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Cathode Performance of LiMn_2O_4 Thick Films Prepared by Gas-Deposition for Lithium Rechargeable Battery

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Lithium manganese oxide thick films were prepared on aluminum foils without any conductive agent or binder material by means of gas-deposition (GD) method. Charge/discharge performances were investigated on the coin-type cells consisting of the GD'ed cathode and the lithium metal anode, which were compared with the case using the cathode conventionally prepared with conductor and binder. In the case that LiMn_2O_4 powders with the particle size of 10 μm were employed as the cathode material, the GD'ed cathode showed smaller discharge capacities in early cycles in comparison with conventionally prepared cathode. However, by roughly milling the cathode powders to modify the particle size distribution, obvious enhancement of discharge capacity was observed only for GD'ed cathode. In terms of the cycle stability, the GD method was effective to prepare the cathode material having a good performance.

Key Words : Cathode Material, Lithium Battery, Lithium Manganese Oxide, Gas Deposition, Aerosol Deposition

1 Introduction

While LiMn_2O_4 is an attractive cathode material in terms of low cost and environmental compatibility^{1,2)} comparing with the currently used LiCoO_2 , one of the main obstacles for the practical application is the capacity fading during charge/discharge cycling³⁻⁵⁾ which is thought to be due to Jahn-Teller distortion,⁵⁾ Mn^{3+} dissolution into electrolyte,^{4,6)} or structural degeneration during the lithium intercalation/deintercalation reactions.⁷⁾ Considering that this capacity fading was strongly influenced by the microstructure, essentially two strategies have been pursued to improve the electrochemical properties during the cycling: first of all, stabilization of the structure by substituting the other transition metal ions,⁸⁾ and the next, optimization of the morphologies of active materials.^{9,10)} In the latter approach, a lot of effort has been devoted so far to synthesize the homogeneous manganese spinel with small particle size, especially by means of various “soft chemistry” synthesis route.¹¹⁻¹⁵⁾

Producing the electrodes in the practical cells, on the other hand, the synthesized LiMn_2O_4 powders must be spread on a current collector such as aluminum foil with carbonous conducting agents and binder material, which increase the cathode volume and probably lose the virtue of the controlled electrode morphology.¹⁶⁾ Of course, in the case of thin films prepared by CVD,¹⁷⁾ r.f. sputtering,¹⁸⁾ or pulsed laser deposition,^{19,20)} conducting agent free cathodes are available since the lithium intercalation/deintercalation occurs at the surface easily.²¹⁾ To obtain thicker film electrode without conductive additives, porous microstructure is preferred for the electrolyte to percolate into inside of the electrodes, which would be obtained by electrostatic spray deposition^{22,23)}

or sol-gel method.²⁴⁾ Nevertheless, heat treatments are necessary after the deposition for these methods.

Comparing with the above techniques, gas-deposition (GD) method,²⁵⁻²⁹⁾ in which powder sample aerosolized by carrier gas flow impacts on the substrate to form films, seems to be a suitable solution for the cathode formation technique of the film batteries, since the feature of surface morphologies of the original powder particles are expected to be preserved in the deposited film. This GD method, often referred as aerosol-deposition, was originally developed for the fabrication of piezoelectric films.^{26,27)} Recently, Sakaguchi *et al.* adopted this technique to the preparation of lithium storage alloy or oxide electrode for rechargeable batteries, and demonstrated the drastic improvement in the charge/discharge stability.³⁰⁾ In the present study, LiMn_2O_4 thick-film cathodes without any conducting agents were prepared and charge/discharge performance was compared with the conventionally prepared ones.

2 Experimental

Three types of LiMn_2O_4 samples were used as the starting powders in the present study. Sample A is the sintered one obtained through high temperature solid-state reaction method using Li_2CO_3 and Mn_2O_3 , where calcining and sintering temperatures were selected to be 700 and 800 $^\circ\text{C}$, respectively. The sample was then crushed in an alumina mortar. Sample B is the commercially available LiMn_2O_4 powder provided by Nippon Chemical Industrial Co. (Cellseed M-10), and sample C is obtained by milling the sample B using planetary ball milling machine operated at 100 rpm for 2 h.

