

ORIGINAL RESEARCH

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Hydrothermal synthesis of carbon-coated LiCoPO₄ cathode material from various Co sources

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Abstract

LiCoPO₄ has been recognized as a promising cathode material for lithium batteries due to its high stability and high operation voltage. However, poor electronic conductivity of LiCoPO₄ prohibits its practical use. A carbon coating can improve electronic conductivity of LiCoPO₄. A hydrothermal synthesis is a very convenient method because it allows us easy preparation of small particles of carbon-coated LiCoPO₄; however, an effect of precursor for LiCoPO₄ preparation on the performance of the synthesized LiCoPO₄ has yet to be cleared. In this paper, the effect of Co source for carbon-coated LiCoPO₄ (LiCoPO₄/C) preparation on performance as a cathode material for Li-ion battery is investigated. The Co source strongly affects the pH value in the starting solution and final products. The single-phase LiCoPO₄ is obtained only when CoSO₄ or CoCl₂ are used as the Co sources. A quality of carbon layer on the LiCoPO₄ is also affected by the Co source. The carbon layer on the LiCoPO₄ synthesized from CoSO₄ contains graphite carbon with high concentration which provides high electronic conductivity compared with that from CoCl₂. Accordingly, the LiCoPO₄/C synthesized from CoSO₄ shows a superior performance than that from CoCl₂ due to high-quality carbon layer.

Keywords: Hydrothermal synthesis, Co sources, Lithium-ion battery, Carbon-coated LiCoPO₄

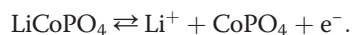
Background

In order to use natural resources such as solar power and wind power, numerous research are done [1-3]. However, a shortcoming on the usage of the natural resources is its difficulty for stable electricity supply. Therefore, energy storage devices must be developed. Lithium rechargeable batteries have high energy and power densities and have been recognized as the most suitable battery for this purpose. The lithium batteries are composed of mainly cathode, anode, and electrolyte. LiCoO₂ and graphite have been used as cathode and anode, respectively, and organic solvent-resolving Li salt has been used for the electrolyte thus far. Both cathode and anode can intercalate Li ion, i.e., Li ion moves from anode to cathode during the discharge process. In the charge process, the Li ion goes back from cathode to anode.

One of the issues of LiCoO₂ is instability of its crystal structure especially under overcharge state. During the charge process, LiCoO₂ releases Li ion, and Li_{1-x}CoO₂ is

formed. The safety circuits in the devices stop charging at $x = 0.5$ (3.9 V). In $x > 0.5$, the structure of LiCoO₂ collapses, and oxygen is released into the electrolyte. This oxygen causes the decomposition of electrolyte by oxidation and sometimes makes serious problems such as fire hazard and battery explosion.

Great attention has been paid to the olivine-type LiMPO₄ (M = Fe, Mn, Ni, Co) cathode materials for lithium-ion batteries in recent years [4-7]. The olivine materials contain PO₄ group in its structure and this strong P-O bond avoids the release of oxygen. Therefore, it is expected that the olivine materials improve the safety of the lithium batteries. Among the olivine-type materials, LiCoPO₄ has been given much attention owing to its high operation voltage close to 4.8 V vs. Li/Li⁺ [8], which allows us to fabricate the lithium batteries with high operation voltage and high energy density because the energy density of the battery is estimated by multiplying the current density by the operation voltage. The electrochemical reaction of LiCoPO₄ in the cathode is shown as follows:



