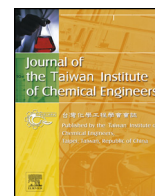




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## Preparation of lithium iron phosphate cathode materials with different carbon contents using glucose additive for Li-ion batteries

Chien-Te Hsieh\*, Chun-Ting Pai, Yu-Fu Chen, I-Ling Chen, Wei-Yu Chen

Department of Chemical Engineering and Materials Science, Yuan Ze University, Taoyuan 32003, Taiwan

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### ABSTRACT

The influence of carbon layer on the cell performance of LiFePO<sub>4</sub> (LFP) has been investigated using charge–discharge cycling and electrochemical impedance spectroscopy. The carbon-coated LFP powders are synthesized using an efficient calcination/pyrolysis method at 650 °C. The amount of glucose additive is chosen as a controlling factor to tune carbon content over the surface of LFP powders. Experimental results show that the moderate carbon layer displays a positive effect in raising the performance of LFP cathodes, *i.e.*, ~161.5 mAh/g at 0.1C and ~99.6 mAh/g at 10C. Excessive amount of glucose additive tends to form an inter-grain LFP aggregate, resulting in slow diffusion rate ( $D_{Li}$ ) and high equivalent series resistance ( $R_{ES}$ ). In this work, the optimal carbon content (2.55 wt%) in C/LFP cathode material significantly assists in lowering the  $R_{ES}$  (43.8 Ω) and rising the  $D_{Li}$  value ( $2.99 \times 10^{-12}$  cm<sup>2</sup>/s) in comparison with other C/LFP cathodes. Analyzed from the Regone plot, the highest specific energy and specific power densities can achieve as high as 400 Wh/kg and 1200 W/kg respectively, showing a feasibility for applications of electric vehicles.

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### 1. Introduction

Olivine-based cathode materials (*i.e.*, LiMPO<sub>4</sub>, M = Fe, Mn, Co or Ni) have been considered as candidate for high-performance Li-ion batteries [1,2]. Among them, LiFePO<sub>4</sub> (LFP) has emerged as the most promising due to its flat voltage plateau (~3.4 V versus Li<sup>+</sup>/Li), moderate theoretical specific capacity (~170 mAh/g), thermal stability, long cycle life, and most importantly, environmental friendliness and abundance of Fe resources in nature [3,4]. So far, LFP has been commercialized as an active cathode material for a new generation of Li-ion batteries, especially for applications in electric vehicles (EVs) and hybrid electric vehicles (HEVs). However, LFP strongly suffers from its limited high rate capability due to its intrinsic low electrical conductivity (~10<sup>-9</sup> to 10<sup>-10</sup> S/cm) [5] and low Li<sup>+</sup> ion diffusion coefficient [6]. Such drawbacks would seriously decrease its full theoretical capacity at high C rates, thereby, limiting the power-demanding applications such as EVs and HEVs [7]. Accordingly, much effort has been devoted in resolving the above problems by reducing particle size and coating conductive layers over the surface of LFP powders. Different synthesis routes such as rheological phase method [8,9], sol–gel

method [4], hydrothermal synthesis [10,11], solid-state reaction [12,13], carbon thermal reduction method [14,15], and co-precipitation [16], have been developed to prepare various LFP powders with different particle sizes and textures. Among these, co-precipitation is a potential method to grow homogeneous hydrated iron phosphates (FePO<sub>4</sub>·xH<sub>2</sub>O) precursor in the nano or submicron scale. The as-grown FePO<sub>4</sub> serves as starting material for preparing LFP powder with relatively small particle size, capable of improving its rate capability.

Expecting for the size effect, surface coating with additives, such as C [5,17,18], SiO<sub>2</sub> [19], Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> [20], onto the surface of LFP have been widely used and reported in past literatures. Carbon coating is still one of commonly-used routes to increase the performance of LFP cathodes because of its low cost, high electrical conductivity, and large-scale feasibility. The as-prepared C/LFP cathodes have been confirmed to exhibit not only high energy density but also high power density if small LFP powders are coated with uniform carbon thin layer [21,22]. The carbon skin-layer provides a circular pathway for electric conduction, inducing an improved power density. However, there are few reports investigating the relationship between electrical conductivity and Li<sup>+</sup> diffusion coefficient in the C/LFP cathodes. In this work, we report a facile method to prepare C/LFP cathode, consisted of the following steps: (i) a spontaneous precipitation to synthesize various FePO<sub>4</sub>·xH<sub>2</sub>O nanoparticles, (ii) well mixing as-prepared

\* Corresponding author. Tel.: +886 3 4638800x2577; fax: +886 3 4559373.  
E-mail address: [cthsieh@saturn.yzu.edu.tw](mailto:cthsieh@saturn.yzu.edu.tw) (C.-T. Hsieh).

