

Fabrication of LiMn_2O_4 thin films by sol–gel method for cathode materials of microbattery

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Abstract

LiMn_2O_4 thin films have received considerable attention as cathode materials for thin-film microbatteries. In this work, LiMn_2O_4 thin films are prepared by a sol–gel method using a spin coator. The precursor powder is investigated by TG–DTA and mass spectroscopy analysis in order to study the decomposition process prior to deposition. The coated films are dried at 310 to 360°C, and annealed at 700 to 800°C to obtain a spinel structure. Films annealed under appropriate conditions exhibit good crystallinity, smooth surface morphology, high capacity, and good rechargeability. This film is therefore suitable for use as a cathode for thin-film microbatteries. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: LiMn_2O_4 ; Microbattery; Sol–gel method; Thin film; Cathode material

1. Introduction

Recently, advances in the microelectronics industry have reduced the current and power requirements of electronic devices. Therefore, thin-film solid-state microbatteries can be employed as power sources for these devices. Thin-film microbatteries have various advantages such as simple design, no gas generation, low internal resistance, and good rechargeability. At present, many research groups and companies [1–15] are interested in using thin-film batteries in the following applications: back-up power for computer memory chips in the advent of a power outage; monolithical hybridization with a CMOSRAM, micromechanics (small sensors); hazard card; miniature hearing aids; ultra-thin watches.

Layered LiCoO_2 , LiNiO_2 and spinel LiMn_2O_4 can be used as cathode materials in thin-film lithium batteries because of their high voltage (about 4 V) and good rechargeability. Among these materials, LiMn_2O_4 is the

most favoured because it has a low cost and does not pose any environmental problems.

To date, thin films of the cathode materials have been usually prepared by chemical vapour deposition [5,6], sputtering [7,8,12], e-beam evaporation [9,15], and pulse laser deposition [11]. These methods, however, have several disadvantages such as difficulty in controlling the stoichiometry, long periods of deposition, and high cost for the fabrication. The sol–gel method is a possible alternative approach to overcoming these problems. This method offers the following advantages:

- excellent control of stoichiometry;
- easy control of crystallinity, density and microstructure;
- easy to be doped in order to produce better properties; and
- low cost and high deposition rate.

Nevertheless, there have been only a few reports of the fabrication of thin films of LiMn_2O_4 by the sol–gel method using a spin coator.

In this study, LiMn_2O_4 thin films are deposited by the sol–gel method, using a spin coator, and spinel-phase

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LiMn_2O_4 films are obtained by means of annealing treatments. The effect of the annealing conditions on the microstructure, the crystallinity and the electrochemical properties of the LiMn_2O_4 thin films are extensively investigated.

2. Experimental

The precursor materials were $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$ (manganese acetylacetonate) and $\text{LiCH}_3\text{COCHCOCH}_3$ (lithium acetylacetonate). Each concentration was controlled to adjust the ratio of Li:Mn to 1:2. 1-Butanol and acetic acid was used as solvent. The latter was mixed at room temperature, stirred for 10 h with a magnetic stirrer, and then passed through a 0.2 μm filter prior to use.

The thermal decomposition behaviour of the precursor powder, which was made from solution by an ageing process at 80°C for 24 h, was examined by thermogravimetry (TG) and differential thermal analysis (DTA). Mass spectroscopy analysis was used in order to obtain more detail information about the deposition behaviour.

Si(100) wafers, covered with 1000 Å of thermally grown oxide, served as the substrate. A Pt (800 Å) current-collector was deposited on the SiO_2/Si wafer by RF-Magnetic sputter. The thin films of LiMn_2O_4 were formed on the Pt/ SiO_2/Si substrate by means of a spin-coating technique. The solution was spin-coated on substrates at 4000 to 7000 rpm for 30 s between six and eight layers were spin coated. Each layer was dried at 310 to 360°C for 10 min in order to evaporate the solvents and remove organic materials from the acetylacetonate sources.

