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# Synthesis of $Li_2FeP_2O_7$/Carbon nanocomposite as cathode materials for Li-ion batteries

Hiroaki Nagano, Izumi Taniguchi*

*Department of Chemical Engineering, Graduate School of Science and Engineering, Tokyo Institute of Technology, 12-1, Ookayama-2, Meguro-ku, Tokyo 152-8552, Japan*

## HIGHLIGHTS

- $Li_2FeP_2O_7$/Carbon nanocomposite was prepared by a novel preparation route.
- $Li_2FeP_2O_7$/Carbon nanocomposite was agglomerates of primary particles.
- The carbon was well distributed on the surface of agglomerates.
- The nanocomposite cathode delivered 100 mAh $g^{-1}$ at 0.05 C.

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## ABSTRACT

A $Li_2FeP_2O_7$/Carbon (C) nanocomposite was successfully synthesized via a combination of spray pyrolysis and wet ball milling followed by annealing from a precursor solution; in which $LiNO_3$, $H_3PO_4$ and $Fe(NO_3)_3 \cdot 9H_2O$ were stoichiometrically dissolved into distilled water. Ascorbic acid was added to the precursor solution as a reduction agent. The peaks of the $Li_2FeP_2O_7$/C nanocomposite obtained by X-ray diffraction analysis were indexed to the monoclinic structure with the space group $P2_1/c$. The $Li_2FeP_2O_7$/C nanocomposite cathode delivered a first discharge capacity of 100 mAh $g^{-1}$ at 0.05 C, which corresponded to 91% of its theoretical capacity. After various higher discharge rates from 0.05 to 2 C in the cycle performance test, a discharge capacity of 93 mAh $g^{-1}$ was achieved at 0.05 C, which showed an excellent capacity retention (93%) after 29 cycles.

## 1. Introduction

Lithium-ion batteries have been widely used in cellular phones, laptop computers and other portable electronic devices owing to their high working voltage, large energy density and long cycle life. They are also considered to be the most promising means of energy storage for practical electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs). It is well known that the cathode materials of lithium-ion batteries have a significant impact on the battery capacity, cycle life, safety and cost. Recently, lithium transition-metal pyrophosphates ($Li_2MP_2O_7$, M=Fe, Mn and Co) [1–7] have been considered as a new promising cathode material of Li-ion batteries owing to their higher theoretical capacities (~220 mAh $g^{-1}$) than other polyanion materials, such as $LiMPO_4$ (M=Fe and Mn) [8]. Especially, $Li_2FeP_2O_7$ cathode material [9–13] has attracted more attention during the past several years, due to its high safety, low material cost and environmental friendliness. However, $Li_2FeP_2O_7$ or $Li_2FeP_2O_7$/Carbon(C) has been synthesized from a relatively expensive precursor ($LiH_2PO_4$) [10–13] or chemically unstable precursors ($Fe(CH_3COO)$, $FeC_2O_4$ or Fe) [3,7,8,10,12,13].

In our previous studies, we developed a novel synthesis route, i.e., a combination of spray pyrolysis (SP) and wet ball milling (WBM) followed by annealing to prepare $LiMPO_4$/C (M=Fe and Mn) [14,15] and $Li_2FeSiO_4$/C [16] nanocomposites to overcome their poor electronic conductivities and slow lithium-ion diffusion. In this study, we have prepared $Li_2FeP_2O_7$/Carbon(C) nanocomposite from relatively cheap and chemically stable precursors ($LiNO_3$, $H_3PO_4$ and $Fe(NO_3)_3 \cdot 9H_2O$) by a combination of SP and WBM followed by annealing. Furthermore, its physical and electrochemical properties have been investigated.

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* Corresponding author. Tel./fax: +81 3 5734 2155.
*E-mail address:* taniguchi.i.aa@m.titech.ac.jp (I. Taniguchi).

