

Short communication

# Fine-sized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ cathode powders prepared by combined process of gas-phase reaction and solid-state reaction methods

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## Abstract

The Ni-rich precursor powders with spherical shape and filled morphologies were prepared by spray pyrolysis from the spray solution with citric acid, ethylene glycol and a drying control chemical additive. The precursor powders with controlled morphologies formed the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders with spherical shape and fine size by solid-state reaction with lithium hydroxide. However, the cathode powders prepared from the spray solution without additives had irregular morphologies and were large in size. The precursor powders with hollow and porous morphologies formed cathode powders with irregular and aggregated morphologies. The composition ratios of the nickel, cobalt and manganese components were maintained in the as-prepared, precursor and cathode powders. The initial discharge capacity of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders with spherical shape and fine size tested at a temperature of 55 °C under a constant current density of 0.5 C was 215  $\text{mAh g}^{-1}$ . The discharge capacity of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders decreased to 81% of the initial value after 30 cycles.

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**Keywords:** Spray pyrolysis; Cathode powder; Solid-state reaction

## 1. Introduction

$\text{LiNiO}_2$  has been studied extensively as a cathode material because of its higher specific capacity, lower cost and because it is less toxic than  $\text{LiCoO}_2$  [1]. However, it has several problems, such as a difficult synthesis, low thermal stability, and a poor cycle life in the charged state [2,3]. To overcome these problems, a small substitution with other elements such as Co, Mn, Fe, Al, Ti and Mg for the nickel component was studied [4–6]. Recently, it has been reported that multiple substitution with each element brings some peculiar advantage on reversibility, capacity fading and thermal stability of the Ni-rich cathode powders [7,8].

The electrochemical performance of the cathode in a secondary lithium battery is strongly affected by the powder properties, such as the powder morphology, the specific surface area, the crystallinity and the composition of the materials [9–12]. With respect to the powder morphology, spherical pow-

ders with narrow size distributions show better electrochemical performance than powders with irregular morphologies because of the former high packing density [9–12]. Fine-sized cathode powders have been intensively investigated to improve the capacity and power output of secondary lithium batteries.

The combined processes of gas-phase reaction and solid-state reaction methods were studied to produce the cathode powders [13,14]. The precursor powders obtained by spray pyrolysis, which is one 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 powders obtained by spray pyrolysis. The precursor powders prepared by conventional spray pyrolysis process using aqueous spray solutions had hollow and porous structure.

In this study, the Ni-rich precursor powders were prepared by spray pyrolysis. Drying Control Chemical Additive (DCCA) and polymeric precursors were added into the spray solution to improve the morphologies of the Ni-rich precursor powders obtained by spray pyrolysis. The characteristics of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders prepared from the pre-

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cursor powders with spherical shape and filled morphologies were investigated.

