

Electrochemical properties of LiMn_2O_4 thin films: suggestion of factors for excellent rechargeability

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Abstract

LiMn_2O_4 thin films are prepared by the sol–gel method. The discharge capacity and cycling performance of the films are determined to investigate the electrochemical properties. By controlling the fabrication conditions, the excellent rechargeability is observed in a test cell which contains the LiMn_2O_4 thin film. Possible factors which have been reported as causes for capacity loss with cycling are reviewed and those producing excellent rechargeability of the LiMn_2O_4 thin films are identified. Attention is especially focused on the relaxation of the stress, which is generated during intercalation/de-intercalation process. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium batteries have attracted much attention in recent years because of their high specific energy and long cycle-life. For a positive electrode material, layered LiNiO_2 , LiCoO_2 and spinel LiMn_2O_4 can be used 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. Unfortunately, however, it can exhibit capacity loss during cycling. Over the past decade, many research groups have investigated the cause of capacity loss, and suggested several possible factors [1,2], namely:

- (i) instability of the organic-based electrolyte in the high-voltage region;
- (ii) dissolution of the $\text{Li}_x\text{Mn}_2\text{O}_4$ electrode in the electrolyte (as Mn^{2+});
- (iii) inhomogeneous local structure of $\text{Li}_x\text{Mn}_2\text{O}_4$ materials;
- (iv) onset of the Jahn–Teller effect in deeply discharged $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes (i.e., at $x = 1$).

Among these factors, instability of the organic-based electrolyte has already been solved by the development of an electrolyte which is stable at high voltage [3,4]. Nevertheless, a slow fade in capacity on repeated charge–discharge cycling has still been observed, the origin of this capacity loss has not been clarified.

To date, many research groups have investigated the characteristics of LiMn_2O_4 thin films and have reported excellent rechargeability when optimal deposition conditions are employed.

Bates et al. [5–7] deposited LiMn_2O_4 thin films by means of a sputtering method over platinum current-collectors on alumina substrates. The as-deposited amorphous films were annealed at 300°C to 800°C in flowing oxygen for 20 min to 1 h. Based on the measured film thickness and on assuming a theoretical density of 4.2 g cm⁻³, the authors reported that the discharge capacity of the LiMn_2O_4 film was 77 $\mu\text{A h mg}^{-1}$ at constant charge–discharge current density of 11.6 $\mu\text{A h}$. After 300 cycles, the capacity loss per cycle was 0.006% in the voltage range of 4.5–3.8 V at 25°C.

Hwang et al. [8,9] also investigated the properties of sputter-deposited LiMn_2O_4 thin films. The films were amorphous but could be crystallized into a spinel structure

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by rapid thermal annealing in an oxygen environment. Cycling tests at room temperature demonstrated that these films had good cycling behaviour.

In the work reported here, the excellent cycling behaviour is displayed by a cell which contains a LiMn_2O_4 thin-film electrode. The film was deposited by means of the sol–gel method using a spin-coater and the spinel phase LiMn_2O_4 film was obtained through a series of annealing treatments.

From the above findings, it is clear that a thin-film electrode of LiMn_2O_4 has better rechargeability than bulk electrode. To the best of our knowledge, however, the reason for this excellent cycling behaviour of the LiMn_2O_4 thin film has still to be explained. In this regard, the present studies focus on the investigation of the factors likely to give excellent rechargeability of the LiMn_2O_4 thin film by surveying several possible factors suspected of contributing to capacity loss during cycle.

2. Experimental

$\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$ (manganese acetylacetonate) and $\text{LiCH}_3\text{COCHCOCH}_3$ (lithium acetylacetonate) were used as precursor materials. The concentrations were controlled to adjust the ratio of $\text{Li}:\text{Mn} = 1:2$. 1-Butanol and acetic acid were employed as solvents. Each solution 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.

Silicon (Si(100)) wafers covered with 1000 Å of thermally grown oxide were used as the substrate. A current-collector of platinum (800 Å) was deposited on the SiO_2/Si wafer by RF magnetic sputter. LiMn_2O_4 thin films were prepared on the Pt/ SiO_2/Si substrate by a spin-coating technique. The solution was spin-coated on substrates at 4000 rpm for 30 s. Eight sol-layers were prepared in this manner. Each layer was dried at 230, 310, 345 and 380°C for 10 min to evaporate solvents and remove organic materials in acetylacetonate sources.

The as-deposited films were annealed at 750°C in flowing oxygen for 10 min for crystallization. Final thickness of the film was about 2000 Å, which was measured by α -step. Phase analysis of the films was carried out by X-ray diffraction with $\text{CuK}\alpha$ radiation using an automated Rigaku X-ray diffractometer. The morphology and structure were examined by scanning electron microscopy (SEM).

