



# Carbon coated lithium cobalt phosphate for Li-ion batteries: Comparison of three coating techniques

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## HIGHLIGHTS

- ▶ Three techniques are adopted to coat carbon on LiCoPO<sub>4</sub> materials.
- ▶ The LiCoPO<sub>4</sub>/C processed via deposition shows a homogeneous carbon coating.
- ▶ LCP-deposition delivers a high capacity of 130 mA h g<sup>-1</sup> with favorable cyclability.
- ▶ A uniform carbon layer is the key to a high and stable electrochemical performance.

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## ABSTRACT

Three techniques, i.e., pyrolysis of sucrose, spray of acetylene black, and propane vapor deposition, are adopted to coat carbon onto the surface of LiCoPO<sub>4</sub> particles, and their effects are compared. The LiCoPO<sub>4</sub>/C composites are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS). The results show that the coating techniques determine the property of carbon films formed on the surface of LiCoPO<sub>4</sub> particles, which further affect the performance of LiCoPO<sub>4</sub>. A complete and homogeneous carbon layer is the key to a high electrochemical activity and stable cycle performance. Among these LiCoPO<sub>4</sub>/C composites, the material processed via the deposition technique shows a more uniform carbon layer than that of the others, thus it exhibits a large reversible capacity of 130 mA h g<sup>-1</sup> with favorable cyclability and rate capability in the voltage range of 3.0–5.0 V.

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## 1. Introduction

Owing to the intrinsically stable nature and good electrochemical properties, olivine structured LiMPO<sub>4</sub> (M = Fe, Mn, Co, Ni) materials have received a lot of attention since their discovery as cathode materials for Li-ion batteries in 1997 [1]. Among them, LiCoPO<sub>4</sub> has recently received particular attention due to its high redox potential of 4.8 V (vs. Li/Li<sup>+</sup>, unless otherwise stated) and thus high energy density of 800 W h kg<sup>-1</sup>, which is essential for batteries to be used in large-format power and energy storage systems. However, the high energy density is difficult to attain, or otherwise it degrades quickly because of poor kinetics and instable cyclability of LiCoPO<sub>4</sub> [2–4]. When operating at a high voltage about 5 V, severe side reaction of electrolyte degradation occurs at

electrode/electrolyte interphase, leading to a drastic capacity fading upon cycling [5–8]. For example, Bramnik et al. reported an initial discharge capacity of 70 mA h g<sup>-1</sup>, and only 10 mA h g<sup>-1</sup> remaining in the 20th cycle [6]. Rabanal et al. also demonstrated a rapid capacity loss for LiCoPO<sub>4</sub> from 80 mA h g<sup>-1</sup> to 40 mA h g<sup>-1</sup> after 20 cycles, and further to 10 mA h g<sup>-1</sup> in the 40th cycle [8].

A variety of strategies have been developed to improve the electrochemical activity of LiCoPO<sub>4</sub>, most of which follow the similar way as the modification of LiFePO<sub>4</sub> material by carbon coating and size reducing [9–14]. These methods enhance the kinetics of LiCoPO<sub>4</sub> and stabilize the interphase as well. The LiCoPO<sub>4</sub>/C core/shell nanocomposite demonstrated high reversible capacities of 144 and 136 mA h g<sup>-1</sup>, as reported by Li et al. [11] and Taniguchi et al. [12], respectively. However, fast capacity degradation was observed in both cases, due probably to the insufficient carbon layer that does not fully cover the surface of all particles. Therefore, electrolyte can easily access the particle surfaces and trigger side reactions. To improve the cyclability, Shui et al. reported a LiCoPO<sub>4</sub> composite consisting of Li<sub>3</sub>PO<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> to achieve

