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$LiMn_2O_4$ particles prepared by spray pyrolysis from spray solution with citric acid and ethylene glycol

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Abstract Spinel $LiMn_2O_4$ particles with fine sizes and regular morphologies were successfully synthesized by ultrasonic spray pyrolysis at the severe preparation conditions from a spray solution with citric acid and ethylene glycol. The as-prepared particles with spherical shapes, porous structures and micron sizes turned into $LiMn_2O_4$ particles with submicron size and narrow size distribution at the post-treatment temperature of 800 °C. The discharge capacities of the particles prepared from the spray solution with citric acid and ethylene glycol changed from 90 to 127 mAh/g when the post-treatment temperature was changed from 700 to 1,000 °C. The $LiMn_2O_4$ particles had maximum discharge capacities at the post-treatment temperature of 800 °C. The discharge capacity of the $LiMn_2O_4$ particles dropped from 127 to 108 mAh/g by the 30th cycle.

Introduction

In secondary lithium batteries, a family of lithium transition metal oxides such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ have been developed as cathode materials [1–5]. Among these cathode materials, $LiCoO_2$ is mainly used as a commercial product. $LiMn_2O_4$ is now being studied extensively as a substitute for $LiCoO_2$ because of its economical and environmental advantages over $LiCoO_2$ [6–10]. $LiMn_2O_4$ particles are usually prepared by the conventional solid-state reaction method. This process has several disadvantages, however, such as inhomogeneity, irregular morphology, large particle size, and broad particle size distribution. It is well-known that the electrochemical performance of the cathode material is strongly affected by the particle properties, such as its morphology, specific surface area, crystallinity and composition [11–14]. In recent years, fine-sized cathode particles have been investigated for the development of high-capacity secondary lithium batteries [15–20]. Various liquid solution methods such as sol-gel, pechini, SCR, emulsion drying, and xerogel have been applied to the preparation of fine-sized cathode particles [21–25].

Ultrasonic spray pyrolysis is classified into the liquid solution and gas phase reaction methods because of its particle formation mechanism. Therefore, ultrasonic spray pyrolysis has the advantages of the liquid solution and gas phase reaction methods [26–30]. The advantage of ultrasonic spray pyrolysis with respect to the liquid reaction method is its ability to control the composition of multicomponent oxide particles, whereas its advantage with respect to the gas phase reaction method is its ability to control the morphology of the particles. Ultrasonic spray pyrolysis is also being applied to the preparation of fine-sized $LiMn_2O_4$ particles [31–34]. Fine-sized $LiMn_2O_4$ particles prepared by ultrasonic spray pyrolysis have spherical shapes and nano-structured morphologies [31].

The characteristics of cathode particles prepared by ultrasonic spray pyrolysis are affected by their preparation conditions. In this study, fine-sized $LiMn_2O_4$ particles with high discharge capacities were prepared by ultrasonic spray pyrolysis at severe preparation conditions such as a high flow rate of the carrier gas and a short residence time of the particles inside the hot wall reactor. Citric acid and

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ethylene glycol were used as polymeric precursors to control the characteristics of the $LiMn_2O_4$ particles. The effects of citric acid and ethylene glycol added into spray solution on the morphologies, discharge capacities, and crystallinities of the $LiMn_2O_4$ particles prepared by ultrasonic spray pyrolysis were investigated.

Experimental

The schematic diagram of the ultrasonic spray pyrolysis system used in this study is cited elsewhere [30]. The length and diameter of the quartz reactor were 1,200 and 50 mm, respectively. The reactor temperature was maintained at 900 °C. The flow rate of the air used as the carrier gas was 40 L/min. The residence time of particle inside the hot wall reactor was 0.4 sec. An aqueous spray solution was prepared by dissolving a stoichiometric ratio of Li carbonate (Li_2CO_3, Aldrich) and manganese acetate hexahydrate [$Mn(CH_3COO) \cdot 4H_2O$, Aldrich], dissolved in distilled water. A polymeric spray solution was prepared by dissolving citric acid and ethylene glycol into an aqueous spray solution. The molar concentrations of citric acid and ethylene glycol were both fixed at 0.3 M. The precursor particles obtained by ultrasonic spray pyrolysis were post-treated at temperatures of 700–1,000°C for 12 h in the air atmosphere.

