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Article / Book Information

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論 文 要 旨

THESIS SUMMARY

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

In order to resolve the currently faced environmental problems, such as the indiscriminate usage and depletion of fossil energy associated CO_2 emission, the lithium-ion batteries are emerging with the development of electrochemical performance as an energy storage device. Among the constituent of the lithium-ion battery, the development of cathode material which determines the energy density has been pursued a high-performance lithium-ion battery. $Li_2MP_2O_7$ (M = Fe and Mn) cathode material is one of promising electrode material for lithium-ion batteries with robust $(P_2O_7)^{4-}$ framework, which provides the structural stability and safety during cycling. Even though the capacity of $Li_2MP_2O_7$ composite is restricted to a one-electron theoretical value of 110 mAh g^{-1}, it is capable of representing twice the theoretical capacity with two Li extraction accompanied with further M^{4+}/M^{3+} redox reaction at high potential beyond 5.2 V. However, a significant problem with this kind of polyanion cathode materials is a low electronic conductivity, impeding the large-scale implementation of lithium-ion battery. To overcome this problem, the pure crystalline $Li_2MP_2O_7$/C (M = Fe and Mn) composites of cathode material for lithium-ion battery have been successfully prepared by spray pyrolysis (SP) method with carbon modification processes, and then their physical and actual electrochemical properties were systematically investigated.

Chapter 1 provides a general background of lithium-ion batteries, including the urgent demand of renewable energy sources, the working principles of electrodes in the battery system. The focus was made on cathode materials for the lithium-ion battery as a promising energy storage system. The brief review of existing preferred cathode materials is presented according to their physical and electrochemical properties. In particular, the synthetical achievements of various polyanionic cathode materials were described with their structural characterizations and electrochemical behavior. Furthermore, the examples of the recent publications on the lithium transition metal pyrophosphate composite were provided, and then the challenges of the reported approaches were pointed out in this chapter. Finally, the objective of this study was presented.

Chapter 2 presents the synthesis and characterization of $Li_2FeP_2O_7$/C composites prepared using spray pyrolysis followed by annealing process. Firstly, the effect of the synthesis conditions was investigated to obtain the pure crystalline $Li_2FeP_2O_7$, and then the

optimal conditions were presented. Secondly, carbon modifications were done *via* two approaches, one was to add organic matter into the precursor solution, and other was to coat the conductive carbon by ball milling process. Although both approaches efficiently enhanced the electrochemical performances, the combined carbon modifications led the superior performances for the cathode material instead. The $Li_2FeP_2O_7$/C composite electrode exhibited the initial discharge capacity of 110 mAh g^{-1} which closed to its theoretical value. Moreover, the influences of transition metal doping on the carbon modified composite were also studied.

Chapter 3 reported concerning the isostructural $Li_2MnP_2O_7$/C prepared using spray pyrolysis followed by annealing process. In consideration of the inactivity of this composite, electrochemical evaluation was performed at an elevated temperature of 60 °C. The relationship between the physical and the electrochemical properties at various synthesis conditions was investigated, the limitations on citric acid addition are discussed with the reaction mechanism in precursor solution and spray pyrolysis process. For the sake of exceeding these limitations, further carbon modification with acetylene black is carried out by ball milling process. The $Li_2MnP_2O_7$/C composite prepared under the optimal conditions delivered 64 mAh g^{-1} with clear redox plateau of Mn^{3+}/Mn^{2+} at near 4.3 V vs. Li/Li^+.

Chapter 4 shows that the solid-solution $Li_2Fe_{1-x}Mn_xP_2O_7$/C ($0 \leq x \leq 1$) composites synthesized under optimal conditions of spray pyrolysis and carbon modification process as established in previous chapters. Indexed XRD patterns showed a consistent shift according to the variation of Fe/Mn ratios in the composite. Electrochemical properties were investigated at a room, and elevated temperature in the potential range from 2.5 to 4.7 V. The initial discharge capacity depended on the Fe contents in the solid-solution composite due to the electrochemical inactivity of Mn constituent at room temperature. However, the thermal promotion allowed to observe the electrochemical activity of Mn constituent in composites. As a result, it was possible to confirm the electrochemical behavior of the prepared solid-solution composites, the discharge capacity and the specific energy density were improved with the appearance of Mn-redox at elevated temperature.

Chapter 5 presents main conclusions based on the above results of the dissertation.