

Short communication

Fine cathode particles prepared by solid-state reaction method using nano-sized precursor particles

Seo Hee Ju, Hye Young Koo, Seung Kwon Hong, Eun Byul Jo, Yun Chan Kang*

*Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong,
Gwangjin-gu, Seoul 143-701, Republic of Korea*

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Abstract

Fine-sized Li–Co–Mn–O cathode particles with various ratios of cobalt and manganese components were prepared by conventional solid-state reaction method using the nano-sized precursor particles. The nano-sized precursor particles of cobalt and manganese components were prepared by spray pyrolysis. The $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ ($0.1 \leq x \leq 0.3$) particles had finer size than that of the pure LiCoO_2 particles. Manganese component disturbed the growth of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ cathode particles prepared by solid-state reaction method. The initial discharge capacities of the layered $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ ($0 \leq x \leq 0.3$) cathode particles decreased from 144 to 136 mAh g^{-1} when the ratios of Co/Mn components were changed from 1/0 to 0.7/0.3. The mean sizes of the spinel $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles decreased from 650 to 460 nm when the ratios of Mn/Co components were changed from 2/0 to 1.8/0.2. The initial discharge capacities of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles decreased from 119 to 86 mAh g^{-1} when the ratios of Mn/Co components were changed from 2/0 to 1.8/0.2.

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1. Introduction

The electrochemical performance of the cathode material in lithium secondary battery is strongly affected by the properties of the particles, such as morphology, specific surface area, crystallinity and phase homogeneity. In recent years, nano-sized cathode materials have been investigated to achieve the high capacity in lithium secondary batteries. The nano-sized cathode materials had high capacity because of high surface area and the raised lithium intercalation efficiency [1–4].

Spray pyrolysis was also studied as a preparation method for fine-sized ceramic particles. Spray pyrolysis had advantages of liquid phase solution and gas phase reaction methods [5–12]. In the respect of liquid phase reaction method, spray pyrolysis had advantage in control the composition of multicomponent oxide particles. Spray pyrolysis had advantage in control the morphology of the particles in the respect of gas phase reaction method. In the said method, spray solutions with polymeric precursors were used in the preparation of various types of oxide particles. Polymeric precursors were added into the spray solution to con-

trol the stoichiometry and morphology of the multicomponent oxide particles in the spray pyrolysis.

In this work, nano-sized Li–Co–Mn–O cathode particles with various ratios of cobalt and manganese components were prepared by conventional solid-state reaction method. Nano-sized precursor particles with uniform morphology and narrow size distribution obtained by spray pyrolysis were used as the source of the cobalt and manganese components.

2. Experimental

The cathode particles were prepared by solid-state reaction method. In the solid-state reaction method, nano-sized precursor particles prepared by spray pyrolysis were used. Nano-sized precursor particles of cobalt and manganese components were prepared by spray pyrolysis from spray solution with organic additives. Ethylene glycol and citric acid used as organic additives enabled the formation of the nano-sized precursor particles in the spray pyrolysis. The spray pyrolysis system consists of droplet generator, quartz reactor, and particle collector. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate large amount of droplets. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. The flow rate of the carrier gas was fixed at 40 l min^{-1} . The

* Corresponding author. Tel.: +82 2 2049 6010; fax: +82 2 458 3504.
E-mail address: yckang@konkuk.ac.kr (Y.C. Kang).

