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The characteristics of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared from precursor particles with spherical shape obtained by spray pyrolysis

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Abstract

Spherical and fine-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles were prepared using spray pyrolysis. Precursor particles with mixed Mn_2O_3, Co_3O_4 and NiO compositions were prepared using spray pyrolysis from aqueous and polymeric precursor solutions. The precursor particles prepared from the aqueous solution had hollow and porous morphologies. The precursor particles prepared from the polymeric precursor solution with citric acid and ethylene glycol were spherical in shape and had filled morphologies. The spherical precursor particles with filled morphologies formed spherical, fine-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles with filled morphologies after post-treatment with LiOH. The mean crystallite sizes of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared from spray solutions with and without lithium at the post-treatment temperature of 800 °C were 56 and 31 nm, respectively. The initial discharge capacities of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared using spray pyrolysis from spray solutions with and without lithium were 178 and 181 mAh g^{-1}, respectively, after a post-treatment temperature of 800 °C.

Keywords: A. Powders: gas phase reaction; E. Batteries

1. Introduction

The electrochemical performance of the cathode in a secondary lithium battery is strongly affected by the powder properties, such as the particle morphology, the specific surface area, the crystallinity and the composition of the materials [1–7]. With respect to the powder morphology, spherical powders with narrow size distributions show better electrochemical performance than powders with irregular morphologies because of the former high packing density. Fine-sized cathode powders have been intensively investigated to improve the capacity and power output of secondary lithium batteries.

The characteristics of the powders used as cathode materials in secondary lithium batteries are strongly affected by their preparation processes. The commercial powders mainly used as cathode materials in secondary lithium batteries are prepared using the conventional solid-state reaction method. The cathode powders prepared using the solid-state reaction method were non-spherical and had large particle sizes. Many liquid solution methods of producing ceramic particles, such as sol–gel, pechini, freeze drying, co-precipitation, and emulsion drying, were applied to the preparation of fine-sized cathode powders with controlled morphologies [4–14].

Spray pyrolosis is a useful method for the synthesis of highly pure, fine-sized, spherical cathode powders [4–9]. Taniguchi et al. synthesized the many types of spherical, fine-sized cathode materials using the spray pyrolysis process [4,6,7]. In the conventional spray pyrolysis process, the as-prepared particles obtained through spray pyrolysis from a spray solution with lithium were post-treated at high temperatures to improve the crystallinity and phase purity of the cathode powders. The morphology of the cathode powders post-treated at high temperatures was strongly affected by the preparation conditions during the spray pyrolysis. $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles are being widely studied as cathode materials for lithium ion batteries because of their high capacity, high working voltage, and high stability. $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles were prepared using solid-state reaction, glycine-

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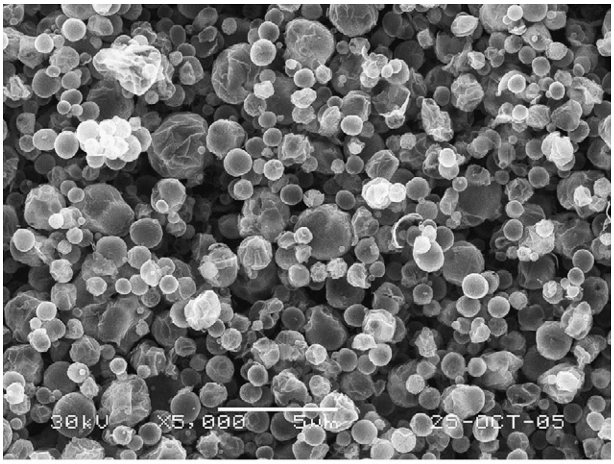
nitrate combustion, spray drying and spray pyrolysis, etc. [4,5,15–17].

In this study, the precursor powders of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ were prepared using spray pyrolysis from spray solutions with and without lithium. The characteristics of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders prepared from two different spray solutions were investigated. The $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders prepared from the spray solution with lithium were non-spherical and had broad size distributions. On the other hand, the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders prepared from the spray solution without lithium were spherical and fine-sized.