The 'as-deposited' films were annealed at 700 to 800°C in flowing O_2 for 10 min. Final film thicknesses were about 2000 Å. Analysis of the phases in the films was

carried out by X-ray diffraction with $\text{CuK}\alpha$ radiation using an automated Rigaku X-ray diffractometer. Film morphology and structure were observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively.

For electrochemical measurements, the LiMn_2O_4 thin film was placed in an open beaker cell which contained 1 M LiClO_4 in propylene carbonate (PC) and lithium foil counter and reference electrodes, and was located inside an Ar-atmosphere glove box. Charge–discharge tests were controlled with an EG&G Electrochemical Analysis System (model 273A).

3. Results and discussion

3.1. Decomposition properties of LiMn_2O_4 precursor

In making thin films via the sol–gel method, a dry process is essential for removing organic materials. The properties of thin films are usually very sensitive to ambient conditions such as temperature, time, etc. Therefore, it is important to determine the dry conditions based on the detailed data on the decomposition behaviour of the precursor which is used for fabrication of the thin films.

The TG and DTA results for the LiMn_2O_4 precursor powder are shown in Fig. 1. The TG curve displays three discrete weight-loss steps, and no more weight loss above 400°C. The first step at below 250°C is associated with the removal of absorbed water, acetic acid, and other solvents. The second and third steps located at 250 to 330°C and 330 to 400°C, respectively, are due to the decomposition of the inorganic and the organic constituents of precursor. The exothermic peaks at 309.8 and 374.7°C are attributed to the decomposition of precursors.

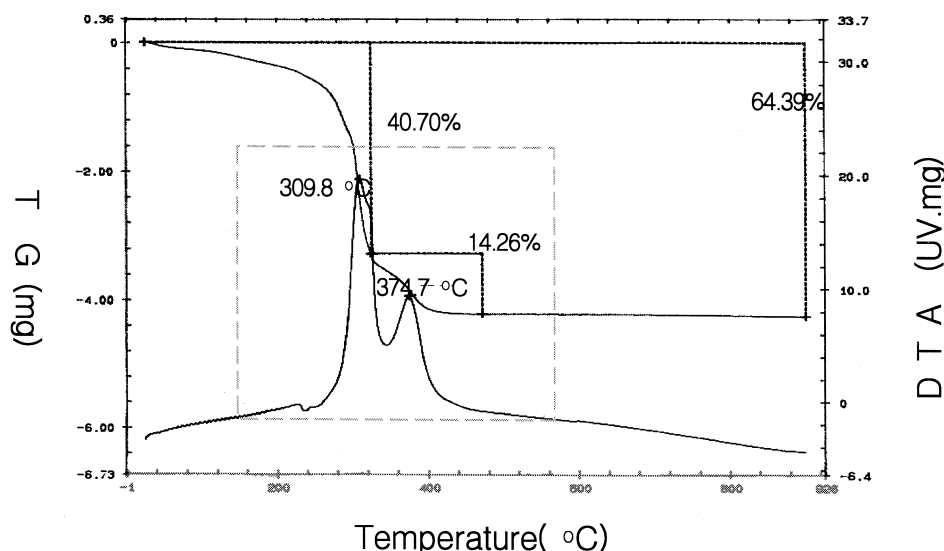


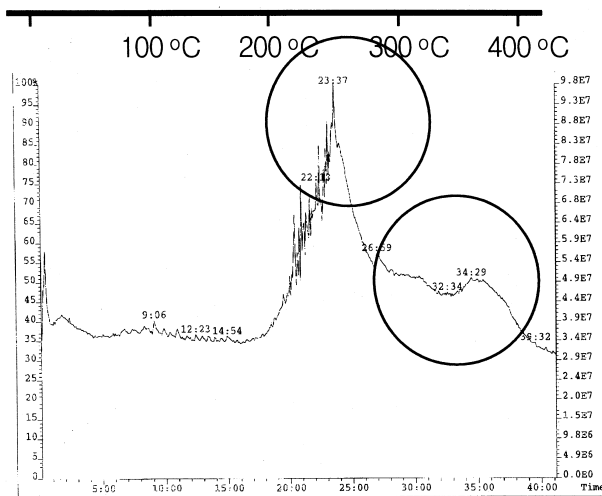
Fig. 1. TG-DTA curve for LiMn_2O_4 precursor powder aged at 80°C for 48 h.