FePO<sub>4</sub>·xH<sub>2</sub>O particles with glucose, used as carbon precursor, and (iii) subsequent sintering and carbonization at 650 °C. To inspect the influence of carbon layer, the LFP cathodes coated with different carbon ratios are systematically investigated using charge–discharge curve and electrochemical impedance spectroscopy (EIS). Our key feature, here, is to examine the influence of carbon layer in determining the electrochemical behavior of C-coated LFP cathodes. Moreover, the Ragone plot of energy density versus power density was also investigated for the effect of carbon layer.

## 2. Experimental

The co-precipitation method was adopted to grow FePO<sub>4</sub>·xH<sub>2</sub>O precursors. In brief, FeSO<sub>4</sub>·7H<sub>2</sub>O was firstly dissolved in de-ionized water to obtain 2.0 M Fe<sup>2+</sup> solution at room temperature. Then 2.0 M H<sub>3</sub>PO<sub>4</sub> (85%) was poured into the iron source solution and the mixture was stirred for 0.5 h. After that, hydrogen peroxide was carefully dropped into the mixture solution, and the molar ratio of H<sub>2</sub>O<sub>2</sub>/FeSO<sub>4</sub> was kept at 1.2:2. A neutralizer, 2 M NH<sub>3</sub>·2H<sub>2</sub>O, was used to titrate the transparent solution at the desired pH value (=3 in this case). Meanwhile, white precipitate started to form immediately in the bottom and the pH value (=3) of the solution was well controlled by using two micropipettes for the titration of NH<sub>3</sub>·2H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>. The slurry mixture was continuously stirred at room temperature for 0.5 h. The precipitate was then separated from the mixtures using filtration and washed several times with de-ionized water. Finally, yellow-white FePO<sub>4</sub>·xH<sub>2</sub>O powders could be obtained after being dried in an oven at 80 °C for 12 h. Prior to any treatment, a dehydration treatment was used to heat the FePO<sub>4</sub>·2H<sub>2</sub>O and Li<sub>2</sub>CO<sub>3</sub> precursors at 200 °C for 2 h. The stoichiometric amount of FePO<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub>, and glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) served as the starting materials. Four types of carbon precursor were set at 5, 10, 15 and 30 g C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> based on 1 mol FePO<sub>4</sub>. In initial step, FePO<sub>4</sub> and Li<sub>2</sub>CO<sub>3</sub> were well mixed by using a planetary ball mill, thus forming a solid reactant mixture. The solid mixture was immersed in the glucose solution to get the mushy slurry. After that, the slurry was placed in an oven and dried at 100 °C overnight. The dried samples were grounded and sieved (Mesh No. 300), and then the fine powders were calcined and carbonized at 650 °C in a furnace for 12 h under nitrogen atmosphere. The four C-coated LFP samples were designated to C1, C2, C3, and C4 according to the ratios of 5, 10, 15 and 30 g C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> to 1 mol FePO<sub>4</sub>, respectively.

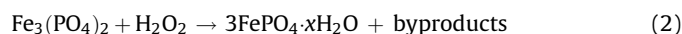
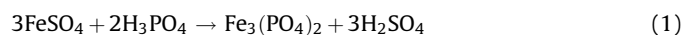
The microstructures of the C/LFP composites, obtained from the co-precipitation followed by calcination, were characterized using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-5600) and a high-resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100). The HR-TEM observation was carried out using a microscope operating at 200 kV. The LFP composite was prepared by ultrasonically dispersing the composite in ethanol. A drop of the suspension was applied onto a copper grid and was dried in air. An X-ray diffraction (XRD, Shimadzu Labx XRD-6000) spectroscopy, equipped with Cu-K $\alpha$  radiation emitter, was adopted to analyze the crystalline structures of the LFP sample.