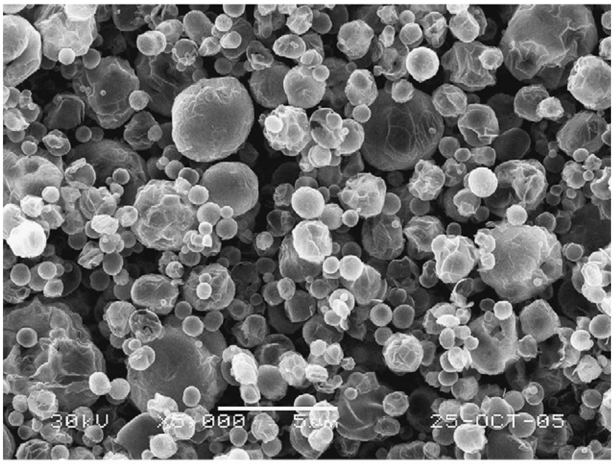
2. Experimental

The $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders were prepared through post-treatment of the precursor powders obtained using spray pyrolysis from two different spray solutions. The precursor powders prepared using spray pyrolysis from the spray solution without lithium were mixed with LiOH powder and post-treated at various temperatures. The precursor powders prepared using spray pyrolysis from the spray solution with lithium were post-treated at 800 °C for 3 h. The spray pyrolysis system consists of a droplet generator, a quartz reactor, and a particle collector [18]. A 1.7 MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets, which are carried into the high-temperature tubular reactor by a carrier gas. The droplets and particles evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. The reactor temperature was maintained at 900 °C. The flow rate of the air used as the carrier gas was changed from 10 to 40 l/min. The precursor solution was prepared by dissolving a stoichiometric ratio of 1:1:1 nickel nitrate hexahydrate [$Ni(NO_3)_2{\cdot}6H_2O$, Aldrich], cobalt nitrate hexahydrate [$Co(NO_3)_2{\cdot}6H_2O$, Aldrich], and manganese acetate tetrahydrate [$Mn(CH_3COO){\cdot}4H_2O$, Aldrich] salts in distilled water. The overall solution concentration of nickel, cobalt and manganese components was 0.5 M. Lithium carbonate was used as the lithium source in the preparation of the spray solution with lithium. Polymeric precursors containing citric acid and ethylene glycol were introduced to control the spherical morphology with micron size precursor particles in spray pyrolysis. The concentrations of citric acid and ethylene glycol were both 0.1 M.

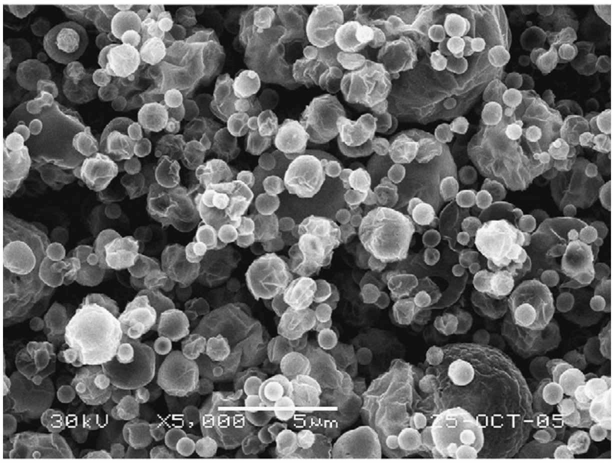
The crystal structures of the as-prepared and post-treated ceria particles were investigated using X-ray diffractometry (XRD, RIGAKU DMAX-33). The morphological characteristics of the particles were investigated using scanning electron microscopy (SEM, JEOL JSM-6060). The charge/discharge characteristics of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders prepared through the solid-state reaction method using spherical precursor powders were compared with those of the powders prepared using the conventional spray pyrolysis method. The cathode electrode was made of 12 mg of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ compounds mixed with 4 mg of a 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 overnight at 120 °C. The lithium metal and polypropylene film were used as the anode electrode and the separator, respectively. The electrolyte was 1 M $LiPF_6$ in a 1:1 mixture by volume of EC/DEC. The entire cell was assembled in a glove box under an argon atmosphere. The charge/discharge characteristics of the samples were measured through cycling in the 2.8–4.5 V potential range at a constant current density of 0.1 C.



