Preparation and morphology of three-dimensional structured LiMn$_2$O$_4$ films

Shinji Koike*, Kuniaki Tatsumi

Ubiquitous Energy Research Institute, National Institute of Advanced Industrial and Technology (AIST), Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan

Abstract

LiMn$_2$O$_4$ films with vertically aligned holes were formed by electrostatic spray deposition (ESD) and subsequent annealing. Different surface morphologies, such as dense grains, 1 μm-diameter pores with 1 μm-thick walls, and 5 μm pores with 3 μm walls, were formed by varying the lithium sources in the precursor solution. The randomly oriented pores in the films prepared using ESD were rearranged in vertical stacks after annealing to produce crystalline LiMn$_2$O$_4$. This process would be suitable for constructing three-dimensional interfaces between active materials and solid-state electrolytes.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Lithium battery; Cathode; LiMn$_2$O$_4$; Porous; ESD

1. Introduction

Lithium batteries that contain solid inorganic electrolytes are promising energy sources for devices that have strict safety requirements, such as those used for in vivo situations. The main limitation of all solid-state lithium batteries is their poor power density. One approach to improving the power density is to elevate the ionic conductivity of the solid electrolytes. A great deal of research has resulted in ionic conductivities of up to 10^{-3} S cm^{-1} being achieved [1,2], approximately 10% of the values for liquid electrolytes. However, the current densities of lithium batteries that contain such solid electrolytes are lower by a much greater factor than the difference in conductivity.

Electrostatic spray deposition (ESD), which is a direct film formation method using electrostatic force, was developed in Schoonman's group [3] by improving on the electrostatic atomization method which was used as a crop spraying and painting. Many kinds of thin films with highly reticular or porous structures, such as TiO$_2$, Li$_3$PO$_4$, LiCoO$_2$, LiNiO$_2$ and LiMn$_2$O$_4$, have been prepared for lithium batteries by

this group [4]. These materials have pores with diameters of the order of 1 μm and narrow pore walls of approximately 1 μm in thickness. These would be suitable structures for providing a high interface area, which is a requirement for all solid-state lithium batteries. However, the substrate temperature used in the preparation of these samples, 240 °C, was inadequate to obtain crystalline films. The effects of annealing on individual structures have not been discussed, and in this paper we show that annealing is necessary in order to obtain films that are suitable lithium battery materials. We have investigated the preparation conditions required to obtain porous structured films using various lithium sources, and we have studied the effects of annealing on their surface morphologies.

2. Experimental

LiMn$_2$O$_4$ films were prepared by spray pyrolysis, using the ESD method. A downward spraying setup was employed for film fabrication [5]. A precursor solution was prepared, containing 0.005 (or 0.0025) mol dm^{-3} of a lithium source and 0.01 mol dm^{-3} of manganese(II) acetate tetrahydrate (MnOAc) in a mixture of ethyl alcohol (15 vol.%) and

---

* Corresponding author. Tel.: +81 72 751 7932; fax: +81 72 751 9609.
  E-mail address: koike@ni.aist.go.jp (S. Koike).

di(ethylene glycol)butyl ether (85 vol.%). The lithium sources used were lithium hydroxide (LiOH), lithium nitrate (LiNO$_3$), lithium acetate (LiOAc) and lithium carbonate (Li$_2$CO$_3$). The precursor solution contained a Li:Mn ratio of 1:2.

Precursor solutions were sprayed onto an aluminum substrate (13 mm in diameter). A high positive voltage was applied between the capillary nozzle against substrate. Precursor solution, which was fed to the nozzle by a pump, was atomized by electrostatic repulsion and simultaneously projected towards the substrate along the electrostatic field stemming from the high voltage. The film was formed by pyrolysis of the precursor solution on the substrate [6].

The flow rate of the precursor solution, the quantity sprayed, the substrate temperature and the distance between the capillary nozzle and substrate were fixed at 0.5 ml h^{-1}, 1.5 ml, 180 °C and 15 mm, respectively. Applied voltages of approximately 4 kV were employed. The surface morphologies and crystal structures of the films were investigated using scanning electron microscopy (JSM-5500LV, JEOL) and X-ray diffraction (RINT 2000, Rigaku).

