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Submicron size $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared by spray pyrolysis from polymeric precursor solution

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Abstract Submicron-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles were prepared by spray pyrolysis. A polymeric precursor solution containing citric acid and ethylene glycol enabled the formation of submicron-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ spherical particles with narrow-sized distribution and non-aggregation characteristics in the spray pyrolysis. The mean sizes of the particles post-treated at temperatures of 800 and 900°C were 380 and 770 nm. On the other hand, the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained from the aqueous solution had irregular morphology and broad-sized distribution. The discharge capacity of the particles prepared from polymeric precursor solution decreased from 88 mAh/g to 135 mAh/g after 50 cycles. The particles prepared from polymeric precursor solution had high discharge capacity and good cyclic properties than those of the particles prepared from the aqueous solution.

1. Introduction

Cathode materials are important in the development of lithium-ion batteries with high energy density, good cycleability, high working voltage, safety properties, etc. The electrochemical characteristics of the cathode materials depend on their morphology, mean size, crystal structure, and phase purity [1–4]. Solid-state reaction method is mainly applied to the commercial production of cathode materials because of the simple process involved and great productivity. However, solid-state reaction method has disadvantages in controlling the morphology and mean size of the cathode materials. The mean sizes of cathode materials prepared by solid-state reaction method range from several microns to several tens of microns. Recently, cathode materials with fine size and regular morphology are much in demand in the development of high-energy lithium-ion batteries. Nanostructured materials have been also examined for use as cathode materials in lithium-ion batteries [4–7]. It has been demonstrated that nanostructured electrodes for lithium-ion batteries show better rate capacities than conventional electrodes composed of the same materials due to the short diffusion distance of Li^+ in the nanostructured electrodes. Therefore, various kinds of preparation methods such as sol-gel, coprecipitation, hydrothermal, emulsion drying, and spray pyrolysis have been developed to obtain the nanostructured cathode materials for lithium-ion batteries [4–15].

Spray pyrolysis is one of the most promising processes for the preparation of the improved cathode materials with spherical structure, fine particle size, narrow-sized distribution, and non-aggregation characteristics because of its particle-formation mechanism [4–10]. The morphology of particles prepared by spray pyrolysis is strongly affected by preparation conditions and type of precursors.

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles as cathode material for lithium-ion batteries are widely studied because of their high capacity, high working voltage, and high stability. $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles were prepared by solid-state reaction, glycine–nitrate combustion, spray dry and spray pyrolysis, etc [4,16–18].

In this work, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles with submicron size, spherical particle structure and narrow-size distribution were prepared by large-scale spray pyrolysis

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process. Polymeric precursor solutions applying ethylene glycol and citric acid were used as spray solution to improve the morphology and electrochemical properties of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles. The electrochemical properties of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared by spray pyrolysis from spray solutions with aqueous and polymeric precursor solutions were studied by means of charge–discharge test in half cell.

2. Experiments

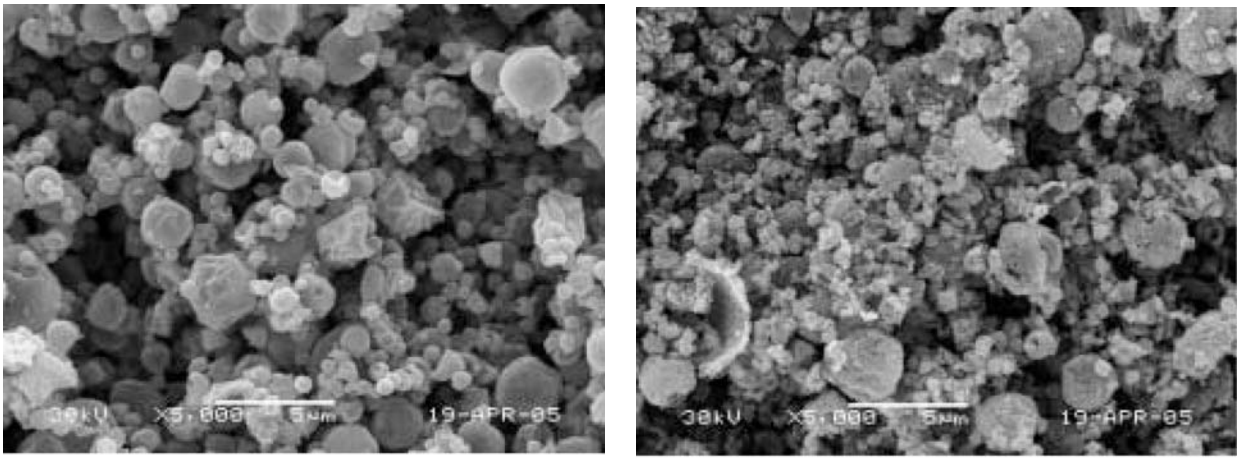
The schematic diagram of spray pyrolysis system used in this work is given elsewhere [19]. The spray pyrolysis system consists of droplet generator, quartz reactor, and particle collector. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets, which are carried into the high-temperature tubular reactor by a carrier gas. 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 air used as carrier gas was 40 l/min. The precursors used in this work were lithium carbonate ($LiCO_3$, Aldrich), nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, Aldrich), cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, Aldrich), and manganese acetate hexahydrate ($Mn(CH_3CO_2).4H_2O$, Aldrich). The polymeric precursor solution was prepared by dissolving ethylene glycol and citric acid into an aqueous solution. The concentrations of ethylene glycol and citric acid in polymeric precursor solution were 0.3 M. The as-prepared particles obtained by spray pyrolysis were post-treated at temperatures between 600 to 1000°C for 12 h.