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a high retention of 86% upon 35 cycles [13]. Alternatively, Jang et al. reported a  $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4/\text{LiFePO}_4$  core/shell structure, and obtained 70% retention after 20 cycles. It is supposed that both  $\text{LiFePO}_4$  and  $\text{Li}_3\text{PO}_4$  components significantly suppress the surface side reaction, and thus improve the cycling behavior [14]. The major problem is that neither  $\text{Li}_3\text{PO}_4$  nor  $\text{LiFePO}_4$  is an electronic conductor, which may affect the capacity delivery and rate capability. On the other hand, ion doping has been proven to be an effective way to enhance conductivity and thus the electrochemical property of  $\text{LiCoPO}_4$  [15,16]. Particularly, Allen et al. have proposed a  $\text{Fe}^{3+}$ -doped structure to suppress the reactivity of  $\text{LiCoPO}_4$ , and successfully raised the cycling stability up to 500 cycles with 80% capacity retention [17]. However, the discharged capacity and cycling rate data are not available.

Among versatile modifications, an efficient coating layer seems to be critical to a high-performance and stable  $\text{LiCoPO}_4$  electrode. Particularly, coating by carbon is promising because it addresses the conductivity and stability issues simultaneously. However, previous work often adopted an ex situ coating method by ball milling  $\text{LiCoPO}_4$  with carbon black [10–12]. Due to limitation of this method, although partial surfaces are covered, the coverage is far from complete and uniform. Consequently, the coated samples still exhibit a fast fading in capacity. In this work, we adopt three techniques to coat  $\text{LiCoPO}_4$  with carbon and compare their effect on the formed  $\text{LiCoPO}_4/\text{C}$  composites. The structure, morphology, homogeneity of coating layer, and electrochemical activities of the  $\text{LiCoPO}_4/\text{C}$  composites are examined in detail. These results are correlated to illustrate how the coating techniques can determine the quality of the carbon layer and the performance of  $\text{LiCoPO}_4$ .

## 2. Experimental

Pure  $\text{LiCoPO}_4$  material was prepared by an aqueous precipitation route using  $\text{LiOH}$ ,  $\text{CoSO}_4$ , and  $\text{H}_3\text{PO}_4$  as starting materials following Delacourt's report [18]. In a typical processing, a 10 mmol  $\text{CoSO}_4$  aqueous solution was mixed with 10 mmol  $\text{H}_3\text{PO}_4$  at vigorous agitation. A  $\text{LiOH}$  solution was added dropwise to the mixture until the pH value reaching  $\sim 7$ . After filtration, the precipitate was carefully collected and dried. Finally, the resultant purple powder was heated at  $600^\circ\text{C}$  for 5 h to obtain a crystalline phase. The phase was identified by X-ray diffraction as a pure olivine structure.

To fabricate carbon coated  $\text{LiCoPO}_4$  samples, a static pyrolysis technique and two dynamic techniques of spray and deposition were adopted to coat about 5 wt.% carbon. Accordingly, the resultant  $\text{LiCoPO}_4/\text{C}$  products are denoted as LCP-pyrolysis, LCP-spray, and LCP-deposition, respectively. Fig. 1 schematically shows the processes. For the pyrolysis approach, 1.0 g  $\text{LiCoPO}_4$  powder was mixed with 0.23 g sucrose in a planetary mill, and then the milled mixture was heated at  $650^\circ\text{C}$  for 1 h under Ar flow (Schematic 1a in Fig. 1). During the heating process, sucrose was carbonized and coated on the surface of  $\text{LiCoPO}_4$  particles. As for the spray method, typically, a suspension containing 5 wt.% acetylene black and 1 wt.% polyvinyl alcohol (PVA) was fed into a coating facility (Powrex, Japan) where  $\text{LiCoPO}_4$  powder was rotated. By spraying, the acetylene black was loaded onto the surface of material particles (Schematic 1b in Fig. 1). Then the admixture was heated at  $600^\circ\text{C}$  to carbonize residual PVA. For processing LCP-deposition sample, 0.6 g  $\text{LiCoPO}_4$  material was loaded into a home-made rotary kiln, while a continuous propane flow was also directed into the kiln. The furnace was kept at  $650^\circ\text{C}$  for 1 h when the propane was degraded to carbon and deposited onto the  $\text{LiCoPO}_4$  material (Schematic 1c in Fig. 1). Note that heating at  $650^\circ\text{C}$  is essential to obtain highly conductive carbon degraded from organic precursors [19], while the temperature does not result in substantial reduction of  $\text{LiCoPO}_4$  [9].

