

The properties of Li-Ni-Mn-O powders prepared by spray pyrolysis

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Li-Ni-Mn-O cathode powders with various ratios of nickel and manganese components were prepared by ultrasonic spray pyrolysis from polymeric precursor solutions. The precursor powders obtained from the polymeric precursor solutions containing citric acid and ethylene glycol were several micrometre in size, had a spherical shape and hollow morphology irrespective of the ratios of nickel and manganese components. However, the morphology of the post-treated Li-Ni-Mn-O cathode powders were affected by the ratios of nickel and manganese components. The $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode powders were several micrometre in size, had a hollow and spherical morphology. However, the LiMn_2O_4 and $\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$ cathode powders had a fine size and regular morphology. The mean sizes of the LiMn_2O_4 and $\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$ cathode powders were 1.2 and 0.26 μm , respectively. The initial discharge capacities of the prepared Li-Ni-Mn-O cathode powders were changed from 120 to 206 mAhg^{-1} according to the ratios of nickel and manganese components.

Key words: spray pyrolysis, cathode material, lithium secondary batteries.

Introduction

LiNiO_2 and LiMn_2O_4 materials are studied extensively as cathode materials for lithium secondary batteries. LiNiO_2 has advantages of higher specific capacity, lower cost and less toxic than LiCoO_2 [1]. However, it has several problems, such as a difficult synthesis, low thermal stability, and poor cycle life in the charged state [2, 3]. LiMn_2O_4 is also an attractive cathode material because of its low cost and friendly environmental characteristics [4, 5]. However, LiMn_2O_4 can exhibit significant capacity fading during cycle performance [6]. To overcome the disadvantages of LiNiO_2 and LiMn_2O_4 cathode materials, lithiated metal oxides of manganese and nickel components were studied. The new layer-structured $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ materials reported by Makimura and Ohzuku [7] and Lu et al. [8] are very interesting since the combination of nickel and manganese may provide advantages such as low cost and toxicity, high thermal stability and capacity. The spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were also studied as candidate cathode materials with good electrochemical properties [9, 10].

The electrochemical performance of the cathode in a lithium secondary battery is strongly affected by the powder properties, such as the powder morphology, the specific surface area, the crystallinity and the composition of the material [11-14]. Spray pyrolysis is a useful method for the synthesis of highly pure, fine-sized,

spherical cathode powders [11-14]. However, the characteristics of the cathode powders prepared by ultrasonic spray pyrolysis are affected by the compositions.

In this study, Li-Ni-Mn-O cathode powders were prepared by ultrasonic spray pyrolysis from polymeric precursor solutions. The effects of the ratios of nickel and manganese components on the morphological and electrochemical properties of Li-Ni-Mn-O cathode powders were studied.

Experimental Procedure

The Li-Ni-Mn-O cathode powders were prepared by ultrasonic spray pyrolysis from the polymeric precursor solutions. Citric acid and ethylene glycol were added into the spray solution as polymeric precursors. The ultrasonic spray pyrolysis system consists of a droplet generator, a quartz reactor, and a powder collector. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate large amount of droplets, which were carried into the high-temperature tubular reactor by a carrier gas. The flow rate of air used as the carrier gas was 40 liter per minute. The length and diameter of the quartz reactor were 1200 and 50 mm, respectively. The precursors used in this study were lithium carbonate (LiCO_3 , Aldrich), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aldrich), and manganese acetate hexahydrate ($\text{Mn}(\text{CH}_3\text{CO}_2)_4 \cdot 4\text{H}_2\text{O}$, Aldrich). The concentration of lithium carbonate, nickel nitrate hexahydrate, and manganese acetate hexahydrate was fixed at 0.3 M. The concentrations of citric acid and ethylene glycol were each 0.3 M. The precursor powders obtained by ultrasonic spray pyrolysis at 700 °C were post-treated at temperature of 800 °C for 3 h in an oxygen atmosphere.

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The morphological characteristics of the powders were investigated by scanning electron microscopy (SEM, JEOL JSM-6060). The crystal structures of the powders were investigated by X-ray diffraction (XRD, RIGAKU DMAX-33). A cathode electrode was made of 12 mg of Li-Ni-Mn-O cathode powders mixed with 4 mg of conductive binder (3.2 mg of teflonized acetylene black and 0.8 mg of graphite), which was pressed between two aluminum plates and then vacuum dried at 120 °C overnight. Lithium metal and polypropylene film were used as the anode electrode and the separator, respectively. The electrolyte was 1 M LiPF₆ in a 1:1 mixture by volume of EC/DMC (ethylene carbonate/dimethyl carbonate). The entire cell was assembled in a glove box under an argon atmosphere. The electrochemical performance of the Li-Ni-Mn-O cathode powders was measured by charge/discharge curves cycled between 2.8–4.5 V at a constant current density of 0.1 C.