The crystal structures of the as-prepared and post-treated particles were investigated using X-ray diffractometry (XRD, RIGAKU, DMAX-33). The mean size and morphology of the particles were investigated using scanning electron microscopy (SEM, JEOL, JSM 6060). The charge/discharge characteristics of the fine-sized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained from the polymeric precursor solution were compared with those of the particles obtained from the aqueous solution. The cathode electrode was made of 12 mg of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ mixed with 4 mg of 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 at 120°C overnight. The lithium metal and polypropylene film were used as the anode electrode and the separator, respectively. The electrolyte was 1 M $LiPF_6$ in 1:1 mixture by volume of EC/DMC. The entire cell was assembled in the glove box under argon atmosphere. The electrochemical performances of the various $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ samples were measured by charge/discharge curves of $Li/Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell cycled in 2.8–4.5 V at a constant current density of 0.5 C.

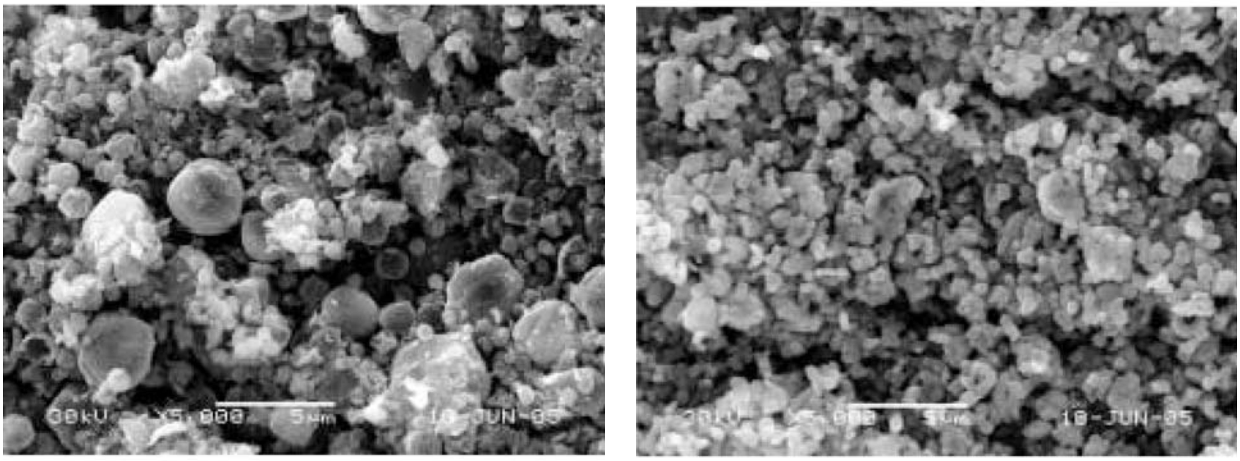
3. Results and discussion

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles were prepared by spray pyrolysis from aqueous and polymeric precursor solutions. The effect of the spray solution on the morphology of the as-prepared and post-treated $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles was investigated. In Fig. 1, the as-prepared particles obtained by spray pyrolysis from aqueous and polymeric precursor solutions at 900°C were post-treated at various temperatures. The as-prepared particles obtained from the aqueous solution were micron-sized and spherical. However, the as-prepared particles obtained at the severe preparation conditions such as high solution concentration, short residence time, high temperature variation induced by large-scale process and high gas flow rate had hollow and porous