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Fine-sized $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ cathode particles prepared by spray pyrolysis from the polymeric precursor solutions

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Abstract

Fine-sized $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ cathode particles with high discharge capacities and good cycle properties were prepared by spray pyrolysis from the polymeric precursor solutions. The cathode particles obtained from the spray solution without polymeric precursors had irregular morphology and hardly aggregated morphology. On the other hand, the cathode particles obtained from the spray solution with citric acid and ethylene glycol had fine size and regular morphologies. The cathode particles obtained from the spray solution containing adequate amounts of citric acid and ethylene glycol had several hundreds nanometer and narrow size distribution. The maximum discharge capacity of the cathode particles was 218 mAh/g when the excess of lithium component added to the spray solution was 6 mol% of the stoichiometric amount to obtain the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles. The discharge capacities of the fine-sized $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles dropped from 218 to 213 mAh/g by the 50th cycle at a current density of 0.1 C.

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

1. Introduction

Commercial lithium ion batteries presently employ the $LiCoO_2$ cathodes, but only 50% of the lithium could be reversibly extracted form $LiCoO_2$, which corresponds to a practical capacity of 140 mAh/g. With an aim to increasing capacity, layered cathode materials such as $LiNiO_2$, Li(Ni, Co)O_2 or Li(Ni,Mn)O_2 are being intensively pursued [1,2]. Among them, $LiNiO_2$ with lower cost and higher energy density has aroused significant interest in recently years. However, it has been reported that the synthesis of stoichiometric $LiNiO_2$ is difficult because a high temperature treatment of $LiNiO_2$ results in the decomposition of $LiNiO_2$ into $Li_{1-x}Ni_{1+x}O_2$ ($x > 0$), which has a partially dis-ordered cations distribution at the lithium site [3]. To overcome this problem such as $LiNi_{1-y}Co_yO_2$ have provided promising results that the Co substitution for Ni stabilizes the two-dimensional layered structure and decreases the initial capacity loss with the improvement of cycle performance [4–6]. Nevertheless, these studies have also demonstrated that $LiNi_{1-y}Co_yO_2$ materials are yet not able to improve the thermal stability at charged state satisfactorily, which is a key issue of safety consideration for lithium ion batteries. It has been suggested and confirmed that the addition with another doping metal element (Al, Mn, Mg, Fe, Y, Sr, Ti, etc.) may further improve cycle performance and thermal stability of $LiNi_{1-x}Co_xO_2$ [7–11]. In recent, Mn-doped $LiNi_{1-x}Co_xO_2$ particles are considered as cathode material in high capacity lithium secondary battery. Manganese doping in $LiNi_{1-x}Co_xO_2$ particles brings about the increase in the unit cell dimensions of a and c. The partial substitution of Mn has a positive effect on the maintenance of lithium stoichiometry. Therefore, Mn-doped $LiNi_{1-x}Co_xO_2$ particles had good capacity and suppressed capacity loss upon cycling [11,12].

The electrochemical performance of the cathode in a lithium ion battery is strongly affected by the particle properties such as the particle morphology, the specific surface area, the crystalline and the composition of the materials [13–17]. With respect to the particle morphology, spherical particles with narrow size distributions show better electrochemical performance than particles with irregular morphologies because of the former high packing density [13–17]. Fine-sized cathode particles have