3. Results and discussion

Fig. 1 shows the surface morphologies of as-prepared LiMn$_2$O$_4$ films sprayed by ESD using various lithium sources. Reticular structure was apparent in these films except when Li$_2$CO$_3$ was used as the lithium source (Fig. 1(a)). Reticular films were obtained not only for the LiOAc source (previously reported by Chen et al. [4]), but also for the LiOH and LiNO$_3$ sources (Fig. 1(b)–(d)). The processes giving rise to reticular structure have been reported by Chen et al. [7], and can be summarized as follows. Atomized droplets reach the substrate surface and gradually spread, but the substrate temperature at the edge of the spreading droplet is higher than at the center. Therefore, evaporation of the solvent at the edge of the droplet occurs more quickly than at the center. The result of this process is a ring-shaped nucleation and precipitation on the substrate surface. The observation that Li$_2$CO$_3$ is the only lithium source of the four that does not give rise to reticular structure can be explained by undissolved particles in the sprayed solvent hindering the spread of the solvent on the substrate.
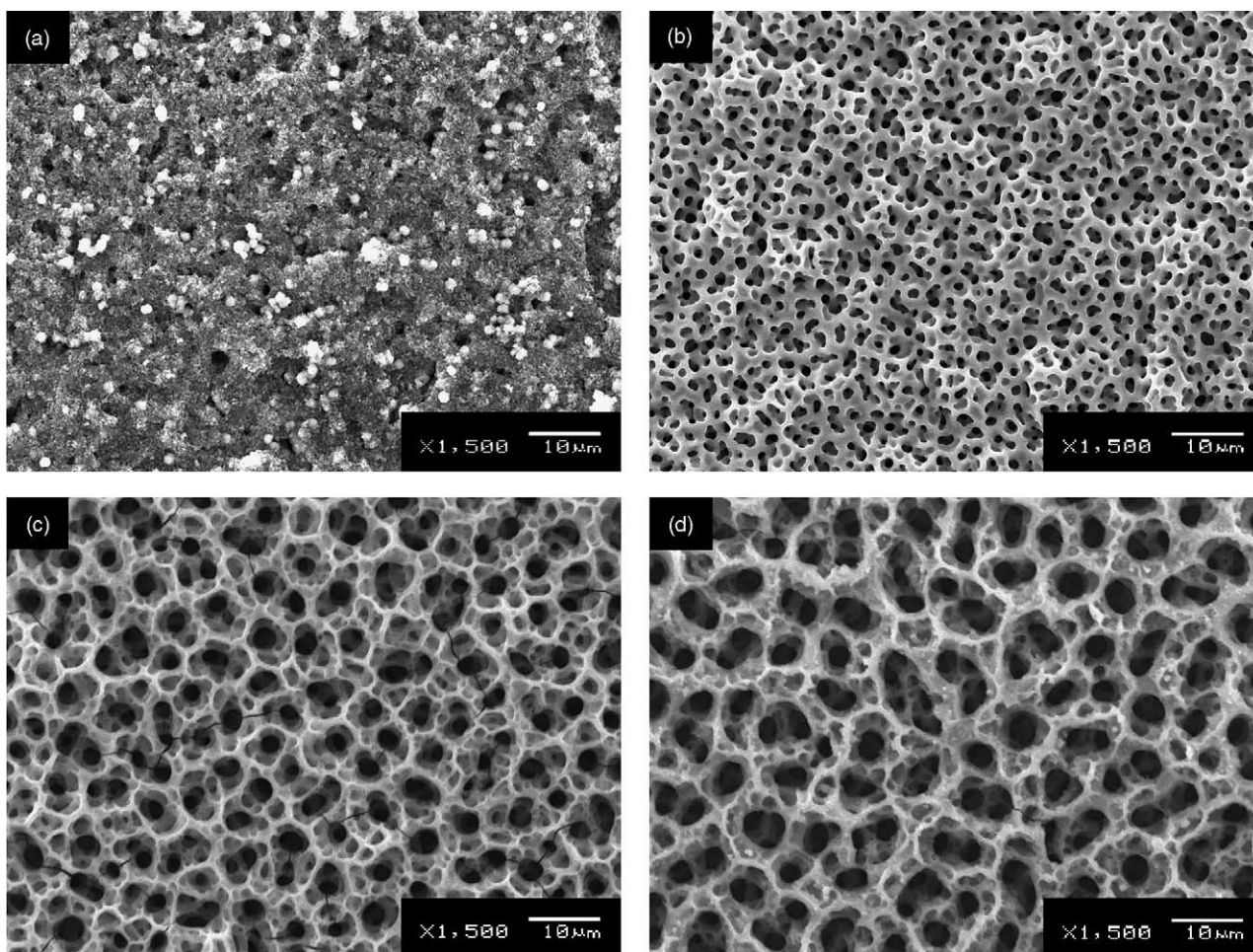