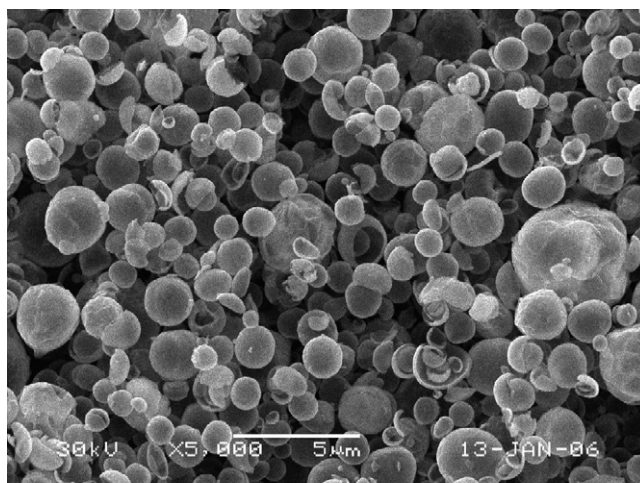
## 2. Experimental

The spray pyrolysis system consists of a droplet generator, a quartz reactor, and a powder collector [15]. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large quantity of droplets, which were carried into the 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<sup>-1</sup>. The precursor solution was prepared by dissolving a stoichiometric ratio of 0.8:0.15:0.05 nickel nitrate hexahydrate [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Aldrich], cobalt nitrate hexahydrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Aldrich] and manganese acetate tetrahydrate [Mn(CH<sub>3</sub>COO)<sub>4</sub>·4H<sub>2</sub>O, Aldrich] salts in distilled water. The overall solution concentration of nickel, cobalt and manganese components was 1 M. DCCA, citric acid and ethylene glycol were added into 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 M. The concentrations of citric acid and ethylene glycol were both 0.1 M. The Ni-rich precursor powders obtained by spray pyrolysis were reacted with lithium hydroxide by the solid-state reaction method. The mixture of the precursor powders and lithium hydroxide were post-treated at a temperature of 800 °C for 3 h under an oxygen atmosphere.

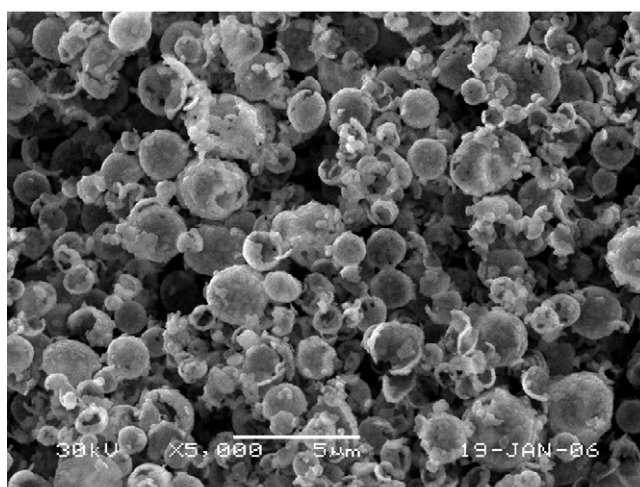
The crystal structures of the as-prepared and post-treated powders were investigated using X-ray diffractometry (XRD, RIGAKU DMAX-33) using Cu K $\alpha$  radiation at room temperatures in the 2 $\theta$  range 10–80°. The morphological characteristics of the powders were investigated using scanning electron microscopy (SEM, JEOL JSM-6060) and a high-resolution transmission electron microscope (TEM, FEI, TECHNAI 300 K). The charge/discharge capacities and cycle properties of the prepared LiNi<sub>0.8</sub>Co<sub>0.15</sub>Mn<sub>0.05</sub>O<sub>2</sub> powders were measured by 2032-type coin cells. The cathode electrode was made of 12 mg of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Mn<sub>0.05</sub>O<sub>2</sub> 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 (TECHNO Semichem Co.) was 1 M LiPF<sub>6</sub> 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 constant current densities of 0.1 and 0.5 C.

## 3. Results and discussion

The morphologies of the as-prepared and post-treated precursor powders obtained by the spray pyrolysis were affected by the types of the spray solutions. Fig. 1 shows the SEM photographs



(a)



(b)

Fig. 1. SEM photographs of the powders obtained from the spray solutions without additives: (a) as-prepared and (b) post-treated.

of the powders obtained by spray pyrolysis from the aqueous solution. The as-prepared powders obtained by spray pyrolysis were post-treated at a temperature of 800 °C for 3 h. The as-prepared powders had spherical shape and several micron sizes. On the other hand, the as-prepared powders had hollow and porous morphologies because of the high drying and decomposition rates of the droplets. The residence time of the powders inside the hot wall reactor was as short as 2.4 s because of the high flow rate of the carrier gas. The as-prepared powders with hollow and porous morphologies had low thermal stabilities at a high post-treatment temperature. Therefore, the post-treated powder had irregular morphologies. The precursor powders with spherical shape and dense morphologies were necessary to prepare the cathode powders with spherical shape and dense structure by solid-state reaction with a lithium component.