(a) 10 1/min



(b) 20 1/min



(c) 40 1/min

Fig. 1. (a–c) SEM micrographs of precursor particles prepared by spray pyrolysis from aqueous solutions at different gas flow rates.

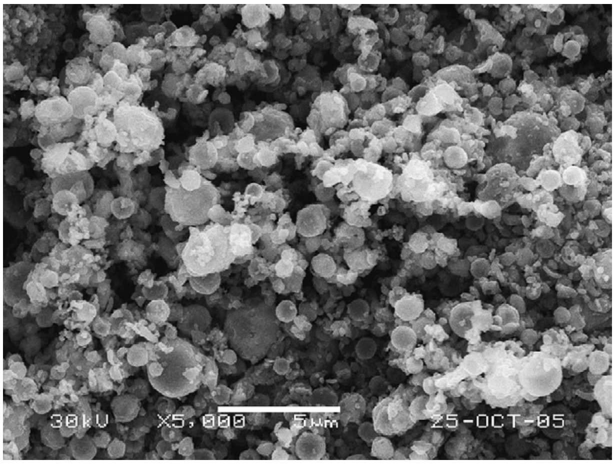


Fig. 2. SEM micrograph of post-treated $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles.

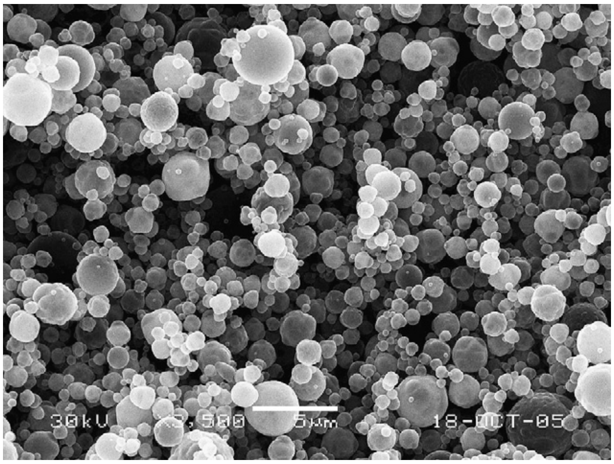
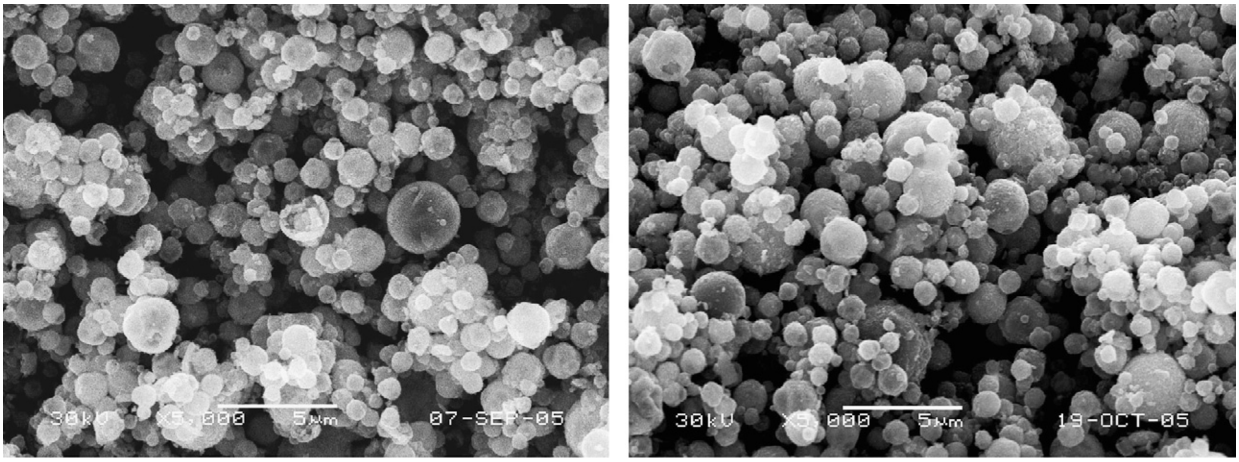


Fig. 3. SEM micrograph of precursor particles prepared by spray pyrolysis from polymeric precursors solution.

