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Article / Book Information

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Title(English)	Study on Novel Preparation Process of Olivine Cathode Materials with High Working Potentials and Their Cathode Performance for Lithium Batteries
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種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Lithium cobalt phosphate ($LiCoPO_4$) and Lithium nickel phosphate ($LiNiPO_4$) are expected to be the next generation cathode materials for lithium ion batteries, mainly because of their thermally stable structures, high working potentials and high theoretical capacity (167 mAh g^{-1}). Nevertheless, poor electronic and ionic conductivities of the $LiCoPO_4$ and $LiNiPO_4$ cathode materials hinder their applications. To overcome those problems, the $LiCoPO_4$ and $LiNiPO_4$ cathode materials were prepared by aerosol and powder technologies in this study. The objective of this study was to improve the electrochemical performance of $LiCoPO_4$ and $LiNiPO_4$.

In the chapter 1, the background of energy crisis and the importance of development of renewable energy systems were demonstrated. The rechargeable batteries were introduced as energy storage systems, especially the lithium ion batteries. The cathode materials for lithium ion batteries, particularly $LiCoPO_4$ and $LiNiPO_4$, were laid emphasis on, since they could exhibit very high energy densities. The most significant problems of the $LiCoPO_4$ and $LiNiPO_4$ cathode materials were revealed. Furthermore, the examples of the recent publications on the $LiCoPO_4$ and $LiNiPO_4$ cathode materials were introduced, and then the challenges of the reported synthesis approaches were pointed out in this chapter. Finally, the objective of this study was presented.

In the chapter 2, $LiCoPO_4$/C composites were prepared by a combination of spray pyrolysis and wet ball milling followed by further heat treatment. The effect of various synthesis parameters, such as annealing temperature, rotation speed, content of carbon and

various carbon sources on the physical and electrochemical properties of $LiCoPO_4$/C composites were studied. The effect of crystallinity, carbon content and impurity phase Co_2P on the electrochemical properties of $LiCoPO_4$/C composites was confirmed. The $LiCoPO_4$/C composites showed a high discharge capacity of 97 mAh g^{-1} in a voltage range of 3.5-5.1 V at 0.1C rate and good cycle performance after 50 cycles, due to the reduced particle size and introduced conductive carbon. However, this discharge capacity was still low compared with the theoretical capacity, probably because of the large particle size (200 nm) of the $LiCoPO_4$/C composites.

In order to restrict the particle size of $LiCoPO_4$, the citric acid was added in the precursor solution as a dispersing agent in the chapter 3. Then, the spherical nanostructured $LiCoPO_4$ particles (SN-$LiCoPO_4$) were successfully synthesized by citric acid assisted spray pyrolysis in air atmosphere. The effect of the spray pyrolysis temperature and addition of the citric acid additive in the precursor solution on the physical and electrochemical properties of the $LiCoPO_4$ samples were investigated. The field-emission scanning electron microscopy images showed that with addition of citric acid in the precursor solution, the growth of primary particle sizes of synthesized SN-$LiCoPO_4$ could be restricted and the specific surface area of the SN-$LiCoPO_4$ increased significantly. When evaluated as cathode in lithium batteries in a voltage range of 2.0-5.1 V at 0.05C, the SN-$LiCoPO_4$ electrode showed a high discharge capacity of 135 mAh g^{-1}, which reached to 81% of the theoretical capacity. The electrochemical impedance spectroscopy (EIS) data demonstrated that the SN-$LiCoPO_4$ electrode had lower resistances and faster redox reaction kinetics compared with bare $LiCoPO_4$. The excellent electrochemical performance of SN-$LiCoPO_4$ electrode could be attributed to the diminished primary particle size that shortened the lithium ion diffusion pathway.

Due to the possibility that $LiNiPO_4$ can deliver higher working potential, in the chapter 4, $LiNiPO_4$/C composites were prepared by a combination of spray pyrolysis and wet ball milling followed by further heat treatment. The effect of spray pyrolysis temperature,

annealing temperature and rotation speed on the physical and electrochemical properties of synthesized $LiNiPO_4$/C composites were examined. $LiNiPO_4$/C composites showed a charge capacity of 73 mAh g^{-1} with a voltage plateau at 5.1 V and an extremely low discharge capacity of 8 mAh g^{-1} in a voltage range of 3.5-5.3 V at 0.1C rate, which was due to the poor electronic conductivity of $LiNiPO_4$.

To further improve the electrochemical properties of $LiNiPO_4$, Co doping was considered in the chapter 5, since the electronic conductivity of $LiCoPO_4$ is higher than that of $LiNiPO_4$. Then, $LiNi_{1-x}Co_xPO_4$/C (x=0, 0.2, 0.5, 0.8, 1) nanocomposites were prepared by a combination of spray pyrolysis and wet ball milling followed by further heat treatment. The effect of cobalt doping content, wet ball milling and carbon introduction on the physical and electrochemical properties of synthesized $LiNi_{1-x}Co_xPO_4$/C nanocomposites were studied. The formation of $LiNi_{1-x}Co_xPO_4$ solid solutions was confirmed from the linearly change of lattice parameter (*a*, *b*, *c*) with content of Co (x). The first discharge capacities of $LiNi_{1-x}Co_xPO_4$/C nanocomposites were superior to those of bare $LiNi_{1-x}Co_xPO_4$ samples. In addition, the electrochemical activity of Ni^{2+}/Ni^{3+} redox couple in the $LiNi_{0.5}Co_{0.5}PO_4$/C electrode was firstly discovered from the reduction peak of the cyclic voltammetry curve at 4.7 V in the normal electrolyte system. The EIS data demonstrated that the $LiNi_{0.5}Co_{0.5}PO_4$/C electrode had low resistances and fast redox reaction kinetics. The excellent electrochemical properties of $LiNi_{0.5}Co_{0.5}PO_4$/C were due to the reduced particle sizes and introduced conductive carbon.