



# Effect of conductive carbon additives on electrochemical performance of LiCoPO<sub>4</sub>



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## HIGHLIGHTS

- Surface area of carbon greatly affects the electrochemical performance of LiCoPO<sub>4</sub>.
- Acetylene black with a moderate surface area (AB-MS) enhances cyclability of LiCoPO<sub>4</sub>.
- AB-MS minimizes side reaction with electrolyte and PF<sub>6</sub><sup>-</sup> intercalation.
- AB-MS also maintains a good conductive network among LiCoPO<sub>4</sub> particles upon cycling.

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## ABSTRACT

The effect of conductive carbon additives (acetylene black with various specific surface areas and ketjen black) on the electrochemical performance of LiCoPO<sub>4</sub> is investigated to develop 5 V-class lithium-ion batteries with good cyclability. The irreversible reactions between electrolyte and LiCoPO<sub>4</sub> electrode can be kept small in addition to realizing reversible and a small amount of intercalation/deintercalation of PF<sub>6</sub><sup>-</sup> into/from the graphite structure of carbon when using acetylene black with a low surface area as a conductive additive. However, the low surface area reduces the utilization of LiCoPO<sub>4</sub>, and degrades its cycle performance owing to the decrease of contact area between LiCoPO<sub>4</sub> and carbon during charge and discharge cycles. On the other hand, ketjen black with a high surface area enhances the capacity of LiCoPO<sub>4</sub>, while it induces a large amount of irreversible reactions and the anion intercalation, leading to the rapid capacity fading. By using acetylene black with a moderate surface area as a conductive additive for LiCoPO<sub>4</sub> electrode, the superior cycle performance can be achieved, which is attributed to the formation of good conductive network among LiCoPO<sub>4</sub> particles by the carbon additive with an appropriate surface area to minimize the irreversible decompose reactions of electrolyte and the anion intercalation.

## 1. Introduction

Lithium-ion batteries with higher energy density and safety are promising as energy storage devices for renewable energy such as solar and wind energy, as well as power sources for plug-in hybrid electric vehicles and electric vehicles [1]. One of effective approaches to improve the energy density is a high voltage operation of batteries, for example, the voltage increase from present 4 V to 5 V. Lithium cobalt phosphate (LiCoPO<sub>4</sub>) has attracted great attention owing to its high operating potential (4.8 V vs. Li/Li<sup>+</sup>) and good theoretical capacity (167 mA h g<sup>-1</sup>), leading to high energy density compared with currently used materials [2]. In addition, LiCoPO<sub>4</sub> with an olivine structure is considered as an excellent safe cathode material, since it has high

thermal and structural stability derived from the strong P–O covalent band [3]. Thus, the improvement of energy density and safety of lithium-ion batteries is achieved by applying LiCoPO<sub>4</sub> to the cathode. However, the low cyclability of LiCoPO<sub>4</sub> obstructs its practical application. It is well known that the high operating potential of LiCoPO<sub>4</sub> is far beyond the electrochemical potential window of conventional electrolytes [4–6]. This high potential leads to irreversible reactions such as decomposition of electrolyte solutions [7] and degradation of LiCoPO<sub>4</sub> by HF included in electrolyte solutions as an impurity [8], resulting in the low coulombic efficiency and the fast capacity fading of batteries upon cycling. Thus, many approaches including the surface modification of electrode materials [9–11], the substitution of anodically stable electrolyte solution for conventional one [12,13], and the

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inclusion of additives in the electrolyte solutions [14–16] have been implemented to overcome this problem.