morphology. The post-treated particles had different morphology according to the post-treatment temperatures. The as-prepared particles post-treated at temperatures below 700°C maintained their micron size and spherical structure. On the other hand, the post-treated particles at temperatures above 800°C had non-spherical shape and irregular morphologies. The as-prepared particles turned fine-sized and aggregated at a post-treatment temperature of 800°C. Crystal growth occurred at high post-treatment temperatures. The mean size of the primary particles increased from several hundreds nanometers to several microns when the post-treatment temperature changed from 800 to 1000°C.

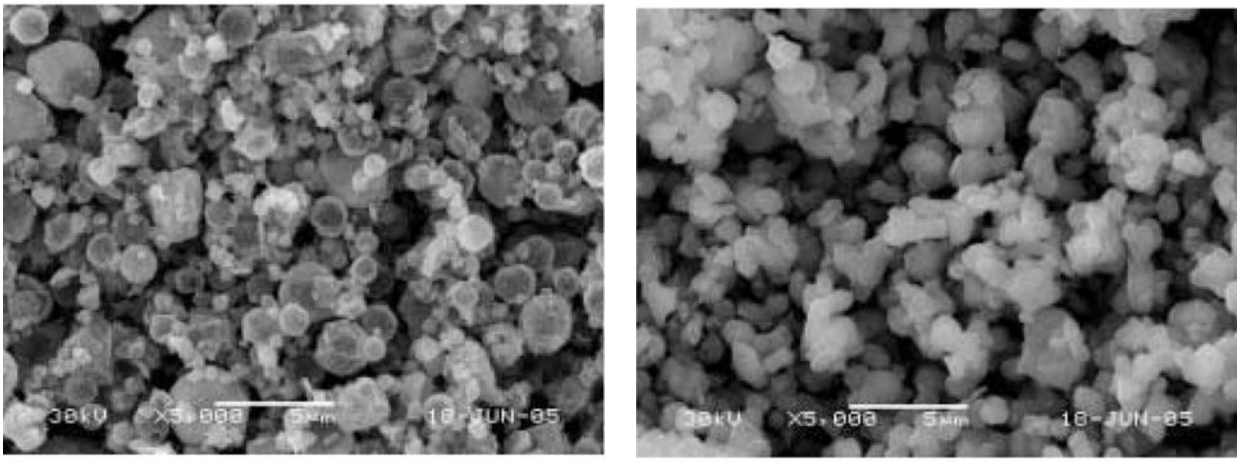
Fig. 2 shows the SEM photographs of the as-prepared and post-treated $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles obtained from the polymeric precursor solution. The concentration of citric acid and ethylene glycol added into the spray solution were 0.3 M, respectively. The as-prepared particles obtained by spray pyrolysis at 900°C had a spherical structure, hollow, and thin walled. Polymeric precursors changed the morphology of the as-prepared particles in the spray pyrolysis. The high evolving rate of gas from the decomposition of ethylene glycol and citric acid changed the morphology of the as-prepared particles. The post-treated particles had also morphologies different from those of the particles prepared from the aqueous solution. The post-treated particles at the temperature of 600°C were nonspherical, hardly aggregated, and had nanostructured morphology. However, the post-treated particles at temperatures between 700 and 900°C had fine size and regular morphology. $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles prepared by spray pyrolysis from polymeric precursor solution were fine sized and had narrow-size distribution without a milling process. The mean size of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles changed from several tens of nanometers to several microns according to the



