Preparation and electrochemical property of Li$_{4}$Mn$_{5-x}$Ti$_{x}$O$_{12}$ cathode materials for lithium ion battery by spray pyrolysis

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Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ ($x = 0–0.5$) powders were successfully prepared by ultrasonic spray pyrolysis. As-prepared Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ powders were calcined from 500 to 700°C. The chemical and physical properties of as-prepared Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ powders and the calcined powders were characterized by XRD, TG-DTA, and SEM. The crystal phases of as-prepared Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ powders crystallized to the spinel structure (Fd-3m) by the calcination at 500°C. As-prepared Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ powders and the calcined powders obtained by spray pyrolysis exhibited spherical morphology with approximately 2 μm. The electrochemical measurement showed that the discharge capacity of the Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ $(x = 0)$ cathodes was 111 mAh/g at the rate of 0.2 C. The discharge capacity of the Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ cathodes increased with the concentration of Ti ion increased. The discharge capacity of the Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ $(x = 5)$ cathodes increased to 171 mAh/g (0.2 C) with increasing up to $x = 5$. The retention rates of the Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ $(x = 0, 2, 3, 5)$ cathodes discharge capacities were approximately 84, 66, 61, and 98% after 100 cycles at the rate of 1 C, respectively.

Key-words : Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$, Spray pyrolysis, Cathode, Lithium ion battery, Spinel, Powder

1. Introduction

Lithium ion batteries have been extensively used as energy storage device for portable electronics. Recently, large-scale lithium ion batteries have been well noted as the power sources for vehicle such as electric vehicles, hybrid electric vehicles, and power supplies used for load leveling in wind power generation and solar power generation.1) In cathode materials for large-scale lithium ion batteries, LiMn$_2$O$_4$ and LiFePO$_4$ have attracted much attention because of their cost effectiveness, low toxicity, relatively high energy density and thermal stability. In addition, lithium ion batteries of various voltages are required in order to use in a variety of applications.

LiFePO$_4$, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, LiMn$_2$O$_4$, LiNi$_{0.5}$Mn$_{1.5}$O$_4$, LiTi$_2$O$_4$, Li$_2$Mn$_{2}$O$_{12}$, and Li$_3$Ti$_2$O$_12$ have been studied as cathode materials. The theoretical capacities of LiFePO$_4$ (electric potential; 3.4 V), LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (electric potential; 3.6 V), LiMn$_2$O$_4$ (electric potential; 3.8 V), LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (electric potential; 4.6 V), LiTi$_2$O$_4$ (electric potential; 1.3 V), Li$_2$Mn$_{2}$O$_{12}$ (electric potential; 3.0 V), and Li$_3$Ti$_2$O$_12$ (electric potential; 1.5 V) were 170, 277, 148, 135, 160, 162 and 175 mAh/g, respectively. Both Li$_2$Mn$_{2}$O$_{12}$ and Li$_3$Ti$_2$O$_12$ are spinel structure.

We considered that spinel-type Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ cathode materials for lithium ion batteries of various voltages are required in order to satisfy process when Ti dope to Li$_3$Mn$_2$O$_{12}$. When their powder characteristics such as the particle size, morphology, and chemical composition are controlled well, the excellent rechargeable performance is expected. Furthermore, the spray pyrolysis easily and quickly leads to the formation of oxide with above powder characteristics in one step. In this work, Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ powders were prepared by ultrasonic spray pyrolysis. The powder characteristics of Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ and the effects of Ti doping on the electrochemical property of Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ cathode were investigated.