In addition to electrolyte and cathode materials, conductive carbon additives in the cathode are subject to the undesirable reactions at high potentials [17–19]. Generally, conductive carbon additives, such as acetylene black (AB) and ketjen black (KB), are added to electrodes to create a continuous conductive network among active materials [20,21]. The carbons may be inert in conventional lithium-ion batteries at 4 V, while they become electrochemically active to react with electrolyte in the high-voltage system at around 5 V. The anion intercalation into the graphite structure of carbons is included in the reaction in addition to the electrolyte oxidation [17–19,22–25]. Some studies have reported that the electrochemical behaviors of carbons at high potentials are strongly dependent on their nature. For example, the irreversible capacity, which is due to the oxidation of electrolyte and the formation of solid electrolyte interphase (SEI) on the carbon surface, is dependent on the surface area of carbon [17]. Kajiyama et al. have demonstrated that both crystallinity and specific surface area of carbons are related to the intercalation of anion species into the carbon matrix in high-potential regions [18]. Furthermore, Zheng et al. have investigated the effect of several commonly used carbon additives on the electrochemical performance of high-voltage spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  [19]. The high surface area carbons, such as KB and graphene, are generally considered to provide the better electrochemical properties to composite electrodes than AB with a low surface area owing to their higher electrical conductivity. However, it has been reported that AB realizes the superior cycle performance compared with KB and graphene. This is due to the acceleration of electrolyte oxidation on the higher surface area carbons of KB and graphene at high potentials, resulting in lower coulombic efficiency and faster capacity fading. Therefore, the cycle performance of  $\text{LiCoPO}_4$  is probably enhanced by using the low surface area carbon as a conductive additive. However, little is known about which low surface area carbon is effective to improve the cycle performance of  $\text{LiCoPO}_4$ . The carbon additives are expected to greatly affect the electrochemical performance of  $\text{LiCoPO}_4$  because of its intrinsically poor electrical conductivity [26] and slow ionic diffusion [27].

In this work, we focused on the several ABs as carbon additives with low surface areas to improve the cycle performance of  $\text{LiCoPO}_4$ . Firstly, the electrochemical behaviors of the carbons with various surface areas (three types of ABs and KB) were examined in high-potential regions. Then, their effect as conductive additives on the electrochemical performance of  $\text{LiCoPO}_4$  were investigated and discussed in terms of the differences in the specific surface area and irreversible reactions with an electrolyte solution in detail.

## 2. Experimental

### 2.1. Synthesis and characterization of $\text{LiCoPO}_4$

Carbon-coated  $\text{LiCoPO}_4$  was synthesized by one-pot hydrothermal process according to our previous report [28]. Briefly, 0.09 mol of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (Wako Pure Chemical Industries, Ltd.), 0.09 mol of  $\text{Li}_3\text{PO}_4$  (Kojundo Chemical Lab. Co., Ltd.), and 2.0 g of carboxymethylcellulose sodium salt ( $M_w = 9.0 \times 10^4 \text{ g mol}^{-1}$ , Sigma-Aldrich Co.) were dissolved into degassed water (30 ml) and heated at 200 °C for 24 h under  $\text{N}_2$  atmosphere. After the hydrothermal treatment, the resulting precipitation was separated centrifugally, washed with water, and subsequently freeze-dried at below  $-100$  °C for 12 h. The dried powder was heat-treated at 700 °C for 1 h under 97%  $\text{Ar}/3\%$   $\text{H}_2$  atmosphere and carbon-coated  $\text{LiCoPO}_4$  was obtained. The X-ray diffraction (XRD, RINT 2000/PC, Rigaku Co.) pattern of the product was assigned to phospholivine  $\text{LiCoPO}_4$  with orthorhombic  $Pnma$  space group. The size and morphology of the prepared  $\text{LiCoPO}_4$  were observed by a scanning electron microscope (SEM, JSM-7500F, JEOL Ltd.). The specific surface area of the sample was calculated using the Brunauer–Emmet–Teller

(BET) equation from the adsorption isotherm of  $\text{N}_2$  gas at 77 K determined by a BELSORP-mini II apparatus (MicrotracBEL Corp.). The carbon content of the sample was determined by a thermogravimetric analysis (DTG-60H, Shimadzu Co.).

### 2.2. Characterization of conductive carbon additives

Four different carbon additives were characterized: three types of ABs (Li-100, Li-400, and Li-435, Denka Co., Ltd.) and KB (EC300J, Lion Specialty Chemicals Co., Ltd.). The size and morphology of carbon additives were observed by SEM. Their specific surface areas were determined by the BET method.