The polymeric precursors and DCCA were added into the spray solution to control the characteristics of the Ni-rich precursor powders obtained by spray pyrolysis. The as-prepared powders obtained by spray pyrolysis from the spray solutions with polymeric precursors and DCCA may contain residue car-

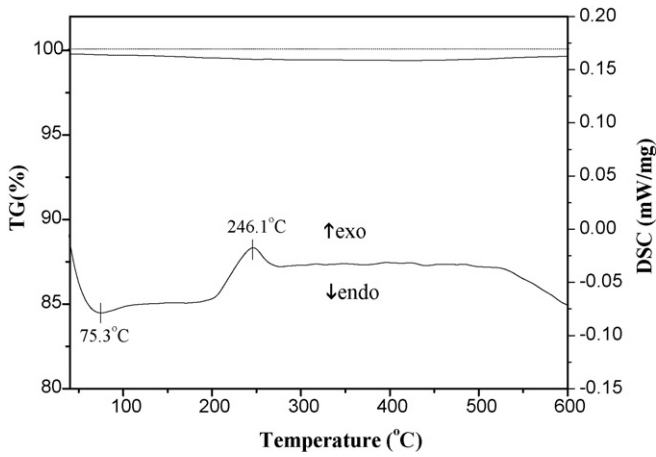
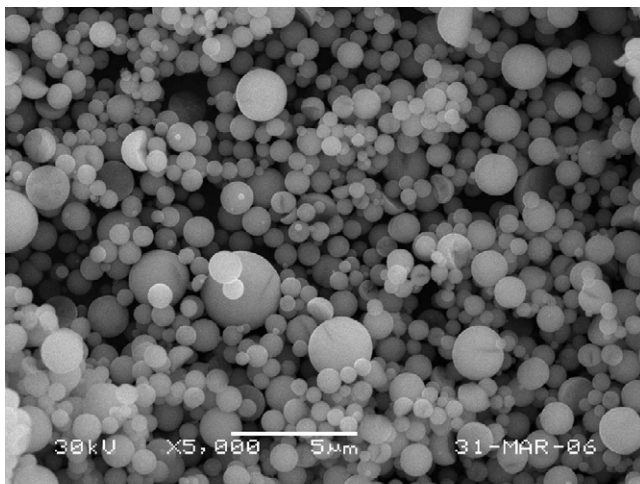
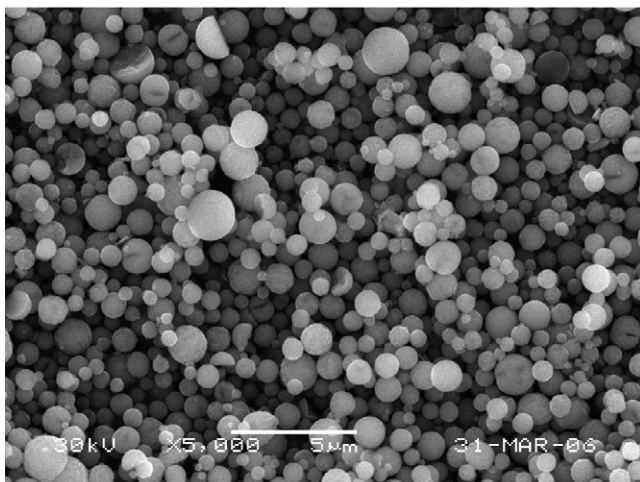


Fig. 2. TG/DSC curves of the as-prepared powders.

bon components inside the powders. Fig. 2 shows the TG/DSC curves of the as-prepared powders. In the DSC curve, the residue carbon components of the as-prepared powders decomposed at a temperature of 246 °C. However, the weight loss of the as-