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During the charge process, LiCoPO_4 releases a Li^+ into the electrolyte, and an electron (e^-) into a current collector (usually Al foil). Co^{2+} is oxidized to Co^{3+} at the same time. In the discharge process, reverse reaction occurs. The redox voltage of Co is high compared with other olivine materials, and it contributes to the high operation voltage of LiCoPO_4 . According to the equation, immigration of the Li^+ and the electron in the cathode is needed. Therefore, the cathode materials require high Li^+ and electronic conductivity. However, the most serious problem of these olivine-type compounds is low intrinsic Li-ion and electronic conductivities [9,10]. To improve the Li-ion conductivity, preparation of small particles of the LiMPO_4 which derives a short Li-ion diffusion path is very effective [11,12]. Drezen et al. claimed that the particle size of LiMnPO_4 prepared by a sol-gel method strongly affected their performance [13]. On the other hand, to overcome the low electronic conductivity, electronic conductive carbon-coating on the surface of the particles has been applied in many groups [11,14-18]. Zhou et al. reported that the discharge capacity of LiFePO_4 prepared by the coprecipitation method had an increase of 110 to 147 mAh g^{-1} by carbon coating [19].

By hydrothermal synthesis, the carbon-coated small particles can be prepared easily with only an addition of a carbon source to starting materials. In fact, Mizuno et al. have succeeded in the preparation of carbon-coated small particles of LiFePO_4 [20] and LiMnPO_4 [7], and they have exhibited a good performance as the cathode material. In the hydrothermal synthesis, starting materials strongly affect the morphology and performance of the final products. Zhao et al. synthesized LiCoPO_4 from various phosphate sources such as H_3PO_4 and $(\text{NH}_4)_2\text{HPO}_4$ through the hydrothermal route and observed a hexagonal prism-like crystal in the range of 10 to approximately 15 μm synthesized from H_3PO_4 and irregular agglomeration particles with the size of 10 to approximately 40 μm synthesized from $(\text{NH}_4)_2\text{HPO}_4$ [21]. However, studies on different start materials, Li and Co sources, have yet to appear. In order to find a better preparation procedure for LiCoPO_4 , an effect of Li and Co sources on properties of produced LiCoPO_4 should be tested. Therefore, the purpose of this paper is to investigate the effect of the Co source for LiCoPO_4 prepared by the hydrothermal route on its performance as the cathode of lithium-ion battery.

Methods

LiCoPO_4 was synthesized by a hydrothermal process according to previous reports for LiFePO_4 and LiMnPO_4 [22-24]. Li_3PO_4 was dissolved into purified water with various Co sources, i.e., $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, CoCl_2 , $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Co}(\text{OH})_2$. To prevent oxidation of Co^{2+} to Co^{3+} , this process was

performed under N_2 atmosphere. A molar ratio of Li/Co/P was 3:1:1. Carboxy methyl cellulose was used as a carbon source and was put into the precursor solution. A glass-lined Parr reactor with the precursor solution and N_2 gas was sealed in a stainless steel autoclave. After that, the hydrothermal synthesis was performed at 200°C for 3 h with stirring at 680 rpm.

Precipitation was separated centrifugally and then freeze-dried at -50°C for 12 h. Yield was always higher than 95%. Synthesized powder was annealed at 700°C for 1 h under 3% H_2/Ar flow to convert carbon species to graphite with high electronic conductivity.

To clarify the crystalline phase of the synthesized powder, X-ray diffraction (XRD, RINT-Ultima, Rigaku Co., Shibuya-ku, Japan) with $\text{Cu K}\alpha$ radiation was used. Raman measurements (NRS-1000, JASCO Ltd., Tokyo, Japan) were carried out at room temperature by a laser radiation of 532 nm. Morphologies of the synthesized powder were observed by means of a scanning electron microscope (SEM, JEOL Ltd., Akishima-shi, Japan).

