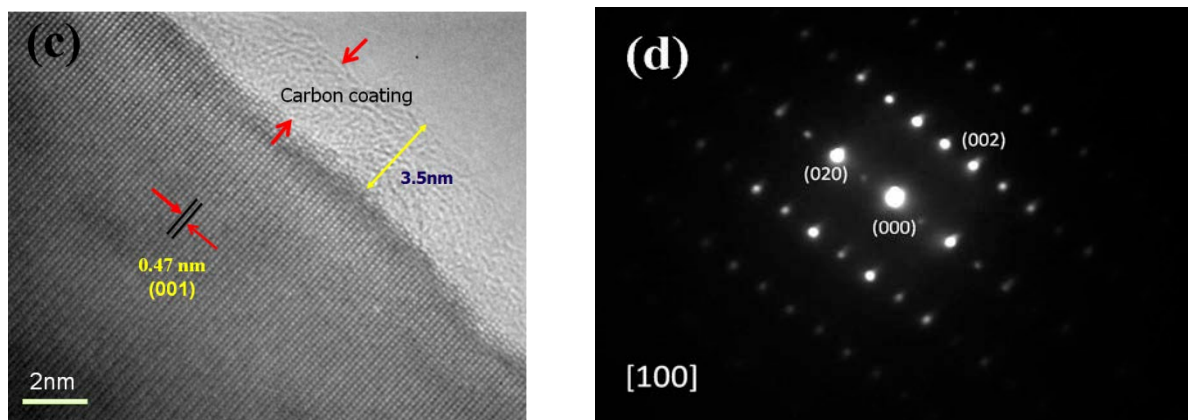
The corresponding selected area XEDS spectrum collected from the particles shown in Fig. 3a is given in Fig. 4. It shows that the as-prepared particles consist of all the elements of the crystal phase and the amorphous carbon element.