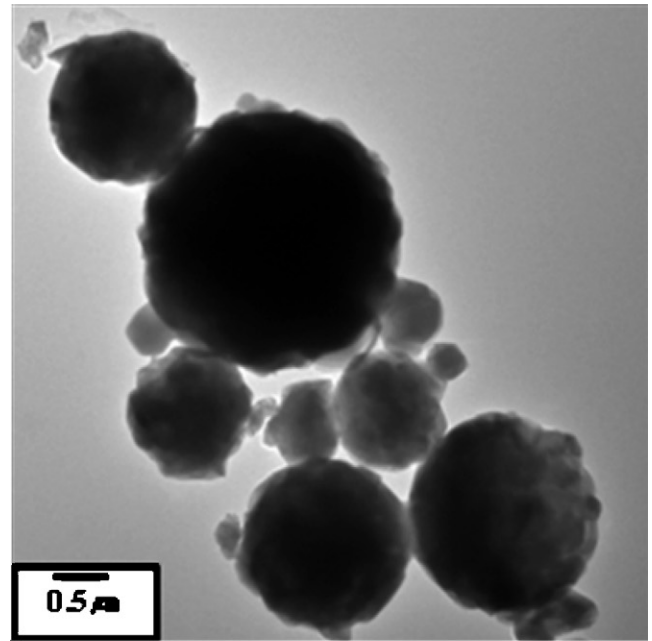


(a)

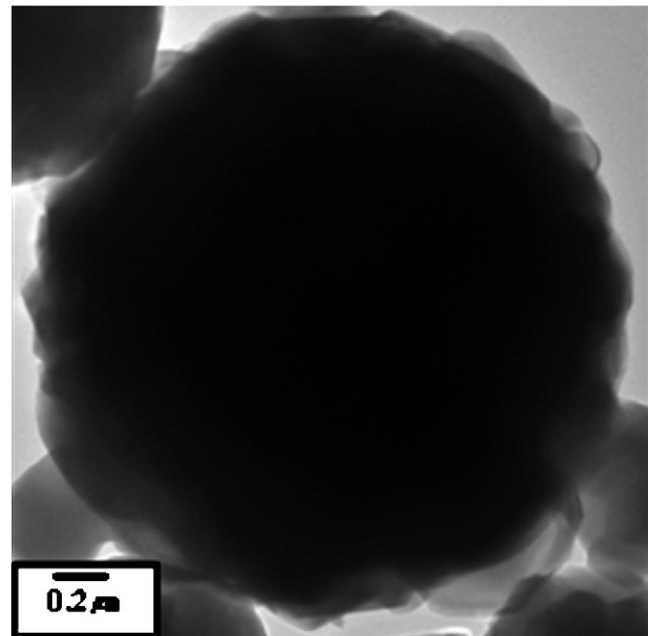


(b)

Fig. 3. SEM photographs of the powders obtained from the spray solutions with additives: (a) as-prepared and (b) post-treated.



(a)



(b)

Fig. 4. TEM photographs of the post-treated precursor powders obtained from the spray solutions with additives: (a) low magnification; (b) high magnification.

prepared powders was low as 0.15 wt%. The post-treatment of the as-prepared powders was also effective in clarifying the crystal structures of the components composing the precursor powders. The correct crystal structures of the precursor powders are necessary in the reaction with lithium components. Therefore, the as-prepared powders obtained by spray pyrolysis were post-treated at a temperature of 800 °C for 3 h in order to prepare the precursor powders. The morphologies of the as-prepared and post-treated powders obtained from the spray solutions with polymeric precursors and DCCA are shown in Fig. 3. Fig. 4

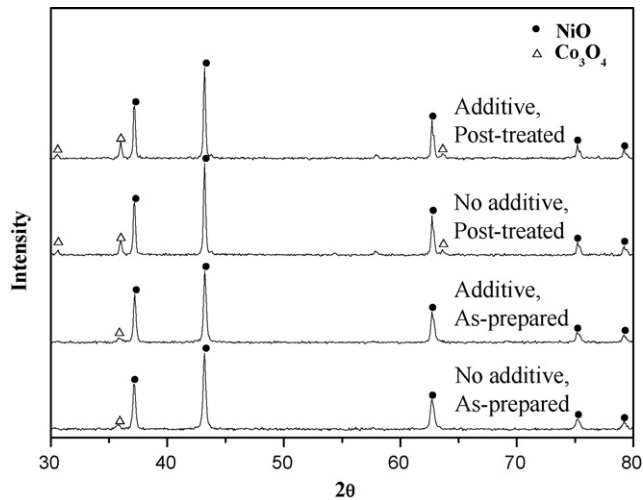


Fig. 5. XRD spectra of the post-treated precursor powders.