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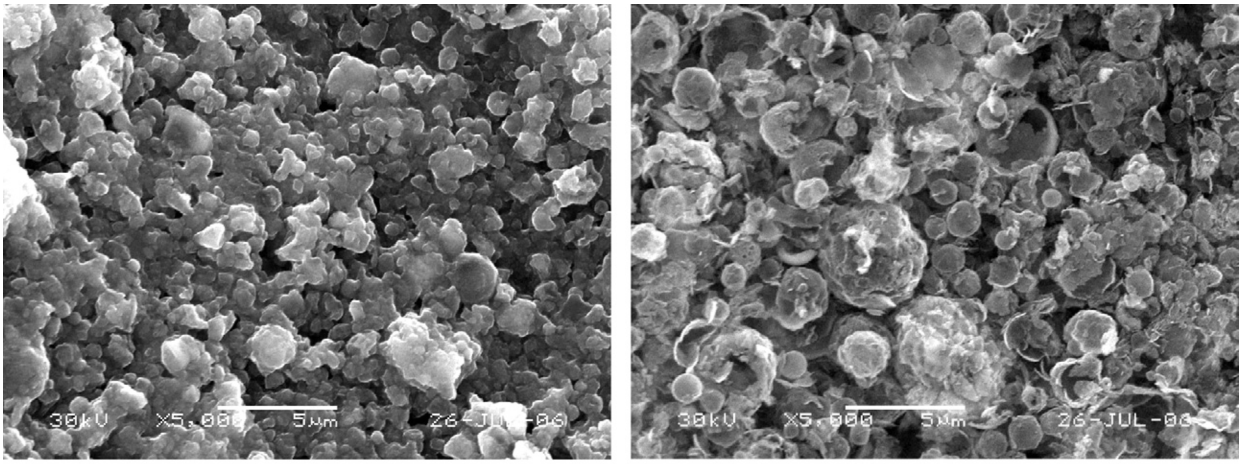
been intensively investigated to improve the capacity and power output of lithium ion batteries.

In this study, fine-sized $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ precursor particles were prepared by spray pyrolysis from the spray solutions which containing polymeric precursors. Citric acid and ethylene glycol were added to the spray solution as the polymeric precursors. The effects of polymeric precursors on the electrochemical properties, morphologies and mean sizes of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ cathode particles were investigated.

2. Experimental

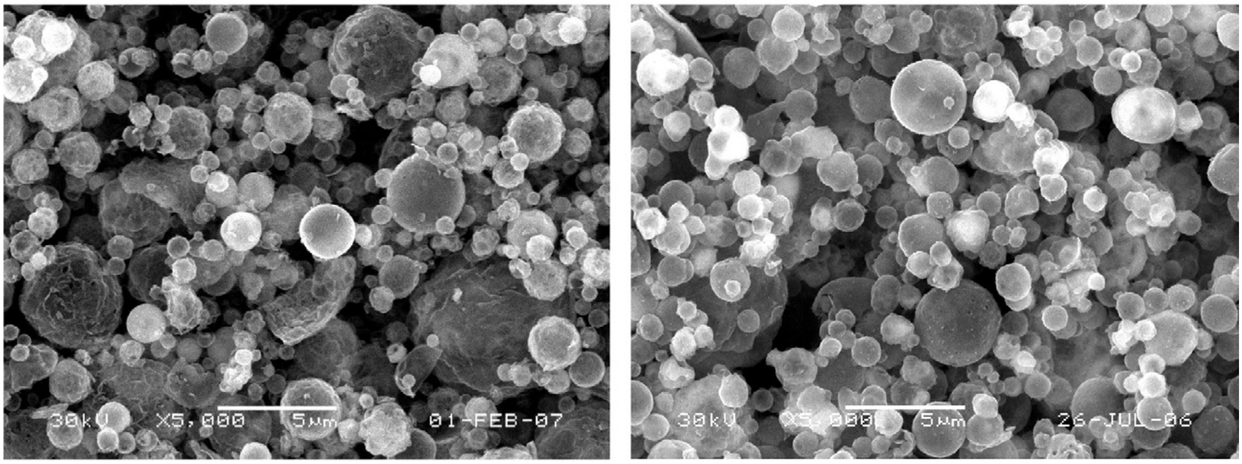
The spray pyrolysis system consists of a droplet generator, a quartz reactor, and a particle collector [18]. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets, which are carried into the high-temperature tubular reactor by a carrier gas. The droplets 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 40 l/min. The precursor solution was prepared by dissolving lithium carbonate [Li_2CO_3, Aldrich], 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 lithium, nickel, cobalt and manganese components was 0.3 M. The concentrations of citric acid and ethylene glycol were both changed from 0.1 to 1 M. The precursor particles obtained by spray pyrolysis were post-treated at various temperatures under oxygen atmosphere.

