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Short communication

# Fine-sized $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ 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 $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ 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 $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ 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 mAh $g^{-1}$. The discharge capacity of the $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ cathode powders decreased to 81% of the initial value after 30 cycles.


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

## 1. Introduction

$LiNiO_2$ has been studied extensively as a cathode material because of its higher specific capacity, lower cost and because it is less toxic than $LiCoO_2$ [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 powders 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 $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ 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$^{-1}$. The precursor solution was prepared by dissolving a stoichiometric ratio of 0.8:0.15:0.05 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 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*-dimethlyformamide 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 Kα 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 $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ powders were measured by 2032-type coin cells. 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 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 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

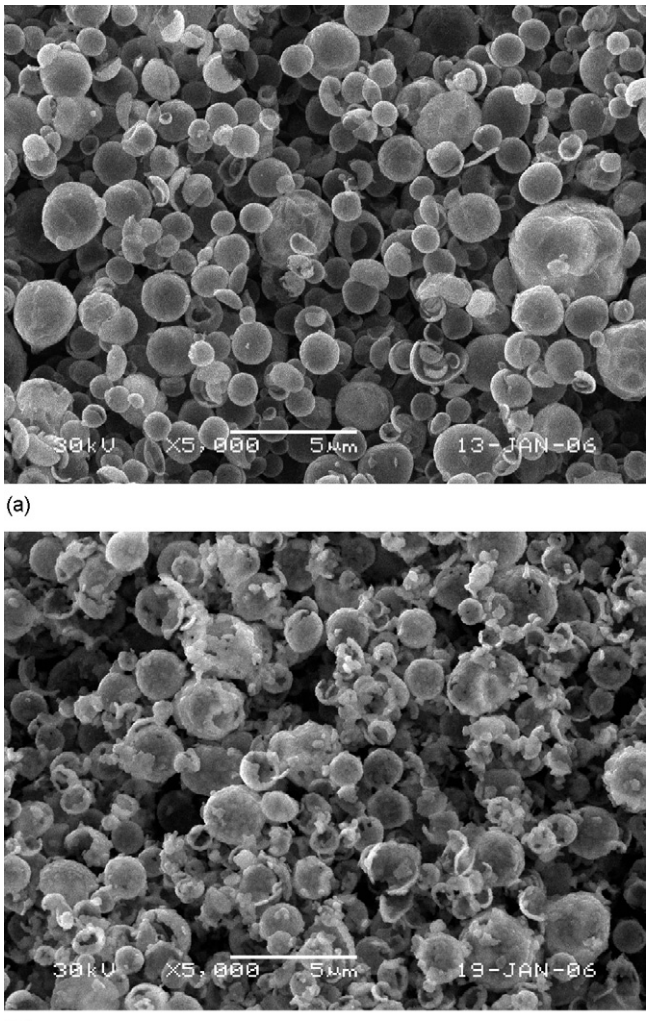


Fig. 1. SEM photographs of the powders obtained from the spray solutions without additives: (a) as-prepared and (b) post-treated.

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-