

The effect of manganese oxide precursors on the characteristics of LiMn_2O_4 cathode particles

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Manganese oxide particles with nanometre and several micrometre sizes were prepared by spray pyrolysis from aqueous and polymeric spray solutions. The LiMn_2O_4 particles prepared from Mn_2O_3 particles obtained from an aqueous solution with a manganese nitrate precursor had micrometre sizes and a spherical shape. On the other hand, the LiMn_2O_4 particles prepared from nano-sized Mn_2O_3 particles obtained from polymeric spray solutions had a fine size, a narrow size distribution, and regular morphology irrespective of the type of manganese precursors. The discharge capacities of the LiMn_2O_4 particles obtained from an aqueous spray solution with a manganese nitrate precursor dropped from 136 to 115 mAh/g by the 25 th cycle at a current density of 0.1 C. On the other hand, the discharge capacities of the LiMn_2O_4 particles obtained from a polymeric spray solution with a manganese nitrate precursor dropped from 121 to 105 mAh/g.

Key Words: Spray pyrolysis, Nano particle, Lithium manganate.

Introduction

Spinel LiMn_2O_4 has been widely studied as a cathode material for lithium secondary batteries due to its low cost and environmental friendliness [1-5]. LiMn_2O_4 particles are prepared by various ceramic processing methods such as solid-state reaction and liquid solution methods. The characteristics of LiMn_2O_4 particles such as their morphology, mean particle size, crystallinity and phase homogeneity are affected by the preparation method. It is well-known that the electrochemical performance of the cathode material is strongly affected by the particle properties [6-8]. In recent years, fine-sized cathode materials have been investigated to achieve the high capacity in lithium secondary batteries [9-14].

Spray pyrolysis has been studied as a preparation method for fine-sized ceramic particles [15-20]. The characteristics of the ceramic particles were strongly affected by the preparation conditions such as type of precursor, flow rate of carrier gas, and preparation temperature. In this study, manganese oxide particles with nanometre and several micrometre sizes were prepared by spray pyrolysis with different preparation conditions. The effects of the type of manganese precursor on the characteristics of the manganese oxide particles prepared by spray pyrolysis from aqueous and polymeric spray solutions were investigated. The manganese oxide particles prepared by spray pyrolysis were mixed with LiOH powder and

post-treated at high temperatures. The characteristics of the LiMn_2O_4 particles prepared by a conventional solid-state reaction method using the Mn_2O_3 particles prepared were investigated.

Experimental procedure

Manganese oxide particles were prepared by spray pyrolysis from various types of spray solution. A schematic diagram of the spray pyrolysis system used in this study is given elsewhere [19]. The system consists of a droplet generator, a quartz reactor, and a particle collector. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate large amounts of droplets, which are carried into the high-temperature tubular reactor by a carrier gas. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. The manganese precursors used in this study were hydrated forms of manganese acetate, chloride and nitrate. The concentration of the manganese precursor was fixed at 0.3 M. The flow rate of air used as the carrier gas was 40 l/minute. The precursor particles obtained by spray pyrolysis at 900 °C were post-treated at a temperature of 800 °C in an air atmosphere to change their crystallinity and morphology. The LiMn_2O_4 particles were prepared by a solid-state reaction method using the manganese oxide particles obtained by spray pyrolysis. Manganese oxide particles were mixed with LiOH powder and post-treated at a temperature of 800 °C for 3 h.

The crystal structures of the particles were investigated by X-ray diffractometry (XRD, RIGAKU DMAX-33). The morphological characteristics of the particles were investigated by scanning electron microscopy (SEM, JEOL

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JSM-6060F). The cathode electrode was made of 12 mg of LiMn_2O_4 compound 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. 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 ethylene carbonate (EC)/dimethyl carbonate (DMC). The entire cell was assembled in a glove box under an argon atmosphere. The electrochemical performance of the various LiMn_2O_4 samples were measured by charge/discharge curves of Li/ LiMn_2O_4 cells cycled from 3.0–4.3 V at a constant current density of 0.1 C.