Performance of a synthesized LiCoPO_4 as a positive electrode was evaluated by a charge-discharge test. A composite LiCoPO_4 electrode was prepared by mixing LiCoPO_4 , Ketjen black, and polyvinylidene difluoride in the weight ratio of 75:15:10 in 1.2 ml of N-methyl pyrrolidone. The LiCoPO_4 electrode was painted onto a thin Al sheet and dried overnight at 85°C under reduced pressure. The LiCoPO_4 composite electrode (14 mm in diameter) was set in a coin cell 2032 with a mixture of ethylene carbonate and ethyl methyl carbonate (volume ratio = 3:7) containing 1 $\text{mol}\cdot\text{dm}^{-3}$ LiPF_6 as an electrolyte and with lithium metal as a negative electrode. The galvanostatic charge/discharge tests of the coin cell with LiCoPO_4 positive electrode were performed using the HJ1001SM8A (Hokuto Denko Ltd., Tokyo, Japan). In the test, the charge process was performed at constant current (CC)-constant voltage (CV) mode, charging at a constant current of 0.1 C until 5.1 V vs. Li/Li^+ , then at a constant voltage of 5.1 V until the current dropped to 0.01 C. A discharge process proceeded at a CC mode of 0.1 C. Cut-off voltages of charge and discharge processes were 5.1 and 3.0 V vs. Li/Li^+ , respectively.

Results and discussion

Results

In the hydrothermal synthesis, it has been well known that pH value in the starting solution influences the phase components and shapes and sizes of particles of the final products [25,26]. Thus, the pH value in the starting solution was checked at first. The pH values were widely changed depending on the Co sources, i.e., 3.7, 3.7, 4.4, 5.5, and 7.8 in the starting solution containing $\text{Co}(\text{NO}_3)_2$, CoCl_2 , CoSO_4 , $\text{Co}(\text{CH}_3\text{COO})_2$, and $\text{Co}(\text{OH})_2$, respectively.

Figure 1 shows XRD patterns of samples synthesized under hydrothermal condition using various Co sources. Obviously, the Co sources strongly influenced the final products. The diffraction peaks were completely different in various Co sources. CoSO_4 and CoCl_2 could produce a single-phase LiCoPO_4 , i.e., the diffraction peaks were consistent with the standard peaks of LiCoPO_4 . On the contrary, only diffraction peaks of starting materials (Li_3PO_4 and Co(OH)_2) were detected from Co(OH)_2 , suggesting no reaction under this condition. The product from $\text{Co(CH}_3\text{COO)}_2$ also contained Li_3PO_4 with some unknown peaks. In the case of $\text{Co(NO}_3)_2$, the diffraction peaks of LiCoPO_4 was confirmed. The diffraction peaks of Co(OH)_2 and $\text{Co(NO}_3)_2$ were also observed.

Pure LiCoPO_4/C was obtained only from CoSO_4 and CoCl_2 . Thus, LiCoPO_4/C synthesized from CoSO_4 and CoCl_2 (denoted as $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ and $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$, respectively) were supplied for further analysis. SEM images of synthesized LiCoPO_4/C are displayed in Figure 2. In both cases (Figure 2a,c), the LiCoPO_4/C particles aggregated each other and formed secondary particles whose sizes were below 20 μm . Interestingly, primary particles had different shapes depending on the Co source. Square-like particles whose sizes were 0.5 to approximately 2 μm were observed in $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$, while the shapes of the primary particles of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ were irregular, and the sizes were 200 to approximately 500 nm. In both cases, the sizes of primary particles were below 2 μm and small enough as the cathode.

Raman measurement (Figure 3) was performed to detect small amounts of impurities on the surface of LiCoPO_4/C , which could not be confirmed in the XRD patterns. Nakano et al. have succeeded in the detection of even small amounts of impurities on the LiFePO_4 synthesized by the hydrothermal process [20]. In both the Raman spectra, shown in Figure 3, a small peak at 948 cm^{-1} was observed. This was attributed to the symmetric vibration