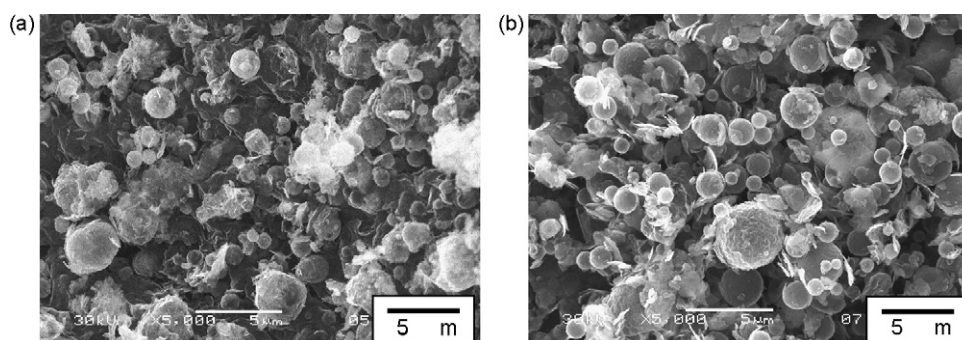


Fig. 1. SEM photographs of the as-prepared Co-rich particles: (a) Co/Mn = 1/0; (b) Co/Mn = 0.7/0.3.

temperature of the reactor was fixed at 900 °C. To prepare the precursor solution, cobalt nitrate and manganese nitrate were dissolved in distilled water. The overall solution concentration of cobalt and manganese components was 0.3 M. The concentrations of citric acid and ethylene glycol used as polymeric precursors were each 0.3 M. The as-prepared particles obtained by spray pyrolysis were post-treated at temperature of 800 °C for 3 h under atmosphere to obtain the nano-sized precursor particles. The nano-sized precursor particles prepared by spray pyrolysis were mixed with LiOH particles and post-treated at temperature of 800 °C for 3 h. An excess of lithium component ($\text{Li}/(\text{Co} + \text{Mn}) = 1.03$) was used to compensate for lithium loss during the post-treatment.

The crystal structures of the particles were investigated by X-ray diffractometry (XRD, RIGAKU DMAX-33). The morphological characteristics of the particles were investigated by scanning electron microscopy (SEM, JEOL JSM-6060). The cathode electrode was made of 12 mg of cathode compounds 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. 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 the glove box under argon atmosphere. The electrochemical performances of the various cathode samples were measured by charge/discharge curves of Li/Li–Co–Mn–O cell cycled in 3.0–4.3 V at a constant current density of 0.1 C.

3. Results and discussion

The morphologies of the as-prepared Co-rich particles obtained by spray pyrolysis were shown in Fig. 1. The as-prepared Co-rich particles had micron size, hollow and spherical morphology. The high flow rate of the carrier gas and the gas evolution from the decomposition of the citric acid and ethylene glycol formed the as-prepared particles with micron size, hollow and porous morphologies.

The as-prepared particles obtained by spray pyrolysis from spray solution with citric acid and ethylene glycol were post-treated at 800 °C for 3 h. The morphologies of the post-treated precursor particles were shown in Fig. 2. The post-treated cobalt oxide particles had submicron size and regular morphology. The as-prepared particles obtained from spray solution with ethylene glycol and citric acid turned to fine-sized and non-aggregated precursor particles during the post-treatment process. The addition of manganese component into the spray solution decreased the mean sizes of the Co-rich particles. The mean sizes of the Co-rich particles were decreased from 440 to 180 nm when the ratios of Co/Mn components were changed from 1/0 to 0.7/0.3.

Fig. 3 shows the XRD spectra of the post-treated Co-rich precursor particles obtained by spray pyrolysis. The main crystal structure of the precursor particles prepared from cobalt nitrate and manganese nitrate solutions was Co_3O_4 . The peaks of the manganese component were not observed in the XRD spectra. However, the mean crystallite sizes of the Co-rich precursor particles were decreased by addition of manganese component.

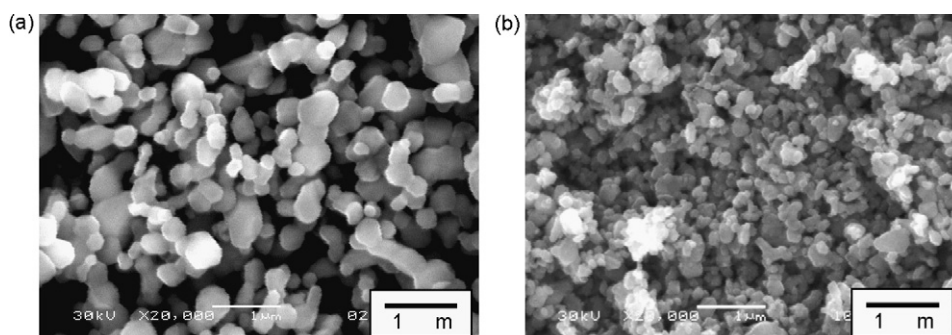


Fig. 2. SEM photographs of the post-treated Co-rich particles: (a) Co/Mn = 1/0; (b) Co/Mn = 0.7/0.3.