Results and Discussions

The effects of the ratio of nickel and manganese components on the morphology of the Li-Ni-Mn-O cathode powders prepared by ultrasonic spray pyrolysis from the polymeric precursor solutions are shown in Figs. 1 and 2. The precursor powders obtained from the spray solution were several micrometre in size, had a spherical shape and hollow morphology irrespective of the ratios of nickel and manganese components. The mean size of the precursor powders were decreased with an increase in the content of the nickel component. The mean size of the precursor powders of LiMn₂O₄ mea-

sured from SEM micrograph was 3.2 µm. In the spray pyrolysis, one powder was formed from one droplet by drying and decomposition of the droplet. Therefore, the size of the powder prepared by ultrasonic spray pyrolysis was affected by the size of the droplet. The mean size of droplets generated by the ultrasonic spray generator with frequency of 1.7 MHz is smaller than 5 µm. Therefore, the powders prepared by the ultrasonic spray pyrolysis under mild preparation conditions had a submicrometre size. However, in this study, precursor powders with a size of several micrometre were prepared by ultrasonic spray pyrolysis. The addition of citric acid and ethylene glycol into the spray solution produced precursor powders with a large size, and with hollow and porous structures. The evolution of gases by decomposition of organic polymers formed precursor powders with a size of several micrometre and hollow structures.

Figure 2 shows the SEM photographs of the Li-Ni-Mn-O cathode powders post-treated at a temperature of 800 °C. The post-treatment of the precursor powders was performed under an oxygen atmosphere for the formation of cathode powders with layered crystal structures. The morphologies of the post-treated Li-Ni-Mn-O cathode powders were affected by the ratios of nickel and manganese components. The LiMn_{1.5}Ni_{0.5}O₄ and LiNi_{0.5}Mn_{0.5}O₂ cathode powders had a size of several micrometre, with spherical and hollow morphologies. The spherical shapes of the LiMn_{1.5}Ni_{0.5}O₄ and LiNi_{0.5}Mn_{0.5}O₂ precursor powders were maintained after post-treatment at a temperature of 800 °C. On the other hand, the spherical shapes of the precursor powders