The crystal structures of the particles were investigated using x-ray diffractometry (XRD, RIGAKU DMAX-33). The morphological characteristics of the particles were investigated using scanning electron microscopy (SEM, JEOL JSM-6060). Specific surface areas of the particles were measured by Brunauer-Emmett-Teller (BET) method. The cathode electrode was made of 12 mg of $LiMn_2O_4$ 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. Lithium metal and polypropylene film were used as the anode electrode and the separator, respectively. The electrolyte 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 electrochemical performances of the various $LiMn_2O_4$ samples were measured using the charge/discharge curves of the Li/$LiMn_2O_4$ cell cycled from 3.0 to 4.3 V at a constant current density of 0.1 C.

Results and discussions

The morphologies of the particles prepared by ultrasonic spray pyrolysis were affected by the preparation conditions such as the flow rate of the carrier gas, the reactor temperature, and the residence time of the particles inside the hot wall reactor. Among these conditions, the flow rate of the carrier gas played a key role in the large-scale production of the particles in ultrasonic spray pyrolysis. The effect of the flow rate of the carrier gas on the morphologies of the lithium manganese particles prepared by ultrasonic spray pyrolysis is shown in Fig. 1. The particles prepared at a low carrier gas flow rate the had filled morphologies and narrow size distributions, whereas the particles prepared at a high carrier gas flow rate had hollow morphologies and broad size distributions because of the high drying rate of the droplets and the short residence time of the particles inside the hot wall reactor.

The lithium manganese oxide particles directly prepared by ultrasonic spray pyrolysis at a high carrier gas flow rate had poor crystal $LiMn_2O_4$ structures because of the short residence time of the particles inside the hot wall reactor. Therefore, the $LiMn_2O_4$ particles prepared by ultrasonic spray pyrolysis at a high carrier gas flow rate were post-treated at high temperatures for homogeneity and high crystallinity. In Fig. 2, the as-prepared particles obtained by ultrasonic spray pyrolysis at the 40 L/min carrier gas flow rate were post-treated at various temperatures for 12 h. The particles post-treated below 750 °C had spherical shapes and hollow morphologies, of which one post-treated particle was obtained from one as-prepared particle. On the other hand, the $LiMn_2O_4$ particles obtained at the post-treatment temperature of 800°C had non-spherical shapes and broad size distributions. The as-prepared particles with spherical shapes and hollow morphologies turned into $LiMn_2O_4$ particles with irregular morphologies at the post-treatment temperature of 800 °C. The mean sizes of the particles increased with increasing post-treatment temperatures. The $LiMn_2O_4$ particles post-treated at 900 and 1,000 °C had several microns and aggregated morphologies between the particles. The BET surface areas of the $LiMn_2O_4$ particles post-treated at temperatures of 800 and 900 °C were 1.6 and 0.8 m^2/g, respectively.

Citric acid and ethylene glycol were added to the spray solution to control the morphologies of the $LiMn_2O_4$ particles prepared by ultrasonic spray pyrolysis. The as-prepared particles obtained by ultrasonic spray pyrolysis from the spray solution with citric acid and ethylene glycol had hollow and porous morphologies. The morphologies of the post-treated particles obtained from the spray solution with citric acid and ethylene glycol differed from those of the particles obtained from the aqueous spray solution. The particles post-treated at 700 and 750 °C had more hollow and more porous morphologies than those obtained from the aqueous spray solution. The particles post-treated at 800 °C had fine sizes, regular morphologies and narrow size distributions, however, in which the spherical morphologies of the as-prepared particles disappeared after