The crystal structures of the as-prepared and post-treated particles were investigated using X-ray diffractometry (XRD, RIGAKU DMAX-33). Measurement of the thermal properties of the precursor powders was performed on a thermo-analyzer (TG-DSC, Netzsch, STA409C, Germany) in the temperature range from 40 to 900 °C (10 °C/min). The morphological characteristics of the particles were investigated using scanning electron microscopy (SEM, JEOL JSM-6060) and transmission electron microscopy (TEM, FEI TECHNAI 300K). The charge/discharge capacities of the prepared $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles were measured. The cathode electrode was made of 12 mg of $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ compounds mixed with 4 mg



(a) No additive

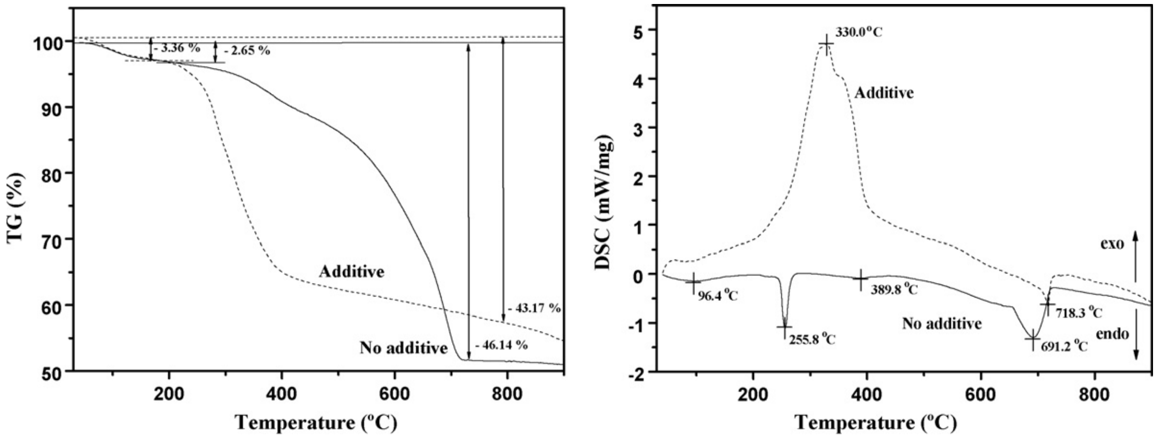
(c) 0.3 M CA and 0.3 M EG



(b) 0.1 M CA and 0.1 M EG

(d) 1 M CA and 1 M EG

Fig. 1. SEM photographs of the precursor particles obtained by spray pyrolysis.



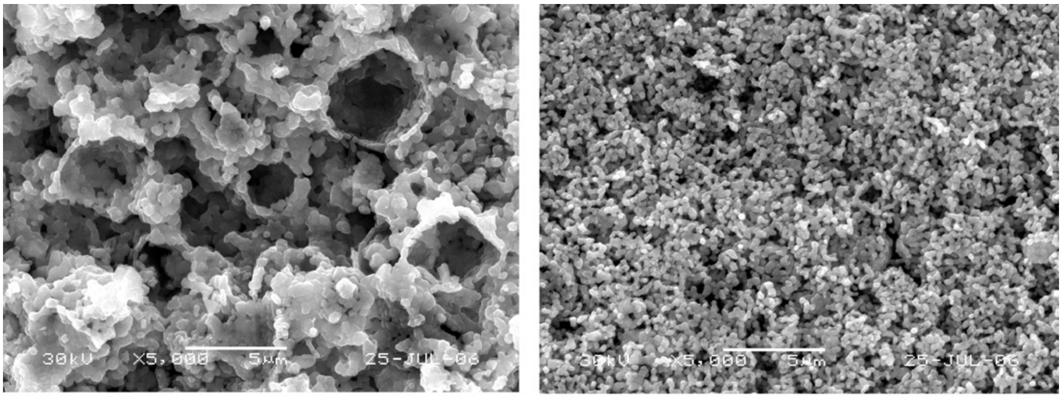
(a) TG (b) DSC

Fig. 2. TG/DSC curves of the precursor particles obtained by spray pyrolysis.

