Investigation of Carbon-coating Effect on the Electrochemical Performance of LiCoPO₄ Single Particle

Yuto YAMADA, a Yusaku NODA, a Hirokazu MUNAKATA, a Shuhei YOSHIDA, b Daisuke SHIBATA, b and Kiyoshi KANAMURA a, *

a Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan
b DENSO CORPORATION, 1-1 Showa-cho, Kariya, Aichi 448-8661, Japan

* Corresponding author: kanamura@tmu.ac.jp

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ABSTRACT
The effect of carbon-coating on the electrochemical properties of LiCoPO₄ was investigated by single particle measurement. For this analysis, micrometer-scale LiCoPO₄ particles with and without carbon-coating were synthesized by hydrothermal method (LiCoPO₄/C0 with 0.3 wt%, LiCoPO₄/C1 with 0.8 wt%, LiCoPO₄/C2 with 1.7 wt% carbon-coating and pristine LiCoPO₄). In the electrochemical tests using the conventional composite electrodes, all the samples showed the similar electrochemical properties with potential plateaus at ~4.7 V vs. Li/Li⁺. In contrast, single particle measurement showed clear differences in the charge and discharge curves. The pristine LiCoPO₄ showed the potential plateau only in the discharge curve due to a large overpotential of charging. LiCoPO₄/C0 also showed large overpotential. On the other hand, good electrochemical responses were obtained for the LiCoPO₄/C1 and LiCoPO₄/C2 particle electrodes even though their carbon-coating amounts were different. This result suggests that 0.8 wt% or higher carbon-coating enables to improve the electrochemical performance of one particle of LiCoPO₄.

Keywords : Lithium-Ion Battery, Single Particle Measurement, Lithium Cobalt Phosphate, Carbon-coating

1. Introduction
Lithium ion batteries have been used as power sources for portable electric devices due to their high energy density. Recently, their applications have been expanded for larger scale devices such as electric vehicles. Lithium metal phosphates (LiMPO₄, M = Fe, Mn, Co, Ni) having olivine structures have been expected as promising cathode materials for such large lithium ion batteries, because they have excellent thermal and structural stability due to strong covalent bond of P-O. In fact, LiFePO₄ has already commercialized and used as a cathode for large lithium ion batteries. However, the operating potential of LiFePO₄ is as low as 3.4 V vs. Li/Li⁺ compared to ~4 V vs. Li/Li⁺ of other conventionally used cathode materials such as LiCoO₂ and LiMn₂O₄. In order to obtain high energy density of batteries, cathode materials having higher operating potentials are required. LiCoPO₄ is an attractive phosphate cathode material since it has high operation potential (4.7 V vs. Li/Li⁺) and large theoretical capacity (167 mA h g⁻¹). However, the electronic and lithium ionic conductivities of LiMPO₄ are basically low. To solve this problem, many researchers have been done, in which carbon-coating and particle design have been mainly performed. Active materials for lithium ion batteries are usually evaluated by making their composite electrodes including conductive carbon and polymer binder. To investigate the electrochemical properties of composite electrode is important for battery design. However, it is not necessarily effective to investigate the intrinsic electrochemical properties of active materials, because the electrochemical responses of composite electrode is influenced by the mixing ratio of materials, electrode porosity and thickness. Especially, for the cases of active materials with poor conductivity including LiMPO₄, the electrochemical properties of composite electrode are strongly influenced by those factors. Therefore, porous composite electrode is not suitable to investigate the intrinsic electrochemical properties of LiMPO₄. In order to overcome this problem, we have employed single particle measurement, which can evaluate one active material particle, resulting in the effective elimination of additive and structure effects on the electrochemical responses of active material in the composite electrode.

In this study, the carbon-coating effect on the electrochemical properties of LiCoPO₄ was investigated by single particle measurement to clarify its optimal coating. Micrometer-scale particles are suitable not only for single particle measurement but also for the suppression of electrolyte decomposition in a high voltage region. Therefore, the LiCoPO₄ particles with and without carbon-coating were synthesized in micrometer-scale sizes by hydrothermal method, which is one of useful methods to control the particle size of active materials. To prepare larger size particles for single particle measurement, hydrothermal treatment with a carbon source is not suitable, because some carbon sources prevent the particle growth. Therefore, carbon-coating process was carried out after synthesizing pristine LiCoPO₄. Sucrose has been used as a carbon source, which is a typical material for carbon-coating after synthesizing LiMPO₄.