2. Experimental procedure

Ultrasonic spray pyrolysis(10) was used to prepare Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ powders. LiNO$_3$, Mn(NO$_3$)$_2$·6H$_2$O, and Ti(iso-OC$_3$H$_7$)$_4$ (TTIP) were used as starting materials. These compounds were dissolved in distilled water. Further, citric acid was used in order to dissolve TTIP in distilled water. The molar ratio of the metal component was set to Li:Mn:Ti = 4.5 − $x$:x $(x = 0, 2, 3, 5)$ in the solution. The concentration of starting solution was 0.1 mol/dm$^3$. The mist of starting solutions were generated using an ultrasonic nebulizer at a frequency of 1.6 MHz. Air was used as the carrier gas during the preparation of Li$_3$Mn$_{6-x}$Ti$_x$O$_{12}$ powders. The flow rate of the carrier gas was 7 dm$^3$/min. The mists were carried to an alumina tube (internal diameter, 50 mm; length, 2000 mm) that was heated by four electric furnaces and then pyrolyzed. The temperatures of two furnaces in drying zone were set to 250°C. The temperatures of two furnaces in pyrolysis zone were set to 500°C. The as-prepared powders were collected by the cyclone system. The as-prepared powders were calcined from 500 to 700°C for 5 h in an electric furnace under an air atmosphere. The heating and cooling rates were 5°C/min. The thermal behaviors of the obtained powders were observed using thermogravimetric-differential thermal analysis (TG-DTA, Shimadzu, DTG-60) at a heating rate of 10°C/min in an air atmosphere. The crystal phases...
of the obtained powders were identified by a powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using Cu Kα radiation. The particle size and morphology of the obtained powders were determined by using a scanning electron microscope (SEM, JEOL, JSM-6390). In the SEM images, 200 particles were randomly sampled to determine the average particle size.

The electrochemical measurements were examined using a 2032 coin type cell. The cathode slurry was prepared by mixing 70 wt% Li4Mn5O12 powders, 20 wt% acetylene black as conductive agent and 10 wt% polyvinylidene fluoride (PVdF) as binder in N-methyl-2-pyrrolidinone. The cathode slurry was coated on aluminum foil with 0.15 mm thickness by using doctor blade and dried under vacuum at 120°C for 24 h. Lithium sheet was used as an anode. The polypropylene sheet was used as a separator. The electrolyte was a 1.0 mol dm⁻³ solution of LiPF₆ in EC-DMC (EC:DMC = 1:1). 2032 coin type cells were assembled in globe box under an argon atmosphere. The rechargeable capacity and cycle stability of Li4Mn5O12 were measured with a battery tester (Hosen, BTS2004) at the voltages between 2.2 and 3.5 V. The rechargeable capacity and cycle stability were calculated using a battery tester (Hosen, BTS2004) at the voltages between 1.5 and 3.5 V, and the voltages between 1.0 and 2.5 V, respectively.

3. Results and discussions

3.1 Powder characteristics

The thermal behavior of the as-prepared LiₓMn₅₋ₓTixO₁₂ powders obtained by ultrasonic spray pyrolysis was observed using the TG–DTA. Figure 1 shows the TG–DTA curves of as-prepared LiₓMn₅₋ₓTixO₁₂ (x = 0, 2, 3, 5) powders. The weight loss with the endothermic reaction and exothermic reaction was observed from 300 to 500°C in all samples. In DTA curves of LiₓMn₅₋ₓTiO₁₂ (x = 0) powders, the endothermic reaction was observed. On the other hand, the exothermic reaction was observed in DTA curves of LiₓMn₅₋ₓTixO₁₂ (x = 2, 3, 5) as-prepared powders. It was found that the undecomposed residues derived from citric acid led to the exothermic reaction. Therefore, it was necessary for as-prepared powders to calcine at a temperature above 500°C. It is considered that the weight loss at 950°C in the LiₓMn₅₋ₓTixO₁₂ (x = 0) powders was attributable to volatilization of lithium.