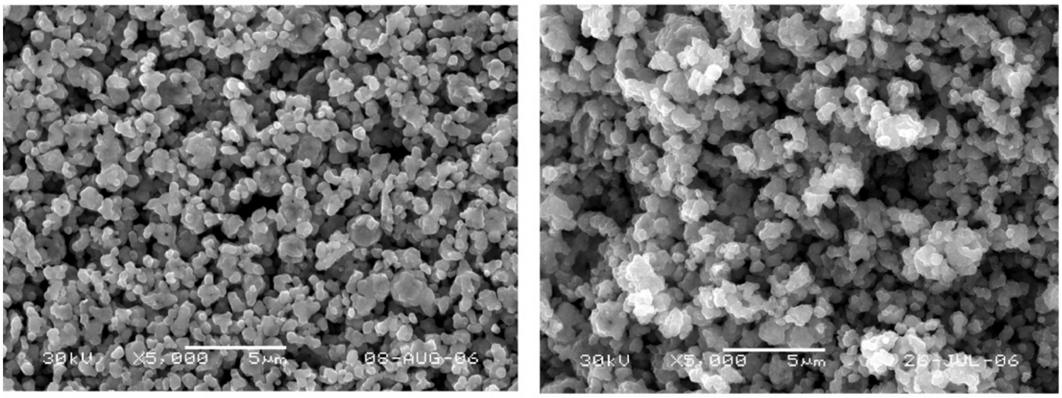
of a conductive binder (3.2 mg of teflonized acetylene black and 0.8 mg of graphite), which was pressed between two aluminum plates and then vacuum-dried overnight at 120 °C. The lithium metal and polypropylene film were used as the anode electrode and the separator, respectively. The electrolyte (TECHNO Semichem. Co.) was 1 M $LiPF_6$ in a 1:1 mixture by volume of EC/DMC. 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.

3. Results and discussion

The precursor particles were prepared by spray pyrolysis from the spray solutions with and without polymeric



(a) No additive (c) 0.3 M CA and 0.3 M EG



(b) 0.1 M CA and 0.1 M EG (d) 1 M CA and 1 M EG

Fig. 3. SEM photographs of the post-treated $Li(Ni_{0.8}Co_{0.15}Mn_{0.05})O_2$ cathode particles.

precursors. The morphology of the precursor particles were affected by the types of spray solution as shown in Fig. 1. The precursor particles obtained from the spray solution without polymeric precursors had non-spherical shape and aggregated morphology. On the other hand, the precursor particles obtained from the spray solutions with citric acid and ethylene glycol as polymeric precursors had spherical shape and several microns size. The thermal analyses of the precursor particles obtained by spray pyrolysis from the spray solutions with and without polymeric precursors are shown in Fig. 2. The TG curves of the precursor particles clearly show that there are two weight losses at temperatures below 900 °C. The first pronounced weight loss at temperatures below 200 °C is related to the evaporation of water molecules adsorbed to the precursor particles obtained from the spray solutions with and without polymeric precursors. However, the second weight losses were different in the precursor particles obtained from the spray solutions with and without polymeric precursors. DSC curve of the precursor particles obtained from the spray solution without polymeric precursors showed endothermic peak with high intensity at 256 °C. The endothermic peak at 256 °C was due to the decomposition of reactants. On the other hand, the endothermic peak at 256 °C in the DSC curve of the precursor particles obtained from the spray solution with polymeric precursors was not observed. The complete decomposition of the reactants occurred in the spray pyrolysis process using spray solution with polymeric precursors. The heat evolved from the decomposition of polymeric precursors inside the particles increased the temperature of the precursor particles. Therefore, complete decomposition of the reactants occurred at the preparation condition of short residence time of the particles inside the hot wall tubular reactor. The exothermic peak of the precursor particles obtained from the spray solution with polymeric precursors at 330 °C was appeared by decomposition of carbon component contained inside the precursor particles. In this work, the precursor particles were prepared by spray pyrolysis at high flow rate of carrier gas of 40 l/min. So, the residence time of the particles inside the hot wall reactor was short as 0.5 s. Therefore, the precursor particles obtained from the spray solution without polymeric precursors had non-spherical shape and aggregated morphology because of incomplete decomposition of the reactants inside the hot wall reactor. On the other hand, the precursor particles obtained from the spray solution with citric acid and ethylene glycol had spherical shape at the same preparation conditions by complete decompositions of reactants. The sphericity of the precursor particles improved with increasing the concentrations of citric acid and ethylene glycol added to the spray solutions.