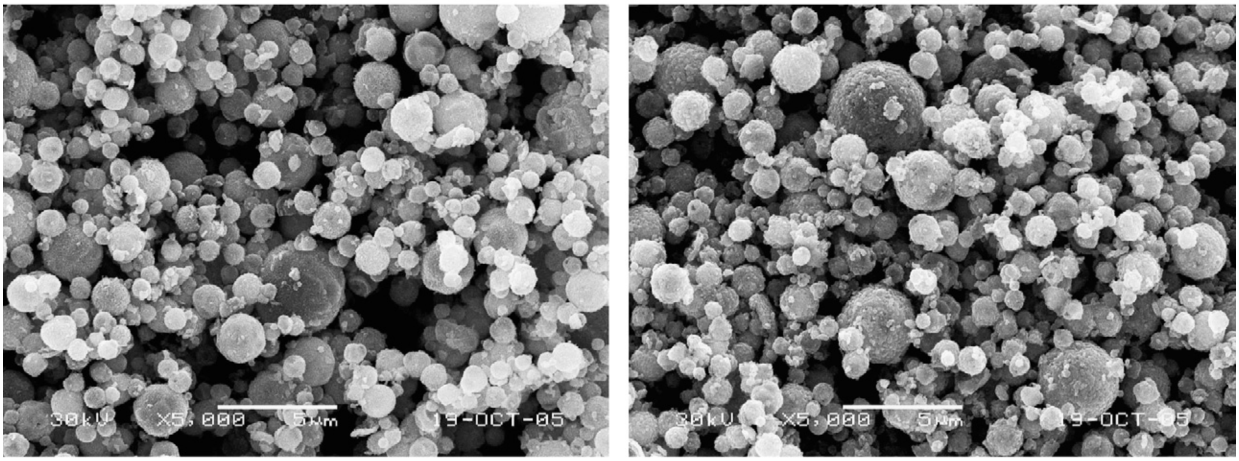
3. Results and discussion

The morphology of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained through post-treatment of the mixture of precursor particles and LiOH was affected by the characteristics of the precursor particles obtained using spray pyrolysis. Spherical precursor particles with dense morphologies were necessary in preparing spherical $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles with non-aggregated characteristics. Fig. 1 shows SEM micrographs of the precursor particles obtained using spray pyrolysis from



(a) A 500°C

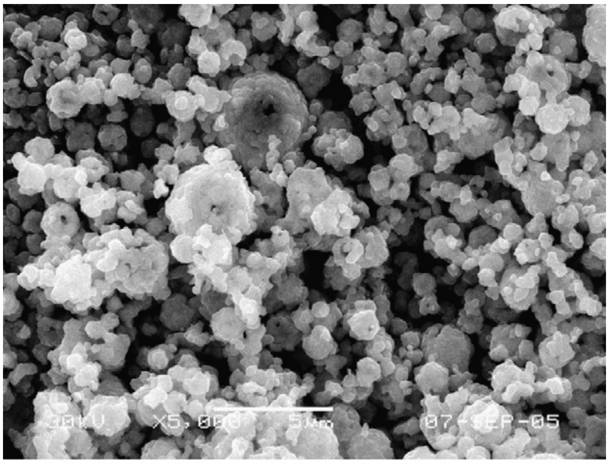
(c) A 700°C



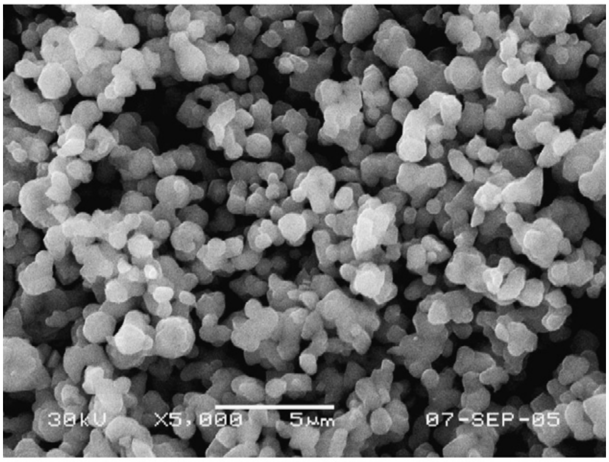
(b) A 600°C

(d) A 800°C

Fig. 4. (a–f) SEM micrographs of post-treated $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles at different post-treatment temperatures.



