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The characteristics of Ni–Co–Mn–O precursor and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders prepared by spray pyrolysis

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Abstract

Ni–Co–Mn–O precursor powders with spherical shape and dense structure were prepared by spray pyrolysis from a spray solution containing a drying control chemical additive (DCCA) and polymeric precursors. In contrast, the Ni–Co–Mn–O precursor powders obtained from a spray solution without additives had a hollow and porous morphology. Ni–Co–Mn–O precursor powders with a spherical shape and dense structure yielded $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders with a spherical shape and fine size by means of a solid-state reaction with lithium hydroxide. The mean size of the spherical cathode powder was 1.1 μm. The discharge capacity of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders with spherical shape and filled morphology was 195 mA h g^{-1} at a current density of 0.1 C. The discharge capacities of the cathode powders with spherical shape and filled morphology at 55 °C decreased from 183 to 154 mA h g^{-1} by the 30th cycle at a current density of 0.5 C.

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

1. Introduction

The electrochemical performance of a cathode in a secondary lithium battery is strongly affected by powder properties such as the powder morphology, specific surface area, crystallinity, and material composition [1–7]. With respect to the powder morphology, spherical powders with narrow size distributions exhibit a better electrochemical performance than powders with irregular morphologies because of their high packing density [4–9]. Fine-sized cathode powders have been extensively investigated with a view to improving the capacity and power output of secondary lithium batteries.

A combined process involving liquid solution and solid-state reaction methods was developed to produce cathode powders with spherical shape and large size [10,11]. Precursor powders with spherical shape were prepared by liquid solution methods such as coprecipitation. Precursor powders with spherical shape and dense morphology formed spherical-shaped cathode powders by means of a solid-state reaction with lithium components. A combined process involving a gas-phase reaction and solid-state reaction was also studied to produce these cathode powders [5,12,13]. The precursor powders obtained by spray pyrolysis—a type of gas-phase reaction—had spherical shape and fine size. However, the characteristics of the cathode powders obtained by the solid-state reaction method were affected by the morphologies of the precursor powder obtained by spray pyrolysis.

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders have been extensively studied from the viewpoint of applications as a cathode material for lithium ion batteries because of their high capacity, high working voltage, and high stability [4,5,14–17]. In a previous study, Ni–Co–Mn–O precursor powders with spherical shape and fine size were prepared by ultrasonic spray pyrolysis [5]. On the other hand, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders formed by solid-state reaction method using Ni–Co–Mn–O precursor powders obtained by spray pyrolysis had non-spherical shape. The spherical shape of the precursor powders disappeared after solid-state reaction at high temperature. In this study, the precursor powders of Ni–Co–Mn–O components were prepared by spray pyrolysis. The precursor powders prepared by the conventional spray pyrolysis process using aqueous spray solutions had a hollow and porous structure because of fast drying and decomposition rates of droplets or powders inside the hot wall reactor. Therefore, in

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this study, a drying control chemical additive (DCCA) and polymeric precursors were applied to a spray solution of nickel, cobalt, and manganese components in order to improve the morphologies of the precursor powders obtained by spray pyrolysis. $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders with spherical shape and fine size were prepared by a solid-state reaction method using the Ni–Co–Mn–O precursor powders obtained by spray pyrolysis. The charge/discharge capacities of the prepared $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders were investigated.

2. Experimental

The spray pyrolysis system comprises a droplet generator, quartz reactor, and powder collector [18]. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets; these are carried into a high-temperature tubular reactor by a carrier gas. The droplets and powders 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 10 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 the nickel, cobalt, and manganese components was 0.5 M. DCCA, citric acid, and ethylene glycol were added to the spray solution to control the morphology of the precursor powders. The concentrations of *N*,*N*-dimethylformamide used as DCCA were changed from 0.3 to 1.5 M. The concentrations of citric acid and ethylene glycol were both 0.1 M. The Ni–Co–Mn–O precursor powders obtained by spray pyrolysis were reacted with lithium hydroxide by the solid-state reaction method. The mixture of precursor powders and lithium hydroxide was post-treated at a temperature of 800 °C for 3 h under air atmosphere. The lithium component added to the spray solution reacted with the precursor powders exceeded the stoichiometric amount by 3% so that $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ could be obtained.