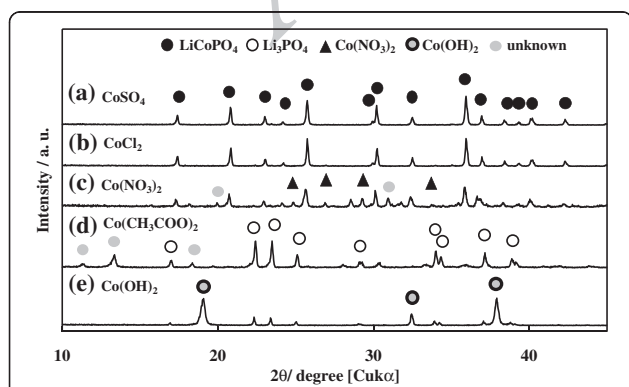


Figure 1 XRD patterns of hydrothermally synthesized LiCoPO_4 from various Co sources. (a) CoSO_4 , (b) CoCl_2 , (c) $\text{Co(NO}_3)_2$, (d) $\text{Co(CH}_3\text{COO)}_2$, and (e) Co(OH)_2 .

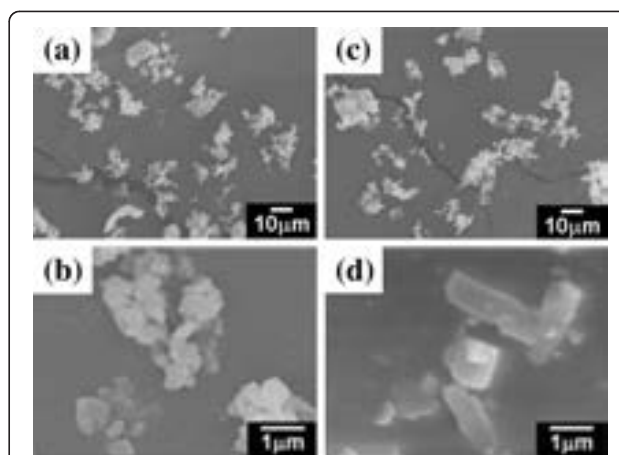


Figure 2 SEM images of hydrothermally synthesized LiCoPO_4 from various Co sources. (a), (b) CoSO_4 and (c), (d) CoCl_2 .

of the PO_4 group [27]. Therefore, it is said that the synthesized powder contained a PO_4 group. As mentioned above, clear diffraction peaks of the LiCoPO_4 were observed in the XRD patterns. The peak at 948 cm^{-1} was consistent with the result of the XRD. It is concluded that LiCoPO_4 has been synthesized successfully from CoSO_4 and CoCl_2 . A peak at 1,610 cm^{-1} was also observed in both spectra and was assigned to the graphite carbon (G band) [28]. This G band is generated by a presence of SP^2 carbon, which has high electronic conductive nature. However, the peak was very weak in both spectra. The carbon amounts of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ and $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ determined by thermogravimetry measurement were 0.9 and 3.6 wt.%, respectively. It is sure that carbon species existed but not very sensitive for the Raman measurement.

In a previous paper [20], Nakano et al. reported that electronic conductivity of hydrothermally synthesized LiFePO_4/C was improved by annealing at 700°C in reductive or inert atmosphere. Consequently, the synthesized LiCoPO_4/C was annealed at 700°C for 1 h under 3% H_2/Ar flow.

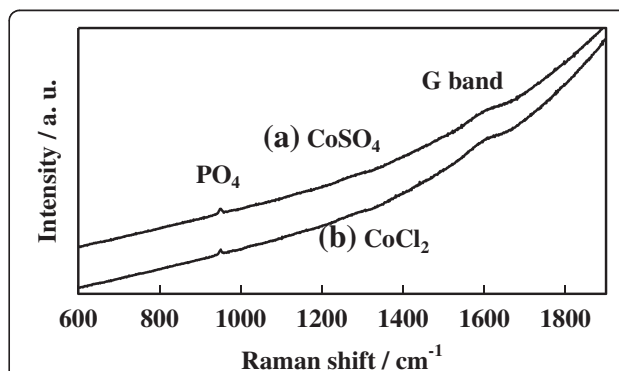


Figure 3 Raman spectra of hydrothermally synthesized LiCoPO_4 from various Co sources. (a) CoSO_4 and (b) CoCl_2 .