(a) P900°C (d) A800°C

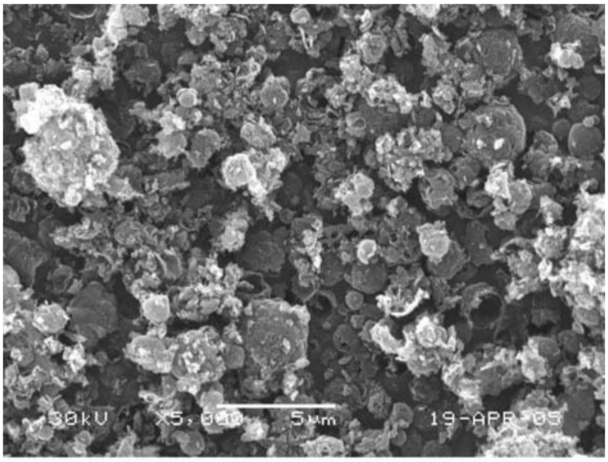


(b) A600°C (e) A900°C

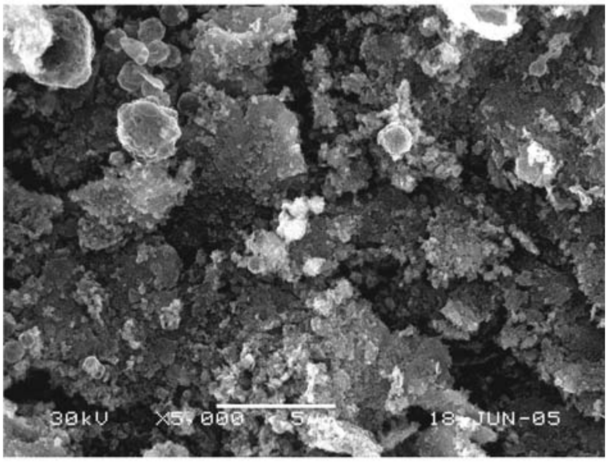


(c) A700°C (f) A1000°C

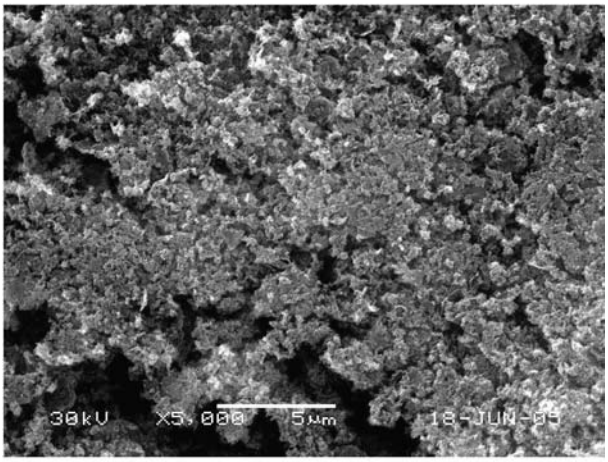
Fig. 1 SEM photographs of as-prepared and post-treated Li($Ni_{1/3}Co_{1/3}Mn_{1/3}$)O_2 particles prepared by spray pyrolysis from aqueous solution (P: preparation temperature, A: post-treatment temperature)