SEM images of the C- $\text{LiFePO}_4$  particles assemblies

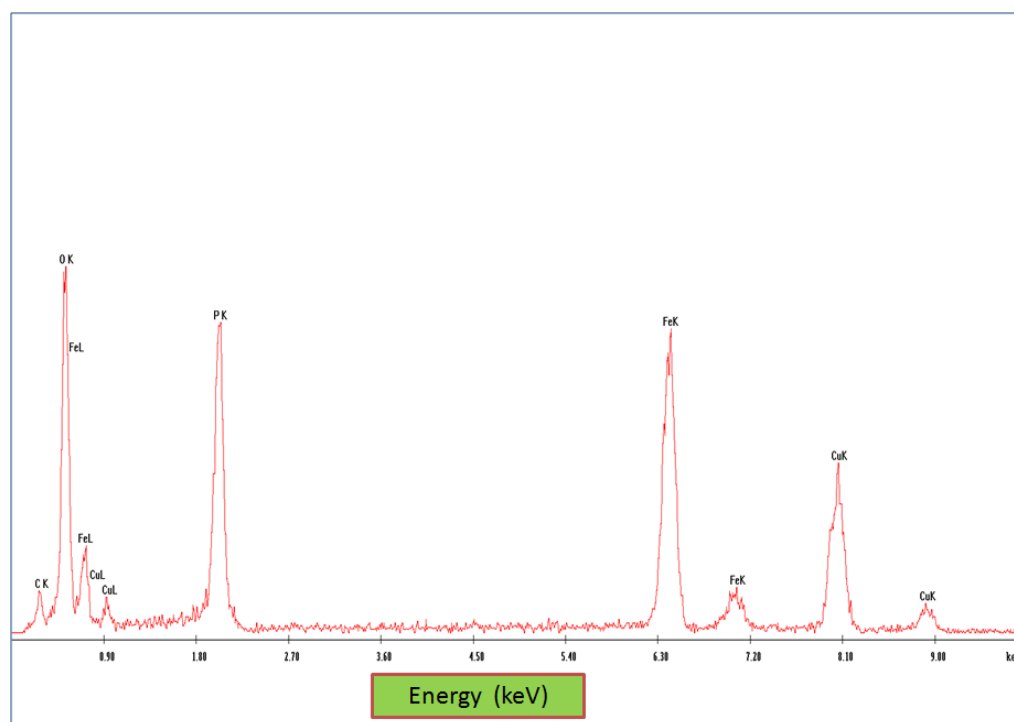
Figure 2(a,b). SEM images





TEM and HRTEM images and SAED patterns of the C-LiFePO<sub>4</sub> particles

**Figure 3(a,b,c,d).** TEM and HRTEM images and SAED pattern



XEDS spectrum of the C-LiFePO<sub>4</sub> particles

**Figure 4.** The XEDS spectrum

From the above analysis, it convincingly shows that the as-prepared C-LiFePO<sub>4</sub> particle assemblies possessed unique core-shell structure and carbon interconnection networks. This is ideal for producing the cathode with enhanced electric conductivity and excellent rate capabilities. As mentioned previously that the nano-sized C-LiFePO<sub>4</sub> particles reduce the solid-state diffusion path[13-18], which further expedite the electron and ion transport during charge-discharging processing as the cathode. These improved characteristics meet all the prerequisites for generating an excellent rate capability and a high volumetric discharge capacity in the development of the higher energy density lithium ion batteries in terms of stability, safety and excellent electrochemical properties[21-23].

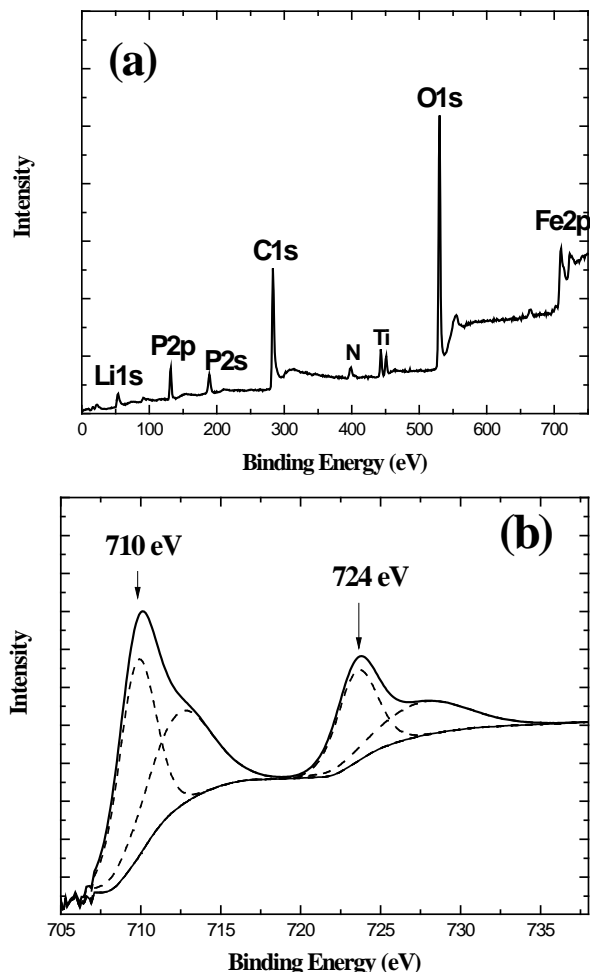
The typical XPS spectrum survey profile and the

core-scan spectrum of Fe 2p are acquired and shown in the Fig.5a and Fig.5b, respectively. The main binding energy (BEs) of Fe 2p<sub>3/2</sub>, O 1s, and C 1s peaks are determined to be 710 eV, 531 eV, and 285 eV, respectively, the appearance of the Ti and N peaks was from the sample support. It is also clearly seen from the Fig.5b that the Fe 2p spectrum split into 2p<sub>1/2</sub> and 2p<sub>3/2</sub> due to the spin-orbit coupling. Each part consists of a main peak and a corresponding satellite peak at BEs of 710.9 eV and 724.4 eV for Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>, respectively. In fact, the appearance of satellite peaks or shoulder peaks is a characteristic feature of transition metal ions with partially filled d-orbits[24, 26], which indicated that two distinct peaks at binding energies of 710.9 eV and 724.4 eV were observed in the core-scan spectrum of Fe 2p. This means that the chemical oxidation state of Fe is +2.

Indeed, the two peaks could be ascribed to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>, which is characteristic of the valence of Fe<sup>2+</sup> state in the olivine-type LiFePO<sub>4</sub> products[25-29].