2. Experimental
0.09 mol of Li₃PO₄ (Kojundo Chemical Laboratory Co., Ltd) as Li and P sources, and 0.09 mol of CoSO₄ (CoSO₄ 7H₂O, Wako Pure Chemical Industries, Ltd.) as Co source were dissolved into 30 mL of water deaerated with N₂ gas. This process was carried out under N₂ atmosphere. The prepared precursor solution was put into an autoclave. Then, hydrothermal treatment was carried out at 200°C for 48 h with stirring. After the hydrothermal treatment, the LiCoPO₄ particles were separated, collected by centrifugation and freeze-dried. As a carbon source, 0.05, 0.1 or 0.2 g of sucrose (Wako Pure Chemical Industries, Ltd.) was dissolved into 1 mL of water and stirred for 3 min. 2.0 g of the synthesized LiCoPO₄ was mixed with this solution. After stirring for 15 min, the mixed solution was
dried under air at 110°C, and then heated at 700°C for 1 h under a mixed gas of Ar and H2 (97:3 in volume) to obtain carbon-coated LiCoPO4. The carbon-coated LiCoPO4 prepared with 0.05 g, 0.1 g and 0.2 g sucrose were described as LiCoPO4/C0, LiCoPO4/C1 and LiCoPO4/C2, respectively.

Crystal structures of synthesized samples were identified by X-ray diffraction (XRD, RINT 2000/PC, Rigaku Co.) with CuKα radiation. The particle size and morphology were observed by scanning electron microscopy (SEM, JSM-7500F, JEOL Ltd.). Raman spectroscopy was conducted with NRS-1000 (Jasco Co.) to confirm the coating states of carbon on sample particles. The elemental mapping of the sample particles was obtained by energy dispersive X-ray spectroscopy (EDX, X-Max 50, Oxford Instruments plc). The amount of carbon was evaluated by thermogravimetric analysis (DTG-60H, Shimadzu Co.).

Electrochemical properties of the synthesized samples were evaluated by single particle measurement. Figure 1 shows an original measurement system. A measurement cell including an electrolyte, a counter electrode and active material particles was put on the stage of an optical microscope (VHX-1000, KEYENCE Co.). A mixed solvent of ethylene carbonate and ethyl methyl carbonate in a volume ratio of 3:7 containing 1 mol dm⁻³ LiPF₆ (Kishida chemical Co., Ltd.) was used as the electrolyte. A piece of lithium foil attached on Ni wire was used as the counter electrode. A micro current collector of Au wire with a diameter of 10 µm was used, whose side was surrounded by glass to reduce a background current caused by double layer capacitance. The tip of micro current collector was contacted to one particle of LiCoPO4 samples by using a manipulator system (QuickPro, Micro Support Co., Ltd.) under observation with an optical microscope. The charge/discharge tests were carried out with an electrochemical analyzer (SP-200, BioLogic Science Instruments plc). The measurement was carried out in a vacuum (<10⁻⁶ Torr) at room temperature under Ar atmosphere.

Electrochemical properties of LiCoPO4 were also evaluated by making their composite electrodes with a weight ratio of synthesized LiCoPO4, ketjen black and PVdF in 75:15:10. These materials were dispersed in N-methyl-2-pyrrolidone to prepare the slurry. The slurry was coated on Al foil as a current collector and then dried under air at 110°C and then heated at 700°C for 1 h under a mixed gas of Ar and H2 (97:3 in volume) to obtain carbon-coated LiCoPO4. The carbon-coated LiCoPO4 prepared with 0.05 g, 0.1 g and 0.2 g sucrose were described as LiCoPO4/C0, LiCoPO4/C1 and LiCoPO4/C2, respectively.

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amount of carbon for LiCoPO₄/C₀, LiCoPO₄/C₁ and LiCoPO₄/C₂ were determined by the weight loss as 0.3 wt%, 0.8 wt% and 1.7 wt% respectively (Fig. 6). Theoretical values calculated from the amounts of sucrose used for carbon-coating were 1.04 wt% (LiCoPO₄/C₀), 2.06 wt% (LiCoPO₄/C₁) and 3.94 wt% (LiCoPO₄/C₂), respectively. Therefore, it can be seen that some amount of sucrose was not converted to carbon in the synthesis process.