shows the TEM image of the post-treated powders. The concentrations of citric acid and ethylene glycol were fixed as 0.1 M. The optimum concentration of DCCA was 0.7 M. The addition of citric acid, ethylene glycol and DCCA into the spray solution improved the structure of the as-prepared Ni-rich powders. The as-prepared powders had a spherical shape and a filled inner structure. The filled inner structure of the as-prepared powders could be estimated from the fractured powders. The controlled drying and decomposition rates of the droplets applying the polymeric precursors and DCCA formed the as-prepared powders with spherical shape and filled morphologies in the spray pyrolysis. Citric acid and ethylene glycol formed the viscous polymers by the esterification reaction during the drying of the droplets. Viscous polymers and DCCA controlled the drying and decomposition rates of the droplets to form the as-prepared powders with filled inner structure. In the SEM and TEM photographs, the post-treated powders also had spherical shape and filled inner structure because of the high thermal stability of the as-prepared powders. The mean size of the precursor powders measured from the SEM photograph (Fig. 3b) was 1.0  $\mu\text{m}$ .

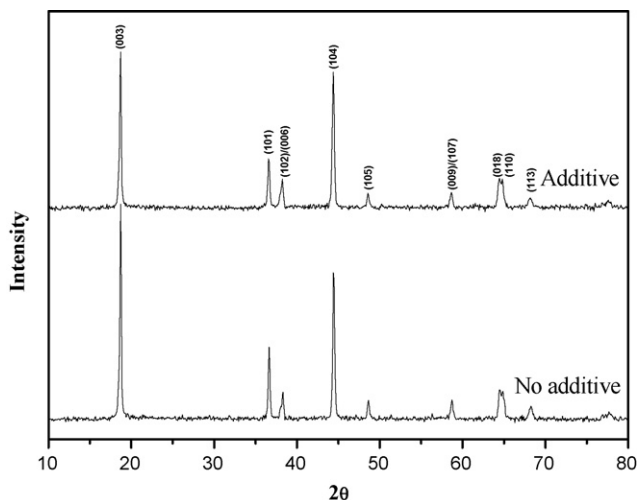
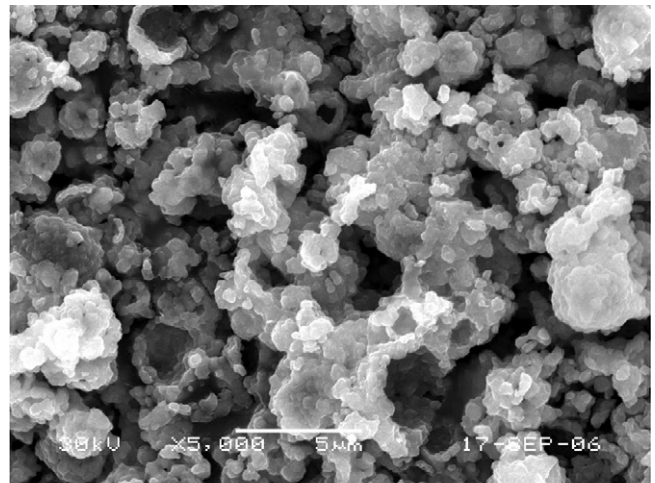
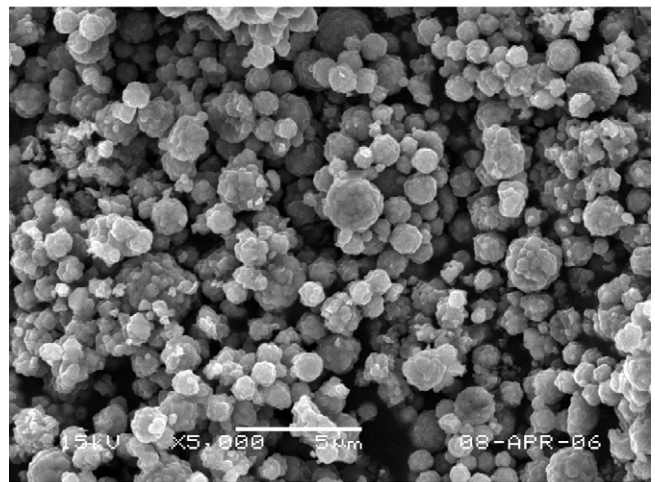


Fig. 6. XRD spectra of the  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05})\text{O}_2$  cathode powders.