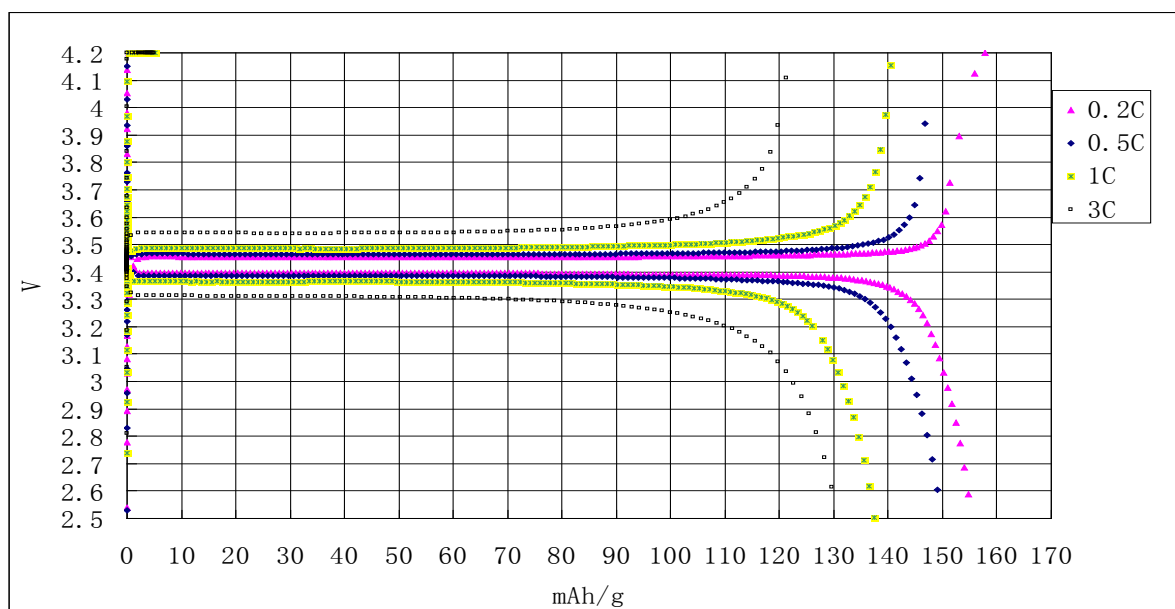
The binding energy of C 1s spectrum in 285 eV shown at Fig.5a is clearly assigned amorphous carbon with sp<sup>2</sup> C-C bonds (284.7 eV)[25]. Meanwhile, the O 1s peak in the binding energy of 531 eV represents the PO<sub>4</sub><sup>3-</sup> group oxide ions in LiFePO<sub>4</sub>. It is believed that the O 1s spectra and P 2p spectra exhibit features at 531.6 and 133.5 eV due to the phosphate structure[25-29]. As a result, the XPS analysis further confirms the co-existence of the olivine phase and amorphous carbon in the as-prepared C-LiFePO<sub>4</sub> cathode samples, which is in good agreement with the above both XRD and HR-TEM analysis.

Galvanostatic discharge-charge testing was electrochemically performed and with the data showed in Fig.6. It is very clear that as-prepared C-LiFePO<sub>4</sub> particles delivered and achieved an initial discharge capacity of nearly 160 mAh/g at a 0.2 C rate as the cathode in a Li-ion cell. The peaks of capacity profiles are rather symmetric, indicating good cycle reversibility. Moreover, it also showed an excellent capacity retention ratio of 97% after the 50th charging/discharging cycles, which also was indicating high rate power performance as well. Obviously, such a full 3-4 nm carbon coating layer (i.e. carbon interconnection networks) can effectively improve particles surface electronic conductivity during discharge-charge processing. In particular, it has been believed from many reports that, the crucial role played by the surface carbon coating on the LiFePO<sub>4</sub> particles has been responsible for the improved electrochemical performance due to the increasing of both electron and ionic transport of the LiFePO<sub>4</sub> cathode composite particles[26-34].



The typical XPS spectrum and (b) the core-XPS spectra of Fe 2p of the C-LiFePO<sub>4</sub> particles

Figure 5. (a) The typical XPS survey spectrum and (b) the core-scan spectra of Fe 2p



The discharge and charge profiles of C-LiFePO<sub>4</sub> nanoparticles at different current rates

Figure 6. The discharge and charge profiles

## 4. Conclusions

1), Carbon coated LiFePO<sub>4</sub> (C-LiFePO<sub>4</sub>) powders products with the olivine-type structure has been successfully synthesized at commercial scale. XRD, SEM, SAED, HR-TEM image, and XPS analyses clearly provide a comprehensive view of the structure-correlated performance of the C-LiFePO<sub>4</sub> products. It demonstrates that each LiFePO<sub>4</sub> particle has a sp<sup>2</sup> amorphous carbon-coating shell and a phospho-olivine type crystal core.

2), The unique olivine-type C-LiFePO<sub>4</sub>, combined with its full coating of conductive carbon, effectively enhances its electrochemical performance due to the presence of the carbon coating networks for both electronic and ionic transport increasing during the electrochemical testing.

3), The present mass production procedure is very valuable to optimize the process for producing carbon coated LiFePO<sub>4</sub> cathode materials, this method is likely to be easy to scale up for industrial production.

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