Schematic illustration of GD apparatus was represent-

Fig. 1 Schematic illustration of gas-deposition (GD) apparatus.

ed in Fig. 1. An aluminum foil of 25 μm thick (Nilaco Co.) used as a substrate was sandwiched by two aluminum plates (holder), the one of which was employed as a screen with a $\phi 10$ hole at the deposition, and they were set in front of the deposition nozzle. Nozzle diameter and nozzle-substrate distance were selected to be $\phi 1.0$ and 13 mm, respectively. The sample powders charged in the guide tube were poured into the vacuum chamber by Ar gas pressured into 7×10^5 Pa within 1 s. After 4 times injection to cover the deposition area, the sample powder remaining on the foil was removed gently, resulting in 0.1–0.2 mg of deposited cathode film.

In addition to the GD'ed film cathodes, a conventional cathode was prepared for the comparison; the mixture of LiMn_2O_4 powders, acetylene-black as a conductor, and PVdF (polyvinylidene difluoride) as a binder (92: 4: 4 in weight) was painted on an Al foil (30 mm in side) with a small amount of NMP (N-methyl-2-pyrrolidone), which was then dried under vacuum at room temperature for 24 h. Typical amount of LiMn_2O_4 active material was 3 mg. We referred this as “slurry” cathode.

Coin-type cells of 2032 size were assembled in an argon-gas filled dry-box, using the GD'ed or conventionally prepared LiMn_2O_4 electrodes as cathodes, 1M $\text{LiClO}_4/\text{EC-DEC}$ (1: 1 v/v) as the electrolyte, Celgard 2400 as a separator, and lithium foil ($\phi 16$ in diameter and 0.75 mm in thickness) as an anode. Charge/discharge experiments were performed on the constructed cell galvanostatically between 3.0 and 4.2 V using multi-charge battery testers in an incubator controlled at 30 $^\circ\text{C}$. The current was selected to be 0.1 and 0.04 mA for slurry and GD'ed electrodes, respectively.

3 Results and Discussion

Figure 2 shows the particle size distribution and SEM photographs of LiMn_2O_4 powders used for GD. The surface photographs of the corresponding GD'ed films are also represented at the right side in this figure. Sample A, prepared by sintering, seemed to consist of 5 μm sized particles as observed in both particle size measurements and SEM images. While the particle size of sample B (Cellseed M-10) was dispersed around 10 μm , SEM

photographs revealed that very fine particles with sub-micrometer size are agglomerated into the secondary particles. The sample C, obtained by milling sample B for 2 h, appeared to be partly crushed into sub-micrometer sized fine particles ($\sim 0.3 \mu\text{m}$) accompanied by remaining coarse ones ($\sim 7 \mu\text{m}$). Thick-film cathodes can be similarly formed on Al foils for all the type LiMn_2O_4 powders by means of GD method. Although the general morphologies of all the GD'ed films showed similar feature from the surface micrographs, smaller particles were partially found in the films A and C, and the microstructure of the initial particles were vaguely remained in B.

Figure 3 shows the second charge-discharge curves of the coin-type cells ($\text{Li} \mid \text{LiMn}_2\text{O}_4$) using conventional slurry and GD'ed cathodes. The current density employed in the slurry cathodes were 50.6, 31.3 and 27.3 mA g^{-1} for samples A, B and C, respectively, while those of corresponding GD'ed ones were 571, 133 and 333 mA g^{-1} . Although the charge/discharge profiles in GD'ed cathodes were a little shrunk, the potential plateau appeared similarly to that of slurry electrodes. Therefore, the charge/discharge mechanism was assumed to be the same even in GD'ed cathodes. While discharge capacities of GD'ed cathodes were relatively smaller than those of slurry ones for samples A and B, comparable capacities could be obtained in both of the GD'ed and slurry sample C. Considering that the current densities were much higher in the GD'ed electrodes comparing with the slurry ones, it was not always possible to conclude that the GD'ed cathode was quite inferior in capacity comparing with the conventionally prepared cathode. On the other hand, discharge capacities of well-fabricated LiMn_2O_4 might exceed 130 mAh g^{-1} .³¹⁾ The present result with still smaller capacities even in the conventional slurry cathode would denote that additional conductive agents must be considered for the practical application of thick film electrode despite of the total volume increase.