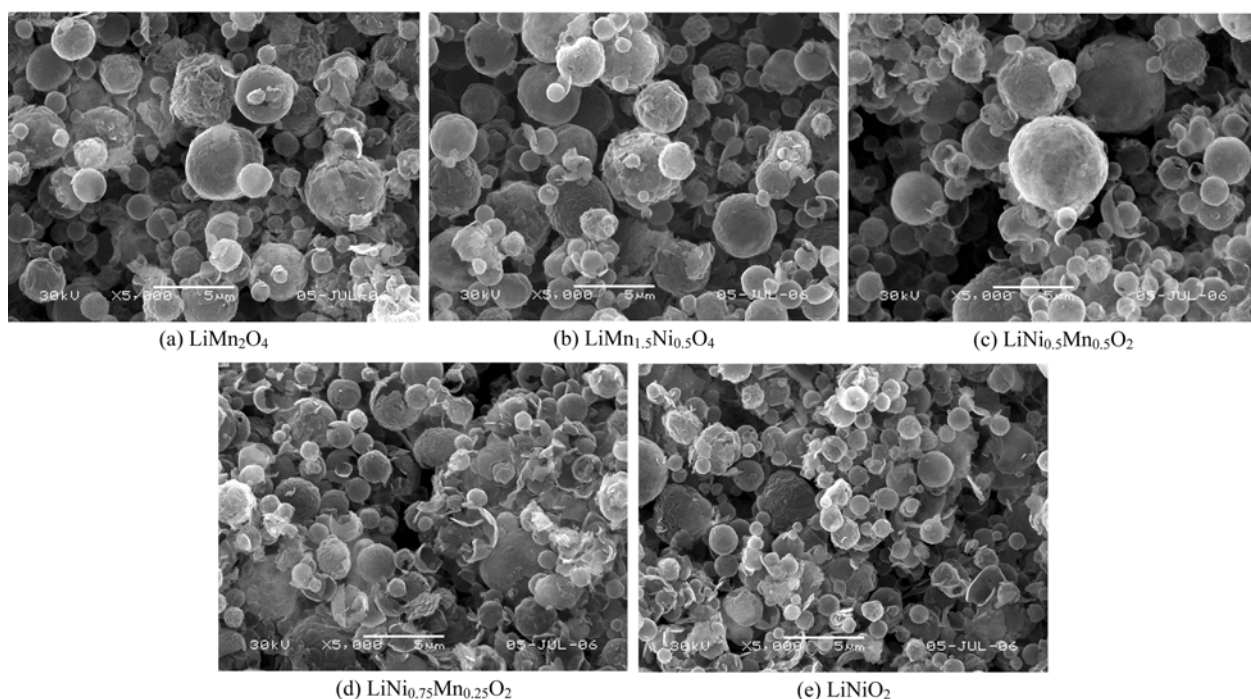


Fig. 1. SEM micrographs of the as-prepared powders obtained by spray pyrolysis.

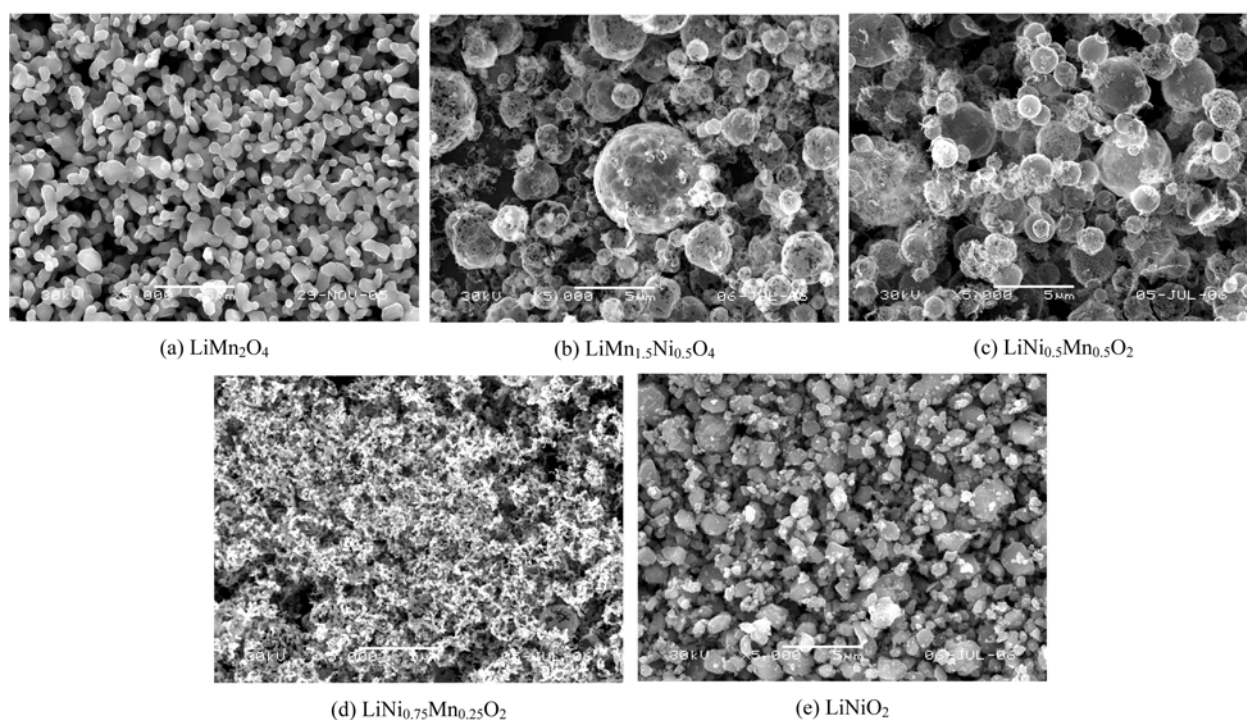


Fig. 2. SEM micrographs of the post-treated powders obtained by spray pyrolysis.