(a)



(b)

Fig. 7. SEM photographs of the  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05})\text{O}_2$  cathode powders. (a) No additive; (b) additive.

Fig. 5 shows the XRD spectra of the as-prepared and post-treated powders obtained from the spray solutions with and without additives. The as-prepared powders had main peaks of NiO irrespective of the types of spray solutions. The post-treatment of the as-prepared powders improved the peak intensities of the  $\text{Co}_3\text{O}_4$  crystal structure. The peaks of manganese component were not observed in the XRD spectra of the as-prepared and post-treated powders because of small content in the powders. Previously, manganese components prepared by spray pyrolysis had the crystal structure of  $\text{Mn}_2\text{O}_3$  at the post-treatment temperature of 800  $^\circ\text{C}$  [16].

The Ni-rich precursor powders obtained by spray pyrolysis were reacted with lithium hydroxide by the solid-state reaction method. Fig. 6 shows the XRD spectra of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  powders prepared from the spray solutions with and without additives. The separations of 018/110 peaks in the XRD spectra, which represent the layered character of structure and good electrochemical properties, appeared in the prepared samples. The mean crystallite sizes of the cathode powders prepared from the spray solutions with and without additives were each 37 and 46 nm.

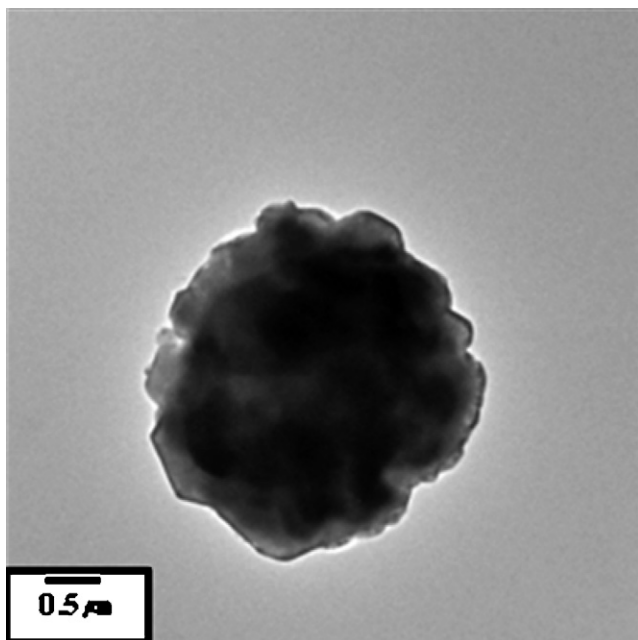
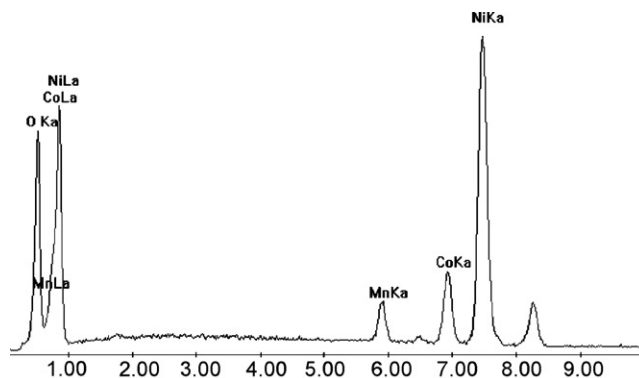


Fig. 8. TEM photograph of the  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05})\text{O}_2$  cathode powders obtained from the spray solutions with additives.

