Investigation of Carbon-coating Effect on the Electrochemical Performance of LiCoPO_4 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

ABSTRACT

The effect of carbon-coating on the electrochemical properties of LiCoPO_4 was investigated by single particle measurement. For this analysis, micrometer-scale LiCoPO_4 particles with and without carbon-coating were synthesized by hydrothermal method ($\text{LiCoPO}_4/\text{C0}$ with 0.3 wt%, $\text{LiCoPO}_4/\text{C1}$ with 0.8 wt%, $\text{LiCoPO}_4/\text{C2}$ with 1.7 wt% carbon-coating and pristine LiCoPO_4). In the electrochemical tests using the conventional composite electrodes, all the samples showed the similar electrochemical properties with potential plateaus at $\sim 4.7\text{ V}$ vs. Li/Li^+ . In contrast, single particle measurement showed clear differences in the charge and discharge curves. The pristine LiCoPO_4 showed the potential plateau only in the discharge curve due to a large overpotential of charging. $\text{LiCoPO}_4/\text{C0}$ also showed large overpotential. On the other hand, good electrochemical responses were obtained for the $\text{LiCoPO}_4/\text{C1}$ and $\text{LiCoPO}_4/\text{C2}$ 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 LiCoPO_4 .

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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 (LiMPO_4 , $\text{M} = \text{Fe, Mn, Co, Ni}$) 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, LiFePO_4 has been already commercialized and used as a cathode for large lithium ion batteries.^{1,2} However, the operating potential of LiFePO_4 is as low as 3.4 V vs. Li/Li^+ compared to $\sim 4\text{ V}$ vs. Li/Li^+ of other conventionally used cathode materials such as LiCoO_2 and LiMn_2O_4 . In order to obtain high energy density of batteries, cathode materials having higher operating potentials are required. LiCoPO_4 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}).³

However, the electronic and lithium ionic conductivities of LiMPO_4 are basically very low. To solve this problem, many researches have been done, in which carbon-coating and particle design have been mainly performed.^{4,5}

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 LiMPO_4 , the electrochemical properties of composite electrode are strongly influenced by those factors.^{6,7} Therefore, porous composite electrode is not suitable to investigate the intrinsic electrochemical properties of

LiMPO_4 . 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.^{2,8–10}

In this study, the carbon-coating effect on the electrochemical properties of LiCoPO_4 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 LiCoPO_4 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.^{5,11,12} 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.⁵ Therefore, carbon-coating process was carried out after synthesizing pristine LiCoPO_4 . Sucrose has been used as a carbon source, which is a typical material for carbon-coating after synthesizing LiMPO_4 .^{13,14}

2. Experimental

0.09 mol of Li_3PO_4 (Kojundo Chemical Laboratory Co., Ltd) as Li and P sources, and 0.09 mol of CoSO_4 ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, Wako Pure Chemical Industries, Ltd.) as Co source were dissolved into 30 mL of water deaerated with N_2 gas. This process was carried out under N_2 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 LiCoPO_4 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 LiCoPO_4 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 CuK α 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 μ m 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) 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 at 80°C overnight. The electrode was punched into a circle in a diameter of 14 mm. 2032 coin-type cells which were composed of the prepared LiCoPO₄ electrode, polypropylene separator, electrolyte and Li foil (Honjo Metal Co., Ltd.) anode were prepared in Ar atmosphere. A mixed solvent of ethylene carbonate and diethyl carbonate with 1:2 in volume containing 1 mol dm⁻³ LiPF₆ (Kishida

chemical Co., Ltd.) was used as an electrolyte. The charge/discharge tests were carried out with a battery charge/discharge system (HJ1001SD8).

3. Results and Discussion

Figure 2 shows the SEM images of LiCoPO₄, LiCoPO₄/C0, LiCoPO₄/C1 and LiCoPO₄/C2. Cubic-shape particles were observed. Several particles had over 10 μ m size. These particles were utilized for single particle measurement. Significant difference in particle size and shape were not observed in these samples. Moreover, carbon was not clearly observed in SEM images of carbon-coated samples.

To confirm the distribution of carbon, the elemental mappings of O, P and C for LiCoPO₄/C0, LiCoPO₄/C1 and LiCoPO₄/C2 were carried out, as shown in Fig. 3. All samples showed distribution of O and P. In addition, C was also observed on the surface of particles, indicating that the carbon-coating was performed. Especially, LiCoPO₄/C2 showed larger amount of carbon compared with other carbon-coated samples.

X-ray diffraction patterns of LiCoPO₄, LiCoPO₄/C0, LiCoPO₄/C1 and LiCoPO₄/C2 are shown in Fig. 4. All patterns were indexed based on olivine structure with orthorhombic *Pnma* space group, suggesting that well-crystallized particles were obtained. From this result, it is confirmed that the carbon-coating process in this study does not effect on the crystal structure of LiCoPO₄.

