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# A two-step solid state synthesis of $LiFePO_4$/C cathode with varying carbon contents for Li-ion batteries

Jihyeon Gim, Jinju Song, Diem Nguyen, Muhammad Hilmy Alfaruqi, Sungjin Kim, Jungwon Kang, Alok Kumar Rai, Vinod Mathew, Jaekook Kim*

*Department of Materials Science and Engineering, Chonnam National University, 300 Yongbong-dong, Bukgu, Gwangju 500-757, South Korea*

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## Abstract

Olivine structured $LiFePO_4$/carbon composites with different amounts of carbon were prepared by a modified two-step solid-state reaction. The iron citrate used as both iron and carbon sources in the reaction resulted in the formation of carbon coatings on the olivine particles as the mixed precursors were heated at three different initial-step temperatures of 200, 300 and 400 °C followed by a second-step annealing at moderate temperatures of 700 °C. The obtained final powders with varying carbon contents were systematically analyzed by characterization techniques of thermo-gravimetric analysis, X-ray powder diffraction, field-emission scanning electron microscopy, and field-emission transmission electron microscopy prior to electrochemical testing in order to determine the structural and calcination effects on the electrochemical properties of the composites. The field-emission transmission electron microscopy images revealed that the morphology of the $LiFePO_4$ composites consist of agglomerated particles surrounded by carbon as a conductive material. Among the prepared samples, the $LiFePO_4$/carbon composite calcined at initial-step temperature of 300 °C showed the highest discharge capacity and the best rate capability in the voltage range of 2.5–4.2 V.

*Keywords:* Lithium iron phosphate; Cathode materials; Solid-state synthesis; Lithium-ion batteries

## 1. Introduction

Rechargeable Li-ion batteries are considered as an attractive power source for a variety of applications including cellular phones, notebook computers, camcorders and even electric vehicles. Although $LiCoO_2$ is currently the most widely applied cathode material in commercial lithium-ion batteries owing to its decent electrochemical properties and convenience of preparation, it is not free from disadvantages of low practical capacity, high cost, toxicity and inferior safety features [1,2]. In recent years, NASICON or olivine-type materials built from $MO_6$ octahedron (where M is Fe, Co, Mn, Ni, V or Ti) and strongly covalent bonded tetrahedral polyanions ($XO_4^{n-}$, where X is P, W, S or Mo), have been investigated as cathodes with significant structural stability [3–6]. Among these, $LiFePO_4$ remains a promising candidate due to its high theoretical capacity (170 mA h $g^{-1}$) [2], low cost [7,8], environmental benignity [9], good cycle life properties [10–15], excellent thermal stability [16,17], and an approximately flat voltage plateau around 3.4–3.5 V versus lithium. Despite its merits, $LiFePO_4$ suffers from rate-limiting characteristics of low electronic conductivity ($\leq 10^{-9}$ S $cm^{-1}$) [18] and lithium ion diffusivity that hinders the practical application of this olivine as Li-ion battery cathodes. Consequently, tremendous efforts are aimed at minimizing the intrinsic disadvantages and improving the electrochemical properties of $LiFePO_4$ using various strategies such as reducing particle sizes [19,20], aliovalent cation substitution [18], particle morphology tailoring [21–23] and developing composites or performing particle coatings with conductive materials [24–29].

Carbon coating on particle surfaces as well as designing carbon-contained composites has been recognized as one of the most effective way to improve the rate capabilities in $LiFePO_4$. Hsu et al. reported that nanosized $LiFePO_4$/carbon composites (noted hereafter as LFP/C) were successfully

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*Corresponding author. Tel.: +82 62 530 1703; fax: +82 62 530 1699.
*E-mail address:* jaekook@chonnam.ac.kr (J. Kim).

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synthesized by a sol–gel method using citric acid as a chelating agent and a carbon source [25]. The reversible capacities for the LFP/C cathode obtained were 148 and 125 mA h g$^{-1}$ at C-rates of 0.025 and 0.1C respectively. Dominko et al. investigated the dependency of varying carbon content on carbon layer thickness formed on the LFP/C nanoparticles via a sol–gel technique by controlling the amount of Hydroxyethylcellulose (HEC) used as a carbon source during synthesis [26]. This study reported that LFP/C with 3.2 wt% carbon content and 1–2 nm thick carbon coating displayed a reversible capacity of about 116 mA h g$^{-1}$ at 5C rate. Nien et al. used a co-precipitation method utilizing a polymer precursor (polystyrene) to develop an LFP/C cathode that demonstrated less than 110 mA h g$^{-1}$ of capacity under 0.5C rate condition [27]. Contrary to solution synthetic routes, the conventional solid-state reaction permits the opportunity for multi-step heat treatments to not only eliminate organic materials but also serves as a prospective approach to introduce carbon sources such as sucrose, glucose or polymer precursors that can directly contribute to surface conducting layers on the formed crystalline particles. Since the approach of forming surface coatings is relatively easier than that followed in solution methods, the strategy to produce high-power performance LFP/C composites by simple solid-state reactions without any complicated separation procedures remains significant.