Fig. 1. Surface morphologies of as-prepared films using various lithium sources: (a) Li$_2$CO$_3$; (b) LiNO$_3$; (c) LiOAc; (d) LiOH.

Table 1
Molecular weights and melting points of lithium sources

Lithium source	Molecular weight	Melting point (°C)
Li_2CO_3	73.89	618–720
$LiNO_3$	68.95	255
LiOAc	65.98	286
LiOH	23.95	471

The reticular morphology obtained using the $LiNO_3$ source differs from the LiOH and LiOAc sources in that the pore diameter is smaller and the pore wall is thinner. It is known that the pore diameter d_p can be expressed as in Eq. (1) [7].

$$d_p = \frac{m}{\pi \rho S_p} \tag{1}$$

Here, m, ρ and S_p are the mass of solute in the primary droplet, the density of the deposit and the cross-sectional area of the ring edge, respectively. If S_p is not changed by other factors, then d_p is proportional to the mass of solute in the primary droplet, m. This mass can be controlled not only by the flow rate but also by the composition of the precursor material. The molecular weights and melting points of the lithium sources are listed in Table 1. In this study, the same type of manganese source and solvent were always used, and hence the solute mass is proportional to the molecular weight of the lithium source. According to Eq. (1), the pore diameters obtained from $LiNO_3$ and LiOAc are almost same, and that obtained from LiOH is slightly smaller. However, Fig. 1 shows that the pore diameter obtained from $LiNO_3$ is smaller than that from the other sources. The value of m includes not only the lithium sources, but also the manganese source and the solvents. The difference in molecular weight of the lithium sources would thus have a negligible effect on the total mass of the droplet. Therefore, the reason for the difference in pore diameters could be the melting points of the lithium sources, which are listed in Table 1. $LiNO_3$ has the lowest melting point of the four sources, close to the 230 °C boiling point of the di(ethylene glycol)butyl ether solvent. Although a second

solvent was also present in the droplet, ethyl alcohol, it must be assumed that evaporation occurs much sooner than for di(ethylene glycol)butyl ether due to its low quantity (15%) and low boiling point (78 °C). The viscosity of the droplet on the substrate would then be increased by partial melting of $LiNO_3$, and the spreading process would be hindered.

The films must be annealed in order to obtain crystalline $LiMn_2O_4$. Fig. 2 shows X-ray diffraction patterns of $LiMn_2O_4$ films that have been annealed for 2 h at 650 °C. No peaks corresponding to the as-prepared films (not shown) were observed, but the patterns shown in Fig. 2(a), (c) and (d) are in good agreement with $LiMn_2O_4$. Thus, $LiMn_2O_4$ was successfully synthesized not only using soluble starting materials, but also by the insoluble lithium source, Li_2CO_3. Only the $LiNO_3$ source gave rise to some extra peaks, shown in Fig. 2(b); these correspond to a small fraction of α-Mn_2O_3 that formed due to a slight deficiency in the Li/Mn ratio.

Fig. 3 shows the surface morphology of the $LiMn_2O_4$ films after annealing, which in all cases resulted in the formation of cracks. The layered structure, $LiCoO_2$, does not crack on annealing [5], but $LiMn_2O_4$, which adopts the spinel structure, shrinks isotropically during the process of crystallization. The cracks are generated perpendicular to the substrate surface and the films are still tightly attached to the substrate.