The cyclability of discharge capacity for above cathodes were represented in Fig. 4, where charge/discharge experiments were extended to 100 and 500 cycles for the slurry and GD'ed cathodes, respectively. While the discharge capacities of the slurry cathodes degenerated obviously down to 54% (A), 46% (B) and 30% (C) of the initial values (maximum ones) within 100 cycles, the GD'ed cathodes retained 84% (A), 80% (B) and 91% (C) of the initial values after 100 cycles, and moreover, 64% (A) and 79% (C) were maintained after 500 cycles. Of course, the cycle performance of the slurry cathode might be improved by increasing the amount of conductive agents and binder additives in the cathode materials. Nevertheless, the present results showing better cycle performance in the GD'ed cathode without any additives exhibited the potential for the cathode thick-film formation technique.

SEM photographs of the GD'ed electrode using sample C, exhibiting the best electrochemical performance in the present study, are represented in Fig. 5. As seen in the cross-sectional image (a), LiMn_2O_4 films are of 7–8 μm thick stuck on an aluminum foil. From the surface micro-

Fig. 2 Particle size distribution and SEM photographs of starting LiMn_2O_4 powders, and the corresponding surface of as-deposited films. Samples A, B and C are sintered, commercially available and roughly milled LiMn_2O_4 powders, respectively.

Fig. 3 Charge/discharge curves of $\text{Li} \mid \text{LiMn}_2\text{O}_4$ cells in the second cycle using (a) conventionally prepared (slurry) and (b) GD²ed cathodes. Curves A, B and C corresponded to the data for sintered, commercially available and roughly milled LiMn_2O_4 powders, respectively used as cathode materials.

Fig. 4 Cycle number dependence of the discharge capacity of the coin-type cells using (a) conventionally prepared and (b) GD cathodes. A: sintered, B: commercially available and C: roughly milled LiMn_2O_4 were employed for the cathode materials.

graphs of as-deposited and after the charge/discharge experiments, various sized particles were found to be mixed and the microstructure of which seemed to be preserved after the long-term charge/discharge experi-

ments, although the deposited particles appeared to be a little swelled. Assuming that even the smaller particles endured on the films during the charge/discharge cycling, roughly milled sample C with a variety of parti-

Fig. 5 SEM photographs of GD'ed LiMn_2O_4 cathode (milled sample). (a): cross-section, (b) and (c): surface of the cathode films. Micrographs (a) and (b) were taken before the charge/discharge cycling, and (c) was obtained after the cycling. Photograph (b), the same as Fig. 2 C, was represented again for the comparison.

cle size would show good cycle stability.

In the present study, we showed the performance of LiMn_2O_4 thick-film cathode prepared by GD method; the GD method was effective to prepare not only anode materials³⁰⁾ but also the cathode ones having good cycle performances. As seen on the roughly milling process of the starting powders for improving the cathode performance, optimization of sample morphology, particle size distribution or amount of the cathode materials would lead the further enhancement of both discharge capacity and cycle performance. Moreover, GD of cathode material mixed with conducting agents is also expected to improve the electrochemical properties. Further investigation should be made on the GD process as the simple and effective cathode thick-film formation method.

4 Conclusion

Charge/discharge performances of LiMn_2O_4 thick-film cathodes prepared by GD method were investigated. GD'ed cathodes generally exhibited the improvement of cycle performance in comparison with the slurry ones containing conductive agents and binder materials. The best cycle performance was observed in commercial LiMn_2O_4 powder roughly milled before GD, where 91 and 79% of initial discharge capacities were retained even without conductive agent or binder after 100 and 500 cycles, respectively in addition to the comparable discharge capacity in early cycles with slurry cathode. SEM observation revealed that the typical deposited film thickness was 7-8 μm and degeneration of microstructure during the charge/discharge cycling is small in GD'ed thick-film cathode.