Mass spectroscopy was employed to obtain more detailed information about decomposition properties. The total mass intensity is presented in Fig. 2a. This parameter is the summation of the vaporization from LiMn_2O_4 precursor powder from room temperature to 400°C . Many materials are detected at 230 to 300°C , which implies that most of the weight loss occurs in second step of the TG curve. The mass vaporization is terminated at 400°C , which is also consistent with the results of the TG analysis.

In the present work, acetylacetonate sources were used to prepare thin films of LiMn_2O_4 . Because acetylacetonate sources are decomposed into CO_2 , CO_3 , CH_3CO , we measured the mass intensities of these molecules from room temperature to 400°C . As shown in Fig. 2b, the intensity of the CO_3 detected at 230 to 270°C is very large,

and a small peak is detected above 300°C . Large CO_2 peaks are detected at 230 to 280°C and at 330 to 400°C (Fig. 2c). The CH_3CO peaks started at 230°C and lasted to 400°C (Fig. 2d). From these, we can conclude that the weight losses at the second and third steps displayed in the TG curve indicate the decomposition of acetylacetonate sources. That is, the decomposition of the acetylacetonate sources starts at 230°C and continues to 400°C . In particular, an abrupt weight loss occurs at 230 to 330°C , and a slow weight loss continues to 400°C .

If a high drying temperature (i.e., above 400°C) is adopted, organic materials can be easily and totally eliminated. A large stress may be generated, however, due to the difference in the coefficient of thermal expansion (CTE) between the substrate and the thin film of LiMn_2O_4 .



(a) Total Intensity

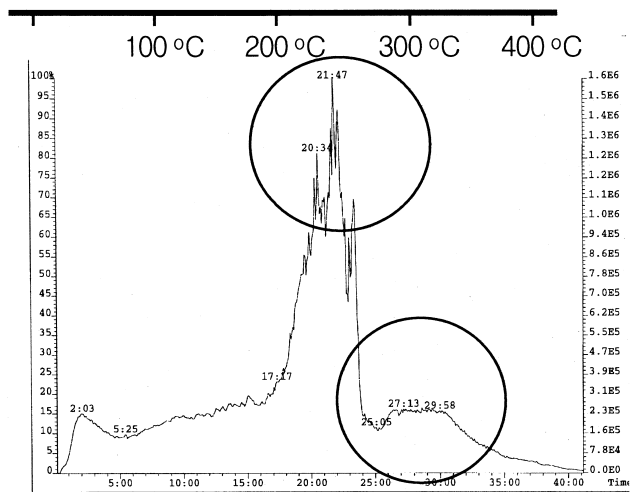
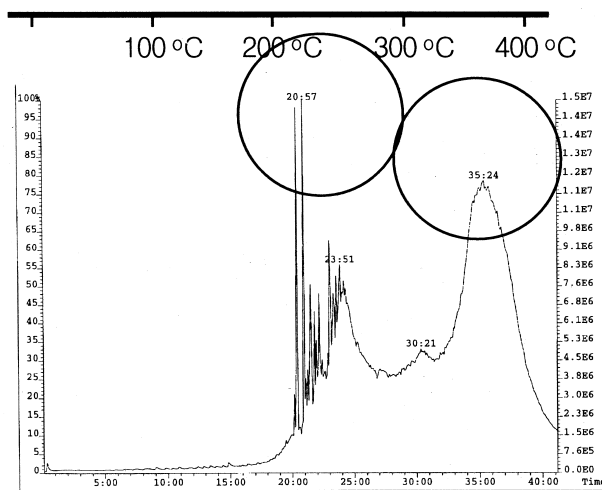
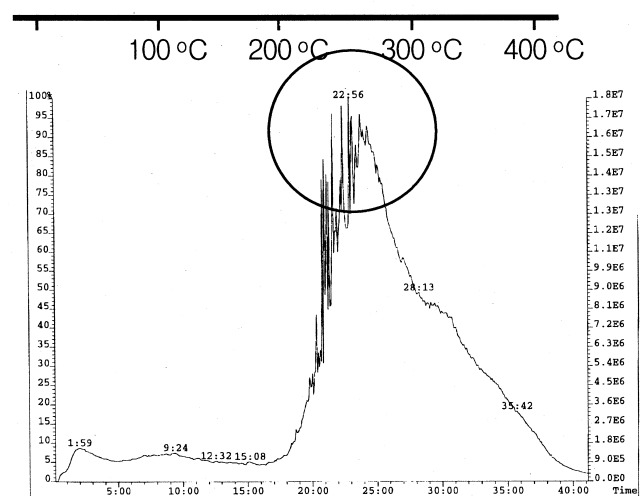
(b) CO_3 Intensity(c) CO_2 Intensity(d) CH_3CO Intensity