The grainy surface of the as-prepared film formed using the insoluble lithium source, Li_2CO_3, changed in appearance on annealing; an ordered arrangement of holes with diameters of a few tens of nanometers became apparent (Fig. 3(a)). The pore diameters of the films formed using the $LiNO_3$, LiOAc and LiOH sources were unchanged by annealing. Interestingly, the randomly oriented pores in the as-prepared samples become aligned in the vertical direction after crystallization. This is much more likely to happen for large pores (Fig. 3(d)) than for small pores (Fig. 3(b)). In addition, small hollows on the pore walls of the film prepared using LiOH disappear after annealing (Fig. 3(d)). In summary, the annealing process results in the cracks propagating from pore to pore, the walls of the pores shrinking by taking up hori-
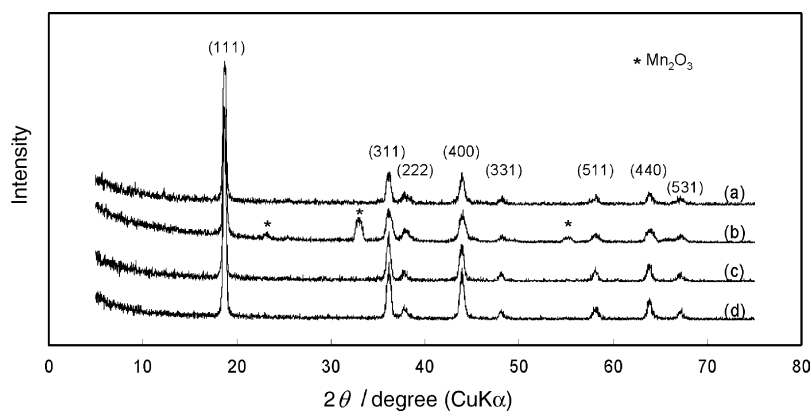