The electrochemical performance of C/LFP composite cathode materials was performed using CR2032-type coin cells. For the cathode assembly, the LFP composite was firstly mixed with a binder (poly-vinylidene fluoride) and two conducting media (Super-P and KS-4) at a weight ratio of 80:10:5:5 in *N*-methyl pyrrolidinone (NMP) solvent to form the electrode slurry. The mixture was blended by a three-dimensional mixer using Zr balls for 3 h to prepare the uniform slurry. Then, the resultant slurry was uniformly pasted on an Al foil substrate with a doctor blade, followed by evaporating the solvent, NMP, with a blow dryer. The

prepared cathode sheets were dried at 135 °C in a vacuum oven for 12 h and pressed under a pressure of approximately 200 kg cm<sup>-2</sup>. The electrode layers were adjusted to control a thickness of ~100  $\mu$ m. The coin cells were assembled in a glove box for the electrochemical characterization. In the test cells, the Li foil and the porous polypropylene film served as the counter electrode and the separator, respectively. The electrolyte solution was 1.0 M LiPF<sub>6</sub> in a mixture of ethylene carbonate, polycarbonate, and dimethyl carbonate with a weight ratio of 1:1:1. The charge/discharge cycling test at different C rates (from 0.1 to 5C) was performed within the voltage region of 2.0–4.0 V vs. Li/Li<sup>+</sup> at ambient temperature. EIS measurement was carried out in the frequency range of 100 kHz to 0.01 Hz at open circuit potential (approximately 3.0 V vs. Li/Li<sup>+</sup> in our case) with an alternating current perturbation of 5 mV. The EIS analysis of cathodes was performed after the charge–discharge cycling at 0.1C (3 cycles) using an impedance analyzer (CH Instrument, Inc., CHI 608), and the equivalent circuit was analyzed by computer software (Z-view).

## 3. Results and discussion

Fig. 1 shows top-view FE-SEM image of dehydrated FePO<sub>4</sub> powders through the co-precipitation at pH = 3. The as-prepared powders show a spherical-like shape with good uniformity. The diameter of the powder ranges from 200 to 350 nm. Concerning the reaction of the precipitation, the growth mechanism for growing FePO<sub>4</sub>·xH<sub>2</sub>O powders can be expressed as [23]



It is recognized that the pH value is a key factor in affecting the morphology of FePO<sub>4</sub> powders in the co-precipitation synthesis. Basically, the co-precipitation synthesis operated at pH = 3–4 would produce amorphous FePO<sub>4</sub> particles with regular shape [9]. To inspect the presence of carbon layer, electron diffraction spectroscopy (EDS) was employed to measure atomic C ratios of as-synthesized LFP powders. The variation of C atomic ratio with the ratio of glucose/FePO<sub>4</sub> (in units of g/mol), as shown in Fig. 2, displays a linearity plot. The C content is a linearly increasing function of the ratio of glucose/FePO<sub>4</sub>, and the carbon content over the LFP powders ranges from 1.05 to 4.89 wt%. This linear increase can be attributed to the fact that the constant rate of glucose loss takes place during the thermal treatment, including evolution

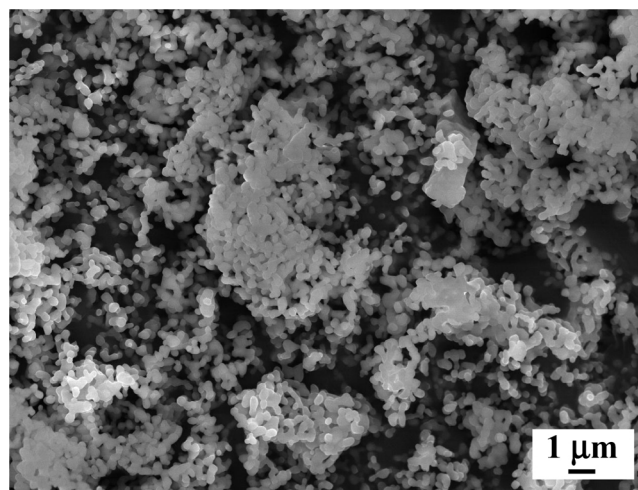


Fig. 1. FE-SEM images of spherical-like FePO<sub>4</sub> precursors through the co-precipitation synthesis at pH = 3.

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