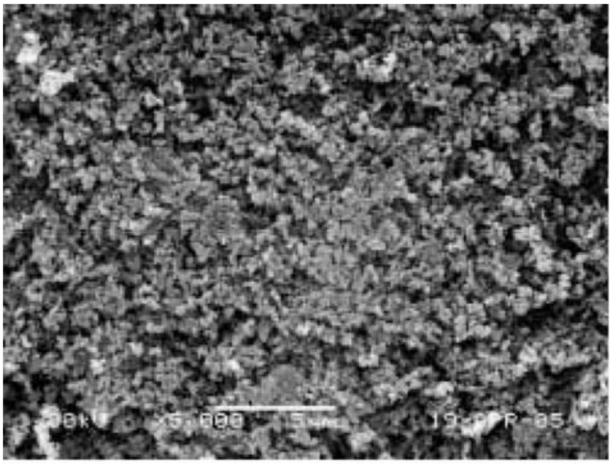
(a) P900°C



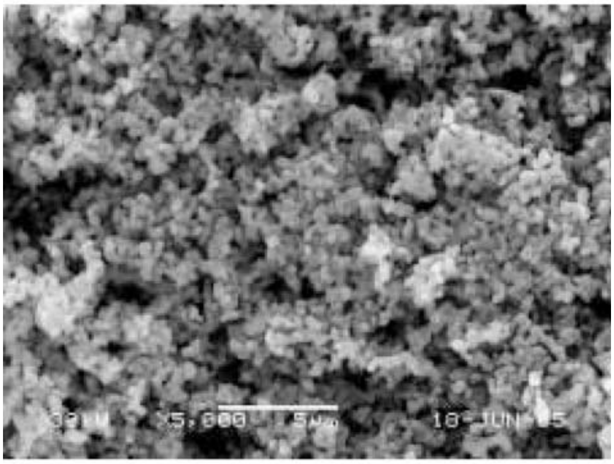
(b) A600°C



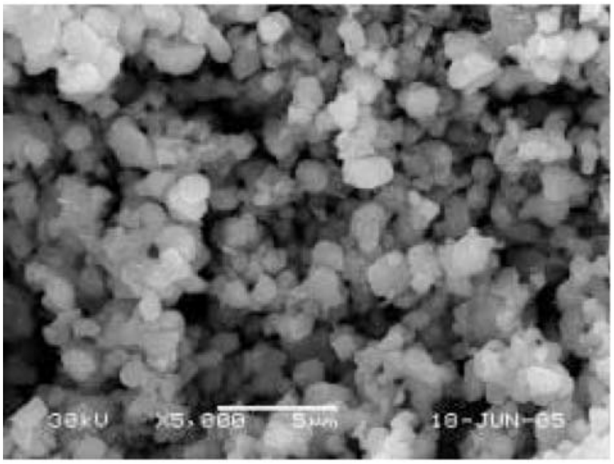
(c) A700°C



(d) A800°C



(e) A900°C



(f) A1000°C

Fig. 2 SEM photographs of as-prepared and post-treated Li($Ni_{1/3}Co_{1/3}Mn_{1/3}$)O_2 particles prepared by spray pyrolysis from polymeric precursor solution (P: preparation temperature, A: post-treatment temperature)

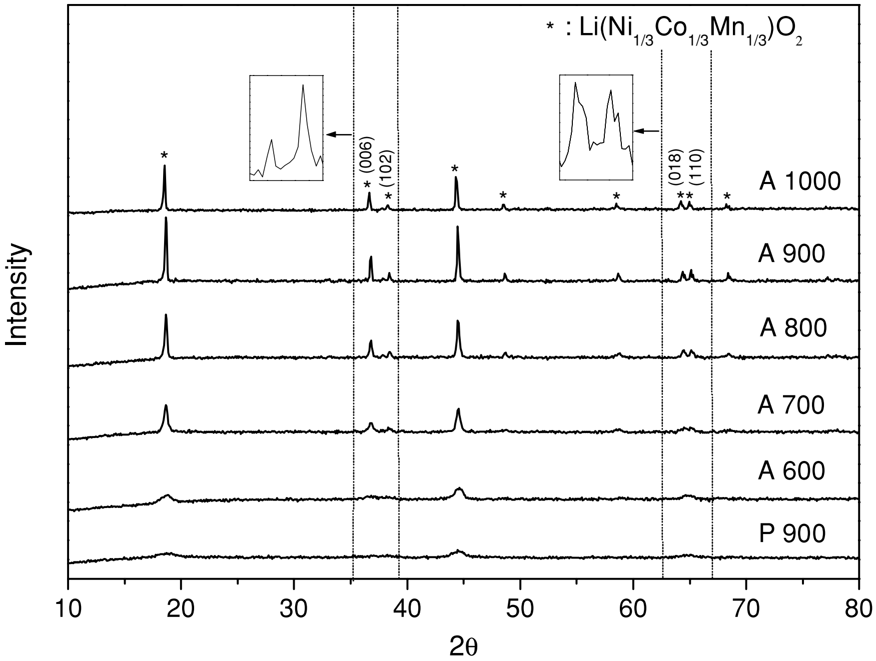


Fig. 3 XRD spectra of as-prepared and post-treated Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ particles prepared by spray pyrolysis from aqueous solution