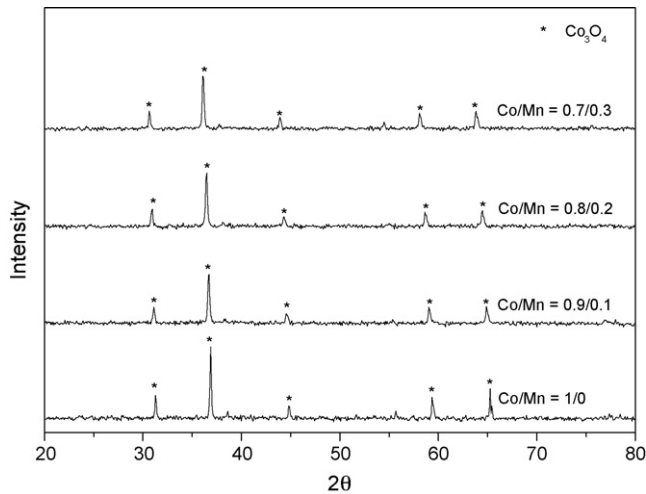


Fig. 3. XRD spectra of the post-treated Co-rich particles.

The Co-rich precursor particles obtained by spray pyrolysis were reacted with LiOH by solid-state reaction method at temperature of 800°C. Fig. 4 shows the SEM photographs of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ cathode particles with various ratios of cobalt and manganese components. The $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ cathode particles formed from the fine-sized precursor particles had submicron size and regular morphology. The mean sizes of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ ($0 \leq x \leq 0.3$) cathode particles were decreased from 570 to 280 nm when the ratios of Co/Mn components were changed from 1/0 to 0.7/0.3. Manganese component disturbed the growth of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ cathode particles prepared by solid-state reaction method.

Fig. 5 shows the XRD spectra of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ ($0 \leq x \leq 0.3$) cathode particles. The prepared cathode particles had pure layered crystal structure irrespective of the ratios of cobalt and manganese components. However, the mean crystallite sizes of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ cathode particles calculated from the Scherrer's equation were decreased with increasing the content of the manganese component. The mean crystallite sizes of the LiCoO_2 and $\text{LiCo}_{0.7}\text{Mn}_{0.3}\text{O}_2$ cathode particles were each 46 and 26 nm.

Fig. 6 shows the initial charge/discharge capacities of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ ($0 \leq x \leq 0.3$) cathode particles. The pure LiCoO_2 cathode particles had initial discharge capacity of 144 mAh g^{-1} . The initial discharge capacities of the

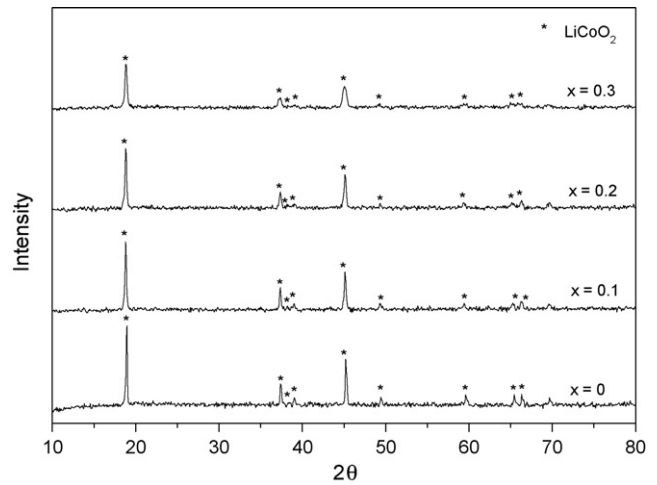


Fig. 5. XRD spectra of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ cathode particles.