Figure 4 shows SEM images of LiCoPO_4/C after annealing. LiCoPO_4 particles aggregated each other and formed secondary particles like those before annealing. In the case of $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$, the sizes of the secondary particles were $<20 \mu\text{m}$, and the size of the primary particle was estimated as 0.5 to approximately $2 \mu\text{m}$. The size of primary particles were the same as those before annealing, indicating that the annealing did not affect the particle size of $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$. On the contrary, large secondary particles ($<60 \mu\text{m}$) were obtained in $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$. Additionally, the size of the primary particle increased as 1 to approximately $2 \mu\text{m}$, and the particles became round shaped by annealing.

XRD patterns of LiCoPO_4 after annealing are depicted in Figure 5. All diffraction peaks were attributed to LiCoPO_4 , indicating that the annealing did not produce any impurity phase. In order to estimate lattice parameters of LiCoPO_4/C , Si internal standard was added in the sample (A peak at $2\theta = 28.4^\circ$ is assigned as Si internal standard). Lattice parameters of the LiCoPO_4 estimated using these XRD patterns were revealed in Table 1. $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ possessed shorter lattice constant in the b -axis direction (5.929 \AA in $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ and 5.935 \AA in $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$), but larger ones in the a - and c -axis directions compared with $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$. As a result, a lattice volume of $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ was 0.40% larger than $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$.

Figure 6 displays the Raman spectra of the LiCoPO_4 after annealing. By annealing, the Raman spectra changed dramatically, especially the Raman shift of 1,200 to approximately $1,700 \text{ cm}^{-1}$ region. A new peak appeared at $1,345 \text{ cm}^{-1}$ and was assigned as the disordered carbon (D band) [28], which has poor electronic conductivity, and a distinct G band could also be confirmed. The peak area ratios of G to D bands of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ and $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ were

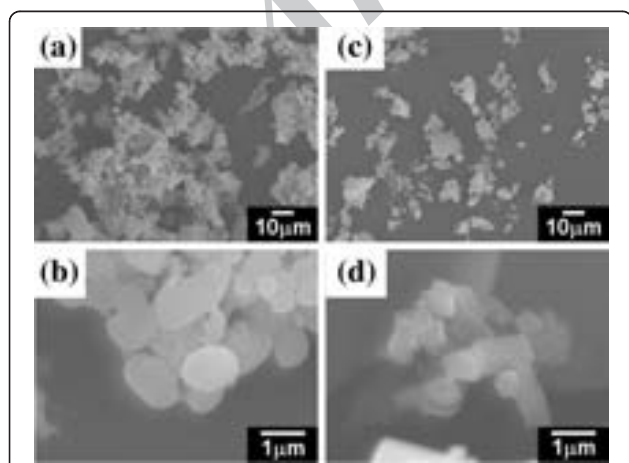


Figure 4 SEM images of hydrothermally synthesized LiCoPO_4 from various Co sources after annealing. (a) and (b) CoSO_4 and (c) and (d) CoCl_2 .

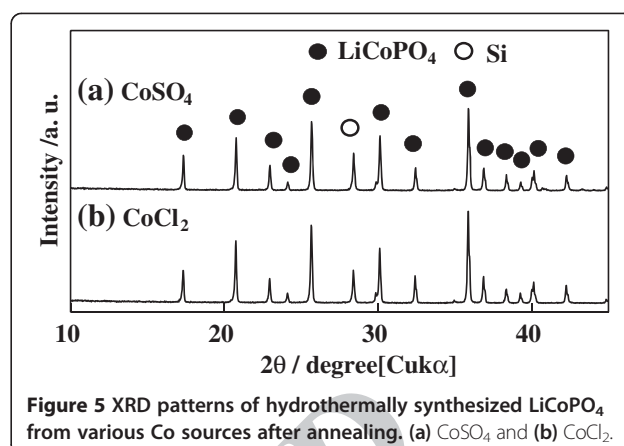


Figure 5 XRD patterns of hydrothermally synthesized LiCoPO_4 from various Co sources after annealing. (a) CoSO_4 and (b) CoCl_2 .