The crystal phases of the obtained powders were investigated by using the XRD. The calcination temperatures were from 500 to 700°C under an air atmosphere. Figure 2 shows the XRD patterns of the as-prepared powders and the powders obtained by changing the calcination temperature. The crystallinity of the as-prepared powders was low regardless of Ti concentration, because the pyrolysis temperature in spray pyrolysis process was low. However, the as-prepared powders were crystallized by calcining above 500°C and then had a spinel structure. The crystal phase of LiₓMn₅₋ₓTiO₁₂ (x = 0, 2) powders was in good agreement with the spinel structure (space group: Fd-3m) regardless of the calcination temperature, and the other phases were not observed. On the other hand, the crystal phases of LiₓMn₅₋ₓTixO₁₂ (x = 3) powders calcined at 500°C were spinel and anatase-type TiO₂. However, the crystal phases of LiₓMn₅₋ₓTixO₁₂ (x = 3) powders calcined at 600 and 700°C were uniform spinel structure (space group: Fd-3m). The crystal phases of LiₓMn₅₋ₓTixO₁₂ (x = 5) powders calcined at 500°C were also spinel and the anatase-type TiO₂. A rutile-type TiO₂ phase was still observed in the LiₓMn₅₋ₓTiO₁₂ (x = 5) powders calcined at 600°C when the calcination temperature was 700°C, the crystal phases of LiₓMn₅₋ₓTiO₁₂ (x = 5) powders were uniform spinel structure (space group: Fd-3m), and no other impurity phases were observed. This suggested that the reactivity of Li and TiO₂ was low in the solid state reaction. All diffraction patterns of the spinel-type LiₓMn₅₋ₓTixO₁₂ (x = 0, 2, 3, 5) powders was identified as the spinel phase of LiₓMn₂O₄ (JCPDS, No. 46-0810) and Li₂TiO₃ (JCPDS, No. 49-0207).

Figure 3 shows the SEM images of the as-prepared powders and LiₓMn₅₋ₓTixO₁₂ powders obtained by changing the calcination temperature. The LiₓMn₅₋ₓTiO₁₂ (x = 0, 5) as-prepared powders were calcined at 700°C. The LiₓMn₅₋ₓTiO₁₂ (x = 2, 3) as-prepared powders were calcined at 600°C. The as-prepared powders obtained by ultrasonic spray pyrolysis exhibited spheri-
ical morphology and were non-aggregated, regardless of Ti concentration. As-prepared Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0$) powders and Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0$) calcined powders had a porous microstructure. The average primary particle size and secondary particle size of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0$) calcined powders were 0.18 and 2.3 μm, respectively. On the other hand, hollow particles were observed in the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 2, 3, 5$) calcined powders. From the results of the TG–DTA and SEM, it is considered that the hollow morphology was formed, because the undecomposed residues derived from citric acid generated the decomposition gas with exothermic reaction when as-prepared Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 2, 3, 5$) powders were calcined. The average particle sizes of them were 1.48 μm ($x = 2$), 2.30 μm ($x = 3$) and 2.54 μm ($x = 5$), respectively.

3.2 Electrochemical properties

The electrochemical properties of Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0, 2, 3, 5$) powders as cathode for lithium ion battery were examined. Figure 4 shows the first rechargeable curves of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0, 2, 3, 5$) cathodes calcined from 500 to 700°C in the indicated voltage range. The rechargeable rate was 0.2 C. The plateaus were observed clearly at approximately 2.8 V in the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0$) cathodes and 1.5 V in the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 5$) cathodes, regardless of the calcinations temperature. On the other hand, in the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 2$) cathodes calcined at 500 and 600°C, the plateaus were observed at approximately 2.6 V. However, the plateau of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 2$) cathodes calcined at 700°C was observed at approximately 2.8 V. In the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 3$) cathodes calcined at 500°C, the plateau was observed at approximately 2.5 V similarly to that of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 2$) cathodes calcined at 500 and 600°C. The plateaus of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 3$) cathodes calcined at 600°C were observed at approximately 2.3 and 1.8 V, respectively. The results of changing the plateau voltage exhibited the existence of the redox process associated with Mn and Ti reduction. This result corresponded to the assumptions of Le et al. that both Mn and Ti are involved in the redox process of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ cathode. In addition, it was found that the Ti concentration influenced the electric potential of a Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ cathode. The electric potential of a Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ cathode became low with increasing the concentration of Ti ion. It is considered that the redox reactions of Ti$^{4+}$ and Ti$^{3+}$ led to a lowering of the electric potential. Furthermore, the calcination temperature influenced the discharge capacity of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0, 2, 3, 5$) cathodes. The discharge capacities of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0, 2, 3, 5$) cathodes were 111 mAh/g ($x = 0, 700°C$), 163 mAh/g ($x = 2, 600°C$), 154 mAh/g ($x = 3, 600°C$), and 171 mAh/g ($x = 5, 700°C$), respectively.

