Research Article

Powder Characterization and Electrochemical Properties of LiNi_{0.5}Mn_{1.5}O_{4} Cathode Materials Produced by Large Spray Pyrolysis Using Flame Combustion

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Received 2 April 2011; Accepted 7 June 2011

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LiNi_{0.5}Mn_{1.5}O_{4} cathode materials were produced by spray pyrolysis apparatus using the flame combustion. SEM revealed that as-prepared powders had spherical morphology with porous microstructure which had an average diameter of about 2 μm with broad size distribution. After the calcination, LiNi_{0.5}Mn_{1.5}O_{4} powders with polygonal morphology and narrow particle size distribution were obtained. XRD showed that LiNi_{0.5}Mn_{1.5}O_{4} was well crystallized after the calcination at 900°C. Rechargeable measurement of LiNi_{0.5}Mn_{1.5}O_{4} cathode showed that the long plateau was observed at 4.7 V in discharge curve of LiNi_{0.5}Mn_{1.5}O_{4} cathode and its discharge capacity was 145 mAh/g at 1 C. The capacity retention of LiNi_{0.5}Mn_{1.5}O_{4} cathode were 95% at 1 C after 100 cycles. The discharge capacity and capacity retention of LiNi_{0.5}Mn_{1.5}O_{4} cathode were 125 mAh/g and 88% at 20 C. LiNi_{0.5}Mn_{1.5}O_{4} cathode exhibited also stable cycle performance at 50°C.

1. Introduction

Lithium ion batteries have been extensively used as energy storage devices for portable electronics. Recently, these are well noted as the power sources for the vehicles such as EV and HEV [1]. Both layered type LiCoO_{2} and spinel type LiMn_{2}O_{4} is the most important cathode materials because of their high operating voltage at 4 V [2, 3]. LiCoO_{2} have been mostly used as cathode material of commercial lithium ion batteries. However, LiCoO_{2} has a problem related to capacity fading due to the instability in rechargeable cycles. Cobalt is also expensive and its resource is not sufficient. Furthermore, the thermal stability is very low in the rechargeable process. Therefore, LiCoO_{2} cathode material is not suitable as a lithium ion battery for EV and HEV. On the other hand, LiMn_{2}O_{4} cathode material is suitable due to their advantages such as low cost, abundance, nontoxicity, and thermally stable [4]. It was known that Ni-substitute lithium manganese oxide spinel (LiNi_{x}Mn_{1-x}O_{4}) was exhibited rechargeable behavior at about 5 V [5–7].

LiNi_{0.5}Mn_{1.5}O_{4} has attracted significant attention as a cathode material with high energy density. It was important to control the chemical composition to obtain homogeneous LiNi_{0.5}Mn_{1.5}O_{4} powders. So far, LiNi_{0.5}Mn_{1.5}O_{4} powders have been prepared via the solution techniques such as coprecipitation [8, 9], spray drying [10], sol-gel [11, 12], polymer gel [13] and chemical wet process [14]. LiNi_{0.5}Mn_{1.5}O_{4} powders have been also prepared via the improved solid state reaction [15–18] and molten salt reaction [19, 20].

We have noted spray pyrolysis in order to prepare a homogeneous LiNi_{0.5}Mn_{1.5}O_{4} powder. It was well known that the spray pyrolysis was an effective process for the rapid synthesis of homogeneous multicomponent oxide powders [21]. We have tried to synthesize various type cathode materials for lithium ion battery by spray pyrolysis [22–24]. The rechargeable capacity and cycle performance of lithium ion battery were improved by using the cathode materials for lithium ion battery derived from spray pyrolysis. Park and Sun [25] have reported that homogeneous LiNi_{0.5}Mn_{1.5}O_{4} powders can be obtained by ultrasonic spray pyrolysis. However, spray pyrolysis has not been applied as an industrial process because it is difficult to homogeneously pyrolyze the mist of inorganic salts in the electrical furnace that the scale-up was done. The difference of pyrolysis temperature...
inside and outside of the electrical furnace increases with increasing the dimension of electrical furnace. So far, we have also offered the two types of spray pyrolysis apparatuses by using gas burner to produce cathode materials [26, 27]. The advantage of these apparatuses is that it is possible to pyrolyze a large amount of mist during the short time compared with that of electrical furnace. The spray pyrolysis using the flame combustion has also the high effect of energy saving compared with that using the heating of conventional electric furnace. In this work, we modified the flame combustion type spray pyrolysis apparatus [26] in which the mist flowed from the bottom to the top and then tried to produce LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders. In this paper, the powder characterization and electrochemical properties of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders produced by large spray pyrolysis apparatus using the flame combustion were described.