Fig. 2. Mass spectroscopy analysis of LiMn_2O_4 precursor powder aged at 80°C for 48 h: (a) total intensity; (b) intensity of CO_3 ; (c) intensity of CO_2 ; (d) intensity of CH_3CO .

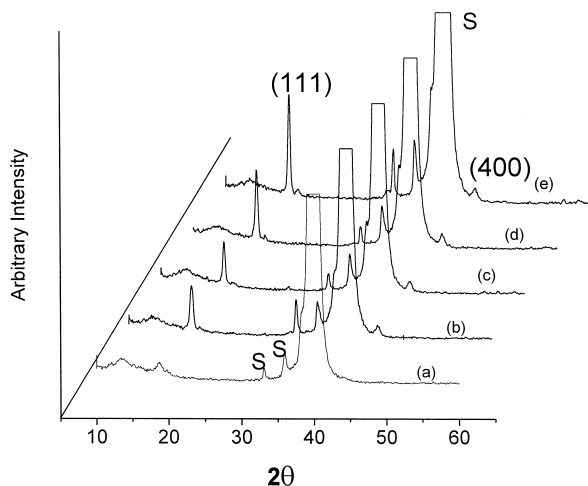


Fig. 3. X-ray diffraction patterns of: (a) as-deposited film; LiMn_2O_4 films annealed at (b) 700°C for 10 min; (c) 750°C for 1 min; (d) 750°C for 10 min; (e) 800°C for 10 min.

Therefore, in this study, the films were dried at 310 to 360°C . Organic materials may be retained in the as-deposited films. Nevertheless, FTIR analysis of the as-deposited films dried at 310 to 360°C revealed that the residual amounts of organic materials is very small.

3.2. Analysis of crystallinity and microstructure

As-deposited films were annealed at 700°C (10 min), 750°C (10 min, 1 min) and 800°C (10 min) in an oxygen atmosphere. X-ray diffraction patterns for the as-deposited and annealed films are given in Fig. 3. The films change from amorphous to crystalline after annealing. Only (111) and (400) peaks are observed; the (311) peak may be hidden under the silicon peak. Peaks marked with S correspond to the substrate silicon wafer and platinum layer. On increasing the annealing temperature, the crystallinity of the films improved.