Results and Discussion

Figs. 1 and 2 show SEM images of the manganese oxide particles prepared by spray pyrolysis from an aqueous spray solution. The as-prepared particles obtained by spray pyrolysis were post-treated at a temperature of 800 °C for 3 h. The as-prepared manganese oxide particles had different morphologies according to the type of manganese precursor. The as-prepared particles obtained from the manganese acetate and chloride precursors had hollow and porous morphologies. On the other hand, the as-prepared particles obtained from the manganese nitrate precursor had a completely spherical shape and filled structure. In the spray pyrolysis, the morphologies of the particles were affected by the type of precursor because of their different drying, decomposition and

crystallization characteristics. The morphologies of the manganese oxide particles were changed after post-treatment. The spherical shape of the as-prepared particles obtained from the manganese acetate precursor disappeared after post-treatment. The particles with a hollow and thin walled structure turned to particles with an irregular morphology after post-treatment. The post-treated manganese oxide particles obtained from the manganese chloride precursor had an aggregated morphology of the fine sized primary particles. However, the particles obtained from the manganese nitrate precursor had a spherical shape and regular morphology after post-treatment. The spherical shape of the as-prepared particles obtained from the manganese nitrate precursor was maintained after post-treatment.

Figs. 3 and 4 show SEM images of the manganese oxide particles prepared by spray pyrolysis from polymeric spray solutions containing citric acid and ethylene glycol. The concentrations of citric acid and ethylene glycol were each 0.3 M. The as-prepared particles obtained by spray pyrolysis were post-treated at a temperature of 800 °C for 3 h. The citric acid and ethylene glycol added into the spray solution changed the morphologies of the as-prepared manganese oxide particles. The as-prepared particles obtained by spray pyrolysis from polymeric spray solutions had sizes of several micrometres, hollow and porous morphologies irrespective of the type of manganese precursor. Gas evolution from the decomposition of the polymeric precursors formed the manganese oxide particles with hollow and porous morphologies. The manganese oxide particles prepared from polymeric spray solutions

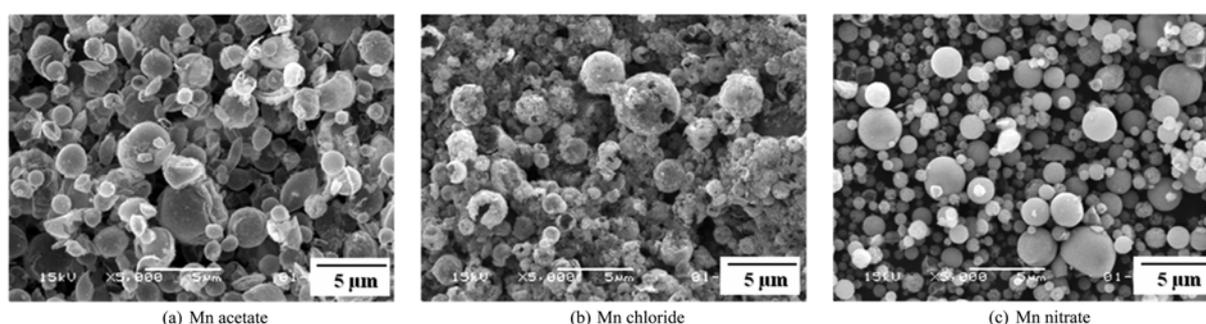


Fig. 1. The as-prepared manganese oxide particles obtained from aqueous spray solutions.

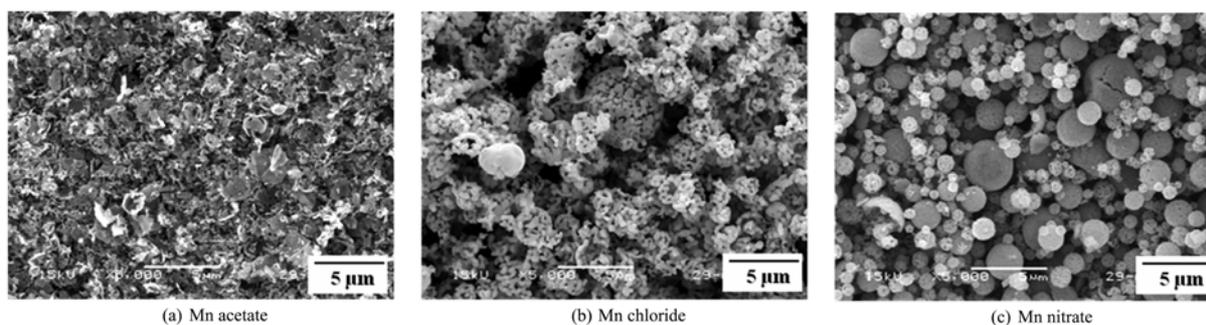


Fig. 2. The post-treated manganese oxide particles obtained from aqueous spray solutions.