Electrochemical performance of LiCoPO₄ samples were evaluated by charge/discharge tests of coin-type cells using their composite electrodes. The charge was performed at 0.1 C until the potential reached to 5.1 V vs. Li/Li⁺ and then the potential was hold until the current declined to 0.01 C. The discharge was conducted at 0.1 C until potential reached to 2.5 V vs. Li/Li⁺. A potential plateau was clearly observed at 4.7 V vs. Li/Li⁺. The initial discharge capacity was 71 mA h g⁻¹ which was lower than the half of theoretical capacity (167 mA h g⁻¹), due to low electric conductivity of LiCoPO₄. An irreversible capacity due to electrolyte decomposition was observed. The charge and discharge curves of LiCoPO₄/C₀, LiCoPO₄/C₁ and LiCoPO₄/C₂ are shown in Figs. 7(b), (c) and (d), respectively. The discharge and charge conditions were the same as those for pristine LiCoPO₄.
with those used for the LiCoPO₄ evaluation. Both the potential plateau and irreversible capacity were observed as similar to those of pristine LiCoPO₄. The larger initial discharge capacities of 105, 110 and 114 mA h g⁻¹ were observed for LiCoPO₄/C₀, LiCoPO₄/C₁ and LiCoPO₄/C₂, respectively. This is due to an improvement of electric conductivity by carbon-coating on the surface of LiCoPO₄.

Figure 8 shows the charge and discharge curves of pristine LiCoPO₄ single particle. The particle size was 50 µm in diameter. The particle was charged at 0.2 nA until the potential reached to 5.1 V vs. Li/Li⁺ and then the potential was held at 5.1 V for 2 hours. The discharge was carried out at 0.2 nA until the potential reached to 2.5 V vs. Li/Li⁺. When the charge was started, the potential rapidly increased and then reached to 5.1 V vs. Li/Li⁺. In the discharge process, the potential plateau was observed at 4.5 V vs. Li/Li⁺ in the 1st cycle and those appeared at lower potentials in the following cycles (4.3 V vs. Li/Li⁺ in 2nd, 4.2 V vs. Li/Li⁺ in 3rd). These values were lower than theoretical operating potential.3 In addition, LiCoPO₄ showed very small discharge capacity. These results indicate that LiCoPO₄ particle without carbon-coating has very high electrochemical impedance. In the case of composite electrode including binder and conductive material, LiCoPO₄ without carbon-coating showed a clear potential plateau at 4.7 V vs. Li/Li⁺ in the discharge process. Probably, the difference between the single particle and composite electrodes of LiCoPO₄ is due to the improvement of electric conductivity by the conductive material in the composite electrode.

Figure 9(a) shows the charge and discharge curves of LiCoPO₄/C₀ single particle at initial 3 cycles. The particle size was 20 µm in diameter. The particle was charged at 3 nA until the potential reached to 5.1 V vs. Li/Li⁺ and then the potential was held until the charge current dropped to 0.3 nA. The discharge was carried out at 3 nA until the potential reached to 2.5 V vs. Li/Li⁺. This current was higher than that for pristine LiCoPO₄ single particle measurement. LiCoPO₄/C₀ single particle showed potential plateaus in the 1st charge process and the 1st–3rd discharge processes. Figure 9(b) shows the discharge rate capability of LiCoPO₄/C₀. All charge processes were carried out at 3 nA until the potential reached to 5.1 V vs. Li/Li⁺ and then the potential was held until the charge current dropped to 0.3 nA. The discharge processes were carried out at various current values from 0.3 nA to 5 nA. In the discharge process at 0.3 nA, the potential plateau was observed at 4.7 V vs. Li/Li⁺, which corresponds to the plateau in composite electrode shown in Fig. 7(b). These results indicate the improvement of electrochemical performance of LiCoPO₄ particle by the carbon-coating. However, the polarization was still large.

Figure 10(a) shows the charge and discharge curves of LiCoPO₄/C₁ single particle during initial 3 cycles at the same current value for LiCoPO₄/C₀ single particle measurement. The particle size was 20 µm in diameter. The potential plateaus were observed in both
charge and discharge curve. Although irreversible capacity and capacity fading were observed during 3 cycles, the charge and discharge curves similar to those of composite electrodes were obtained. Figure 10(b) shows the discharge rate capability of LiCoPO₄/C0 single particle measurement. The discharge processes were carried out at various current values from 0.3 nA to 20 nA. The electrochemical performance was greatly improved by coating 0.8 wt% of carbon.