2. Experimental

2.1. Powder Preparation. LiNO$_3$, Mn(NO$_3$)$_2$·6H$_2$O, and Ni(NO$_3$)$_2$·6H$_2$O were used as starting reagents. They were weighted out to attain the molar ratio of metal component (Li : Mn : Ni) of 2 : 3 : 1 and were dissolved in distilled water to prepare the starting solution. The concentration of the starting solution was 1 mol/dm$^3$. Figure 1 shows schematic diagram of flame spray pyrolysis apparatus used in this work. The apparatus is a prototype developed in order to verify the industrial production of cathode materials by the spray pyrolysis. This consisted of a two-fluid nozzle atomizer (the diameter of nozzle was 10 $\mu$m), a furnace (1800 mm × 580 mm) with six gas burners, a cooling line, and a bag filter. In comparison with the spray pyrolysis apparatus developed in a past study [26], the scale-up of the furnace was done. The flame combustion was generated using the liquefied petroleum gas and then the temperature of it was maintained at 500°C. The mist of the starting solution was continuously generated by two-fluid nozzle atomizer with the flow rate of 10 dm$^3$/h. The mist was introduced to the furnace by using the air carrier gas and pyrolyzed in the furnace at 500°C. The temperature in the furnace was monitored by the thermometer using Pt thermocouple. The thermometer was set in the centre of the furnace. The cooling line was naturally cooled by the radiation of heat using air. The potential of powders production increased up to 5 kg/day compared with the spray pyrolysis apparatus (3 kg/day) developed in a past. Both as-prepared LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders and outgas were cooled less than 100°C by a cooling line before the powder collection in the bag filter because the temperature of outgas was more than 200°C. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders were continuously produced for 5 h at the rate of 200 g/h. As-prepared LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders were calcined from 700°C to 1000°C for 2 h under the air atmosphere.

2.2. Characterization of Powders. The crystal phases of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders were identified with powder X-ray Diffraction (XRD-6100, Shimadzu). The particle morphology, microstructure, and state of aggregation of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders were observed with a scanning electron microscope (SEM, JSM-6390, JEOL). The chemical component of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders was determined by induced coupled plasma analysis (ICP, SII, SPS-7800). Specific surface area of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders was measured by BET method (SSA, BEL India, BELSORP-miniII). The particle density of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders was determined with the pycnometer (Pycnomatic, Thermoelectron) using He gas.

2.3. Electrochemical Measurement. Cathode was prepared using 80 wt% LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders, 10 wt% acetylene black as a conductive agent, and 10 wt% polyvinylidene fluoride resin as a binder. They were homogeneously mixed.
with N-methyl-2-pyrrolidone. They were dried at 120°C for 24 h in a vacuum oven. Metal lithium sheet was used as the anode. Microporous polypropylene membrane was used as a separator. 1 mol/dm³ LiPF₆ in ethylene carbonate/diethyl carbonate (EC : DEC = 1 : 1 in volume ratio) was used as the electrolyte. The coin type cell (CR2032) was assembled in a glove box filled with an argon gas. The rechargeable capacity of cathode was measured at 900°C. When as-prepared LiNi₀.₅Mn₁.₅O₄ powders were calcined at 900°C for 2h, the primary particles were sintered to form uniform polygonal morphology. The average particle size and σₚ of them were 1.01 μm and 1.3, respectively. It was found that the particle size and size distribution became small and narrow. Specific surface area of LiNi₀.₅Mn₁.₅O₄ cathode was measured 4.17 g/m³ due to the sintering of the primary particles. This led to the improvement for the dispersibility of LiNi₀.₅Mn₁.₅O₄ powders in N-methyl-2-pyrrolidone solvent, so that the homogeneous slurry of them was obtained for the preparation of cathode.