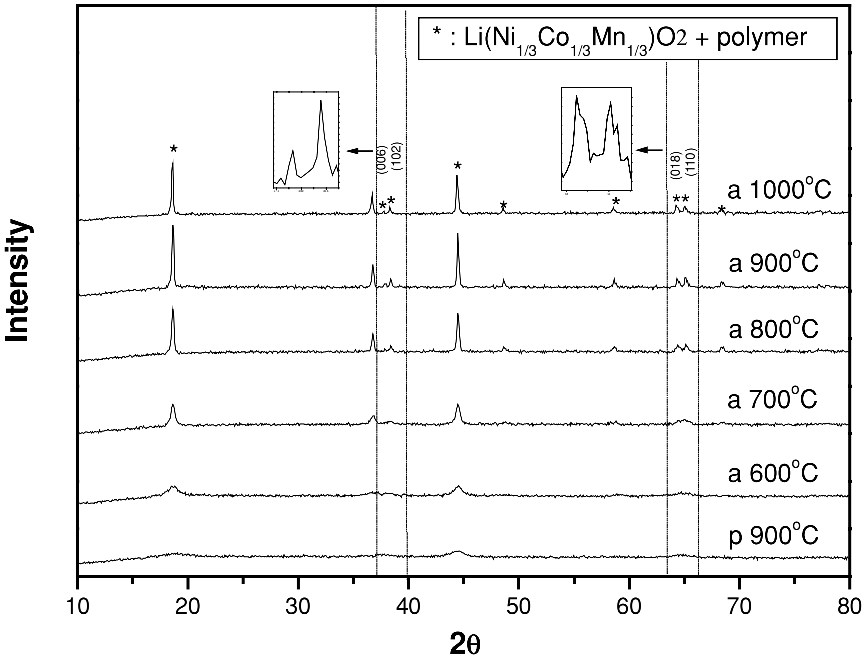


Fig. 4 XRD spectra of as-prepared and post-treated Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ particles prepared by spray pyrolysis from polymeric precursor solution

post-treatment temperatures. The mean sizes of the particles post-treated at temperatures of 800 and 900°C measured from the SEM photographs were 380 and 770 nm. The post-treatment temperature of 1000°C was too high for the preparation of submicron-sized Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ particles.

The XRD spectra of the as-prepared and post-treated Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ particles obtained from aqueous and polymeric precursor solutions are shown in Figs. 3 and 4. The as-prepared particles obtained by spray pyrolysis from aqueous and polymeric precursor solutions at 900°C had poor crystallinity because of the particles' short residence time of only 0.6 s inside the hot-walled reactor. The post-treated particles at all post-treatment temperatures had pure crystal structures of Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ particles regardless of the types of spray solutions. In the spray pyrolysis, the phase separation of each component consisting of the Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ particles was minimized inside the micron-sized particles. Therefore, the purity of as-prepared and post-treated particles of Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ was ensured. The crystallinity of the particles increased with the

Fig. 5 Charge/discharge curves of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell operated in voltage of 2.8–4.5V at a constant current density of 0.5 C

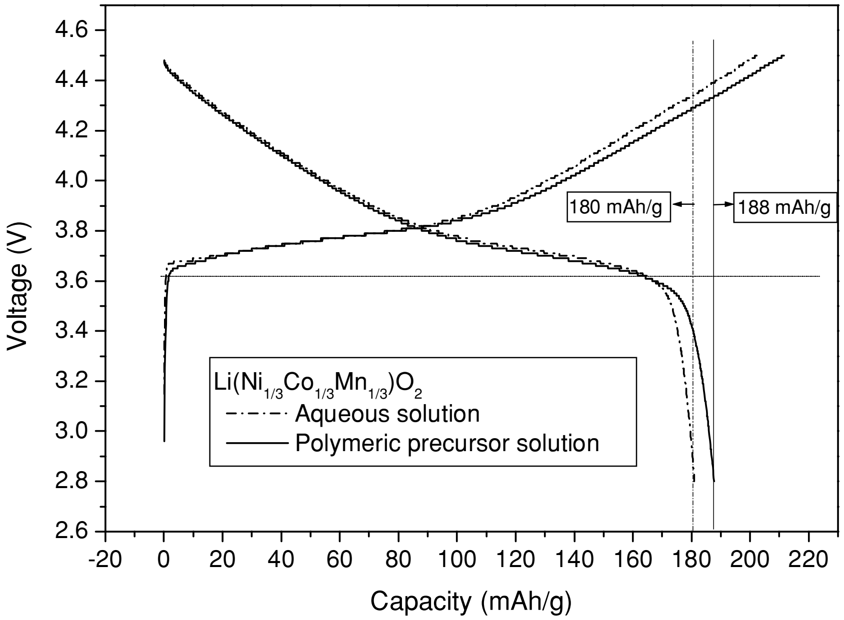
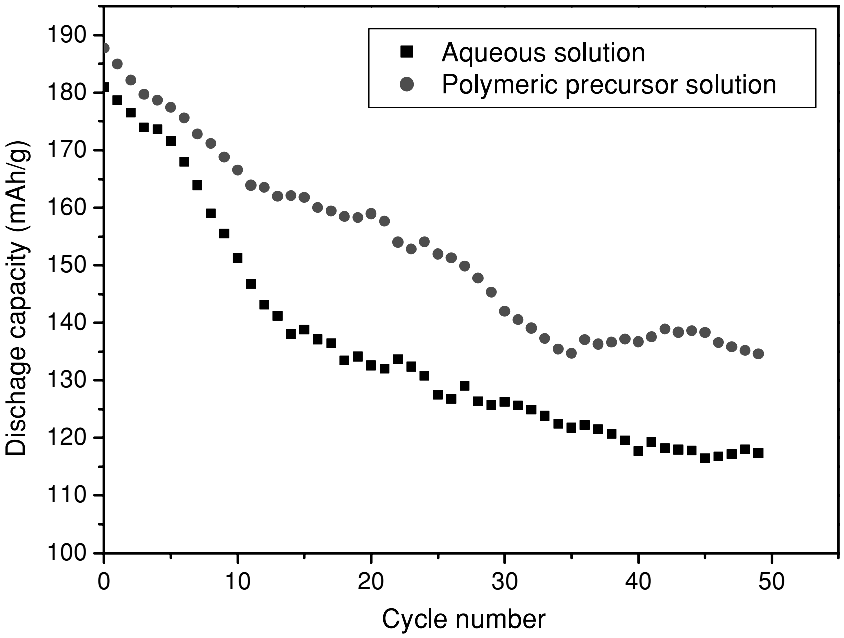