The crystal structures of the as-prepared and post-treated powders were investigated using X-ray diffractometry (XRD, RIGAKU DMAX-33) using Cu Kα radiation at room temperature in the 2θ range 10–80°. The morphological characteristics of the powders were investigated using scanning electron microscopy (SEM, JEOL JSM-6060) and high-resolution transmission electron microscopy (TEM, FEI, TECHNAI 300K). The compositions of the powders were analyzed by using energy dispersive X-ray (EDX).

The pore structures of the precursor powders were measured using the mercury porosimetry (AutoPore4 9500). The charge/discharge capacities of the prepared $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders were measured. The cathode electrode was made of

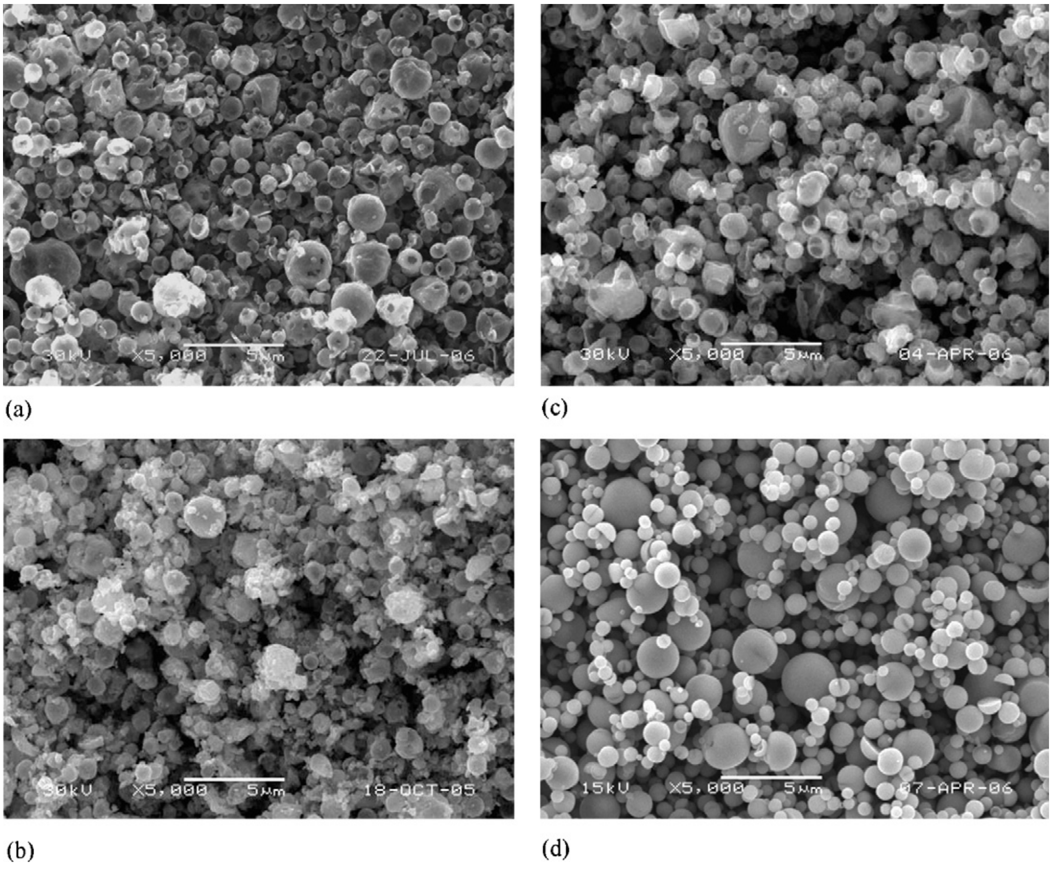

Fig. 1. SEM photographs of the as-prepared powders. (a) Aqueous solution. (b) 0.1 M CA/EG. (c) 0.7 M DCCA. (d) 0.1 M CA/EG, 0.7 M DCCA.