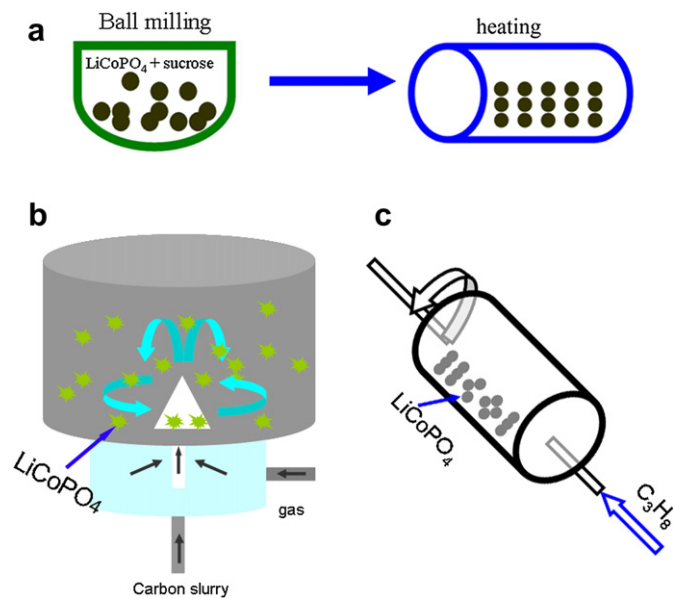


Fig. 1. Schematic presentation of the three techniques used for carbon coating on  $\text{LiCoPO}_4$ .

The structure of the  $\text{LiCoPO}_4/\text{C}$  composite was identified by X-ray diffraction (XRD) using a Rigaku Dmax-2400 automatic diffractometer equipped with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406$  nm). The diffraction data were collected from  $10$  to  $100^\circ$  employing a step scanning procedure at an interval of  $0.02^\circ$  with a count time of 2 s [20]. The structural analysis was performed with the Rietveld method on the program Rietan-2000 [21]. The morphology of the product was examined by scanning electron microscopy (SEM, JEOL JSM-6390). Carbon coating layer was examined by transmission electron microscopy (TEM, FEI Tecnai G2 T20). Element mapping was recorded on an energy dispersive X-ray spectroscopy (EDS, Oxford).

The electrochemical properties of the  $\text{LiCoPO}_4$  materials were examined using 2032 coin cells. The cell comprises a lithium foil anode, a polypropylene separator and a composite cathode sheet consisting of 80 wt.% active material, 10 wt.% carbon black, and 10 wt.% polyvinylidene fluoride, with a typical material loading of  $3\text{ mg cm}^{-2}$ . The coin cells were assembled in an Ar-filled glove box (MBraun) with both  $\text{O}_2$  and  $\text{H}_2\text{O}$  concentration below one ppm. The organic electrolyte is  $1\text{ mol L}^{-1}$   $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 by volume). All the cells were tested on a Land battery program-controlled test system in the voltage range of 3.0–5.0 V at room temperature. The cells were first activated by performing one cycle before subject to various tests.

Electrochemical impedance spectroscopy (EIS) was carried out using a Solartron SI 1280B electrochemical unit. The spectra were measured with the frequency ranging from 20 kHz to 0.1 Hz and the oscillation voltage being 10 mV.

## 3. Results and discussion

### 3.1. Structure

XRD spectra of the carbon-coated  $\text{LiCoPO}_4$  materials are shown in Fig. 2a. It can be seen that all the patterns display well resolved diffraction peaks, which can be indexed to olivine  $\text{LiCoPO}_4$  (PDF #32-0552). Peaks due to carbon are not visible, because of the low degree of crystallinity. Structural analysis based on Rietveld refinement was implemented on the recorded XRD data. Fig. 2b

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