Figure 4 shows XRD patterns of as-prepared LiNi₀.₅Mn₁.₅O₄ powders and LiNi₀.₅Mn₁.₅O₄ powders calcined at 900°C for 2h. XRD revealed that the crystallinity of as-prepared powders was low, but that was well crystallized by the calcination at 900°C. It was seemed that these diffraction patterns of LiNi₀.₅Mn₁.₅O₄ powders were identified with a cubic spinel structure with Fd3m of space group. The diffraction patterns of impurities except for spinel phase were not observed. From ICP analysis of LiNi₀.₅Mn₁.₅O₄ powders calcined at 900°C, the molar ratio of LiNi₀.₅Mn₁.₅O₄ powders was 1.0 : 0.49 : 1.49 and showed good agreement with that of starting solution. This suggested that Li⁺ ion, Ni²⁺ ion and Mn⁴⁺ ion were uniformly mixed at molecular level in each mist which was played a role as a microreactor.

3. Results and Discussion

3.1. Particle Characterization of LiNi₀.₅Mn₁.₅O₄ Powders. LiNi₀.₅Mn₁.₅O₄ powders were continuously produced at rate of 200 g/h. Figure 2 shows an SEM image of LiNi₀.₅Mn₁.₅O₄ powders obtained after 5 h. SEM image revealed that as-prepared LiNi₀.₅Mn₁.₅O₄ particles had spherical morphology with broad particle size distribution. The average particle size and geometrical standard deviation (σₚ) of them were 1.68 μm and 1.34, respectively. The follow particles or spheroidal particles were also observed in Figure 2. This result suggested that the large mist derived from two-fluid nozzle atomizer with about nozzle size of 10 μm led to large particle size and broad size distribution of LiNi₀.₅Mn₁.₅O₄ powders. Specific surface area and particle density of as-prepared LiNi₀.₅Mn₁.₅O₄ powders were 24.6 m²/g and 3.32 g/cm³, respectively. These results suggested that LiNi₀.₅Mn₁.₅O₄ particles obtained had the porous microstructure which was consisted of primary particles.

Figure 3 shows the particle morphology of LiNi₀.₅Mn₁.₅O₄ powders calcined at 900°C for 2h. When as-prepared LiNi₀.₅Mn₁.₅O₄ powders were calcined at 900°C, the primary particles were sintered to form uniform polygonal morphology. The average particle size and σₚ of them were 1.01 μm and 1.3, respectively. It was found that the particle size and size distribution became small and narrow. Specific surface area of LiNi₀.₅Mn₁.₅O₄ powders decreased to 1.03 m²/g. The particle density of them increased to 4.17 g/m³ due to the sintering of the primary particles. This led to the improvement for the dispersibility of LiNi₀.₅Mn₁.₅O₄ powders in N-methyl-2-pyrrolidone solvent, so that the homogeneous slurry of them was obtained for the preparation of cathode.

3.2. Electrochemical Properties of LiNi₀.₅Mn₁.₅O₄ Cathode. Figure 5 shows the charge and discharge curves of LiNi₀.₅Mn₁.₅O₄ cathode at discharge rate indicated. The plateau was observed at around 4.7 V in discharge curves of them. This was attributed to Ni²⁺/Ni⁴⁺ redox couple [28].
The discharge capacity of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode was 145 mAh/g at 1 C. Another plateau was observed at around 4 V in the discharge curve of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode at 1 C. This was attributed to Mn$^{3+}$/Mn$^{4+}$ redox couple. The discharge capacity decreased with increasing the discharge rate. The plateau at 4 V disappeared at more than 10 C. The discharge capacity of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode was 125 mAh/g when the discharge rate was 20 C. The voltage of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode also lowered about 0.1 V at 20 C. The disappearance of plateau and the decrease of voltage may result in the increase in the polarization of cell. This was reported in the literature [29].