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) that 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 and the separator, respectively. The electrolyte used (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 initial charge/discharge capacities 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. The cycle performances of the cathode powders at an elevated temperature of 55 °C were measured at a constant current density of 0.5 C.

3. Results and discussion

The Ni–Co–Mn–O precursor powders were prepared by spray pyrolysis from spray solutions with and without additives. The effects of polymeric precursors and DCCA on the morphologies of the as-prepared and post-treated precursor powders were investigated. The as-prepared powders obtained by spray pyrolysis from the spray solutions with citric acid and ethylene glycol used as polymeric precursors had residual carbon components within the powders. Therefore, the as-prepared powders obtained by spray pyrolysis were post-treated at a temperature of 800 °C for 3 h for the removal of carbon components. The post-treatment of the as-prepared powders was also effective in clarifying the crystal structures of the components comprising the precursor powders. In this study, the post-treated powders were defined as the precursor powders. Fig. 1 shows SEM photographs of the as-prepared powders obtained by spray pyrolysis. The as-prepared powders obtained from the spray solution without additives had a size of the order of microns, in addition to a spherical shape and hollow morphology. The addition of citric acid and ethylene glycol to the spray solution slightly improved the structure of the as-prepared powders. The as-prepared powders formed from the polymeric precursor solution had a more filled structure than those formed from the spray solution without additives. The as-prepared powders obtained from the spray solution with DCCA also had a hollow morphology. The addition of DCCA to the spray solutions with polymeric precursors improved the morphological characteristics of the as-prepared powders. The concentrations of the DCCA were varied from 0.3 to 1.5 M. The as-prepared powders obtained from the spray solutions with polymeric precursors and DCCA had a spherical shape and filled morphology irrespective of the concentrations of DCCA. The filled inner structure of the as-prepared powders could be estimated from the fractured powders. The as-prepared powders obtained from the spray solutions with polymeric precursors and DCCA had a more smooth surface and filled morphology than those obtained from the spray solutions without additives. Fig. 2 shows SEM photograph of the precursor powders. The as-prepared powders (Fig. 1(d)) were post-treated at a temperature of 800 °C. The precursor powders formed from the spray solution without additives had a hollow and porous structure. However, the precursor powders obtained from the spray solutions with polymeric precursors and DCCA had a spherical shape and filled morphology as shown in Fig. 2. The mean size of the precursor powders (Fig. 2) as measured from the SEM photograph was 1.1 μm.

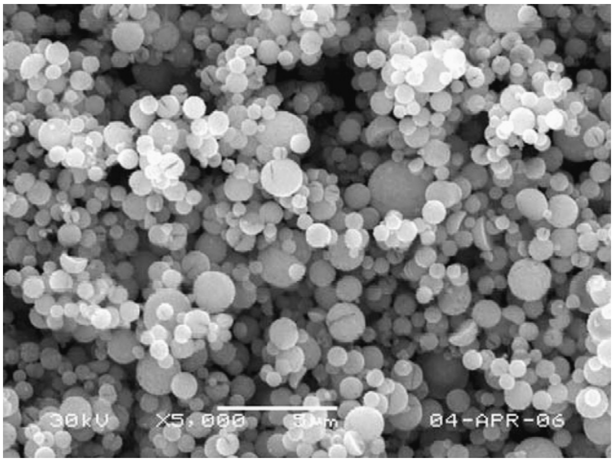

Fig. 2. SEM photograph of the precursor powders.

Fig. 3 shows the pore size distributions, and cumulative intrusion and extrusion volumes of the precursor powders obtained from the spray solutions with and without additives. The concentrations of citric acid, ethylene glycol, and DCCA were 0.1, 0.1, and 0.7 M, respectively. The precursor powders obtained from the aqueous spray solution had larger pore volumes of meso and macro pores than those obtained from the spray solution with additives. Fig. 3(b) shows the cumulative intrusion and extrusion volumes measured by mercury porosimetry. The total pore volume of the precursor powders obtained from the spray solutions with and without additives were 0.9 and 1.1 ml/g, respectively.