Fig. 2. X-ray diffraction patterns (Cu Kα) of $LiMn_2O_4$ prepared using ESD and various lithium sources: (a) Li_2CO_3; (b) $LiNO_3$; (c) LiOAc; (d) LiOH.
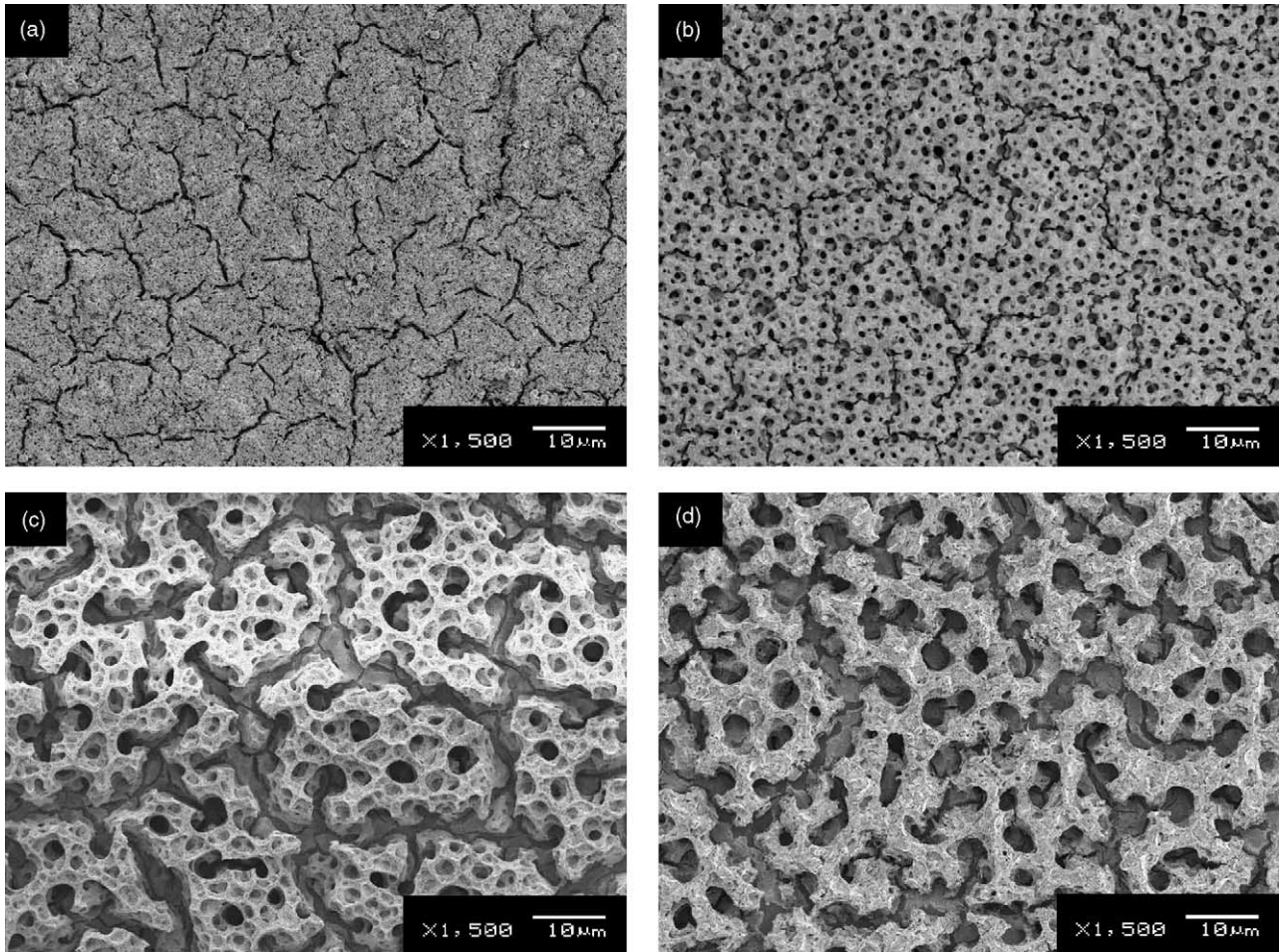
Fig. 3. Surface morphologies of films annealed at 650 °C, prepared using various lithium sources: (a) Li_2CO_3; (b) $LiNO_3$; (c) LiOAc; (d) LiOH.

zontal materials, and the self-assembly of vertically aligned holes during the process of crystallization.

The assembly of upright holes, including cracks, allows solid electrolytes to be pushed and pressed into the pores much more easily than for an assembly of randomly aligned holes, making these films suitable for all solid-state lithium batteries that have high interface areas.

4. Conclusions

Spinel $LiMn_2O_4$ films, with upright pores and pore walls as narrow as one micron, were successfully prepared by ESD and subsequent annealing. The controlled formation of a three-dimensional precursor material with a reticular structure facilitates the preparation of crystalline films with a self-assembled arrangement of vertically-aligned pores. This is a promising approach to improve the conductivity of all-solid lithium batteries through the fabrication of a three-dimensional interface between the active materials and the solid electrolyte.

Acknowledgments

References

[1] U.V. Alpen, A. Rabenau, G.H. Talat, Appl. Phys. Lett. 30 (1977) 621.
[2] J.H. Kennedy, Y. Yang, J. Electrochem. Soc. 133 (1986) 2437.
[3] A.A. Van Zomeren, E.M. Kelder, J.C.M. Marijnissen, J. Schoonman, J. Aerosol. Sci. 25 (1994) 1229–1235.
[4] C. Chen, E.M. Kelder, J. Schoonman, J. Electrochem. Soc. 144 (1997) 289.
[5] S. Koike, K. Tatsumi, J. Schoonman, Lithium/lithium-ion batteries, in: K. Striebel, D. Guyomard, K. Zaghib (Eds.), The Electrochemical Society Proceedings Series, Pennington, NJ, 2003, in press.
[6] C. Chen, E.M. Kelder, P.J.J.M. van der Put, J. Schoonman, J. Mater. Chem. 6 (1996) 765.
[7] C. Chen, E.M. Kelder, J. Schoonman, J. Mater. Sci. 31 (1996) 5437.