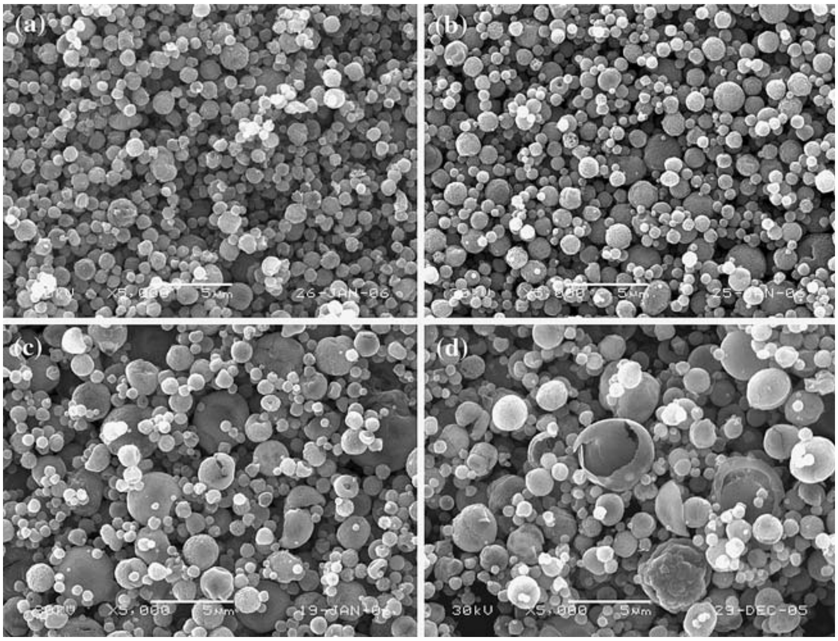


Fig. 1 SEM photographs of the as-prepared particles at different flow rates of carrier gas: (**a**) 5 L/min, (**b**) 10 L/min, (**c**) 20 L/min, (**d**) 40 L/min