The surface morphology of thin films of LiMn_2O_4 annealed at various conditions (temperature, time) is shown in Fig. 4. The heat-treated films have a smooth and dense surface and a relatively small and fairly uniform grain size. The grain size of the film annealed at 700°C is about $0.05\ \mu\text{m}$, and that of films annealed at 750°C is about $0.1\ \mu\text{m}$. This grain size is much smaller than those of the bulk materials. For films annealed at 800°C for 10 min, the grain size increases up to about $0.3\ \mu\text{m}$. In addition, the surface has a porous structure, which may result in short-circuits in thin-film batteries [7]. The arrows in Fig. 4d indicate the pores in the surface.

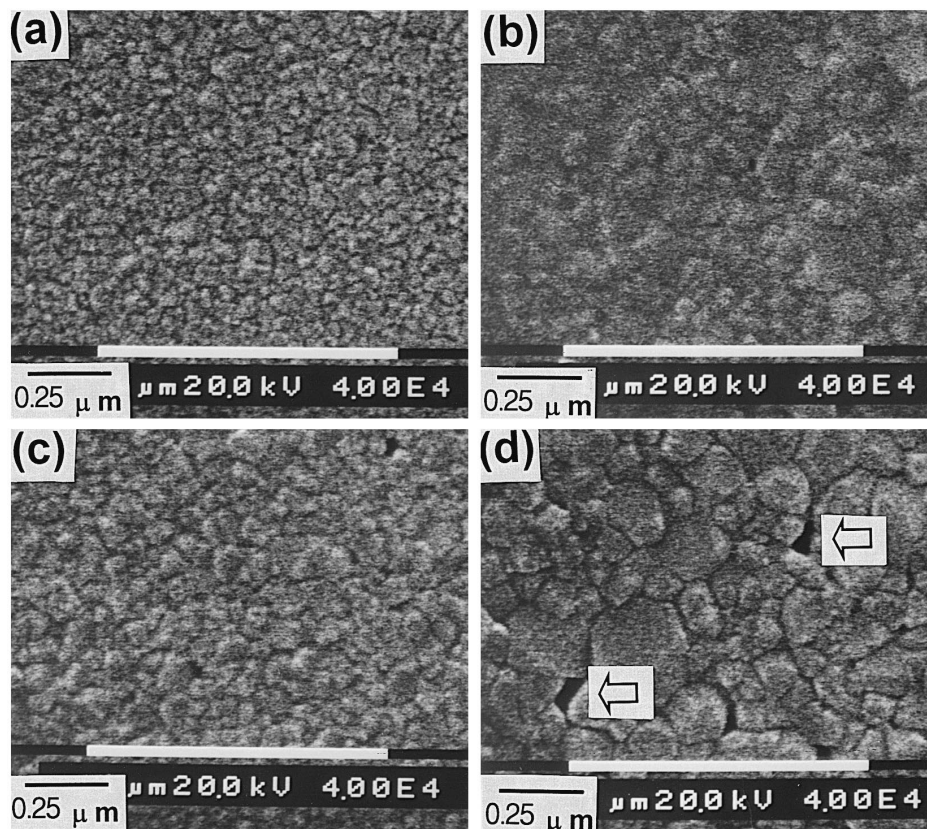


Fig. 4. Electron micrographs of LiMn_2O_4 films annealed at: (a) 700°C for 10 min; (b) 750°C for 1 min; (c) 750°C for 10 min; (d) 800°C for 10 min.