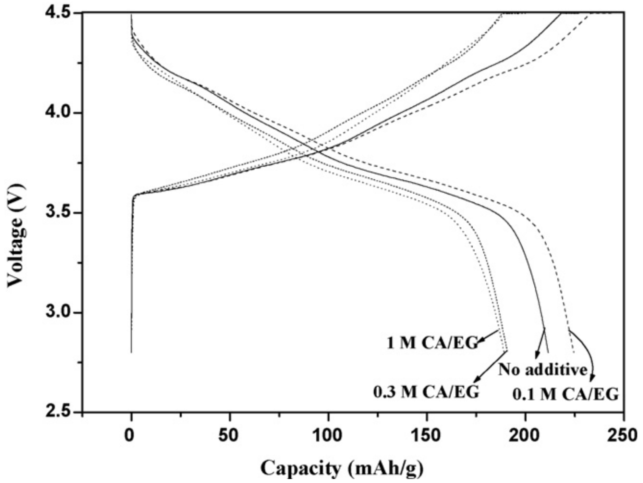


Fig. 5. Initial charge/discharge curves of the Li($Ni_{0.8}Co_{0.15}Mn_{0.05}$)$O_2$ cathode particles.

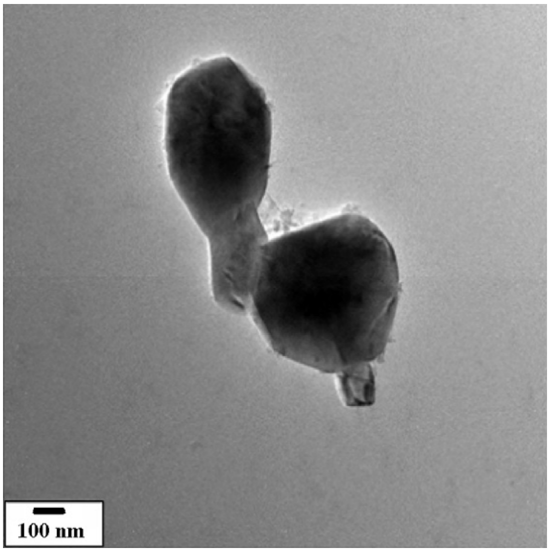


Fig. 4. TEM photograph of the post-treatment $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ cathode particles.

Fig. 3 shows the SEM photographs of the post-treated $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles. The precursor particles obtained from the spray solutions with and without polymeric precursors were post-treated at temperature of 800 °C under oxygen atmosphere. An excess of lithium component [Li/(Ni + Co + Mn) = 1.03] was used to compensate lithium loss during the preparation and post-treatment processes. The

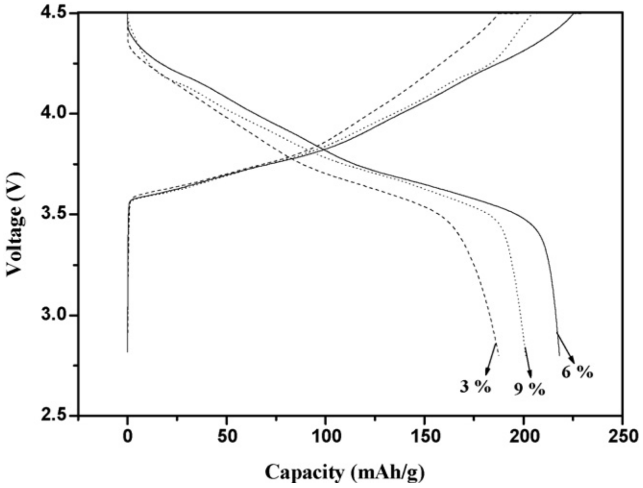
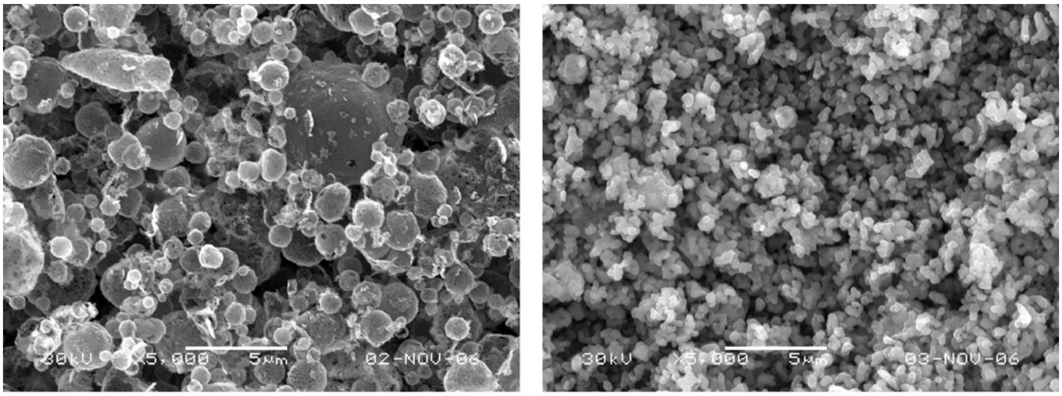