In this work, we demonstrate an effective method to control the thickness of an in-situ surface carbon layer formed on the LFP/C composites via a modified solid-state reaction method. The high temperature reaction uses iron citrate, which acts as a dual source of iron as well as carbon, as one of the starting materials. The main focus on this work has been to study the effect of heat treatment on the residual carbon content and the carbon coating layer formed on the prepared particles. In addition, the present study also investigates the influence of the heating process on particle formation by a coherent understanding obtained from thermo-gravimetric, elemental, morphological and electrochemical analyses.

## 2. Experimental

### 2.1. Material synthesis

LFP/C composites were prepared by the solid state reaction method using lithium carbonate ($Li_2CO_3$, 98% Daejung), iron (III) citrate hydrated ($FeC_6H_5O_7 \cdot xH_2O$, 98% Aldrich) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$, 99% Junsei) as the starting materials. In brief, 0.01 mol $Li_2CO_3$, 0.02 mol iron citrate, and 0.02 mol $NH_4H_2PO_4$ corresponding to 0.02 mol of $LiFePO_4$ was thoroughly milled in an acetone medium using the conventional ball milling apparatus with a rotation speed of about 120 rpm for 24 h. The resultant material was divided into three parts, which were pre-heated at three different temperatures, viz. 200, 300 and 400 °C for 3 h in air. Subsequently, all the heated samples were ground again and then annealed at 700 °C for 6 h under argon (Ar) atmosphere and the final products are marked as LFP/C-200, LFP/C-300 and LFP/C-400 respectively.

### 2.2. Material characterization

The thermal decomposition behavior of the annealed samples was examined with a thermo-gravimetric analyzer (TGA) (TA instruments SDT Q-600) at a scanning rate of 5 °C min$^{-1}$ from room temperature to 800 °C under air flow of 100 mL min$^{-1}$. The structure and morphology of the prepared powders were identified by X-ray diffraction (XRD) using a Shimadzu X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å), field-emission scanning electron microscopy (FE-SEM, S-4700 Hitachi) and high-resolution transmission electron microscopy (HR-TEM, Philips Tecnai F20 at 200 kV). The obtained powders were ultrasonically dispersed in ethanol, dropped onto TEM grids and allowed to evaporate residual solvent in air at room temperature before obtaining TEM images. Elemental analysis was carried out using a Flash-2000 Thermo Fisher model to determine the practical amount of carbon in the annealed LFP/C composites.

### 2.3. Electrochemical measurements

The working electrode was prepared by mixing the active material with 10 wt% of Ketjen black as a conductive reagent and 15 wt% of polytetrafluoroethylene (PTFE) as a binder. The mixture was pressed onto a stainless steel mesh and vacuum dried at 120 °C for 12 h to eliminate residual moisture. A 2032 coin-type cell was fabricated using the lithium metal as a counter electrode, separated by a polymer membrane (Celgard 2400) and subsequently stored for 12 h in a glove box before the electrochemical measurements. The electrolyte employed was a solution of 1 M $LiPF_6$ in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) with 1:1 volume ratio. The galvanostatic tests were carried out with a programmable battery tester (NAGANO, BTS-2400H) at a constant current of 28.9 mA g$^{-1}$ (=0.17 C) and C-rate performances were evaluated at different currents by cycling them for three times at each rate in the potential range of 2.5–4.2 V versus lithium.

## 3. Results and discussion

### 3.1. Characterization of structure and morphology

Thermo-gravimetric and differential thermal analysis (TG/DTA) were used to determine the reaction temperatures for the synthesis of the LFP/C composites. The TG/DTA curves observed under air atmosphere for the ball-milled mixture of starting precursors namely, $Li_2CO_3$, $FeC_6H_5O_7 \cdot xH_2O$ and $NH_4H_2PO_4$ are displayed in Fig. 1(a). There are several stages of weight loss regions in the TG plot that are reflected as corresponding endothermic and exothermic peaks in the DTA plot. The first domain is attributed to the release of physically absorbed water at temperatures below 200 °C. The second temperature domain ranging from 200 to 450 °C shows