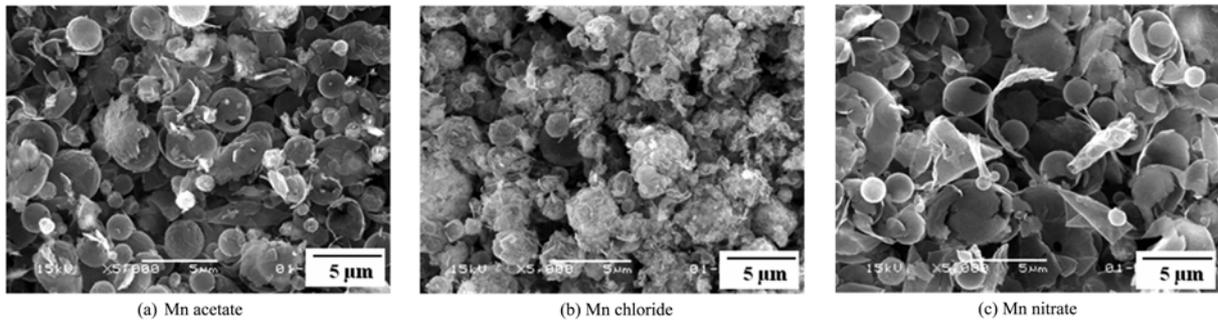


Fig. 3. The as-prepared manganese oxide particles obtained from polymeric spray solutions.

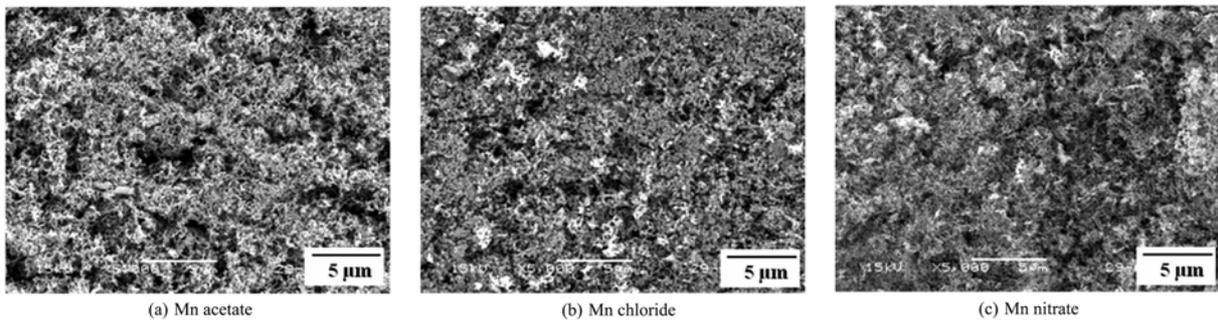


Fig. 4. The post-treated manganese oxide particles obtained from polymeric spray solutions.

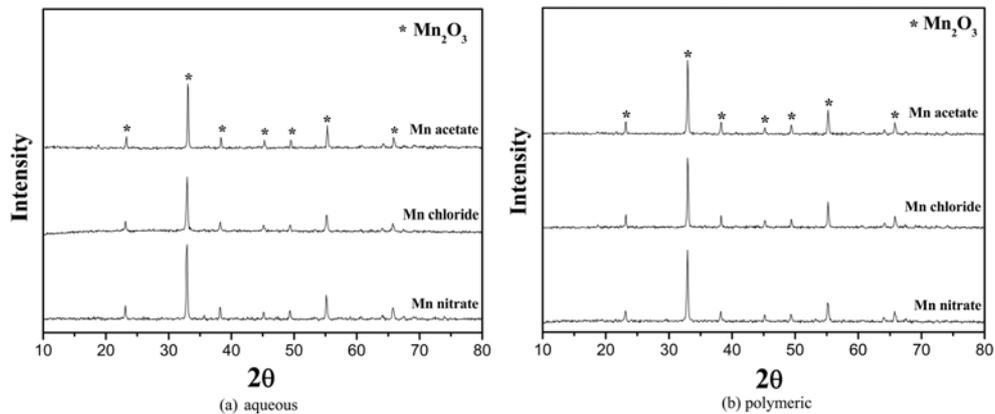


Fig. 5. XRD spectra of the post-treated manganese oxide particles obtained from aqueous and polymeric spray solutions.