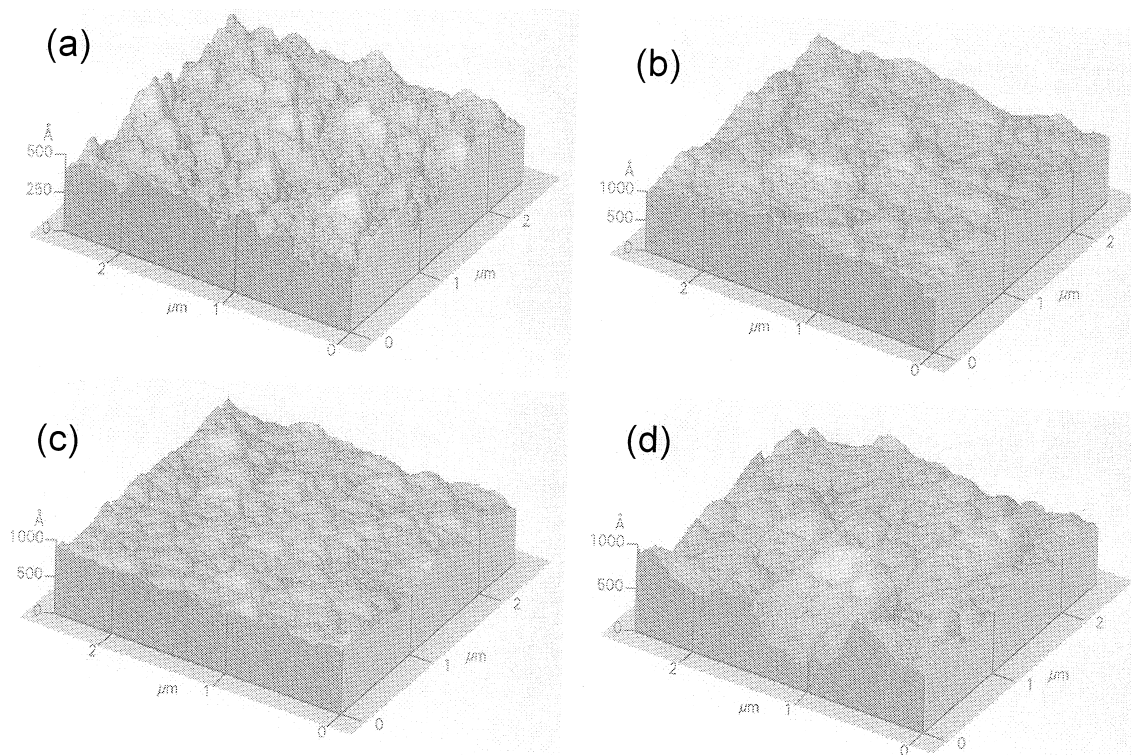


Fig. 5. AFM images of LiMn_2O_4 films annealed at: (a) 700°C for 10 min; (b) 750°C for 1 min; (c) 750°C for 10 min; (d) 800°C for 10 min.

The surface roughness and grain size of thin films of LiMn_2O_4 is observed in detail by atomic force microscopy (AFM). The AFM images of the thin films annealed under various conditions are shown in Fig. 5. The surface of films annealed at 700°C and 750°C are smooth, while that of films annealed at 800°C are relatively rough. The average surface roughness of the LiMn_2O_4 films is presented in Fig. 6. Films annealed at 700 and 750°C for 10 min exhibit a small average surface roughness (below 40

\AA). It should be noted that the film annealed at 750°C for 1 min has a larger average roughness than the film annealed at 750°C for 10 min. This implies that 1 min is an insufficient time for the rearrangement of atoms to make a complete spinel phase and a smooth surface. The film annealed at 800°C for 10 min reports a large average surface roughness (85 \AA). This indicates that the latter condition is unsuitable for making cathode films.

3.3. Electrochemical behaviour

The electrochemical behaviour of various LiMn_2O_4 films was characterized galvanostatically by cycling test

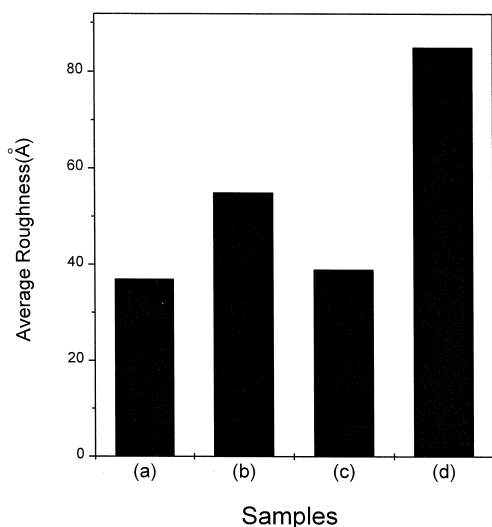


Fig. 6. Surface roughness of LiMn_2O_4 films annealed at: (a) 700°C for 10 min; (b) 750°C for 1 min; (c) 750°C for 10 min; (d) 800°C for 10 min.