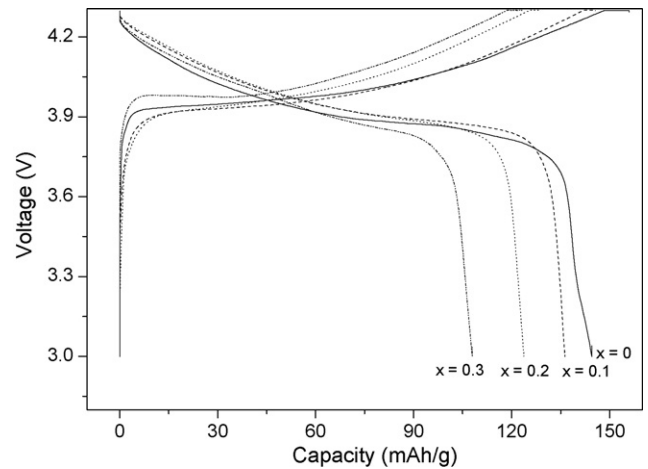


Fig. 6. Initial charge/discharge curves of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ cathode particles.

$\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ ($0 \leq x \leq 0.3$) cathode particles decreased from 144 to 136 mAh g^{-1} when the ratios of Co/Mn components were changed from 1/0 to 0.7/0.3.

Figs. 7 and 8 show the SEM photographs of the as-prepared and post-treated Mn-rich particles obtained by spray pyrolysis. The as-prepared Mn-rich particles had spherical shape, hollow and porous morphology irrespective of the contents of cobalt component. However, the precursor particle post-treated at tem-

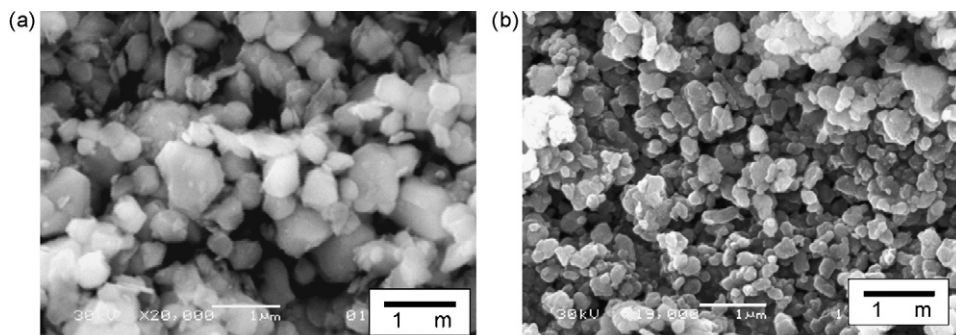


Fig. 4. SEM photographs of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ cathode particles: (a) $x = 0$; (b) $x = 0.3$.

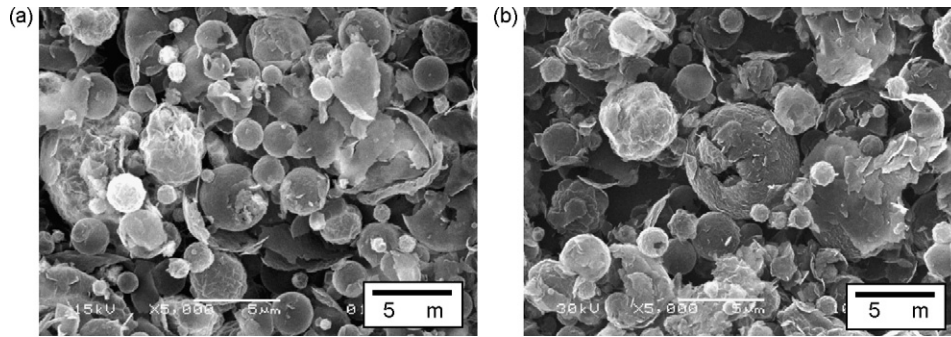


Fig. 7. SEM photographs of the as-prepared Mn-rich particles: (a) Mn/Co = 2/0; (b) Mn/Co = 1.8/0.2.