had similar morphologies after post-treatment irrespective of the type of manganese precursor. The as-prepared particles of a micrometre size with hollow and porous morphologies turned to nano-sized manganese oxide particles after post-treatment without a milling process. The type of manganese precursor affected the mean size of the post-treated manganese oxide particles. The particles prepared from the manganese chloride precursor had a larger mean size than those of the particles prepared from manganese acetate and nitrate precursors.

Fig. 5 shows the XRD spectra of the post-treated manganese oxide particles prepared from aqueous and polymeric spray solutions. The particles post-treated at temperature of 800 °C had the same Mn₂O₃ crystal structure irrespective of the type of manganese precursor.

The mean crystallite sizes of the Mn₂O₃ particles prepared from an aqueous spray solution were changed from 30 to 40 nm according to the type of manganese precursor. On the other hand, the mean crystallite sizes of the Mn₂O₃ particles prepared from a polymeric spray solution were changed from 35 to 44 nm according to the type of manganese precursor.

LiMn₂O₄ particles were prepared by a solid-state reaction method using the manganese oxide particles obtained by spray pyrolysis. Fig. 6 shows SEM images of the LiMn₂O₄ particles, where the Mn₂O₃ particles obtained from an aqueous spray solutions were reacted with LiOH particles. The different characteristics of the Mn₂O₃ particles affected the morphology and the mean size of the LiMn₂O₄ particles obtained by the solid-state reaction

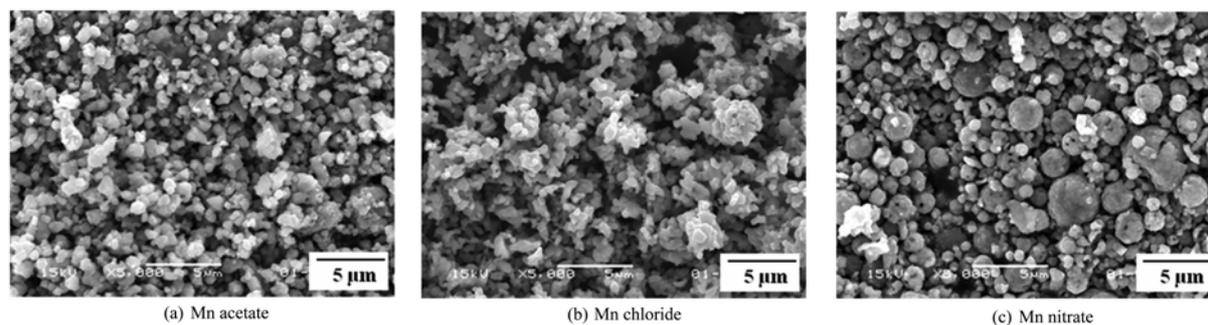


Fig. 6. SEM images of LiMn_2O_4 particles obtained from aqueous spray solutions.

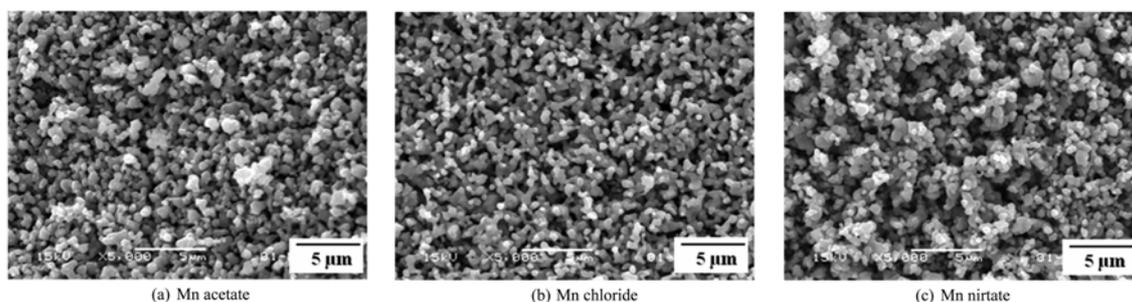


Fig. 7. SEM images of LiMn_2O_4 particles obtained from polymeric spray solutions.