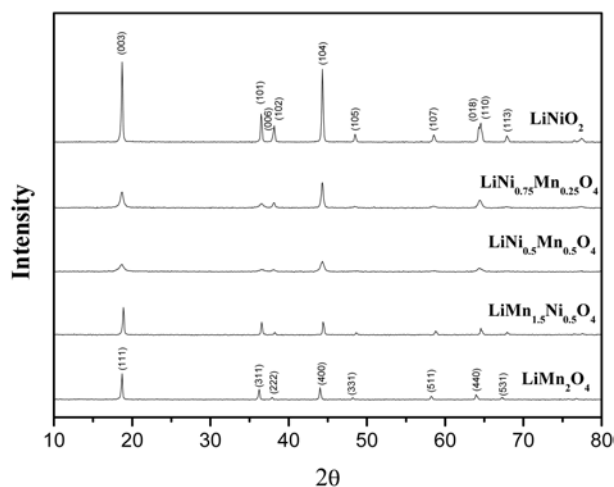


Fig. 3. XRD spectra of post-treated cathode materials obtained by spray pyrolysis from spray solutions with organic additives.

with compositions of LiMn_2O_4 , $\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$ and LiNiO_2 disappeared after post-treatment. Spinel LiMn_2O_4 powders with micrometre sized and with a regular morphology were obtained by post-treatment of the precursor powders with hollow and porous structures. The $\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$ cathode powders also had a fine size and regular morphology. On the other hand, LiNiO_2 cathode powders had a large size and a broad size distribution. The mean sizes of the LiNiO_2 , LiMn_2O_4 , $\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$ cathode powders measured from the SEM micrographs were 1.7, 1.2 and 0.26 μm , respectively.

Figure 3 shows the XRD spectra of the post-treated

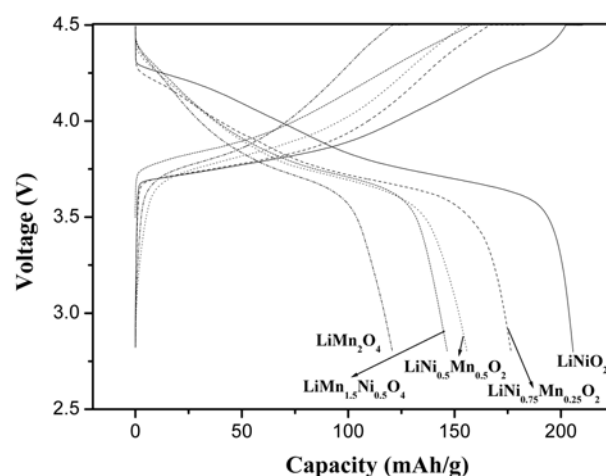


Fig. 4. Initial charge/discharge curves of post-treated powders obtained by spray pyrolysis.

Li-Ni-Mn-O cathode powders obtained from the polymeric precursor solutions. The LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode powders showed typical patterns of a spinel crystal structure. The mean crystallite sizes of the LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode powders were 51 and 43 nm, respectively. The separations of the 018/110 peaks in the XRD spectra, which represents the layered character of structure, appeared in the samples of LiNiO_2 , $\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode powders. The mean crystallite sizes of the cathode powders with layered crystal structures were also affected by the ratios of the nickel and manganese components. The mean crystallite sizes of the LiNiO_2 ,

$\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode powders were 43, 18 and 14 nm, respectively.

The initial charge/discharge curves of the prepared Li-Ni-Mn-O cathode powders obtained from the polymeric precursor solutions at a constant current density of 0.1 C are shown in Fig. 4. The initial discharge capacities of the layered LiNiO_2 , $\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode powders were 206, 176 and 155 mAhg^{-1} , respectively. The initial discharge capacity of the spinel LiMn_2O_4 cathode powders was 120 mAhg^{-1} . On the other hand, the spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode powders prepared by ultrasonic spray pyrolysis from the polymeric precursor solution showed unstable charge/discharge characteristics.

Conclusions

The effects of the ratios of nickel and manganese components on the morphological and electrochemical properties of Li-Ni-Mn-O cathode powders prepared by ultrasonic spray pyrolysis from polymeric precursor solutions were studied. The morphologies and crystal structures of the as-prepared and post-treated powders were affected by the ratios of the nickel and manganese components. The $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode powders obtained from the polymeric precursor solutions maintained their spherical shape and sizes of several micrometre of the as-prepared powders after post-treatment at a temperature of 800°C . However, the as-prepared powders with a size of several micrometre and hollow morphology formed the $\text{LiNi}_{0.75}\text{Mn}_{0.25}\text{O}_2$

and LiMn_2O_4 cathode powders with a fine size and regular morphology after post-treatment.

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