Raman spectroscopy was performed to confirm carbon-coating state of samples.^{15,16} Raman spectra of LiCoPO₄, LiCoPO₄/C0, LiCoPO₄/C1 and LiCoPO₄/C2 are shown in Fig. 5. A sharp peak was observed at 950 cm⁻¹ ascribed to PO₄³⁻ anion's symmetric stretching in all samples. In the carbon-coated samples, the broad peaks also observed at 1350 cm⁻¹ and 1500 cm⁻¹ can be ascribed to D band and G band of carbon, respectively. As increasing amount of carbon, stronger peaks of carbon were observed. However, the peak of PO₄³⁻ was clearly observed even for carbon-coated samples. From this result, two patterns of carbon-coating state are considered. When the thickness of carbon layer is 5–12 nm, very weak PO₄³⁻ peak is observed.¹⁷ Therefore, one of possible reasons is that carbon layer is very thin (less than 5 nm). Another possible reason is that LiCoPO₄ particle is not fully covered with carbon.⁵

The amount of carbon was estimated by thermogravimetric analysis as shown in Fig. 6. The measurement was carried out in air atmosphere with a heating rate of 10°C min⁻¹. In carbon-coated samples, the weight loss due to oxidation of the carbon on LiCoPO₄ surface was observed from 440°C to 660°C. The increase in weight at around 390°C is attributable to the oxidation of cobalt.^{16,18} The

Figure 1. Single particle measurement system.

Figure 2. SEM images of (a) pristine LiCoPO₄, (b) LiCoPO₄/C0, (c) LiCoPO₄/C1 and (d) LiCoPO₄/C2.

Figure 3. EDX mappings of C, O and P for $\text{LiCoPO}_4/\text{C0}$, $\text{LiCoPO}_4/\text{C1}$ and $\text{LiCoPO}_4/\text{C2}$.

Figure 4. XRD patterns of pristine LiCoPO_4 , $\text{LiCoPO}_4/\text{C0}$, $\text{LiCoPO}_4/\text{C1}$ and $\text{LiCoPO}_4/\text{C2}$.

Figure 5. Raman spectra of pristine LiCoPO_4 , $\text{LiCoPO}_4/\text{C0}$, $\text{LiCoPO}_4/\text{C1}$ and $\text{LiCoPO}_4/\text{C2}$.

Figure 6. Thermogravimetric analysis of pristine LiCoPO_4 , $\text{LiCoPO}_4/\text{C0}$, $\text{LiCoPO}_4/\text{C1}$ and $\text{LiCoPO}_4/\text{C2}$.

amount of carbon for $\text{LiCoPO}_4/\text{C0}$, $\text{LiCoPO}_4/\text{C1}$ and $\text{LiCoPO}_4/\text{C2}$ 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% ($\text{LiCoPO}_4/\text{C0}$), 2.06 wt% ($\text{LiCoPO}_4/\text{C1}$) and 3.94 wt% ($\text{LiCoPO}_4/\text{C2}$), respectively. Therefore, it can be seen that some amount of sucrose was not converted to carbon in the synthesis process.

Electrochemical performance of LiCoPO_4 samples were evaluated by charge/discharge tests of coin-type cells using their composite electrodes. The charge and discharge curves of the coin-type cell of LiCoPO_4 without carbon-coating are shown in Fig. 7(a). 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 mAh g^{-1} which was lower than the half of theoretical capacity (167 mAh g^{-1}), due to low electric conductivity of LiCoPO_4 . An irreversible capacity due to electrolyte decomposition was observed.¹⁹ The charge and discharge curves of $\text{LiCoPO}_4/\text{C0}$, $\text{LiCoPO}_4/\text{C1}$ and $\text{LiCoPO}_4/\text{C2}$ are shown in Figs. 7(b), (c) and (d), respectively. The discharge and charge conditions were the same

Figure 7. Charge/discharge curves of (a) pristine LiCoPO_4 , (b) $\text{LiCoPO}_4/\text{C0}$, (c) $\text{LiCoPO}_4/\text{C1}$ and (d) $\text{LiCoPO}_4/\text{C2}$ as composite electrodes.

Figure 8. Charge/discharge curves of pristine LiCoPO_4 single particle.

with those used for the LiCoPO_4 evaluation. Both the potential plateau and irreversible capacity were observed as similar to those of pristine LiCoPO_4 . The larger initial discharge capacities of 105, 110 and 114 mA h g^{-1} were observed for $\text{LiCoPO}_4/\text{C0}$, $\text{LiCoPO}_4/\text{C1}$ and $\text{LiCoPO}_4/\text{C2}$, respectively. This is due to an improvement of electric conductivity by carbon-coating on the surface of LiCoPO_4 .