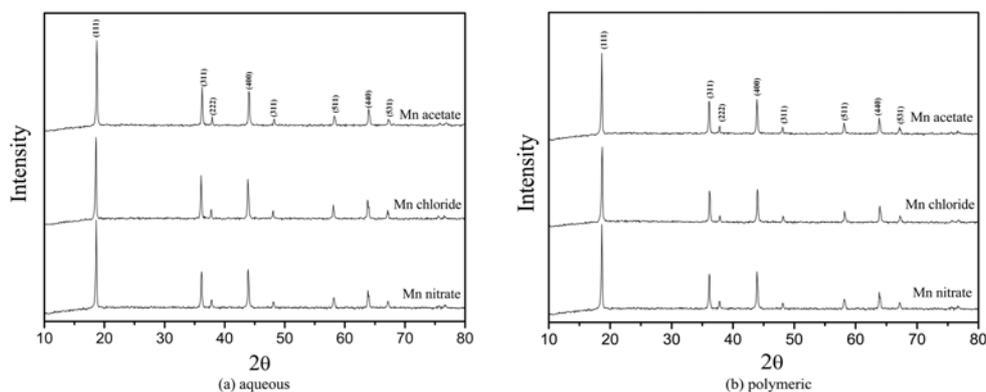


Fig. 8. XRD spectra of LiMn_2O_4 particles obtained from aqueous and polymeric spray solutions.

method. The LiMn_2O_4 particles prepared from the Mn_2O_3 particles [Fig. 2(a), (b)] obtained from manganese acetate and chloride precursors had micrometre sizes and aggregated morphologies. On the other hand, the LiMn_2O_4 particles prepared from the Mn_2O_3 particles [Fig. 2(c)] obtained from manganese nitrate precursor had a micrometre size with a spherical shape and regular morphology. The spherical shape of the Mn_2O_3 particles [Fig. 2(c)] was maintained after the reaction with LiOH particles. Fig. 7 shows SEM images of the LiMn_2O_4 particles, in which the Mn_2O_3 particles [Fig. 4(a), (b), (c)] obtained from polymeric spray solutions were reacted with LiOH particles. The nano-sized Mn_2O_3 particles obtained from manganese acetate, chloride and nitrate precursors formed the LiMn_2O_4 particles with a fine size, narrow size distribution, and regular morphology. Fig. 8 shows the XRD spectra of the LiMn_2O_4 particles. The particles had a pure spinel

cubic LiMn_2O_4 crystal structure irrespective of the type of manganese precursor dissolved into aqueous and polymeric spray solutions. The mean crystallite sizes of the LiMn_2O_4 particles calculated by Scherrer's equation changed from 37 to 42 nm according to the type of manganese precursor dissolved into the aqueous and polymeric spray solutions.

Fig. 9 shows the initial charge and discharge curves of the LiMn_2O_4 particles [Fig. 6(a), (b), (c)]. The charge and discharge capacities of the LiMn_2O_4 particles were affected by the type of manganese precursor used as raw materials from the Mn_2O_3 particles. The discharge capacities of the LiMn_2O_4 particles obtained from the manganese acetate and nitrate precursors were 134 and 136 mAh/g, respectively. On the other hand, the discharge capacity of the LiMn_2O_4 particles obtained from the manganese chloride precursor was 128 mAh/g. However,

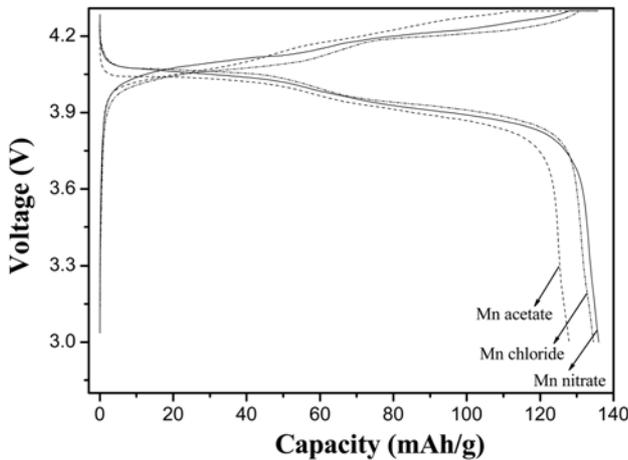


Fig. 9. Initial charge/discharge curves of LiMn_2O_4 particles obtained from aqueous spray solutions.