### 2.3. Electrochemical measurement

The carbon electrodes were fabricated by coating the slurries including the carbon additive and polyvinylidene difluoride (PVDF, Kureha Co.) with a weight ratio of 50:50 in *N*-methyl pyrrolidone on Al foil current collectors (20  $\mu\text{m}$  in thickness) using a doctor blade. The  $\text{LiCoPO}_4$  electrodes were also prepared by a similar procedure with electrode slurries including 80 wt%  $\text{LiCoPO}_4$ , 10 wt% carbon, and 10 wt% PVDF. All electrodes were dried at 120 °C under vacuum for 12 h and punched into a circle shape (14 mm in diameter). The loading amount of carbon was 0.37–0.53  $\text{mg cm}^{-2}$  with a thickness of 7–11  $\mu\text{m}$ . The loading amount of  $\text{LiCoPO}_4$  was 2.2–2.8  $\text{mg cm}^{-2}$  with a thickness of 16–21  $\mu\text{m}$ . Carbon|Li and  $\text{LiCoPO}_4$ |Li half-cells were assembled in the 2032 coin-type cells in an Ar filled glove box. A three dimensionally ordered macroporous polyimide membrane [29–34] and 1  $\text{mol dm}^{-3}$   $\text{LiPF}_6$ /ethylene carbonate:diethyl carbonate = 1:2 (v/v) (Kishida chemical Co., Ltd.) were used as a separator and an electrolyte solution. Cyclic voltammetry (CV) of each carbon|Li half-cell was performed with an automatic polarization system (HSV-110, Hokuto Denko Co.) in the potential range of 3.0–5.3 V at the scan rate of 0.1  $\text{mV s}^{-1}$ . Galvanostatic charge–discharge tests of the cells were carried out with a charge–discharge unit (HJ1001SD8, Hokuto Denko Co.) in the potential range of 3.0–5.1 V at 133.6  $\text{mA g}^{-1}$  for the carbon|Li half-cells and 0.1 C (1 C = 167  $\text{mA g}^{-1}$ ) for the  $\text{LiCoPO}_4$ |Li half-cells. Current densities and specific capacities of carbon electrodes and  $\text{LiCoPO}_4$  electrodes were calculated by normalizing to the weight of carbon and  $\text{LiCoPO}_4$ , respectively. Electrochemical impedance spectroscopy of  $\text{LiCoPO}_4$ |Li half-cells was conducted using a Solartron SI 1287 electrochemical analyzer at open circuit voltage with an AC modulation amplitude of  $\pm 5$  mV in the frequency range from 1 MHz to 0.01 Hz. The spectra were measured at fresh state and after 100 cycles of the galvanostatic charge–discharge test.

### 2.4. Surface characterization

X-ray photoelectron spectroscopy (XPS) analysis of  $\text{LiCoPO}_4$  electrodes was performed by using a JPS-9010MX equipment (JEOL Ltd.) with Al  $K\alpha$  X-ray source (emission current: 10 mA, acceleration voltage: 10 kV). The  $\text{LiCoPO}_4$ |Li half-cells after 100 cycles of charge–discharge test were disassembled in an Ar filled glove box to take out the  $\text{LiCoPO}_4$  electrodes, which were then washed with dimethyl carbonate, vacuum-dried, and transferred to the spectrometer. For comparison, the pristine  $\text{LiCoPO}_4$  electrodes were also investigated as a control. The binding energy of each spectrum was calibrated using the standard energy of C 1s peak of amorphous carbon at 285.0 eV. The peaks observed in the spectra were assigned based on previous reports [8,13]. Quantification was performed from high resolution spectra of C 1s, O 1s, F 1s, P 2p, and Co 2p (pass energy 30 eV, steps 0.1 eV) after a Shirley-type background subtraction by XPS Peak software (SpecSurf Version 1.9.2.12, JEOL Ltd.). The surface morphology of  $\text{LiCoPO}_4$  electrodes before and after cycling were observed by SEM.

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