1.4 and 0.7, respectively. The peak at 948 cm^{-1} was attributed to the symmetric vibration of the PO_4 group as described above. Therefore, it is concluded that LiCoPO_4 structure did not change by annealing.

Figure 7 revealed charge and discharge curves of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ and $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$. Three coin cells were constructed in each sample to check the experimental error. In both cases, the charge capacity was much larger than the theoretical capacity (167 mAh g^{-1}) [6]. Many authors have reported a decomposition of electrolyte at high voltage like 5.1 V vs. Li/Li^+ [29,30]. Therefore, the reason for the large charge capacity is attributed to delithiation of the LiCoPO_4 coincident with the decomposition of the electrolyte. A discharge curve of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ showed a much longer plateau at approximately 4.6 V vs. Li/Li^+ compared with $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$. Discharge capacities of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ and $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ were 99 ± 5 and $32 \pm 3 \text{ mAh g}^{-1}$, respectively. The experimental error was very small. It is obvious that $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ showed better performance as the cathode.

Discussion

An effect of Co source for hydrothermally synthesized LiCoPO_4 on performance as cathode for the lithium-ion battery was studied.

Single-phase LiCoPO_4 particle was obtained only from CoSO_4 and CoCl_2 . The pH value in the starting solution affected the formation of the final products. Huang et al. reported that the formation of pure LiCoPO_4 phase

Table 1 Lattice parameters of hydrothermally synthesized LiCoPO_4 after annealing estimated from Figure 5

Co source	a -Axis (\AA)	b -Axis (\AA)	c -Axis (\AA)	Volume (\AA^3)	$\Delta V/V$
CoSO_4	10.23(2)	5.935(5)	4.708(6)	285.84(6)	-
CoCl_2	10.24(5)	5.929(2)	4.727(5)	286.99(0)	+0.40%

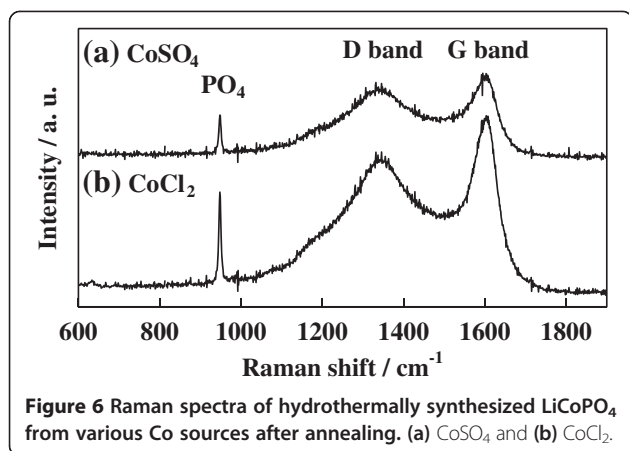


Figure 6 Raman spectra of hydrothermally synthesized LiCoPO_4 from various Co sources after annealing. (a) CoSO_4 and (b) CoCl_2 .

single-phase LiCoPO_4 was obtained only under acidic condition. This discrepancy could be attributed to PO_4 and Li sources. They used LiOH and H_3PO_4 as Li and PO_4 sources, respectively. On the other hand, I used Li_3PO_4 as both Li and PO_4 sources. It is thought that

