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**Synthesis of Carbon-Coated LiCoPO₄ by
Hydrothermal Method and Application to High-
Voltage Lithium-Ion Batteries**

(水熱法によるカーボン被覆 LiCoPO₄ の合成と
高電位リチウムイオン電池への応用)

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General Introduction

In order to solve the global environmental and energy issues, we need to use renewable energy such as solar, wind, wave, and geothermal energy. Energy storage devices play a key role to use the renewable energy. Lithium ion batteries (LIBs) is one of the promising energy storage devices owing to their high energy density compared with other battery technologies, and have been applied to power sources for many portable electronic devices. In recent year, the applications of LIBs have extended to the power sources for electric vehicles and energy storage devices for renewable energy. For requirement of these applications, the energy density and safety of LIBs demand to be improved. The performance of LIBs highly depends on the characteristics of cathode materials. Lithium cobalt phosphate (LiCoPO_4) is considered a promising cathode material, since it possesses a high operating potential (4.8 V vs. Li / Li^+), a flat voltage profile and a good theoretical capacity (167 mA h g^{-1}), improving the energy density of LIBs. Moreover, LiCoPO_4 with olivine structure has high thermal and structural stability derived from the strong P–O covalent band, realizing high safety in LIBs. However, the discharge capacity of LiCoPO_4 is low owing to its intrinsically poor electrical conductivity and slow ionic diffusion. Moreover, the high operating potential of LiCoPO_4 causes irreversible reactions of cell components such as electrolyte, conductive carbon additives, and separators, lowering its cycle stability. To solve these problems, not only the particle design of the cathode material, but also the optimization and development of the cell components are required. In this work, the particle design of the cathode material, the optimization of conductive carbon additives, and the application of new separator were carried out to enhance the capacity and cycle performance of LiCoPO_4 .

Chapter 1 Effect of Organic Additives on Characteristics of Carbon-Coated LiCoPO₄ Synthesized by Hydrothermal Method

In order to improve the electrochemical performance of LiCoPO₄, the particle design of the cathode material is effective approach such as carbon coating on the surface of active materials and decreasing particle size. In this chapter, carbon-coated LiCoPO₄ fine particles have been synthesized by one-pot hydrothermal process using three different organic additives (carboxymethylcellulose sodium salt (CMC), glucose, and ascorbic acid). The effect of the organic additives on particle size, morphology, nature of carbon coating, and electrochemical property of the resulting LiCoPO₄ has been investigated. CMC plays important roles to decrease the particle size and form well-covered carbon coating on the surface. Carbon-coated LiCoPO₄ prepared using CMC delivers higher initial discharge capacity of 135 mA h g⁻¹ at 0.1 C, and shows superior rate capability and cycle performance than the other samples. The improved electrochemical characteristics are attributed to not only the fine particle which allows facile electronic and ionic transport, but also the high coverage of carbon coating which improves the electrical conductivity and prevents the irreversible reactions of the charged LiCoPO₄ with electrolyte.

Chapter 2 Conductive Carbon Additives for Improving Electrochemical Performance of LiCoPO₄

To improve the performance of 5 V-class lithium-ion batteries, the optimization of conductive carbon additives in electrodes are required, since they become electrochemically active above 5 V vs. Li / Li⁺. The high surface area carbons are generally considered better than low surface area ones owing to developed conductive network among active materials, but they accelerate irreversible reactions at high potentials, lowering the cycle performance of high-voltage cathode materials. In this chapter, the effect of conductive carbon additives (acetylene blacks with various specific surface areas and ketjen black) on the electrochemical performance of LiCoPO₄ has been investigated. Acetylene black with a low surface area prevents irreversible reactions between electrolyte and cathode surface, and realizes reversible intercalation/deintercalation of PF₆⁻ into/from its graphite structure. However, the low surface area reduces the capacity, and degrades the cycle performance of LiCoPO₄. On the other hand, ketjen black with a high surface area enhances the capacity of LiCoPO₄, while it induces the irreversible reactions, leading to the rapid capacity fading. By using acetylene black with a moderate surface area as a conductive additive for LiCoPO₄ cathode, the author has achieved the superior cycle performance, which is attributed to high coulombic efficiency and good conductive network among active materials.

Chapter 3 Enhanced Cycle Stability of LiCoPO₄ by Using Three-Dimensionally Ordered Macroporous Polyimide Separator

To enhance the low cycle stability of LiCoPO₄, the development of stable separators in batteries is required, since they are oxidized in the high-voltage system at around 5 V, affecting the cycle performance of high-voltage lithium-ion batteries. The performance of the batteries also depends on the porous structure of separators. In this chapter, the author has achieved the improved coulombic efficiency and capacity retention of LiCoPO₄ by using a three-dimensionally ordered macroporous polyimide (3DOM PI) separator, compared with a conventional polypropylene (PP) separator with heterogeneous pore structure. The uniform current distribution created by the ordered macroporous structure results in the low overpotential during charge process, preventing the oxidation of electrolyte and the growth of the resistive film on the cathode surface during cycling. Furthermore, the high anodic stability of 3DOM PI separator maintains its chemical and macroporous structures after cycling at high potentials, leading to the superior stability of the cell.

General Conclusion

This work demonstrated that the capacity and cycle performance of LiCoPO_4 are greatly enhanced by the decreasing particle size and carbon coating on the surface of the cathode material, the optimization of the surface area of conductive carbon additives, and application of the separator with high anodic stability and the three-dimensionally ordered macroporous structure. From these results, the author found the possibility of realizing the high-voltage lithium-ion battery using LiCoPO_4 as a cathode material. The findings obtained in this work should contribute to further enhancement of energy density and safety in lithium-ion batteries.