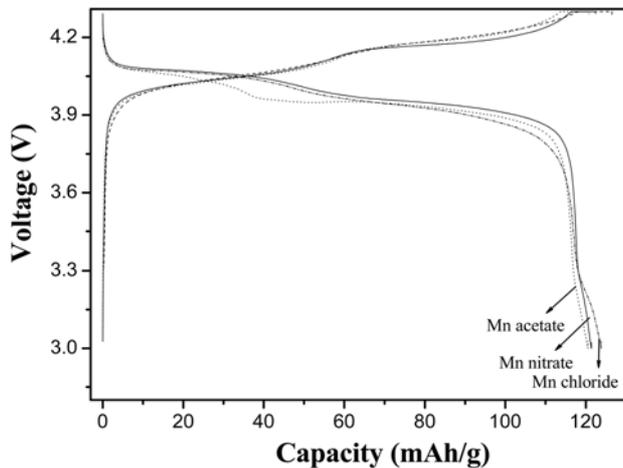


Fig. 10. Initial charge/discharge curves of LiMn_2O_4 particles obtained from polymeric spray solutions.

the LiMn_2O_4 particles [Fig. 7(a), (b), (c)] obtained from the fine-sized Mn_2O_3 particles had similar discharge capacities of 120 mAh/g irrespective of the type of manganese precursor as shown in Fig. 10.

Fig. 11 shows the cycle properties of the LiMn_2O_4 particles [Fig. 6(a), (b), (c)]. The LiMn_2O_4 particles obtained from the manganese nitrate and acetate precursors had good cycle properties. The discharge capacities of the LiMn_2O_4 particles as shown in Fig. 6(a) and (c) decreased to 84 and 85% of their initial values after 25 cycles at a current density of 0.1 C. On the other hand, the discharge capacity of the LiMn_2O_4 particles as shown in Fig. 6(b) decreased to 70% of its initial value after 25 cycles. Fig. 12 shows the cycle properties of the LiMn_2O_4 particles [Fig. 7(a), (b), (c)]. The discharge capacities of the LiMn_2O_4 particles as shown in Fig. 7(a) and (c) decreased to 68 and 87% of their initial values after 25 cycles. On the other hand, the discharge capacity of the LiMn_2O_4 particles as shown in Fig. 7(b) decreased to 44% of its initial value after 25 cycles.

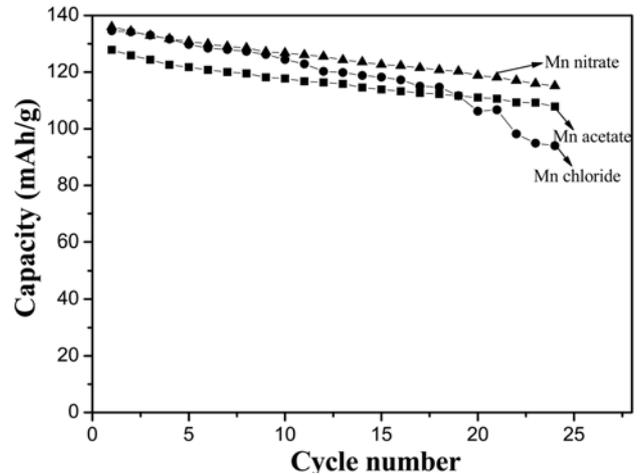


Fig. 11. Cycle properties of LiMn_2O_4 particles obtained from aqueous spray solutions.