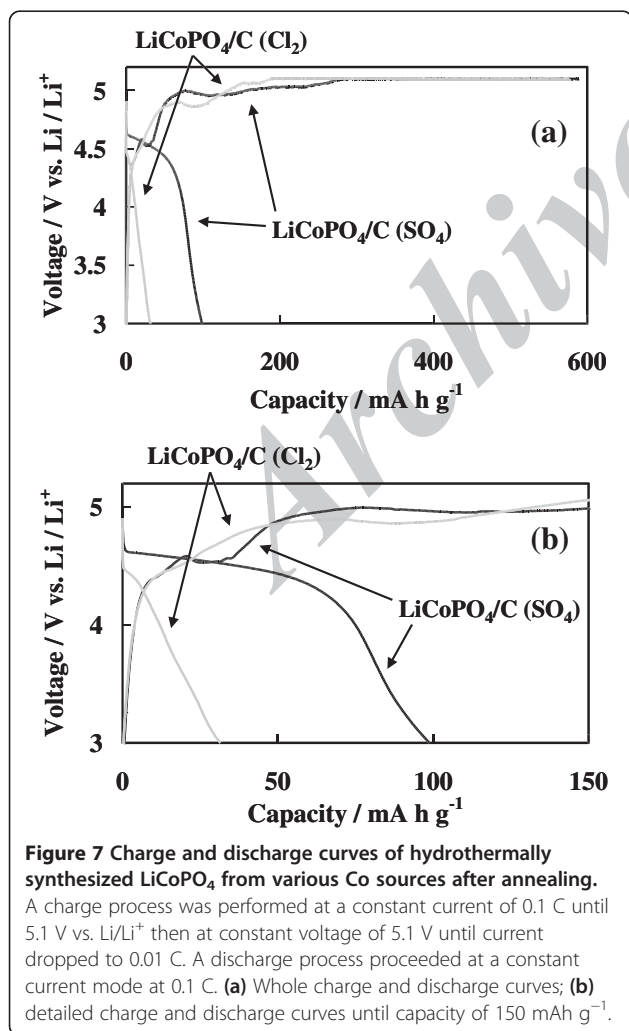


Figure 7 Charge and discharge curves of hydrothermally synthesized LiCoPO_4 from various Co sources after annealing. A charge process was performed at a constant current of 0.1 C until 5.1 V vs. Li/Li^+ then at constant voltage of 5.1 V until current dropped to 0.01 C. A discharge process proceeded at a constant current mode at 0.1 C. (a) Whole charge and discharge curves; (b) detailed charge and discharge curves until capacity of 150 mAh g^{-1} .

solubility of Li_3PO_4 in the range of weak acidic to alkaline conditions would be low. In fact, diffraction peaks of Li_3PO_4 (Figure 1d,e) were observed only in the case of $\text{Co}(\text{OH})_2$ and $\text{Co}(\text{CH}_3\text{COO})_2$, whose pH values were 7.8 and 5.5, respectively. In these conditions, Li_3PO_4 could not dissolve in water even under hydrothermal condition. Therefore, Li_3PO_4 was precipitated on the bottom and could not participate in the reaction. This would be a reason that non-reacted Li_3PO_4 still remain in the final products. As for $\text{Co}(\text{NO}_3)_2$, formation of LiCoPO_4 was confirmed, but some were unknown, and $\text{Co}(\text{NO}_3)_2$ peaks were also observed. The pH value of the starting solution containing $\text{Co}(\text{NO}_3)_2$ was 3.7, same as that of CoCl_2 . Consequently, the counter anion may also play an important role for the formation of LiCoPO_4 , not only the pH value of precursor solution.

After annealing, morphology change of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ was observed, while no large difference of $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ particle shape was confirmed. Thermal stability of produced LiCoPO_4/C particles would also be affected by the Co source.

Discharge capacity of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ and $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ were 99 ± 5 and $32 \pm 3 \text{ mAh g}^{-1}$, respectively. It has been known that Li-ion transport in LiMPO_4 ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) olivine materials occurs along with the b -axis [31]. The lattice constant in the b -axis direction of $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ was shorter than that of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ as shown in Table 1. Additionally, primary particle size of $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ was smaller than that of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$. From the view of the Li-ion transport in the particles, $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ has an advantage against $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ due to a short distance of Li-ion transport. Thus, $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ was expected to demonstrate better electrochemical performance; however, much larger discharge capacity was obtained in $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$. This should relate to the quality of carbon layer on the LiCoPO_4 particle, which can provide high electronic conductivity. As shown in the Raman spectra, there are two kinds of carbon, graphite, and disorder carbons, on the LiCoPO_4 . The graphite carbon possesses high electronic conductivity, and the disorder carbon does not. The ratios of the graphite to the disorder carbon of $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ and $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ were 1.4 and 0.7, respectively. The disorder carbon could not give a high electronic conductivity to the carbon-coating layer on the LiCoPO_4 whereas the graphite carbon could. Therefore, $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ has superior electronic conductivity. This would be a reason why the $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ showed better performance than $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$. It is found that the Co sources affect not only the crystal structure and morphology of LiCoPO_4 but also the nature of the carbon layer, resulting in different cathodic performance among the products. Much attention should be paid for Co source selection to prepare the carbon-coated LiCoPO_4 .