Figure 11(a) shows the charge and discharge curves of initial 3 cycles and discharge rate capability of LiCoPO₄/C2 single particle. The particle size was 20 µm and electrochemical measurement was carried out in the same current values with LiCoPO₄/C1 shown in Fig. 10. In the initial 3 cycles, irreversible capacity and capacity fading were observed as similar to LiCoPO₄/C1. Electrochemical performance was improved compared with pristine LiCoPO₄. The rate capability in Fig. 11(b) was not so different from that for LiCoPO₄/C1. Therefore, it can be concluded that 0.8 wt% or higher of carbon-coating is suitable for single particle electrode of LiCoPO₄.

For more detailed investigation, quasi Tafel plots were made for LiCoPO₄/C1 and LiCoPO₄/C2 single particles from their rate capabilities. Figure 12 shows the quasi Tafel plot of LiCoPO₄/C1 in the state of depth of discharge (DOD) 10%. DOD was calculated from the capacity in the discharge process at 0.3 nA. Current densities were calculated from the discharge current value and the surface area of particle by assuming that the particle is a cube with 20 µm on each side. When the relationship between potential and current density accords to Tafel equation, kinetics of the electrochemical reactions are limited by the charge transfer process.

Tafel equation is given as

\[
\log i = \log i_0 + \frac{\alpha F}{2.303RT} \eta.
\]

Here, \(i\) is current density, \(i_0\) is the exchange current density, \(\alpha\) is the transfer coefficient, \(F\) is the Faraday constant, \(R\) is the gas constant, \(T\) is the reaction temperature, and \(\eta\) is the overpotential. The overpotential \(\eta\) in this study was obtained from the potential difference between the equilibrium potential (\(E_{\text{eq}}\)) and discharge.

Figure 10. (a) Charge/discharge curves at initial 3 cycles and (b) rate capability of LiCoPO₄/C1.

Figure 11. (a) Charge/discharge curves at initial 3 cycles and (b) rate capability of LiCoPO₄/C2.

Figure 12. Tafel plot of LiCoPO₄/C1 in the state of DOD 10%.
The value of \( i_0 \) were limited by the Li diffusion coefficient at various DODs. The charge transfer resistance \( R_{ct} \) is obtained by the intersection point of the Tafel equation and the equilibrium potential. The charge transfer resistance \( R_{ct} \) is calculated with formula (2).

\[
R_{ct} = \frac{RT}{i_0}
\]

In the high current values, the obtained plots deviated from the Tafel equation. This indicates that kinetics of the electrochemical reactions are limited by the Li\(^+\) diffusion process in the LiCoPO\(_4\) particle. In the case of one-dimensional diffusion, the diffusion coefficient \( D \) can be estimated by formula (3).

\[
l = \sqrt{2Dt}
\]

Here, \( l \) is the radius of the particle, \( t \) is the discharge time for the current value at starting of the deviation from the Tafel equation. The value of \( i_0, R_{ct}, \) and \( D \) at various DODs were summarized in Table 1. At the high DOD region, electrochemical parameters could not be obtained due to large deviation from Tafel equation at low discharge currents. \( R_{ct} \) of LiCoPO\(_4\)/C1 showed higher value than that of LiCoPO\(_4\)/C2 except for DOD 20%. Larger amount of carbon may provide lower \( R_{ct} \). \( D \) for LiCoPO\(_4\)/C1 and LiCoPO\(_4\)/C2 were 10\(^{-11}\) to 10\(^{-9}\) cm\(^2\) s\(^{-1}\), which were similar values. This indicated that \( D \) is independent from carbon-coating. These values were comparable to the diffusion coefficient of LiFePO\(_4\) secondary particle estimated by single particle measurement.\(^{2}\) Other studies have reported the \( D \) value of approximately 10\(^{-13}\) cm\(^2\) s\(^{-1}\) using composite electrode of LiCoPO\(_4\).\(^{5,22,23}\) These values are smaller than that of single particle in several orders of magnitude. The difference between this study and other studies is due to the difference of the measurement systems: one active material and composite electrode. Namely, Li\(^+\) diffusion in the composite electrodes is affected by Li\(^+\) diffusion in electrolyte. On the other hand, the single particle electrodes have no effect of diffusion in electrolyte due to spherical diffusion. Moreover, the \( D \) value of carbon-coated LiCoPO\(_4\) estimated by single particle measurement is closer to the values calculated by first-principles method (10\(^{-12}\) cm\(^2\) s\(^{-1}\) and 10\(^{-9}\) cm\(^2\) s\(^{-1}\) for CoPO\(_4\) and LiCoPO\(_4\), respectively), compared with the value estimated using composite electrode.\(^{24}\) However, the D values were not so close to calculated values. This indicates that suitable particle design and crystalline are also important to improve electrochemical performance of LiCoPO\(_4\).