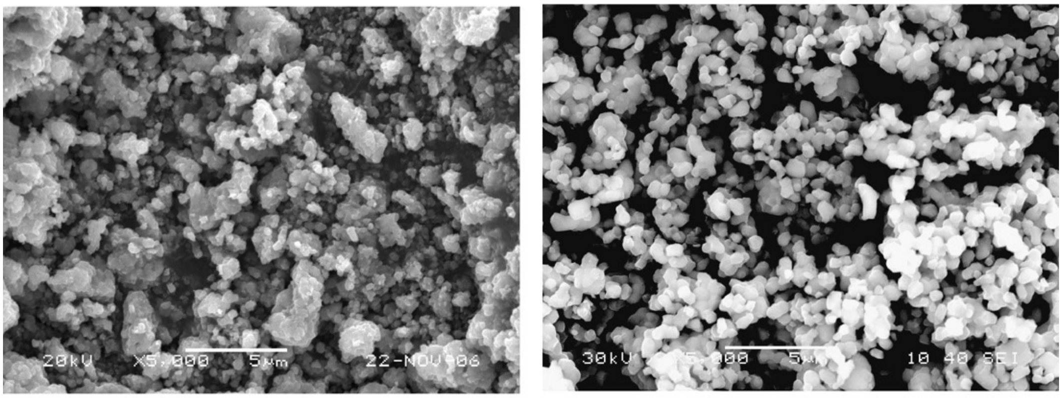
Fig. 6. Initial charge/discharge curves of the Li($Ni_{0.8}Co_{0.15}Mn_{0.05}$)$O_2$ cathode particles with excess of lithium components.

cathode particles obtained from the spray solution without polymeric precursors had irregular morphology and hardly aggregated morphology. On the other hand, the cathode particles obtained from the spray solution with polymeric precursors had regular morphologies. The mean sizes of the cathode particles were affected by the concentrations of citric acid and ethylene glycol added to the spray solutions. The cathode particles obtained from the spray solutions which containing low and high amounts of citric acid and ethylene glycol had micron sizes. On the other hand, the cathode particles obtained from the spray solution containing adequate amounts of citric acid and ethylene glycol had several hundreds nanometer. Fig. 4 shows the TEM photograph of the fine-sized $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ cathode particles as shown in Fig. 3(b). The mean size of the cathode particles with well crystallized structure was 300 nm.

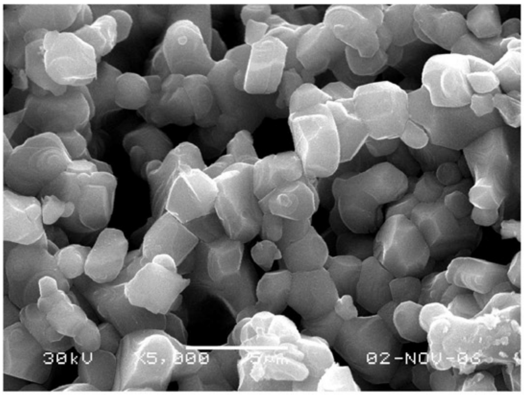
Fig. 5 shows the initial charge/discharge capacities of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles. The initial discharge capacity of the cathode particles obtained from the spray solution without polymeric precursors was high as 211 mAh/g at a constant current density of 0.1 C. However, the initial discharge capacities of the cathode particles obtained from the spray