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## 2. Experimental

The precursor solution used in this study was prepared by dissolving stoichiometric amounts of $LiNO_3$, $H_3PO_4$ and $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water. Ascoribic acid was added into the precursor solution as a reducing agent.

A schematic diagram of the SP setup that we developed has been provided elsewhere [17]. The precursor solution was atomized at a frequency of 1.7 MHz using an ultrasonic nebulizer. The sprayed droplets were transported to a reactor using a 3% $H_2+N_2$ gas with a gas flow rate of 4 $dm^3$ $min^{-1}$, heated at 800 °C and converted into solid particles. The resulting particles were then milled with 5 wt.% acetylene black (AB) in ethanol by planetary high-energy planetary ball milling (Fritsch, Pulverisette 7) at 200 rpm for 1 h and then annealed at 600 °C for 2 h in a 3% $H_2+N_2$ atmosphere to obtain the desired material.

The crystalline phases of the samples were studied by X-ray diffraction (XRD, Rigaku, Ultima IV with D/teX Ultra) analysis using Cu-K$\alpha$ radiation. The carbon, iron and phosphor distributions in the sample were observed by a field emission scanning electron microscopy (FE-SEM, Hitachi, SU9000) with energy-dispersive spectroscopy (EDS, Ametech, Genesis-APEX) at 6.0 kV and a transmission electron microscopy (TEM, JEOL, Ltd., JEM-2010F) system equipped with an energy-dispersive spectroscopy (EDS) system operated at 8 kV. The morphology of the obtained samples was also examined by SEM (Keyence YE-8800). The Brunauer–Emmett–Teller (BET) specific surface area was determined from the nitrogen absorption–desorption isotherm using a Micromeritics TriStar-II analyzer. The carbon content of the samples was estimated using an element analyzer (CHNS, Elementar, Vario Micro Cube).

The electrochemical performance of the $Li_2FeP_2O_7$/C nanocomposite was investigated using coin-type cells (CR2032). A 1 mol $dm^{-3}$ $LiPF_6$ solution in a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 volume ratio (Tomiyama Pure Chemical Co., Ltd.) was used as the electrolyte. The cathode consisted of 70 wt.% $Li_2FeP_2O_7$/C, 10 wt.% polyvinylidene fluoride (PVdF) as a binder and 20 wt.% AB. The cells were galvanostatically cycled in a constant current-constant voltage mode at a 0.05 C rate (1 C = 110 mA $g^{-1}$) to 4.3 V, held at 4.3 V until C/100, and then discharged to 2.0 V at different C-rates.

## 3. Results and discussion

Spray pyrolysis synthesis from the precursor solution; in which stoichiometric amounts of $LiNO_3$, $H_3PO_4$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved into distilled water, was firstly carried out for different synthesis temperatures ranging from 600 to 800 °C. The XRD patterns of all the samples were identified as $Li_3Fe_2(PO_4)_3$ crystal structure. Only those of the sample prepared at 800 °C are shown in Fig. 1a. A further annealing at 600 °C for 2 h in 3% $H_2+N_2$ atmosphere was performed for the spray pyrolysis samples. However, a final product ($Li_9Fe_3(P_2O_7)_3(PO_4)_2$) included $Fe^{3+}$ instead of the desired material ($Li_2FeP_2O_7$) was obtained by the SP followed by annealing (Fig. 1a). This may clearly indicate that a reducing agent should be added to the starting solution. Thus, ascorbic acid was used as a reducing agent. Fig. 1b shows the XRD patterns of the samples prepared from the precursor solution with ascorbic acid additive by SP at 800 °C, and then annealed at 600 °C for 2 h in 3% $H_2+N_2$ atmosphere. While the weak peaks attributed to $LiFePO_4$ crystal structure are observed in the XRD patterns of the SP sample, the XRD patterns of the final sample are identified as a monoclinic structure with space group $P2_1/c$ [4,10].