The precursor powders with hollow and porous structures that were prepared from the post-treatment of the as-prepared powders obtained from the aqueous spray solution formed

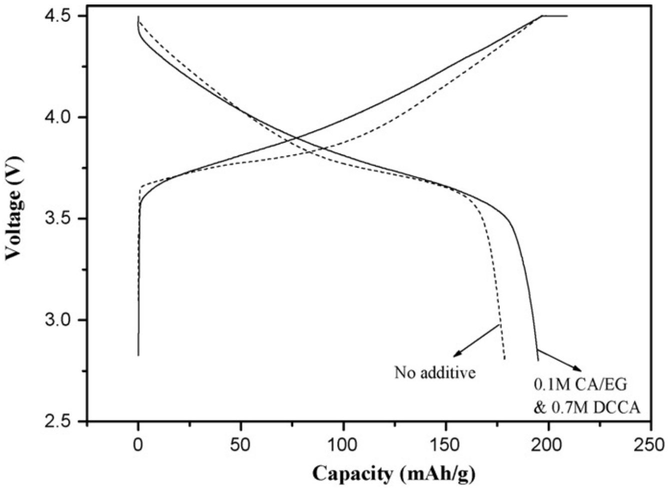

Fig. 3. The pore size distributions and cumulative pore volumes of the precursor powders. (a) Pore size distributions. (b) Cumulative pore volumes of intrusion and extrusion.

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders with a non-spherical shape and fractured structure after the solid-state reaction with lithium hydroxide, as shown in Fig. 4(a). Precursor powders with a hollow morphology formed cathode powders with a hollow morphology and fractured structure. However, the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders (Fig. 4(b)) prepared from the precursor powders with spherical shape and filled morphologies, shown in Fig. 2, had spherical shapes and filled morphologies. A TEM photograph of the cathode powders (Fig. 4(b)) shown in Fig. 5 shows the filled internal structure. Therefore, controlling the morphology of the precursor powders obtained by spray pyrolysis was of importance in the preparation of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders with fine size and regular morphology by the solid-state reaction with lithium hydroxide. The mean size of the cathode powder (Fig. 4(b)) was 1.1 μm.

The compositions and crystal structures of the as-prepared, precursor and cathode powders were investigated from the EDX and XRD spectra. The as-prepared and precursor powders were formed from the spray solutions with DCCA and polymeric precursors. The concentration of DCCA was 0.7 M. In the EDX spectra, the composition ratios of the nickel, cobalt, and manganese components were analyzed. Table 1 shows the compositions of the powders measured from the EDX spectra. The composition ratios of the nickel, cobalt, and manganese components were maintained in the as-prepared, precursor, and cathode powders. Fig. 6 shows the XRD spectra of the as-prepared, precursor, and cathode powders. In the XRD spectra, the as-prepared and precursor powders exhibited sharp crystal structures of Co_3O_4. The crystal structures of the nickel and manganese components could not be suitably observed in the XRD spectra of the as-prepared and precursor powders. In this study, the Ni–Co–Mn–O precursor powders were considered as mixtures of Mn_2O_3, Co_3O_4, and NiO [19]. The prepared cathode powders had pure phases of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. The mean crystallite size of the cathode powders was calculated by Scherrer's equation to be 33 nm.

The charge/discharge capacities of the cathode powders prepared from the precursor powders with different morphologies were investigated. Fig. 7 shows the initial charge/

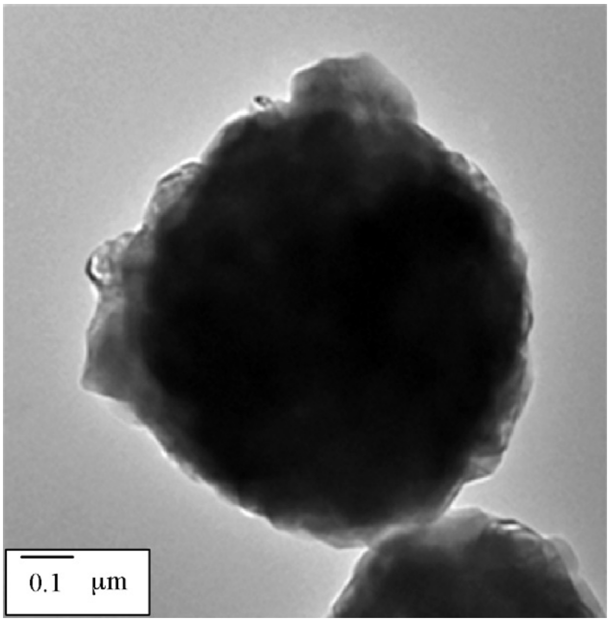

Fig. 5. TEM photograph of the cathode powders obtained from the spray solution with additives.