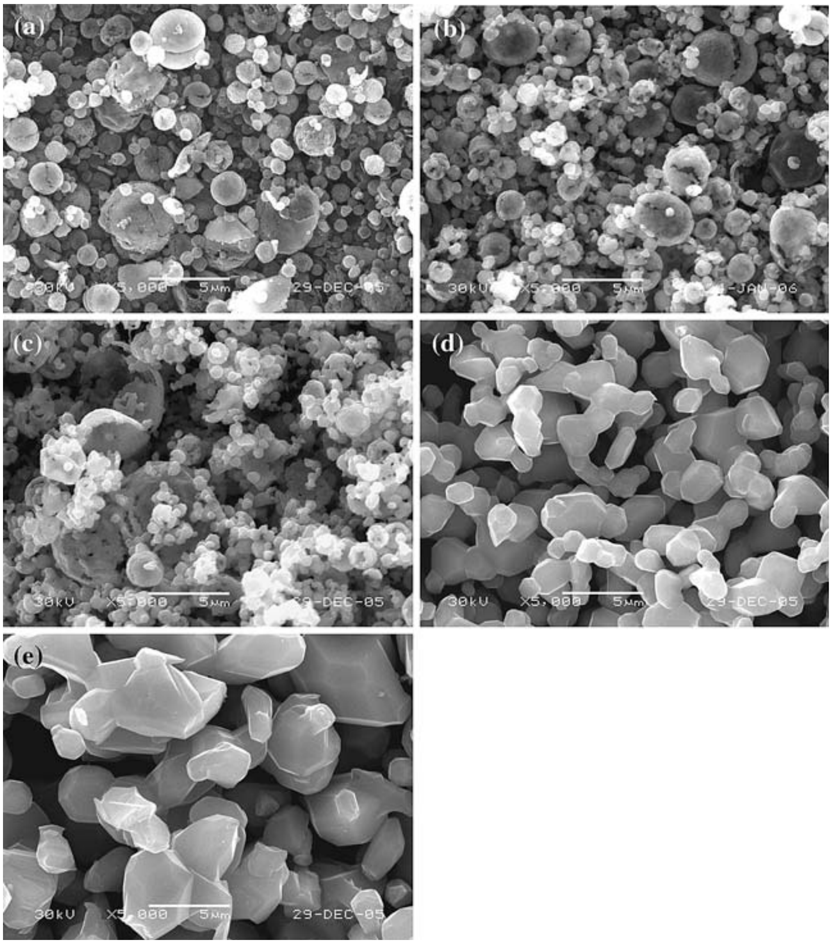
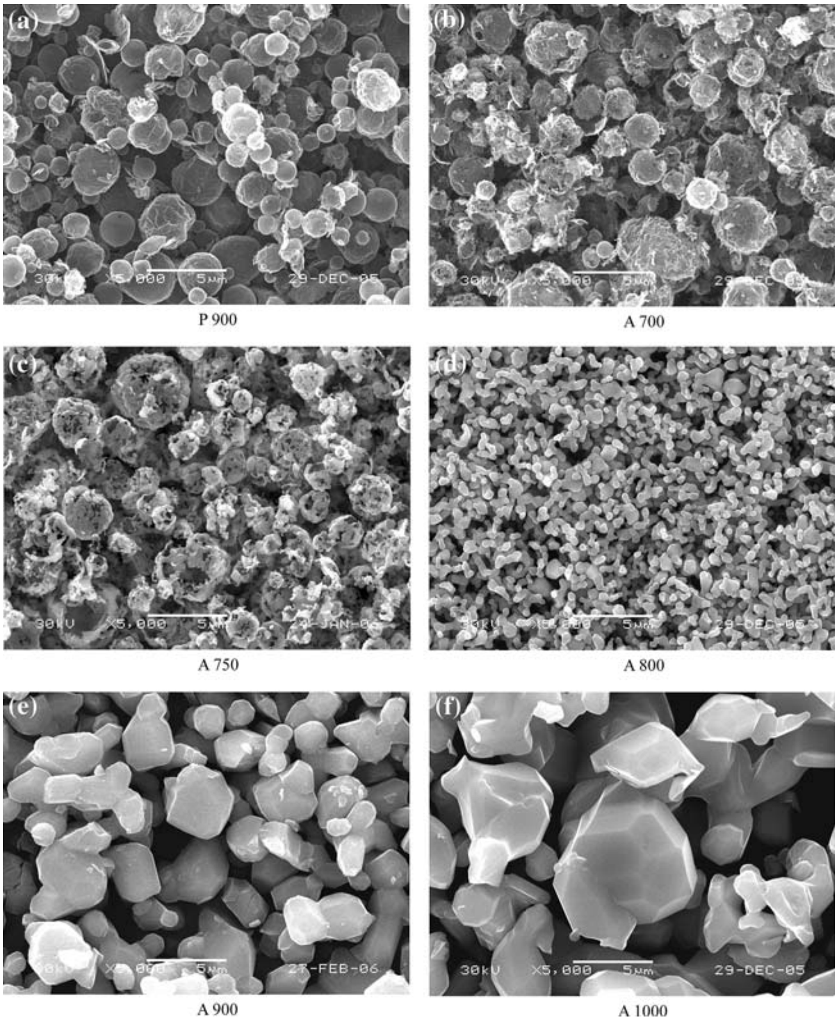


Fig. 2 SEM photographs of post-treated particles prepared from spray solution without citric acid and ethylene glycol (A : post-treatment temperature): (**a**) A700, (**b**) A750, (**c**) A800, (**d**) A900, (**e**) A1000

their post-treatment. The mean size of the particles measured from the SEM photograph (Fig. 3d) was 670 nm at the post-treatment temperature of 800 °C. The morphologies and mean sizes of the particles obtained from the spray solution with citric acid and ethylene glycol were similar to those of the particles obtained from the aqueous

Fig. 3 SEM photographs of as-prepared and post-treated particles prepared from spray solution with citric acid and ethylene glycol (P : preparation temperature): (**a**) P900, (**b**) A700, (**c**) A750, (**d**) A800, (**e**) A900, (**f**) A1000



spray solution at the post-treatment temperatures of 900 and 1,000 °C. The BET surface areas of the $LiMn_2O_4$ particles obtained from the spray solution with citric acid and ethylene glycol were decreased from 4.9 to 0.7 m^2/g when the post-treatment temperature was changed from 700 to 900 °C.