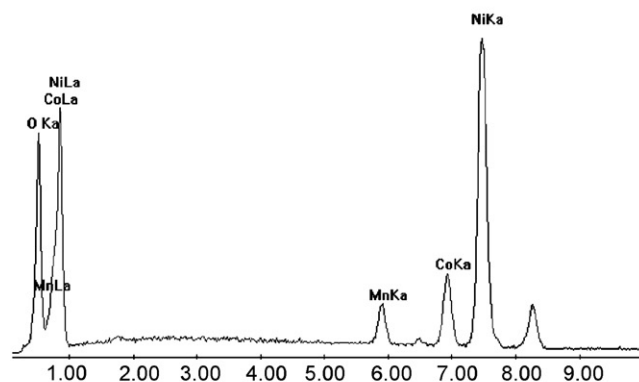
Fig. 7 shows the SEM photographs of the prepared  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders. The cathode powders prepared from the spray solution without additives had irregular morphologies. The precursor powders with hollow and porous morphologies formed the cathode powders with irregular and aggregated morphologies. However, the cathode powders prepared from the spray solutions with additives had spherical shape and non-aggregated morphologies. Fig. 8 shows the TEM image of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powder obtained from the spray solution with additives. The cathode powders had filled inner structure. The Ni-rich precursor powders with spherical shape and filled morphologies formed the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders with spherical shape and non-aggregated morphologies. The mean size of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders measured from the SEM photograph was  $1.1\ \mu\text{m}$ . One cathode powder was formed from one precursor powder by solid-state reaction with lithium hydroxide. Therefore, the mean size of the cathode powders prepared from the spray solution with additives was similar to that of the precursor powders.

Fig. 9 shows the EDAX spectra of the as-prepared, precursor and cathode powders obtained from the spray solution with additives. In the EDAX spectra, the composition ratios of the nickel, cobalt and manganese components were analyzed. Table 1 shows the compositions of the powders measured from the EDAX spectra. The composition ratios of the nickel, cobalt and manganese components were maintained in the as-prepared, precursor and cathode powders.

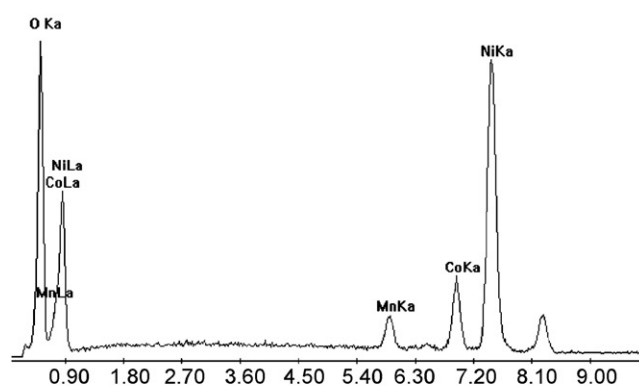
The initial charge/discharge curves of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders, tested at a temperature of  $25\ ^\circ\text{C}$  under a constant current density of  $0.1\text{C}$ , are shown in Fig. 10. The cathode powders prepared from the spray solution without additives had lower charge/discharge capacities



(a)



(b)



(c)

Fig. 9. EDAX spectra of the powders: (a) as-prepared precursor, (b) post-treated precursor, and (c) cathode powder.

than those of the cathode powders prepared from the spray solution with additives. The initial discharge capacity of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders prepared from the spray solution without additives was  $200\ \text{mAh g}^{-1}$ . However, the initial discharge capacity of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders prepared from the spray solution with additives was  $209\ \text{mAh g}^{-1}$ . The cathode powders with spherical shape and fine size had a higher discharge capacity than that of the cathode powders with irregular morphology and large size.