Figure 6 shows the discharge efficiency of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode at the rate indicated. The discharge efficiency of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode was 95% at 1 C. Although, the discharge efficiency of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode decreased with increasing the discharge rate, it kept more than 85% at even 20 C. It is considered that LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles with uniform polygonal morphology and high crystallinity are responsible of these outstanding rechargeable performances.

Figure 7 shows the relation between discharge capacity and cycle number of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode at the discharge rate indicated. The rechargeable test was carried out up to 100 cycles at room temperature. The capacity fading was slightly observed in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode at 1 C after 100 cycles. The capacity retention of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode was 95% at 1 C. That of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode obtained decreased with increasing the discharge rate and then capacity fading increased. The cycle retention of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode was 88% at 20 C after 100 cycles. It was found that LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode had excellent the cycle stability. It was considered that the rechargeable reaction uniformly occurred at the level of interface between particle and electrolyte because of narrow particle size distribution.

Figure 8 shows the cycle performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ when the cycle test was done alternately for 10 cycles at 1 C.
and 10 C. 140 mAh/g of discharge capacity was maintained at 1 C. The discharge capacity of LiNi_{0.5}Mn_{1.5}O_{4} cathode decreased to 130 mAh/g at 10 C. LiNi_{0.5}Mn_{1.5}O_{4} cathode had also good stability for the alternate cycle test at the higher and lower dischargeable rate. This suggested that the spinel structure of LiNi_{0.5}Mn_{1.5}O_{4} was also stable for intercalation of Li⁺ ion at the high and low rechargeable rate. This suggested that LiNi_{0.5}Mn_{1.5}O_{4} spinel structure may lead to the high cycle stability for the volume change during the rapid intercalation of lithium ion.

Figure 9 shows the cycle performance of LiNi_{0.5}Mn_{1.5}O_{4} cathode at 30°C and 50°C. The cycle test was examined at 1 C for 200 cycles. The discharge capacity of LiNi_{0.5}Mn_{1.5}O_{4} cathode at 30°C was 135 mAh/g after 200 cycles. The capacity retention of it was 95%. The discharge capacity of LiNi_{0.5}Mn_{1.5}O_{4} cathode at 50°C was 115 mAh/g after 200 cycles. The capacity retention of it was 91%. It was found that the cycle performance at 50°C was also stable as well as that at room temperature.

4. Conclusions

LiNi_{0.5}Mn_{1.5}O_{4} cathode materials were successfully produced by spray pyrolysis apparatus using the flame combustion. As-prepared LiNi_{0.5}Mn_{1.5}O_{4} powders had spherical morphology with porous microstructure which had an average diameter of 1.68 μm with broad size distribution. After the calcination, LiNi_{0.5}Mn_{1.5}O_{4} powders with polygonal morphology and narrow particle size distribution were obtained. LiNi_{0.5}Mn_{1.5}O_{4} powders were well crystallized after the calcination at 900°C and the chemical composition was in good agreement with that of synthesized solution. Rechargeable measurement of LiNi_{0.5}Mn_{1.5}O_{4} cathode showed that the plateau was observed at 4.7 V in discharge curve of LiNi_{0.5}Mn_{1.5}O_{4} cathode and its discharge capacity was 146 mAh/g at 1 C. The capacity retention of LiNi_{0.5}Mn_{1.5}O_{4} cathode was 95% at 1 C after 100 cycles. The discharge capacity and capacity retention of LiNi_{0.5}Mn_{1.5}O_{4} cathode was 125 mAh/g and 88% at 20 C. LiNi_{0.5}Mn_{1.5}O_{4} cathode exhibited stable cycle performance at 50°C.

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