Figures 4 and 5 show the XRD spectra of the as-prepared and post-treated particles. The as-prepared particles obtained from the spray solutions with and without citric acid and ethylene glycol at the preparation temperature of 900 °C were post-treated at 700–1,000 °C. The as-prepared particles had the crystal structures of the $LiMn_2O_4$ particles irrespective of the types of the spray solution. The as-prepared particles had poor crystallinities, however, because of the short residence time of the particles inside the hot wall reactor. The mean crystallite sizes of the particles prepared from the aqueous spray solution changed from 29 to 62 nm when the post-treatment temperature was changed from 700 to 1,000 °C. On the other hand, the mean crystallite sizes of the particles prepared

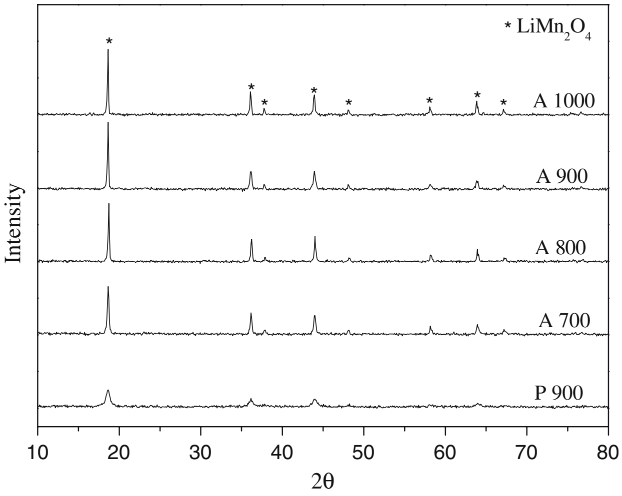


Fig. 4 XRD spectra of as-prepared and post-treated particles prepared from spray solution without citric acid and ethylene glycol

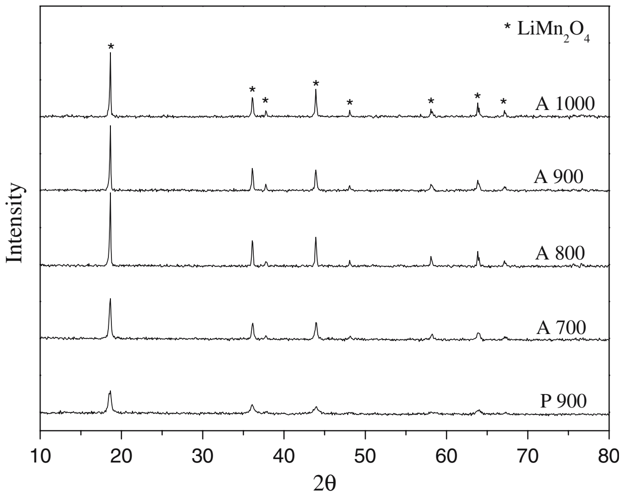


Fig. 5 XRD spectra of as-prepared and post-treated particles prepared from spray solution with citric acid and ethylene glycol

from the spray solution with citric acid and ethylene glycol changed from 32 to 64 nm when the post-treatment temperature was changed from 700 to 1,000 °C.

The charge/discharge characteristics of the $LiMn_2O_4$ particles prepared from the spray solutions with and without citric acid and ethylene glycol are shown in Figs. 6 and 7. The discharge capacities of the particles prepared from the spray solution without citric acid and ethylene glycol changed from 88 to 125 mAh/g when the post-treatment temperatures were changed from 700 to 1,000 °C. At the same post-treatment temperatures, the discharge capacities of the particles prepared from the spray solution with citric acid and ethylene glycol changed from 90 to 127 mAh/g. The $LiMn_2O_4$ particles prepared from the spray solutions with and without citric acid and ethylene glycol had maximum discharge capacities at the post-treatment temperature of 800 °C.