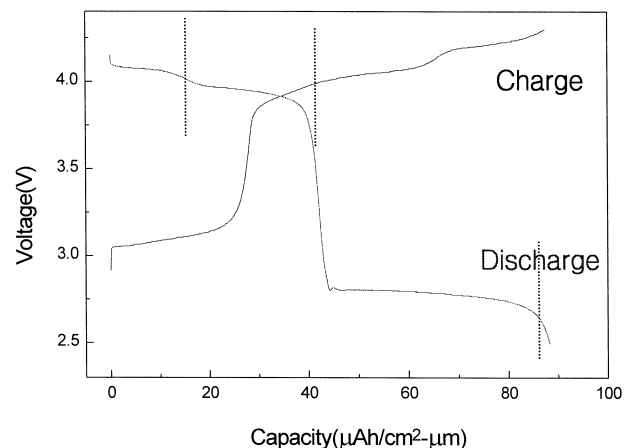


Fig. 7. Charge–discharge curves for cell $\text{Li}/1 \text{ M LiClO}_4\text{-PC solution}/\text{LiMn}_2\text{O}_4$ thin film (current density = $200 \mu\text{A cm}^{-2}$).

cells. The charge–discharge curves for a LiMn_2O_4 (thin film) 1 M LiClO_4 in PC/Li cell operated between 4.3 and 2.5 V are given in Fig. 7. The film annealed at 750°C for 10 min was tested at a constant charge–discharge current density ($200 \mu\text{A cm}^{-2}$). The curves can be divided into three voltage plateaus, i.e., in a manner reported previously by other workers [7,16–18]. The discharge capacity is about $40 \mu\text{A h/cm}^2 \mu\text{m}$ at the 4 V plateau. The results of the first discharge of cells/thin films of LiMn_2O_4 annealed under various conditions are shown in Fig. 8. In this case, the cells were operated at $400 \mu\text{A cm}^{-2}$ between 4.3 and 3.7 V. The film annealed at 700°C for 10 min has a relatively low discharge capacity (about $20 \mu\text{A h/cm}^2 \mu\text{m}$), this indicates that the film does not have sufficient crystallinity to yield a high discharge capacity. The discharge capacity increases as the annealing temperature is increased to 750°C . Moreover, a film annealed for 10 min has a higher discharge capacity than a film annealed for 1 min. This might be due to insufficient crystallinity, as confirmed by X-ray diffraction analysis. The film annealed at 800°C for 10 min has good crystallinity, but the discharge capacity is a little lower than that of a film annealed at 750°C for 10 min. We have mentioned that the film annealed at 800°C for 10 min has a larger grain size than the other films. According to recent studies [3,7,16], the grain size is considered to affect the capacity and cycle-life. Croquennec et al. [16] showed that the larger the surface area, the higher the electrochemical specific capacity and energy. They also reported that lithium intercalation can take place more easily at the surface rather than at the core of the grains. A film annealed at 800°C has a larger grain size and, thus, a smaller grain boundary area. The grain boundary area is the place where the lithium ion can react more easily. Therefore, the larger the grain size, the smaller the discharge capacity.

