# Spherical Nanostructured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Powders Prepared via an Ultrasonic Spray Pyrolysis Process

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Nanostructured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were successfully synthesized via an ultrasonic spray pyrolysis process. The prepared powders were composed of nanosized crystallites and formed a spherical shape. Well-crystallized structure was obtained after calcination at 800 °C. The prepared $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders exhibited a high discharge capacity of 184 mAh/g within the voltage range of 2.5–4.5 V. The capacity retention was 78% after 100 cycles test at 1C charging and 3C discharging rate at 55 °C.

Recently, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has been intensively investigated[1–5] for the application to lithium-ion batteries because of its high discharge capacity and enhanced safety. This material has a $R\bar{3}m$ structure and is generally synthesized via a two-step process for obtaining the high structure ordering material. The first step is the coprecipitation process for preparing the metal hydroxide precursors with high elemental homogeneity, and the second step is to mix lithium oxide or salts with hydroxide precursors. Park et al.[6] employed the ultrasonic spray pyrolysis process instead of the coprecipitation method to prepare $Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ precursors. However, the heating time has to be prolonged to several hours for obtaining the desired powders. Using the above methods to obtain $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders containing nanocrystallites is also difficult.

The ultrasonic spray pyrolysis is considered to be an effective technique to shorten the reaction time and produce particles with homogenous composition.[7–11] In this study, spherical nanostructured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were prepared via the one-step ultrasonic spray pyrolysis method. $LiNO_3$, $Ni(NO_3)_2\cdot 6H_2O$, $Mn(NO_3)_2\cdot 6H_2O$, and $Co(NO_3)_2\cdot 6H_2O$ (Wako Pure Chemical Industries Ltd.) were used as the starting materials. These materials were dissolved in distilled water, and the chemical composition of the metal ions in the aqueous solution was adjusted to $[Li^+]:[Ni^{2+}]:[Co^{2+}]:[Mn^{2+}] = 1:1/3:1/3:1/3$. An ultrasonic nebulizer was utilized to generate mist from the aqueous solution, and the mist was introduced into an electrical furnace for the drying and pyrolysis processes. The temperature in the electrical furnace was kept at 500 °C during the spray pyrolysis. The obtained powder was calcined at 800 °C in air for 3 h.

The crystal structures of the prepared powders were examined by X-ray diffraction (XRD, MAC-MXP18). A scanning electron microscope (SEM, JEOL JSM-6500F) was used to investigate the morphology of the powders. A field emission transmission electron microscope equipped with an energy-dispersive spectrometer (FE-TEM EDS, JEOL JEM-2100F) was utilized to determine the crystalline size and the element distribution in the crystal structure. The TEM sample was prepared by the by ultramicrotomy method before the TEM measurement. Electrochemical analysis was performed via coin cells assembling (2032 type). The cathode materials were prepared by mixing $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, carbon black and PVdF in a weight ratio of 78:12:10 in NMP. Li metal foils, PP, $LiPF_6$ (1 M) with EC/EMC (1:2 by volume ratio) were used as anodes, separators, and electrolytes, respectively.

Figures 1a and 1b illustrate the XRD patterns of the as-prepared $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ precursor powders and the powders calcined at 800 °C for 3 h, respectively. The XRD intensity of the precursor powders was amplified 10 times in the figure. After the spray pyrolysis process, the precursor powders with a layered structure were formed. Further calcination at 800 °C resulted in the formation of well-crystallized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with an $\alpha$-$NaFeO_2$ hexagonal structure. In comparison with the previous studies,[1–6] the required heating temperature and duration for preparing single-phased $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ via the ultrasonic spray pyrolysis were significantly reduced.

The microstructures of the precursor powders and the 800 °C-calcined $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders are shown in Figure 2. Precursor powders with a spherical shape and a size of around 1 µm were formed after the ultrasonic spray pyrolysis process, as shown in Figures 2a and 2b. The spherical shape of the particles was resulted from the agglomeration of primary particles that are several nanometers in size. After calcination at 800 °C, the spherical morphology with the high porosity of the calcined powders were obtained.

The TEM photos and EDS mapping results for the precursor powders and the 800 °C-calcined powders are shown in Figure 3.

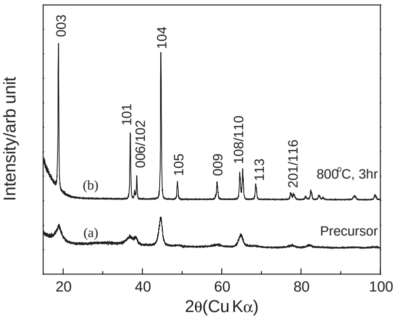

**Figure 1.** X-ray diffraction patterns of (a) precursor powders of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and (b) precursor powders calcined at 800 °C in air for 3 h.