Discharges were carried out at 3 nA after rate capability test for the particle of LiCoPO\(_4\)/C1 and LiCoPO\(_4\)/C2, as shown in Fig. 10 and Fig. 11, respectively. Figure 13(a) shows the discharge curves of LiCoPO\(_4\)/C1 after rate capability test. The discharge capacities of LiCoPO\(_4\)/C1 and LiCoPO\(_4\)/C2 were 0.275 nA h and 0.352 nA h which are 42% and 55% of 1st discharge, respectively. In a high voltage range, electrolyte decomposition actively occurred at the direct contact area of LiCoPO\(_4\) with electrolyte,\(^{26}\) which caused capacity fading.\(^{25}\) Therefore, the better cycleability for LiCoPO\(_4\)/C2 was observed, probably due to larger coverage area of carbon. However, cycle performance was still low even for LiCoPO\(_4\)/C2. To prevent capacity fading, improvement of carbon-coating or development of electrolyte with high stability at high voltages are required.

4. Conclusions

The micrometer-scale LiCoPO\(_4\) particles with and without carbon-coating were prepared by hydrothermal method. Their electrochemical performance was evaluated by single particle measurement. In the charge and discharge curves of coin-type cells with composite electrodes, both pristine LiCoPO\(_4\) and carbon-coated LiCoPO\(_4\) showed clearly a discharge plateau at 4.7 V vs. Li/Li\(^+\), and the carbon-coated LiCoPO\(_4\) showed larger discharge capacity (over 105 mA h g\(^{-1}\)) than that of pristine LiCoPO\(_4\) (71 mA h g\(^{-1}\)).

### Table 1. Electrochemical parameters of LiCoPO\(_4\)/C1 and LiCoPO\(_4\)/C2 single particles at various DODs.

| DOD    | 10%  | 20%  | 30%  | 40%  | 50%  | 60%  | 70%  | 80%  | 90%  |
|--------|------|------|------|------|------|------|------|------|------|
| \( i_0 \) (mA cm\(^{-2}\)) | 0.0229 | 0.028 | 0.0139 | 0.0125 | —    | —    | —    | —    | —    |
| \( R_{ct} \) (Ω cm\(^2\)) | 1120 | 917.9 | 1851 | 2049 | —    | —    | —    | —    | —    |
| \( D \) (cm\(^2\) s\(^{-1}\)) | 2.65 x 10\(^{-9}\) | 2.65 x 10\(^{-9}\) | 7.07 x 10\(^{-10}\) | 7.07 x 10\(^{-10}\) | —    | —    | —    | —    | —    |

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**Figure 13.** Discharge curves of (a) LiCoPO\(_4\)/C1 and (b) LiCoPO\(_4\)/C2 particles at 3 nA after rate capability test.
In contrast, the single particle of pristine LiCoPO$_4$ and 0.3 wt% carbon-coating LiCoPO$_4$ showed poor discharge capacity and lower potential plateau, indicating that 15 wt% of conductive material in the composite electrode played an important role for electric conductivity of electrodes. On the other hand, 0.8 and 1.7 wt% carbon-coating LiCoPO$_4$ single particle showed extremely improved electrochemical performances. Therefore, when using 0.8 wt% carbon-coating LiCoPO$_4$ particles, the amount of conductive carbon additive in the composite electrode can be reduced, which can improve the capacity density of electrode. The diffusion coefficient of Li$^+$ ion in the carbon-coated LiCoPO$_4$ particle showed the values from $10^{-11}$ to $10^{-9}$ cm$^2$s$^{-1}$ at different DODs, which is higher than those reported in the previous studies using composite electrodes. However, these values were lower than the value calculated by first-principle mothed. Moreover, cycle performance of carbon-coated LiCoPO$_4$ particle was still low. Therefore, further improvement is required.

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