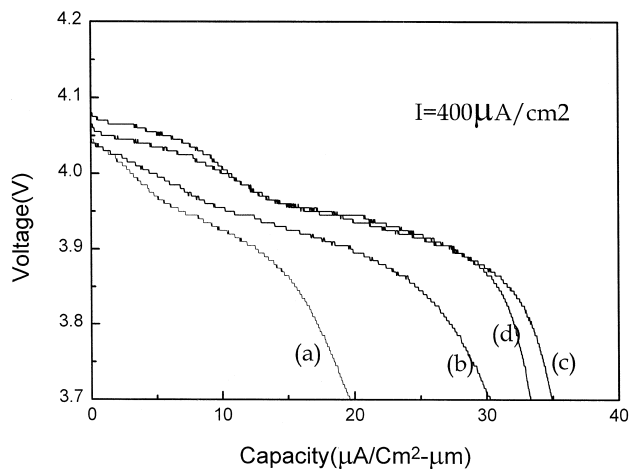


Fig. 8. Discharge curves for cell Li/1 M LiClO_4 -PC solution/ LiMn_2O_4 thin film annealed at: (a) 700°C for 10 min; (b) 750°C for 1 min; (c) 750°C for 10 min; (d) 800°C for 10 min (current density = $400 \mu\text{A cm}^{-2}$).

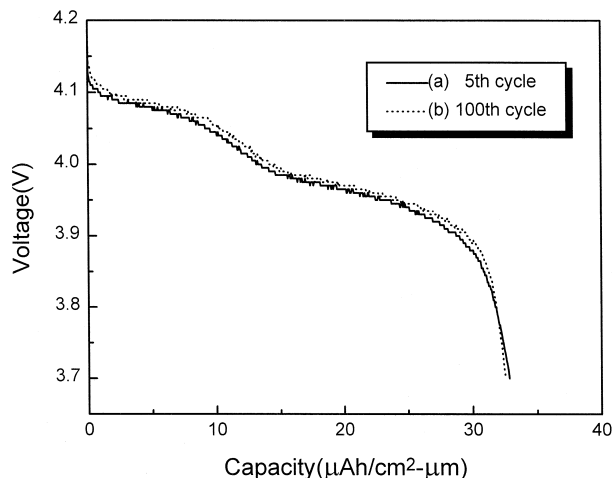


Fig. 9. Comparison of discharge curves for cell Li/1 M LiClO_4 -PC solution/ LiMn_2O_4 thin film annealed at 750°C for 10 min: (a) first cycle; (b) 100th cycle (current density = $100 \mu\text{A cm}^{-2}$).

The rechargeability of thin films of LiMn_2O_4 annealed at 750°C (10 min) are shown in Fig. 9. Test cells were subjected to 100 cycles at a current density of $100 \mu\text{A cm}^{-2}$ between 4.3 and 3.7 V. No appreciable degradation is observed after 100 cycles at room temperature. This result shows that the sol-gel prepared thin films have good rechargeability. It is found that the film annealed at 750°C for 10 min has good properties such as large discharge capacity, a smooth surface, and a relatively small grain size. Thus, it is clear that films fabricated by the sol-gel method and annealing process can be used as the cathode material of thin-film microbatteries.

4. Conclusions

Thin films of LiMn_2O_4 are fabricated by the sol-gel method using a spin coator and an annealing process. The decomposition of the LiMn_2O_4 precursor used in this study commences at 230°C and continues to 400°C . As-deposited films have been annealed at 700°C (10 min), 750°C (1 min, 10 min) and 800°C (10 min) in an oxygen atmosphere. The grain size and crystallinity of the films increases as the annealing temperature is raised. The films annealed at 700 and 750°C have smooth and dense surfaces, but the film annealed at 800°C has a relatively rough and porous surface. Thus, this film is not suitable for microbatteries because of the high possibility of short-circuits. The best discharge capacity is obtained from the film annealed at 750°C for 10 min. The film annealed at 800°C for 10 min has good crystallinity, but the discharge capacity is a little lower than that of the film annealed at 750°C for 10 min. No appreciable degradation is observed after 100 cycles at a current density of $100 \mu\text{A cm}^{-2}$ at room temperature.

From these results, it is clear that films prepared by the sol–gel method and annealing process can serve as the cathode material in thin-film microbatteries.

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