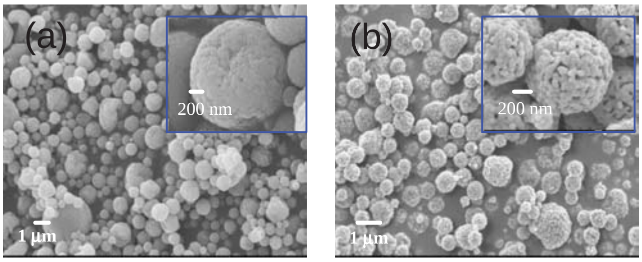

**Figure 2.** Scanning electron micrographs of (a) precursor powders of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and (b) precursor powders calcined at 800 °C in air for 3 h. Inset: The magnified (a) and (b) powders.

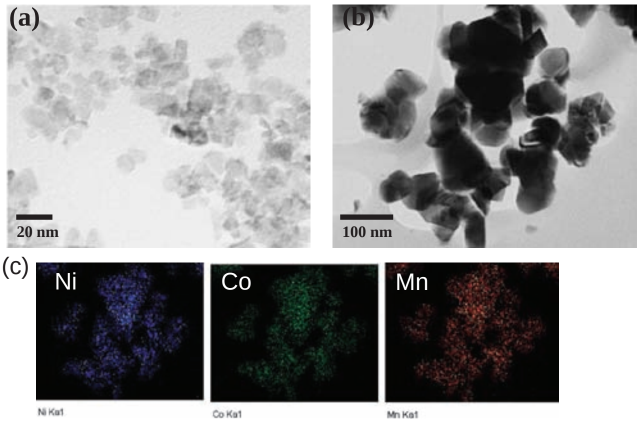

**Figure 3.** Transmission electron micrographs of (a) precursor powders of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, (b) precursor powders calcined at 800 °C in air for 3 h, and (c) elemental mapping of 800 °C calcined powder.

It is observed in this figure that the crystal size of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ precursor powder was around 8 nm. After calcination at 800 °C, the crystal size was enlarged to around 60 nm. From the EDS mapping results, it is clearly observed that nickel, cobalt, and manganese ions were uniformly distributed in the particles. This fact indicates that $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders with a homogeneous chemical composition were prepared via the ultrasonic spray pyrolysis.

Figure 4 shows the charge–discharge curve for the 800 °C-calcined $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as a function of voltage in the range of 2.5 to 4.5 V at 0.1 C rate in the first cycle. The charge and discharge capacities of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ are 203 and 184 mAh/g, respectively, and its irreversible capacity is 10% at first cycle. The high discharge capacity and low irreversible capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ may be attributed to the less cation mixing property in the layer oxide cathode material.[12] For the cycling test performed at 1C charging and 3C discharging rate at 55 °C (see the inset), the capacity retention was 78% after 100 cycles. These results demonstrate that nanostructured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders had high discharge capacity and good cycling performance. The improved characteristics are considered to attribute to the compositional homogeneity in the precursor powders and the unique nanoscaled spherical structure with the high porosity of the synthesized powders.

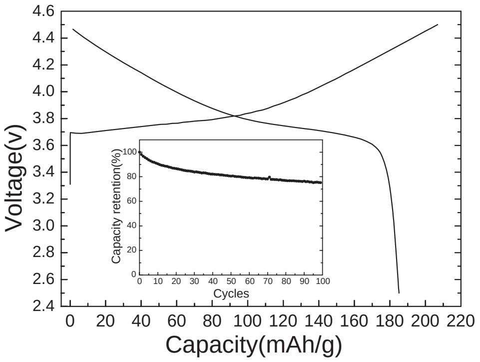

**Figure 4.** Charge and discharge curve of $Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ subjected to a 0.1C rate between 2.5–4.5 V at 25 °C. Inset: Discharge capacity vs cycle number for $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ tested at 1C charging and 3C discharging rate between 2.5–4.5 V at 55 °C.

Nanostructured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders with a spherical shape were successfully synthesized via the ultrasonic spray pyrolysis process. The obtained powders exhibited a high charge–discharge performance. High capacity retention was also achieved after cycling at high C rates at 55 °C. The ultrasonic spray pyrolysis method has been demonstrated to be an effective approach to enhance the electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders.

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