The morphology of the $Li_2FeP_2O_7$ prepared from the precursor solution with ascorbic acid additive by SP with heat treatment is presented in Fig. 2a. The obtained $Li_2FeP_2O_7$ powders are spherical particles with a size ranging from 1 to 3 μm. Although carbon content in the sample was measured by the element analyzer, there was no carbon in it owing to completely decompose of ascorbic acid in the SP synthesis process at 800 °C. The obtained $Li_2FeP_2O_7$ sample was used as a cathode active material and its battery performance was evaluated at a charge–discharge rate of 0.05 C, as shown in Fig. 2b. The $Li_2FeP_2O_7$ electrode delivers 63 mAh $g^{-1}$ at first cycle and 62 mAh $g^{-1}$ at second cycle, corresponding to 57% of its theoretical capacity (110 mAh $g^{-1}$). Also, a narrow potential plateau at approximately 3.4 V in only the discharge profiles, which may attribute to $Fe^{3+}/Fe^{2+}$ reduction reaction, and a large potential difference between charge and discharge profiles can be obviously seen in the figure. These may be due to its poor electronic conductivity, which is a feature of many polyanionic systems, and relatively large particle size of the sample, as shown in Fig. 2a [18].

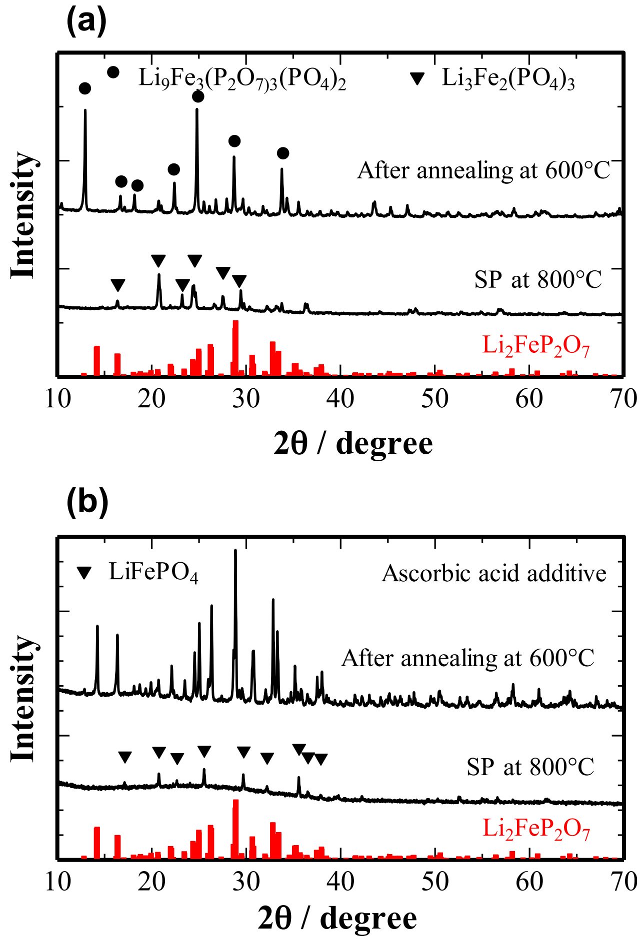

**Fig. 1.** XRD patterns of the sample prepared by SP with annealing from precursor solution with (a) and without (b) ascorbic acid additive.

In order to enhance the electrochemical properties of $Li_2FeP_2O_7$, a novel synthesis route, i.e., a combination of spray pyrolysis and wet ball milling (WBM) followed by annealing was employed to reduce the particle size of $Li_2FeP_2O_7$ and well mix it with carbon. The sample prepared at 800 °C by SP was chosen as the precursor material on the WBM procedure to prepare the $Li_2FeP_2O_7$/C nanocomposite.

Fig. 3a shows the XRD patterns of the sample prepared by a combination of SP and WBM followed by annealing at 600 °C for 2 h. The XRD patterns of the $Li_2FeP_2O_7$ sample prepared by SP with annealing are also shown in the figure as a reference. The XRD