Figure 8 shows the charge and discharge curves of LiCoPO_4 single particle without carbon-coating. 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 were 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, LiCoPO_4 showed very small discharge capacity. These

Figure 9. (a) Charge/discharge curves at initial 3 cycles and (b) rate capability of $\text{LiCoPO}_4/\text{C0}$.

results indicate that LiCoPO_4 particle without carbon-coating has very high electrochemical impedance. In the case of composite electrode including binder and conductive material, LiCoPO_4 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 LiCoPO_4 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 $\text{LiCoPO}_4/\text{C0}$ 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 LiCoPO_4 single particle measurement. $\text{LiCoPO}_4/\text{C0}$ 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 $\text{LiCoPO}_4/\text{C0}$. 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 LiCoPO_4 particle by the carbon-coating. However, the polarization was still large.

Figure 10(a) shows the charge and discharge curves of $\text{LiCoPO}_4/\text{C1}$ single particle during initial 3 cycles at the same current value for $\text{LiCoPO}_4/\text{C0}$ single particle measurement. The particle size was 20 μm in diameter. The potential plateaus were observed in both

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

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/C1. All charge processes were same with 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 same 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.

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%.

Tafel equation is given as

$$\log i = \log i_0 + \frac{\alpha F}{2.303RT} \eta. \quad (1)$$

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

Table 1. Electrochemical parameters of LiCoPO₄/C1 and LiCoPO₄/C2 single particles at various DODs.

	DOD	10%	20%	30%	40%	50%	60%	70%	80%	90%
LCP/C1	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)	2.65×10^{-9}	2.65×10^{-9}	7.07×10^{-10}	7.07×10^{-10}	—	—	—	—	—
LCP/C2	i_0 (mA cm ⁻²)	0.0241	0.0226	0.0191	0.0183	0.0166	0.0161	0.012	—	—
	R_{ct} (Ω cm ²)	1065	1134	1346	1401	1546	1598	2145	—	—
	D (cm ² s ⁻¹)	2.02×10^{-9}	9.90×10^{-10}	9.90×10^{-10}	5.70×10^{-10}	5.70×10^{-10}	2.42×10^{-10}	2.42×10^{-10}	—	—

potential at each current value. Here, E_{equ} was assumed to be the potential value in the discharge process at 0.3 nA, because E_{equ} was difficult to estimate due to the self-discharge of LiCoPO₄.^{20,21} In this experiment, α was considered as 0.5, and T was 298 K. i_0 can be obtained by the intersection point of the Tafel equation and the equilibrium potential. The charge transfer resistance R_{ct} is calculated with formula (2).

$$R_{ct} = \frac{RT}{Fi_0} \quad (2)$$

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 LiCoPO₄ particle. In the case of one-dimensional diffusion, the diffusion coefficient D can be estimated by formula (3).

$$l = \sqrt{2Dt} \quad (3)$$

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 even at low discharge currents. R_{ct} of LiCoPO₄/C1 showed higher value than that of LiCoPO₄/C2 except for DOD 20%. Larger amount of carbon maybe provide lower R_{ct} . D for LiCoPO₄/C1 and LiCoPO₄/C2 were 10^{-11} to 10^{-9} cm² s⁻¹, which were similar values. This indicated that D is independent from carbon-coating. These values were comparable to the diffusion coefficient of LiFePO₄ secondary particle estimated by single particle measurement.² Other studies have reported the D value of approximately 10^{-13} cm² s⁻¹ using composite electrode of LiCoPO₄.^{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 LiCoPO₄ estimated by single particle measurement is closer to the values calculated by first-principles method (10^{-5} cm² s⁻¹ and 10^{-9} cm² s⁻¹ for CoPO₄ and LiCoPO₄, 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 LiCoPO₄.

Discharges were carried out at 3 nA after rate capability test for the particle of LiCoPO₄/C1 and LiCoPO₄/C2, as shown in Fig. 10 and Fig. 11, respectively. Figure 13(a) shows the discharge curves of LiCoPO₄/C1 after rate capability test. The discharge capacities of LiCoPO₄/C1 and LiCoPO₄/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

Figure 13. Discharge curves of (a) LiCoPO₄/C1 and (b) LiCoPO₄/C2 particles at 3 nA after rate capability test.

direct contact area of LiCoPO₄ with electrolyte,²⁰ which caused capacity fading.²⁵ Therefore, the better cycleability for LiCoPO₄/C2 was observed, probably due to larger coverage area of carbon. However, cycle performance was still low even for LiCoPO₄/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 LiCoPO₄ 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 LiCoPO₄ and carbon-coated LiCoPO₄ showed clearly a discharge plateau at 4.7 V vs. Li/Li⁺, and the carbon-coated LiCoPO₄ showed larger discharge capacity (over 105 mA h g⁻¹) than that of pristine LiCoPO₄ (71 mA h g⁻¹).

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 $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at different DODs, which is higher than those reported in the previous studies using composite electrodes. The diffusion coefficient could be evaluated without the effect of Li^+ diffusion in the electrolyte by single particle measurement. However, these values were lower than the value calculated by first-principle method. Moreover, cycle performance of carbon-coated LiCoPO_4 particle was still low. Therefore, further improvement is required.

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