(a) A 700 (c) A800



(b) A750 (d) A850



(e) A 900

Fig. 7. SEM photographs of the post-treated $Li(Ni_{0.8}Co_{0.15}Mn_{0.05})O_2$ cathode particles post-treated at different temperature.

solution with polymeric precursors were affected by the concentrations of citric acid and ethylene glycol added to the spray solution. The maximum discharge capacity of the cathode particles obtained from the spray solution with low concentrations of citric acid and ethylene glycol was 224 mAh/g. The discharge capacities of the cathode particles decreased with increasing the amounts of citric acid and ethylene glycol added to the spray solutions. The discharge capacities of the cathode particles obtained from the spray solutions with high concentrations of citric acid and ethylene glycol had lower discharge capacities than that of the cathode particles obtained from the spray solution without polymeric precursors. The high evaporation rate of lithium component decreased the discharge capacities of the cathode particles obtained from the spray solutions with high concentrations of polymeric precursors. In the spray pyrolysis process, the heat evolved from the decompositions of citric and ethylene glycol evaporated the volatile lithium component.

The concentrations of lithium carbonate added to the spray solution were optimized to improve the capacities of the fine-sized cathode particles obtained from the spray solutions with polymeric precursors. Fig. 6 shows the initial charge/discharge capacities of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles obtained from the spray solutions with excess of lithium components. The concentrations of citric acid and ethylene glycol added to the spray solution were each 0.3 M. The precursor particles obtained by spray pyrolysis were post-treated at temperature of 800 °C for 3 h. The maximum discharge capacity of the cathode particles was 218 mAh/g when the excess of lithium component added to the spray solution was 6 mol% of the stoichiometric amount to obtain the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles.

Fig. 7 shows the SEM photographs of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles post-treated at different temperatures. An excess of lithium component [Li/(Ni + Co + Mn) = 1.06] was used to compensate for lithium loss during the preparation and post-treatment processes. The post-treated particles at temperature of 700 °C had spherical shape and several micron sizes. The morphology and mean size of the precursor particles obtained by spray pyrolysis maintained at post-treatment temperature of 700 °C. On the other hand, the spherical shape of the precursor particles disappeared after post-treatment at temperatures above 750 °C. Fine-sized $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles were obtained at post-treatment temperature of 800 °C. At post-treatment temperature of 900 °C, the cathode particles had large size and aggregated morphology. In Figs. 3(c) and 7(c), the excess amount of lithium component affected the mean size of the cathode particles. The mean size of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles increased with increasing the excess amount of lithium component. Fig. 8 shows the XRD spectra of the cathode particles post-treated at different temperatures. The separations of 0 1 8/1 1 0 peaks in the XRD spectra, which represents the layered character of structure and good electrochemical properties, appeared in the prepared samples. The mean crystallite sizes of the cathode particles increased from 20 to 55 nm when the post-treatment temperatures were changed from 700 to 900 °C. The effects

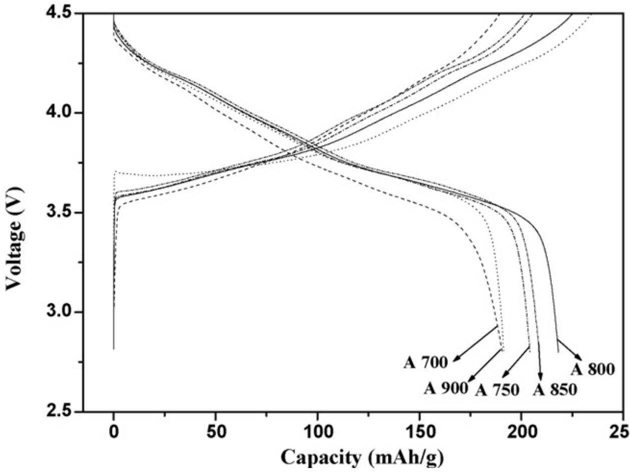


Fig. 9. Initial charge/discharge curves of the $Li(Ni_{0.8}Co_{0.15}Mn_{0.05})O_2$ cathode particles post-treated at different temperature.