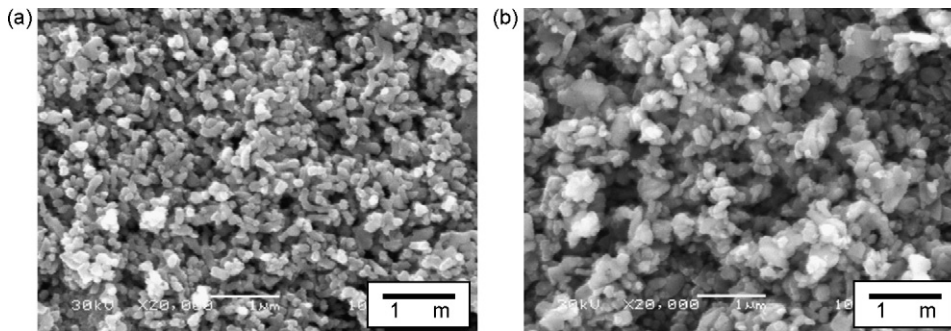


Fig. 8. SEM photographs of the post-treated Mn-rich particles: (a) Mn/Co = 2/0; (b) Mn/Co = 1.8/0.2.

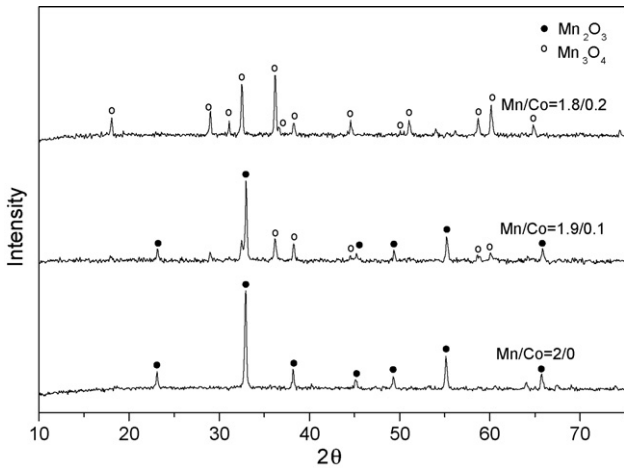


Fig. 9. XRD spectra of the post-treated Mn-rich particles.

perature of 800 °C had fine size and regular morphology. The post-treatment of the as-prepared particles with hollow and porous morphologies formed the fine-sized Mn-rich precursor particles with regular morphologies irrespective of the contents of cobalt component. The mean sizes of the Mn-rich particles were increased from 150 to 270 nm when the ratios of Mn/Co components were changed from 2/0 to 1.8/0.2.

Fig. 9 shows the XRD spectra of the Mn-rich particles post-treated at temperature of 800 °C. The precursor particles prepared from spray solution of manganese nitrate had pure crystal structure of Mn_2O_3 . The addition of cobalt component into the Mn-rich particles formed the new phase of Mn_3O_4 . The Mn-rich particles containing the high content of cobalt component had pure crystal structure of Mn_3O_4 . The Mn-rich precursor particles obtained by spray pyrolysis were reacted with LiOH by solid-state reaction method at temperature of 800 °C.

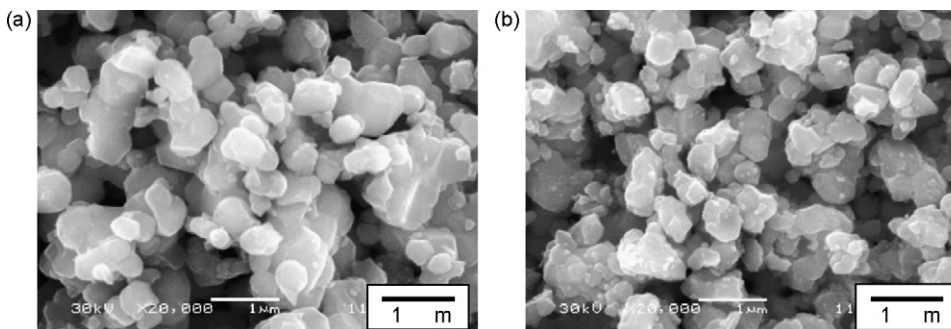


Fig. 10. SEM photographs of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ cathode particles: (a) $y = 0$; (b) $y = 0.2$.