Figure 5 shows the relation between cycle number and discharge capacity of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ cathode calcined from 500 to 700°C in the indicated voltage range. The rechargeable rate was 1 C. The discharge capacities of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ cathodes ($x = 0$) calcined at 600 and 700°C after 100 cycles were maintained at approximately 84 and 31% of the initial discharge capacity. Thackeray et al. reported that Li$_2$MnO$_3$ powders were gradually formed when Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0$) powders were calcined from 650 to 900°C. Li$_2$MnO$_3$ phase was not observed in the crystal phase of Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0$) powders calcined at 700°C in Fig. 2. However, it is considered that the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0$) powders calcined at 700°C contained as an impurity small amounts of Li$_2$MnO$_3$ powders. Therefore, it is considered that the presence of Li$_2$MnO$_3$ lead to poor cycle stability of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ cathodes ($x = 0$) calcined at 700°C. The discharge capacity retention rate of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 2$) cathode calcined at 600°C was approximately 66%. The discharge capacity retention rate of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 3$) cathode calcined at 600°C was approximately 61%. On the other hand, the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 5$) cathode calcined at 700°C exhibited excellent cycle stability. The discharge capacity retention rate of the Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 5$) cathode calcined at 700°C was approximately 98%.

4. Conclusions

Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0, 2, 3, 5$) powders were successfully prepared by ultrasonic spray pyrolysis. The calcination temperature influenced the crystal phase and particle morphology of Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ powders. XRD revealed that the homogeneous crystal phase of spinel-type Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ obtained by calcining from 500 to 700°C. Spinel-type Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ powders were well crystallized and spherical morphology. The average particle

![SEM images of as-prepared Li$_4$Mn$_{5-x}$Ti$_x$O$_{12}$ ($x = 0, 2, 3, 5$) powders and calcined powders.](image-url)
Fig. 4. First rechargeable curves of the Li$_4$Mn$_{3-x}$Ti$_x$O$_{12}$ ($x = 0, 2, 3, 5$) cathodes calcined from 500 to 700°C at a rate of 0.2 C in the voltage range indicated.

Fig. 5. Cycle performances of the Li$_4$Mn$_{3-x}$Ti$_x$O$_{12}$ ($x = 0, 2, 3, 5$) cathodes obtained from 500 to 700°C at a rate of 1 C in the voltage range indicated.
sizes of Li₄Mn₅₋ₓTiₓO₁₂ calcined powders were approximately 2 μm. Electrochemical measurement indicated that the discharge capacities of the Li₄Mn₅₋ₓTiₓO₁₂ cathodes increased with increasing the concentration of Ti ion. At the rate of 0.2 C, the first discharge capacities of Li₄Mn₅₋ₓTiₓO₁₂ cathodes were 111 mAh/g (x = 0), 163 mAh/g (x = 2), 154 mAh/g (x = 3), 171 mAh/g (x = 5), respectively. Li₄Mn₅₋ₓTiₓO₁₂ (x = 0, 5) cathodes exhibited good cycle stability, but Li₄Mn₅₋ₓTiₓO₁₂ (x = 2, 3) cathodes exhibited poor cycle stability.

References