(e) A 900ºC



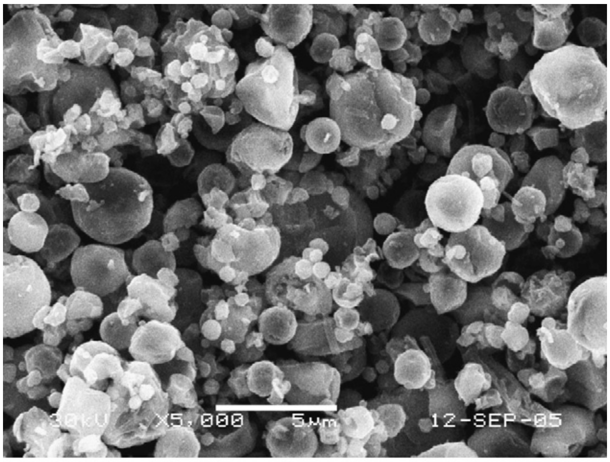
(f) A 1000ºC

Fig. 4. (*Continued*).

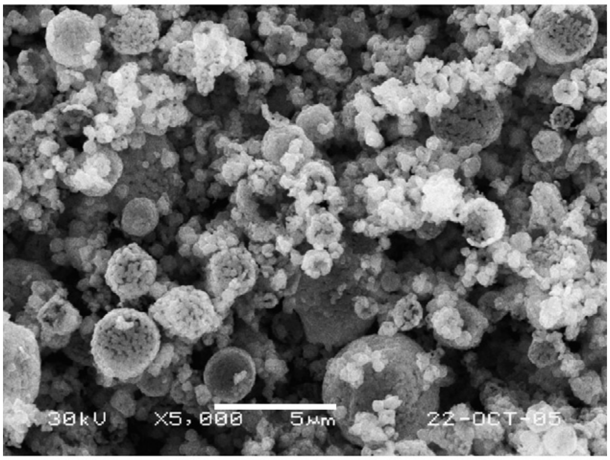
aqueous solutions at different flow rates of the carrier gas. The hollowness of the precursor particles increased with the increase in the flow rate of the carrier gas because of the high drying and decomposition rates of the reactants. The residence time of the particles inside the hot wall reactor changed from 0.6 to 0.15 s when the flow rate of the carrier gas changed from 10 to 40 l/min. Fig. 2 shows SEM micrograph of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained through post-treatment of the mixture of the precursor particles (Fig. 1(a)) and LiOH. The micron-sized, fine-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles had bimodal size distributions. The large precursor particles with hollow, porous structures became fine-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles after post-treatment at 800 °C. On the other hand, one $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particle was obtained from one small precursor particle with a dense structure.

Fig. 3 shows SEM micrograph of the precursor particles prepared from the polymeric precursor solution that contained citric acid and ethylene glycol. Polymeric precursors were introduced to control the morphologies of the precursor particles in spray pyrolysis. The concentrations of citric acid and ethylene glycol were both 0.1 M. The flow rate of the carrier gas was 10 l/min. The precursor particles prepared from the polymeric precursor solution were more spherical and had denser morphologies than those (Fig. 1(a)) prepared from the aqueous solution. The esterification reaction between the carboxyl group in citric acid and the hydroxyl group in ethylene glycol within droplets formed a highly viscous gel that consisted of a three-dimensional network of polymers. The viscous gel promoted volume precipitation and resulted in the formation of spherical particles with filled morphologies and non-aggregated characteristics. Fig. 4 shows SEM micrographs of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained from the precursor particles shown in Fig. 3. The mixture of the precursor particles and LiOH was post-treated at different temperatures for 3 h. The $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles were spherical and had non-aggregated characteristics at post-treatment temperature below 800 °C, in which the morphologies of the precursor particles were maintained after post-treatment with LiOH. One $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particle was obtained from one fine-sized precursor particle with a dense structure at post-treatment temperatures below 800 °C. On the other hand, the morphologies of the spherical precursor particles were destroyed after post-treatment at above 900 °C.