Performance at high temperatures is also important for lithium ion battery application. Fig. 11 shows the cycle properties of the cathode powders prepared from the spray solutions with additives tested at a temperature of  $55\ ^\circ\text{C}$  under a con-

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

Samples	Composition (Ni:Co:Mn atomic ratios)	Average of composition
As-prepared	(80.0:15.1:4.9)	80.0:15.2:4.8
	(79.5:15.5:5.0)	
	(80.6:15.0:4.4)	
Precursor	(79.7:15.4:4.9)	79.8:15.3:4.9
	(80.3:14.9:4.8)	
	(79.5:15.5:5.0)	
Cathode	(80.3:15.0:4.7)	79.8:15.2:5.0
	(79.1:15.7:5.2)	
	(79.9:15.0:5.1)	

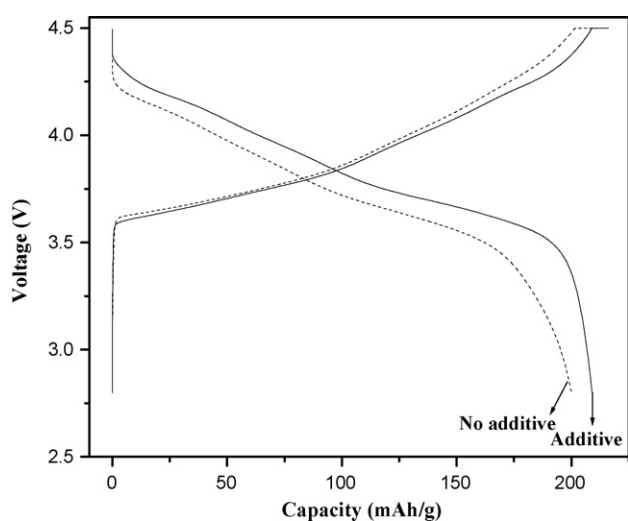


Fig. 10. Charge/discharge curves of the  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05})\text{O}_2$  cathode powders.

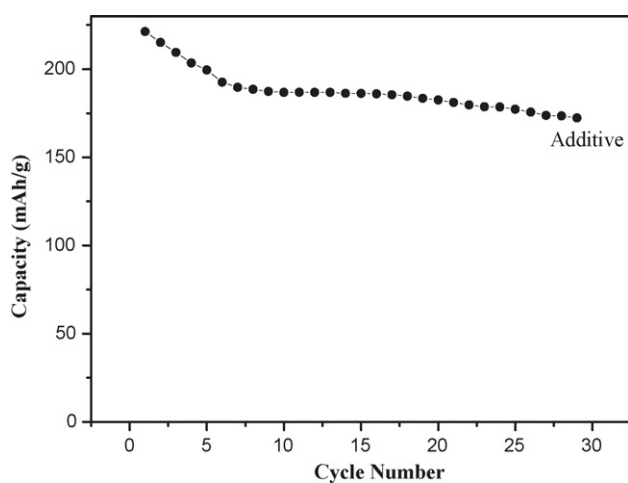


Fig. 11. Cycling performance of the  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05})\text{O}_2$  cathode powders at a temperature of  $55^\circ\text{C}$  between 4.5 and 2.8 V with 0.5 C.

stant current density of 0.5 C. The initial discharge capacity of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders prepared from the spray solution with additives was high as  $215 \text{ mAh g}^{-1}$ , which may be attributed to better kinetics (high mobility of the  $\text{Li}^+$  ions) and lower polarization at elevated temperatures [17]. The discharge capacity of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders decreased to 81% of the initial value after 30 cycles.

#### 4. Conclusions

The morphologies of the Ni-rich precursor powders obtained by spray pyrolysis affected the characteristics of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders prepared by solid-state reaction with lithium hydroxide. The Ni-rich precursor powders with spherical shape and filled morphologies were required to prepare the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders with regular morphologies and fine size. In this experiment, polymeric precursors and DCCA were applied to the spray solution to control the morphologies of the Ni-rich precursor powders. The precursor powders with spherical shape and filled morphologies, which were obtained from the spray solutions with polymeric precursors and DCCA, formed the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  cathode powders with spherical shape and fine size. The cathode powders with spherical shape and fine size had higher charge/discharge capacities than those of the cathode powders with irregular morphologies and large size.

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