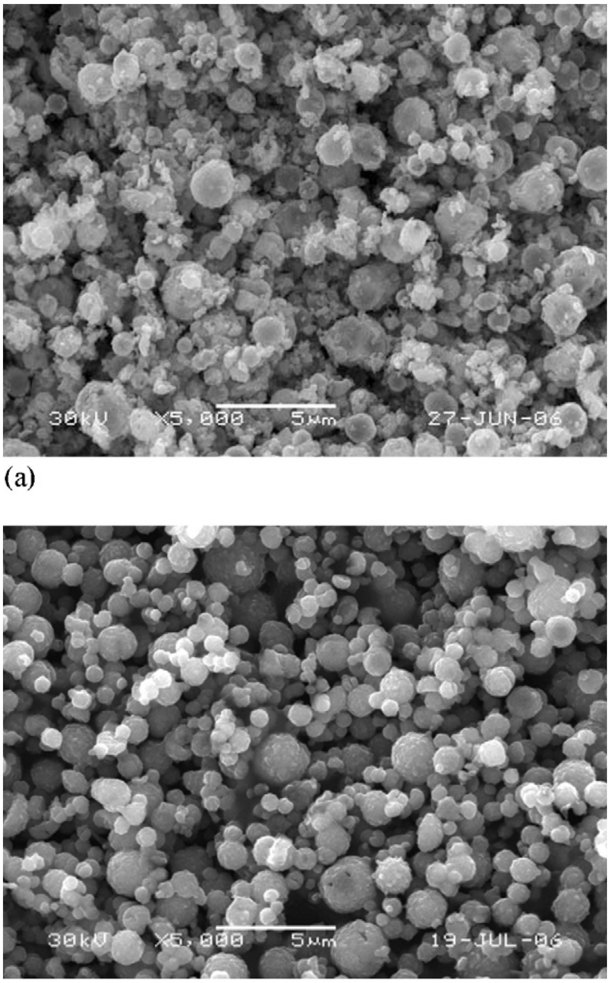

Fig. 4. SEM photographs of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders. (a) Aqueous solution. (b) 0.1 M CA/EG, 0.7 M DCC.

Table 1
Compositions of the as-prepared, precursor and cathode powders

Samples	Composition (Ni:Co:Mn atomic ratios)	Average of composition
As-prepared	(1.11:1.06:1.00) (1.05:1.00:1.01) (1.13:1.09:1.00)	1.10:1.05:1.00
Precursor	(1.05:1.01:1.00) (1.05:1.00:1.03) (1.04:1.01:1.00)	1.05:1.00:1.01
Cathode	(1.04:1.02:1.00) (1.03:1.00:1.01) (1.06:1.00:1.01)	1.04:1.00:1.00

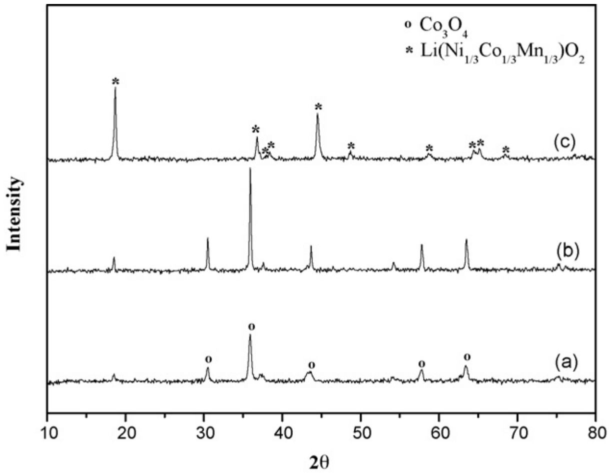

Fig. 6. XRD spectra of the powders: (a) as-prepared, (b) precursor, (c) cathode.