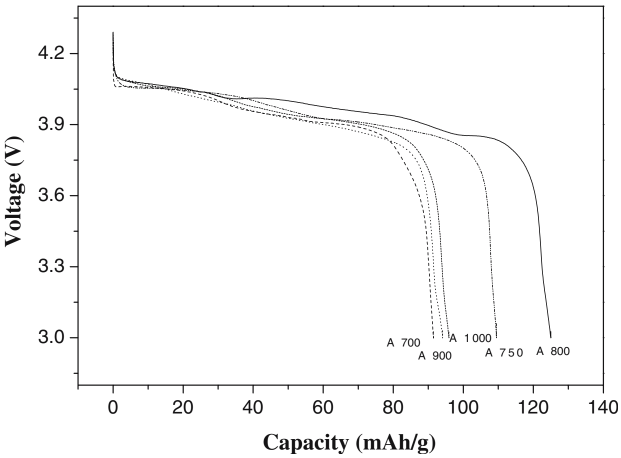


Fig. 6 Initial discharge curves of post-treated particles prepared from spray solution without citric acid and ethylene glycol

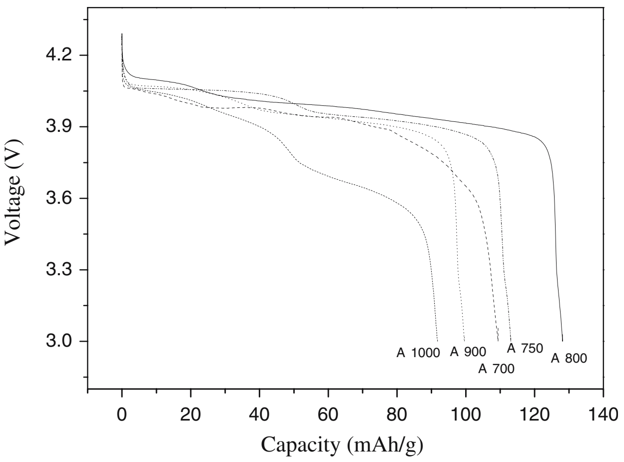


Fig. 7 Initial discharge curves of post-treated particles prepared from spray solution with citric acid and ethylene glycol

Figure 8 shows the cycle properties of the $LiMn_2O_4$ particles prepared by ultrasonic spray pyrolysis. The precursor particles prepared from the spray solution with citric acid and ethylene glycol were post-treated at 800 °C for 3 h. The discharge capacities of the $LiMn_2O_4$ particles dropped from 127 to 108 mAh/g by the 30th cycle.

Conclusions

The addition of citric acid and ethylene glycol to the spray solution affected the morphologies and mean sizes of the $LiMn_2O_4$ particles prepared by ultrasonic spray pyrolysis. The as-prepared particles obtained by ultrasonic spray pyrolysis from the spray solution with citric acid and ethylene glycol turned into $LiMn_2O_4$ particles with fine sizes and regular morphologies at the post-treatment temperature

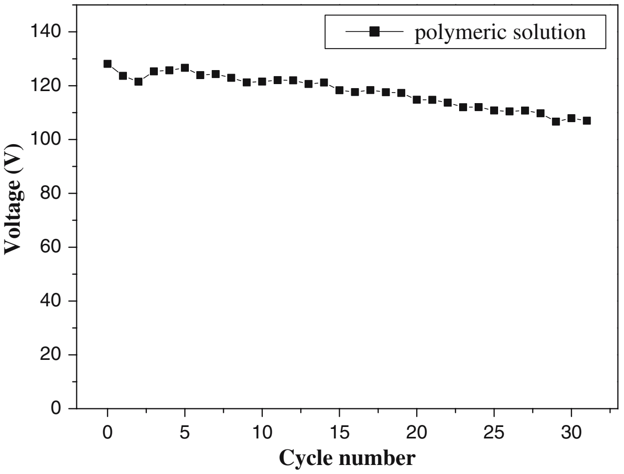


Fig. 8 Cycle properties of the particles prepared from spray solution with citric acid and ethylene glycol

of 800 °C. On the other hand, the $LiMn_2O_4$ particles prepared from the spray solution without citric acid and ethylene glycol had irregular morphologies and broad size distributions at the post-treatment temperature of 800 °C. The $LiMn_2O_4$ particles prepared by ultrasonic spray pyrolysis from the spray solution with citric acid and ethylene glycol had high discharge capacities and good cycle properties.

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