It was reported that the ratio of the graphite to disorder carbon on the LiMnPO_4 depended on the carbon sources [7]. Therefore, further improvement of the performance of LiCoPO_4/C would be possible if suitable carbon source for $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ was found because $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$ is thought to possess a favorable structure with respect to Li-ion transport. This attempt is now underway, and it will be reported.

Conclusions

The LiCoPO_4 cathode material for lithium batteries were synthesized by hydrothermal method using various Co sources. Crystal structure and morphology of hydrothermally synthesized LiCoPO_4 were strongly affected by the Co source. Single-phase LiCoPO_4 could not be obtained from $\text{Co}(\text{NO}_3)_2$, $\text{Co}(\text{OH})_2$, and $\text{Co}(\text{CH}_3\text{COO})_2$. Only CoCl_2 and CoSO_4 could produce single-phase LiCoPO_4 . Before annealing, LiCoPO_4 was not very sensitive against Raman measurement. After annealing, the carbon species on the LiCoPO_4 particles became active for the Raman measurement and clear G and D bands could be observed. LiCoPO_4 synthesized from CoCl_2 possessed shorter lattice constant along with the *b*-axis than that from CoSO_4 , suggesting favorable Li-ion transport. Additionally, Co source also affected a nature of carbon layer on the LiCoPO_4 after annealing. Ratios of G band to D band in the Raman spectra were 1.4 and 0.7 for $\text{LiCoPO}_4/\text{C}(\text{SO}_4)$ and $\text{LiCoPO}_4/\text{C}(\text{Cl}_2)$, respectively. The carbon layer on LiCoPO_4 synthesized from CoSO_4 was converted to graphite carbon easily, resulting in the investment of high electronic conductivity to the LiCoPO_4 particle. As a result, LiCoPO_4 synthesized from CoSO_4 revealed better performance compared with that from CoCl_2 although its particle seems to be inferior in terms of Li-ion transport. Further improvement of performance of LiCoPO_4 from CoCl_2 could be possible if high-quality carbon layer could be prepared because particles of LiCoPO_4 from CoCl_2 possess a favorable structure with respect to Li-ion transport.

Competing interests

The author has no competing interests.

Authors' information

Dr. MK graduated in 1996 and received his M.S. in 1998 from Toyohashi University of Technology. After working at Hino Motors as an engine designer from 1998 to 2002, he received a Ph.D. degree in Engineering from the University of Yamanashi in 2006 under the direction of Prof. Watanabe. He studied on hydrogen production and hydrogen purification catalysts for fuel cell application. After receiving the Ph.D., he worked at the University Ulm, Germany, as an Alexander von Humboldt fellow. He researched on the CO oxidation mechanism on Au catalyst mainly using Temporal Analysis of Product (TAP) reactor under Prof. R. J. Behm. Then, he came back to Japan as an associate professor in Tokyo Metropolitan University in 2009 and researched on lithium battery. Now, he is an associate professor at the Department of Material and Environmental Engineering in Hakodate National College of Technology, Japan. He specializes in lithium battery, solid electrolyte, electrochemistry, and heterogeneous catalysts. More than 40 papers with respect to fuel cell, lithium battery, and heterogeneous catalysts have been published under his name.

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