The morphologies of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared from the precursor particles were compared with those of the particles prepared from the spray solution that contained lithium. In Fig. 5, the as-prepared particles obtained using spray



(a) No additive



(b) Post-treated

Fig. 5. (a and b) SEM micrographs of as-prepared and post-treated $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared by spray pyrolysis containing lithium component.

pyrolysis from the spray solution that contained lithium carbonate salt were post-treated at 800 °C for 3 h. The flow rate of the carrier gas was 10 l/min. The as-prepared particles were micron-sized, spherical, and had hollow morphologies. On the other hand, the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained after post-treatment had broad size distributions and irregular morphologies. The morphologies of the precursor particles obtained using spray pyrolysis were not maintained after post-treatment at 800 °C. In this study, the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared using spray pyrolysis from the spray solution that contained lithium under severe preparation conditions were non-spherical and had broad size distributions.

Fig. 6 shows the XRD spectra of the precursor and post-treated particles obtained using spray pyrolysis. The precursor particles prepared using spray pyrolysis from the spray solution without lithium had mixed Co_3O_4, Mn_2O_3, and NiO crystal structures. The mixture of the precursor particles and LiOH formed the pure-phase $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles after post-treatment at above 500 °C for 3 h. The crystallinity of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles increased with the increase in the post-treatment temperature. The mean crystallite size of the particles changed from 19 to 49 nm when the post-treatment temperature was increased from 500 to 1000 °C. The crystal structures of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained using spray pyrolysis from the spray solutions with and without lithium are shown in Fig. 7. The $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained through post-treatment of the mixture of the precursor particles and LiOH had lower crystallinities than did the particles prepared through post-treatment of the as-prepared particles that contained lithium. The mean crystallite sizes of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared from the spray solutions with and without lithium at the post-treatment temperature of 800 °C were 33 and 47 nm, respectively.

Fig. 8 shows the charge/discharge curves of the $Li/Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell cycled at 2.8–4.5 V at a constant current density of 0.1 C. The charge/discharge characteristics of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared through post-treatment of the mixture of precursor particles obtained using spray pyrolysis from polymeric precursors and LiOH were compared with those of the particles prepared through post-treatment of the as-prepared particles obtained using spray pyrolysis from the spray solution with lithium. The charge/discharge capacities of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared from precursor particles were affected by the post-treatment temperatures. The particles post-treated at low post-treatment temperatures below 700 °C had low charge/discharge capacities because of poor crystallinities, as shown in Fig. 6. The particles post-treated at temperatures between 800 and 1000 °C, however, had high charge/discharge capacities regardless of temperature. The $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles (Fig. 4(d)) post-treated at 800 °C were spherical and had regular morphologies. On the other hand, the morphologies of the

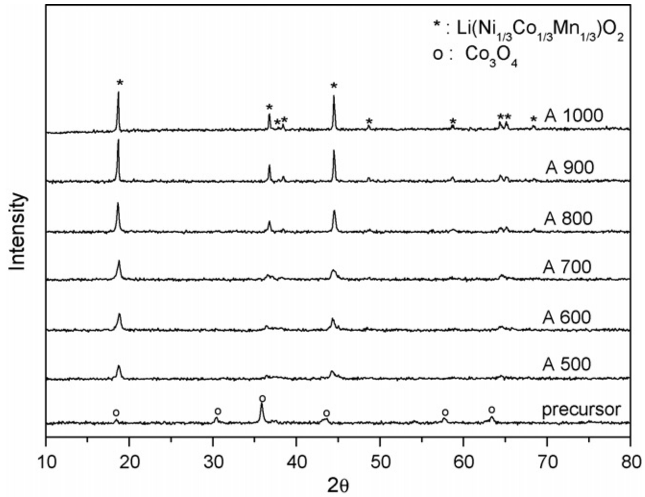


Fig. 6. XRD spectra of precursor and post-treated Li $(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles: A, post-treatment temperature.