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References

- 1) J. M. Tarascon and D. Guyomard, *Electrochim. Acta*, **38**, 1221 (1993).
- 2) J. M. Tarascon, W. R. McKinnon, F. Coowar, T. N. Bowmer, G. Amatucci, and D. Guyomard, *J. Electrochem. Soc.*, **141**, 1421 (1994).
- 3) Y. Gao and J. R. Dahn, *Solid State Ionics*, **84**, 33 (1996).
- 4) Y. Xia, Y. Zhou, and M. Yoshio, *J. Electrochem. Soc.*, **144**, 2593 (1997).
- 5) R. J. Gummow, A. de Kock, and M. M. Thackeray, *Solid State Ionics*, **69**, 59 (1994).
- 6) D. H. Jang, J. Y. Shin, and S. M. Oh, *J. Electrochem. Soc.*, **143**, 2204 (1996).
- 7) A. Yamada, *J. Solid State Chem.*, **122**, 160 (1996).
- 8) L. Guohua, H. Ikuta, T. Uchida, and M. Wakihara, *J. Electrochem. Soc.*, **143**, 178 (1996).
- 9) J. Barker, R. Pynenburg, and R. Koksang, *J. Power Sources*, **52**, 185 (1994).
- 10) H. Huang, C.H. Chen, R. C. Perego, E. M. Kelder, L. Chen, J. Schoonman, W. J. Weydanz, and D. W. Nielsen, *Solid State Ionics*, **127**, 31 (2000).
- 11) Y. -S. Lee, Y. -K. Sun, and K. -S. Nahm, *Solid State Ionics*, **109**, 285 (1998).
- 12) B. J. Hwang, R. Santhanam, and D. G. Liu, *J. Power Sources*, **97-98**, 443 (2001).
- 13) I. Taniguchi, C. K. Lim, D. Song, and M. Wakihara, *Solid State Ionics*, **146**, 239 (2002).
- 14) K. Matsuda and I. Taniguchi, *J. Power Sources*, **132**, 156 (2004).
- 15) P. Kalyani, N. Kalaiselvi, and N. Muniyandi, *J. Power Sources*, **111**, 232 (2002).
- 16) S. Mandal, J. M. Amarilla, J. Ibanez, and J. M. Rojo, *J. Electrochem. Soc.*, **148**, A24 (2001).
- 17) P. Liu, J. -G. Zhang, J. A. Turner, C. E. Tracy, and D. K. Benson, *J. Electrochem. Soc.*, **146**, 2001 (1999).
- 18) S. Komaba, N. Kumagai, M. Baba, F. Miura, N. Fujita, H. Groult, D. Devilliers, and B. Kaplan, *J. Appl. Electrochem.*, **30**, 1179 (2000).
- 19) K. A. Striebel, C. Z. Deng, S. J. Wen, and E. J. Cairns, *J. Electrochem. Soc.*, **143**, 1821 (1996).
- 20) A. Rougier, K. A. Striebel, S. J. Wen, and E. J. Cairns, *J. Electrochem. Soc.*, **145**, 2975 (1998).
- 21) K. Dokko, M. Mohamedi, M. Umeda, and I. Uchida, *J. Electrochem. Soc.*, **150**, A425 (2003).
- 22) F. Cao and J. Prakash, *Electrochim. Acta*, **47**, 1607 (2002).
- 23) J. L. Shui, G. S. Jiang, S. Xie, and C. H. Chen, *Electrochim. Acta*, **49**, 2209 (2004).
- 24) S. R. Das, S. B. Majumder, and R. S. Katiyar, *J. Power Sources*, **139**, 261 (2005).
- 25) S. Kashu, E. Fuchita, T. Manae, and C. Hayashi, *Jpn. J. Appl. Phys., Pt. 2*, **23**, L910 (1984).
- 26) J. Akedo and M. Lebedev, *Jpn. J. Appl. Phys., Pt. 1*, **38**, 5397 (1999).
- 27) J. Akedo and M. Lebedev, *Appl. Phys. Lett.*, **77**, 1710 (2000).
- 28) T. Maki, S. Sugimoto, T. Kagotani, K. Inomata, and J. Akedo, *Mater. Trans.*, **45**, 2626 (2004).
- 29) T. Kagotani, R. Kobayashi, S. Sugimoto, K. Inomata, K. Okayama, and J. Akedo, *J. Mag. Mag. Mater.*, **290**, 1442 (2005).
- 30) H. Sakaguchi, T. Toda, Y. Nagao, and T. Esaka, *Electrochem. Solid-State Lett.*, **10**, J146 (2007).
- 31) T. Yi, X. Hu, and K. Gao, *J. Power Sources*, **162**, 636 (2006).