Fig. 6 Cycling performances of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell operated in voltage of 2.8–4.5V at a constant current density of 0.5 C



increase of the post-treatment temperatures and had the maximum sharpness at post-treatment temperature of 900°C. The crystallite sizes of the particles were calculated by Scherrer's equation. The crystallite sizes of the particles prepared from aqueous and polymeric precursor solutions at post-treatment temperature of 800°C were 35 and 37 nm, respectively. Peak splits of (006)/(102) and (018)/(110) peaks occurred in Figs. 3 and 4. Peak splits in the XRD spectra at (006)/(102) and (018)/(110) peaks indicate the formation of layered structure of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ particles.

The charge/discharge curves of $Li/Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cell cycled in 2.8–4.5 V at a constant current density of 0.5 C are shown in Fig. 5. For the measurement of the electrochemical properties of the cathode materials, the as-prepared particles obtained by spray pyrolysis from aqueous and polymeric precursor solutions were post-treated at a temperature of 800°C for 12 h. The charge/discharge curves were similar to the results of previously reported studies [14,16–18]. The initial charge and discharge capacities of the particles prepared from the aqueous solution were 200 mAh/g and 180 mAh/g, respectively. The charge and discharge capacities of the particles prepared from the polymeric precursor solution were higher than those of the particles prepared from the aqueous solution. The initial charge and discharge capacities of the particles prepared from the polymeric precursor solution were 210 mAh/g and 188 mAh/g, respectively.

Fig. 6 shows the specific discharge capacity versus the number of cycles for Li/ Li($Ni_{1/3}Co_{1/3}Mn_{1/3}$)O_2 cell in the voltage range of 2.8–4.5 V at a constant current density of 0.5 C. The discharge capacity of the particles prepared from the aqueous solution decreased from 180 mAh/g to 128 mAh/g after 50 cycles. On the other hand, the discharge capacity of the particles prepared from polymeric precursor solution decreased from 188 mAh/g to 135 mAh/g after 50 cycles. The discharge capacities of the particles prepared from aqueous and polymeric precursor solutions were 65% and 72% of the initial discharge capacities after 50 cycles. The particles prepared from the polymeric precursor solution had high discharge capacity and good cyclic properties than those of the particles prepared from the aqueous solution.

4. Conclusion

Fine-sized Li($Ni_{1/3}Co_{1/3}Mn_{1/3}$)O_2 particles were prepared by spray pyrolysis from aqueous and polymeric precursor solutions. The as-prepared particles obtained by spray pyrolysis from polymeric precursor solution were micron-sized, were hollow and had thin walls. The as-prepared particles obtained from the polymeric precursor solution turned to fine-sized Li($Ni_{1/3}Co_{1/3}Mn_{1/3}$)O_2 particles after the post-treatment process above 700°C. The mean sizes of the particles increased from several tens of nanometers to micron size when the post-treatment temperature was changed from 600 to 1000°C. The electrochemical properties of the submicron-sized Li($Ni_{1/3}Co_{1/3}Mn_{1/3}$)O_2 particles post-treated at 800°C were characterized. The spray pyrolysis method applying polymeric precursor solutions could be applied to the preparation of fine-sized cathode materials with various compositions.

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