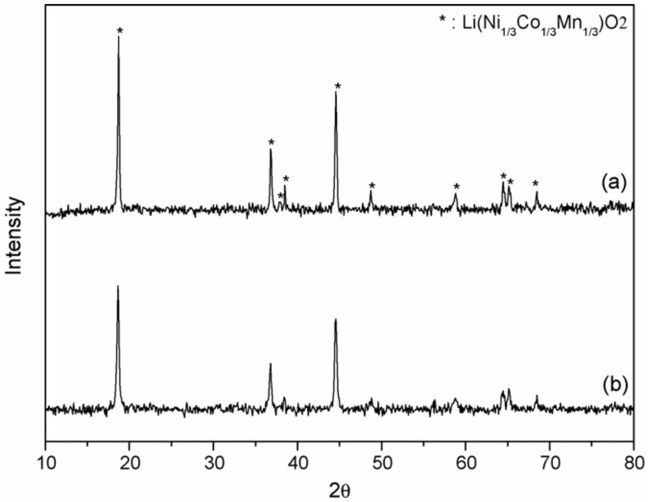


Fig. 7. XRD spectra of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared by spray pyrolysis from spray solutions with and without lithium component: (a) the particles prepared from spray solution with lithium component, (b) the particles prepared from spray solution without lithium component.

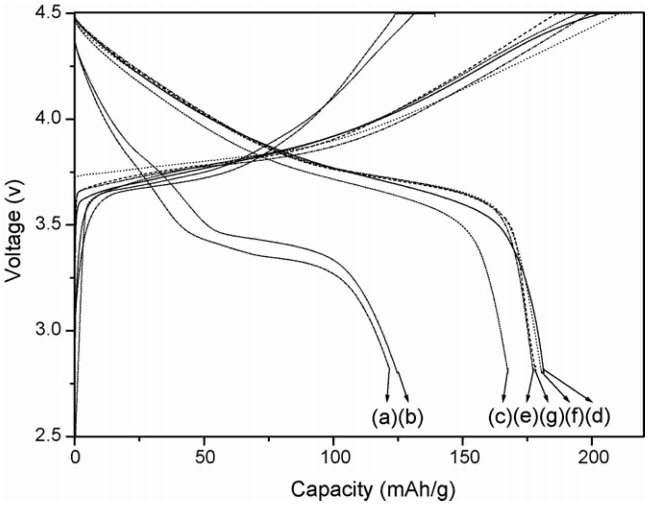


Fig. 8. Initial charge/discharge capacities of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared by spray pyrolysis from spray solutions without lithium component: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C, (f) 1000 °C. (g) Initial charge/discharge capacity of particles prepared from spray solution with lithium component.

spherical precursor particles were destroyed after post-treatment at above 900 °C. Therefore, the optimum post-treatment temperature for obtaining the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles with high charge/discharge capacities and regular morphologies was 800 °C. The charge/discharge capacities of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared through post-treatment of the mixture of precursor particles obtained using spray pyrolysis and LiOH were similar to those of the particles prepared through post-treatment of the as-prepared particles obtained using spray pyrolysis from the spray solution with lithium. The initial discharge capacities of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared using spray pyrolysis from the spray solutions with and without lithium were 178 and 181 mAh g^{-1}, respectively, after post-treatment at 800 °C.

4. Conclusions

The morphologies and electrochemical properties of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared using spray pyrolysis from spray solutions with and without lithium were investigated. The spherical shapes and hollow morphologies of the as-prepared particles obtained from the spray solution with lithium were destroyed after post-treatment at 800 °C. The spherical precursor particles with filled morphologies were prepared using spray pyrolysis from spray solutions that contained citric acid and ethylene glycol to prepare spherical, fine-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles. The precursor particles with mixed Mn_2O_3, Co_3O_4, and NiO compositions produced spherical, fine-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles after post-treatment with LiOH. Spherical precursor particles with filled morphologies were necessary in preparing spherical $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles with filled morphologies using spray pyrolysis.

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