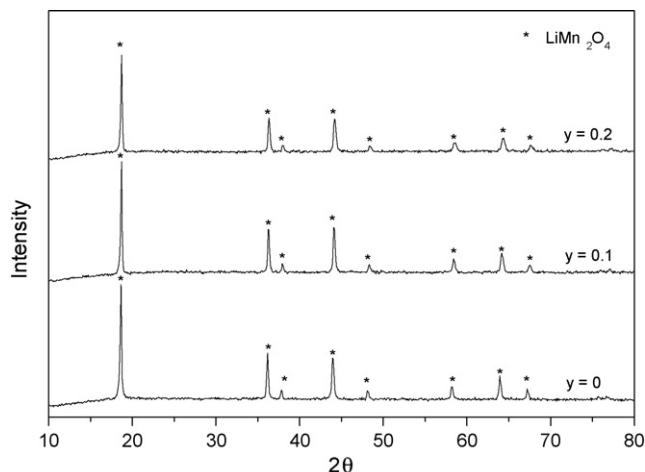


Fig. 11. XRD spectra of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ cathode particles.

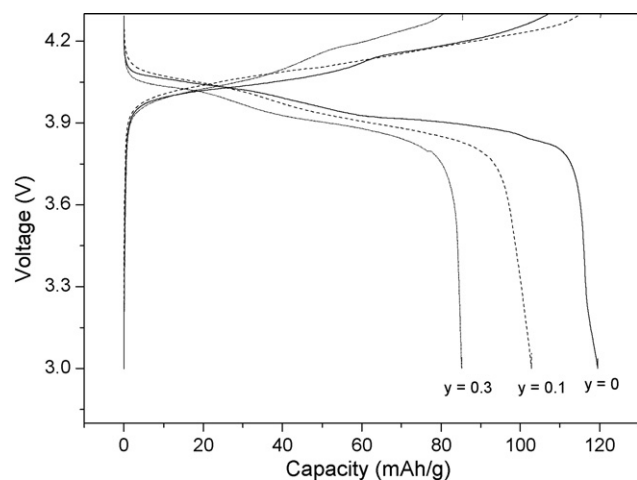


Fig. 12. Initial charge/discharge curves of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ cathode particles.

Fig. 10 shows the SEM photographs of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles. The $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles prepared by solid-state reaction method had fine size and regular morphologies irrespective of the contents of the cobalt component. The mean sizes of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles decreased from 650 to 460 nm when the ratios of Mn/Co components were changed from 2/0 to 1.8/0.2. Fig. 11 shows the XRD

spectra of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles. The prepared $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles had pure spinel crystal structure. However, the discharge capacities of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles decreased abruptly with increasing the contents of the cobalt component. Fig. 12 shows the initial charge/discharge curves of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles. The initial discharge capacities of the $\text{LiMn}_{2-y}\text{Co}_y\text{O}_4$ ($0 \leq y \leq 0.2$) cathode particles decreased from 119 to 86 mAh g^{-1} when the ratios of Mn/Co components were changed from 2/0 to 1.8/0.2.

4. Conclusions

The nano-sized precursor particles of cobalt and manganese components were prepared by spray pyrolysis from spray solutions containing citric acid and ethylene glycol. Nano-sized precursor particles with various ratios of cobalt and manganese components formed the Li–Co–Mn–O cathode particles with fine size and regular morphologies. The ratios of cobalt and manganese components affected the morphologies, crystallinities and discharge capacities of the Li–Co–Mn–O cathode particles prepared by solid-state reaction method. The addition of manganese component to the LiCoO_2 cathode particles decreased the mean sizes and mean crystallite sizes of the Li–Co–Mn–O cathode particles. However, the initial discharge capacities of the $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ decreased with increasing the content of the manganese component.

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