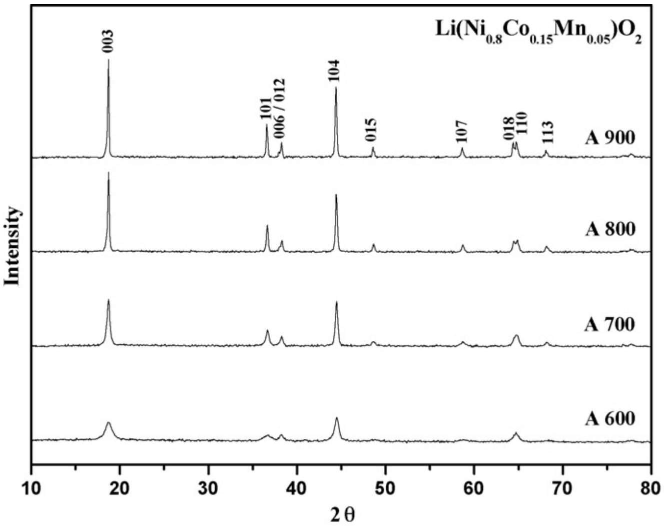


Fig. 8. XRD spectra of the $Li(Ni_{0.8}Co_{0.15}Mn_{0.05})O_2$ cathode particles post-treated at different temperature.

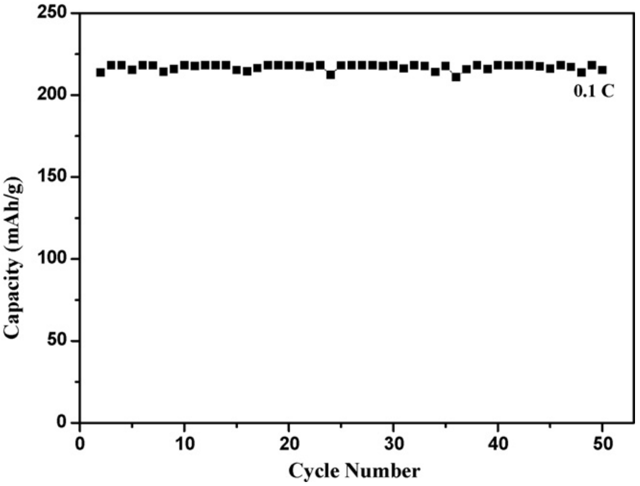


Fig. 10. Cycling performances of the $Li(Ni_{0.8}Co_{0.15}Mn_{0.05})O_2$ cathode particles operated in voltage of 2.8–4.5 V at a constant current density of 0.1 C.

of post-treatment temperatures on the initial discharge capacities of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles are shown in Fig. 9. The initial discharge capacities of the cathode particles were changed from 190 to 218 mAh/g when the post-treatment temperatures were changed from 700 to 900 °C. The maximum initial discharge capacity of the cathode particles was obtained at post-treatment temperature of 800 °C. Fig. 10 shows the cycle properties at a current density of 0.1 C of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles obtained at post-treatment temperature of 800 °C. The fine-sized $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles prepared by spray pyrolysis had good cycle properties. The discharge capacity of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ particles decreases from 218 to 213 mAh/g after 50 cycles with capacity retention of 97.7% at a current density of 0.1 C.

4. Conclusions

Ni-rich cathode particles were prepared by spray pyrolysis from the spray solutions with and without polymeric precursors. The effects of citric acid and ethylene glycol added to the spray solutions as polymeric precursors on the electrochemical properties, morphologies and mean sizes of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ cathode particles were investigated. Citric acid and ethylene glycol affected the morphologies of the precursor and cathode particles by evolving heat and gas in the spray pyrolysis. The capacities of the cathode particles were also affected by the concentrations of citric acid and ethylene glycol. The adequate amounts of citric acid and ethylene glycol added to the spray solution to prepare the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ cathode particles with fine size, regular morphology, high discharge capacity, and good cycle property were each 0.3 M.

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