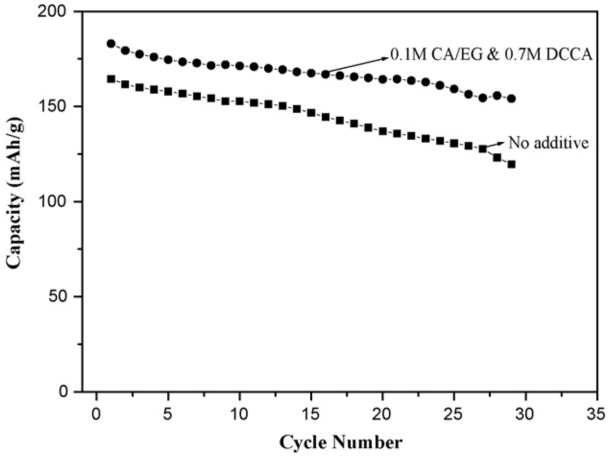

Fig. 8. Cycling performances at elevated temperatures (55 °C) of the cathode powders prepared from spray solution with and without additives at a constant current density of 0.5 C.

discharge curves of the $Li/Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cells cycled at 2.8–4.5 V at a constant current density of 0.1 C. The initial discharge capacity of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders prepared from the precursor powders with hollow morphology, which were obtained from the spray solution without additives, was 179 mA h g^{-1}. However, the initial discharge capacity of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders prepared from the precursor powders with filled morphology, which were obtained from the spray solution with citric acid, ethylene glycol, and DCCA, was 195 mA h g^{-1}. The prepared cathode powders had similar discharge capacity to those of the powders prepared by various preparation methods [5,13,15]. The concentrations of DCCA added to the spray solutions to control the morphologies of the precursor powders did not affect the initial discharge capacities of the cathode powders prepared by the solid-state reaction with lithium hydroxide.

The cycle performances of the cathode powders with hollow and filled morphologies at an elevated temperature of 55 °C are shown in Fig. 8. The discharge capacities of the cathode powders with filled morphology decreased from 183 to 154 mA h g^{-1} by the 30th cycle at a current density of 0.5 C. On the other hand, the discharge capacities of the cathode powders with hollow morphology decreased from 164 to 120 mA h g^{-1} by the 30th cycle at a current density of 0.5 °C.

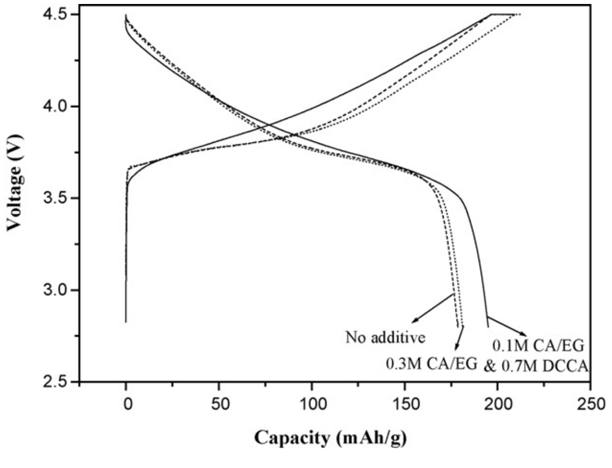

Fig. 7. Charge/discharge curves of the cathode powders prepared from spray solution with and without additives at constant current density of 0.1 C.

4. Conclusions

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders with spherical shape and filled morphology were prepared by the solid-state reaction method using precursor powders with controlled morphology. The morphology of the Ni–Co–Mn–O precursor powders obtained by spray pyrolysis affected the morphology of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders. The precursor powders with hollow and porous structures formed $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders with hollow and fractured morphology. The precursor powders with spherical shape and dense structure, which were obtained from the spray solutions with DCCA and polymeric precursors, formed $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders with spherical shape and filled morphology. The prepared $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powders had good charge/discharge capacities.

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