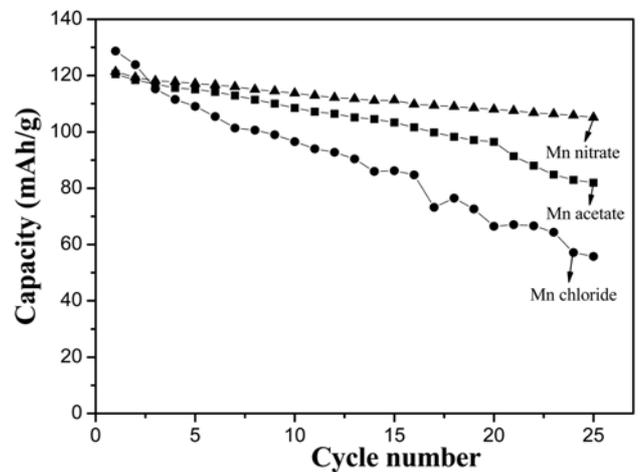


Fig. 12. Cycle properties of LiMn_2O_4 particles obtained from polymeric spray solutions.

Conclusions

The effects of types of manganese precursors on the characteristics of the manganese oxide particles prepared by spray pyrolysis from aqueous and polymeric spray solutions were investigated. The mean size of the manganese oxide particles prepared by spray pyrolysis changed from several tens of nanometres to several micrometres according to the type of spray solution. The mean size, morphology and charge/discharge capacities of the LiMn_2O_4 particles prepared by a conventional solid-state reaction method were affected by the characteristics of the manganese oxide particles. Manganese acetate and nitrate precursors were appropriate for the preparation of nano-sized manganese oxide particles by spray pyrolysis from polymeric spray solutions. Fine-sized LiMn_2O_4 particles with high charge/discharge capacities were prepared by a conventional solid-state reaction method using nano-sized manganese oxide particles.

References

1. Y. Xia, Y. Zhou and M. Yoshio, *J. Electrochem. Soc.* 144 (1997) 2593-2600.
2. J.M. Tarascon and D. Guyomard, *Electrochim. Acta* 38 (1993) 1221-1231.
3. T. Ohzuku, M. Kitagawa and T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769-775.
4. J.M. Tarascon and M. Armand, *Nature* 414 (2001) 359-367.
5. D. Guyomard and J.M. Tarascon, *J. Electrochem. Soc.* 138 (1991) 2864-2868.
6. T. Ogihara, Y. Saito, T. Yanagawa, N. Ogata, K. Yoshida, M. Takashima, S. Yonezawa, Y. Mizuno, N. Nagata and K. Ogawa, *J. Ceram. Soc. Jpn.* 101 (1993) 1159-1163.
7. Y. Li, C. Wan, Y. Wu, C. Jiang and Y. Zhu, *J. Power Sources* 85 (2000) 294-298.
8. C.H. Chen, A.A.J. Buysman, E.M. Kelder, and J. Schoonman, *Solid State Ionics* 80 (1995) 1-4.
9. T. Kawamura, M. Makidera, S. Okada, K. Koga, N. Miura and J. Yamaki, *J. Power Sources* 146 (2005) 27-32.
10. Y. Gu, D. Chen and X. Jiao, *J. Phys. Chem. B* 109 (2005) 17901-17906.
11. O.A. Shlyakhtin, S.H. Choi, Y.S. Yoon and Y.J. Oh, *Electrochim. Acta* 50 (2004) 511-516.
12. T. Tsuji, T. Kakita, T. Hamagami, T. Kawamura, J. Yamaki and M. Tsuji, *Chem. Lett.* 33 (2004) 1136-1137.
13. S.H. Choi, J.S. Kim and Y.S. Yoon, *J. Power Sources* 135 (2004) 286-290.
14. J. Liu, Z. Wen, Z. Gu, M. Wu and Z. Lin, *J. Electrochem. Soc.* 149 (2002) A1405-A1408.
15. K. Matsuda and I. Taniguchi, *J. Power Sources* 132 (2004) 156-160.
16. I. Taniguchi, C.K. Lim, D. Song and M. Wakihara, *Solid State Ionics* 146 (2002) 239-247.
17. K. Matsuda and I. Taniguchi, *Kagaku Kogaku Ronbunshu* 29 (2003) 232-237.
18. I. Taniguchi, *Mater. Chem. Phys.* 92 (2005) 172-179.
19. J.R. Sohn, Y.C. Kang and H.D. Park, *Jpn. J. Appl. Phys.* 41 (2002) 3006-3009.
20. J.M. Han, D.S. Jung, S.H. Lee and Y.C. Kang, *J. Ceram. Proc. Res.* 9 (2008) 140-145.