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 a lithium foil counter and reference electrodes, and was located inside a glove box with an argon atmosphere. Charge–discharge tests were performed with an EG&G Electrochemical Analysis System (Model 273A).

The discharge capacities of the films were obtained in the potential range 4.3 to 3.7 V with a constant current density of 100 $\mu\text{A cm}^{-2}$. The rechargeability of LiMn_2O_4 thin-film electrodes was evaluated by cycling tests at the same current density.

The impedance spectrum was obtained from LiMn_2O_4 electrodes in the electrochemical cell. Electrochemical impedance measurements were performed with a frequency response analyzer (Solatron, SI 1260 FRA) in conjunction with a potentiostat (EG&G Model 273). Impedance spectrum was potentiostatically measured by applying an AC voltage of 20 mV amplitude over the frequency range 10^{-2} to 10^5 Hz. The frequency was scanned from high to low values.

3. Results and discussion

3.1. Fabrication of LiMn_2O_4 thin films

The LiMn_2O_4 spinel structure was obtained by a drying process and an annealing treatment. Referring to the results of previous work [10], all as-deposited films were annealed

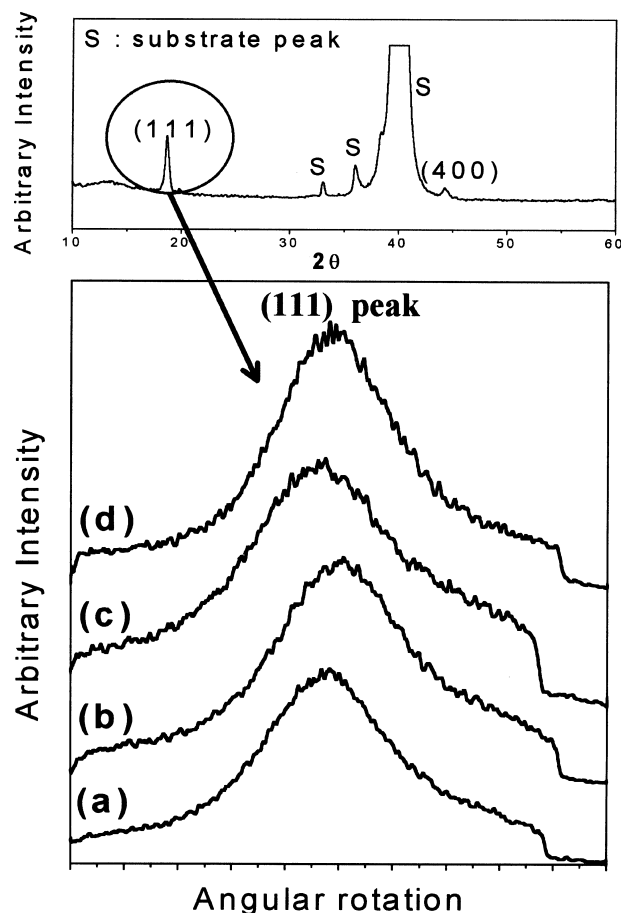


Fig. 1. Rocking curves of (111) peak of LiMn_2O_4 films dried at (a) 230°C for 10 min, (b) 310°C for 10 min, (c) 345°C for 10 min, (d) 380°C for 10 min, and annealed at 750°C for 10 min.

at 750°C in an oxygen atmosphere for 10 min. The present work focuses on the characterization of LiMn_2O_4 thin films prepared with different drying temperatures.

In film preparation by the sol–gel method, drying of the solution coated on the substrate is a critical step. The effects of drying conditions such as temperature, time, etc., on film properties are critical. If the drying temperature is too low, organic materials will not be removed sufficiently, and will remain in the film. These residual organic materials will accumulate in the film during the coating and drying processes, and thereby increase the film thickness. Because the film thickness does not decrease sufficiently during the annealing treatment, the density of the film will be reduced. Too much residual organic material will also cause many defects to appear in the film, and thus affect the film properties [11].

The rocking curves for LiMn_2O_4 films dried under different temperatures and annealed at 750°C for 10 min are shown in Fig. 1. The data show the (111) main peak of LiMn_2O_4 thin film. The difference in crystallinity between the films with different drying temperatures is not critical.

The surface morphology of the films is displayed in Fig. 2 (SEM images). The films have a relatively smooth and dense surface with small grains of fairly homogeneous size. The grain sizes after different drying temperatures are almost same (about 0.1 μm).

The electrochemical behaviour of various LiMn_2O_4 films was characterized galvanostatically by cycling test cells. The discharge curves for LiMn_2O_4 thin film/1 M LiClO_4 in a PC/Li cell operated between 4.3 and 3.7 V are shown in Fig. 3. The discharge capacity of the annealed films increases as the drying temperature is increased, even when the films have the same annealing

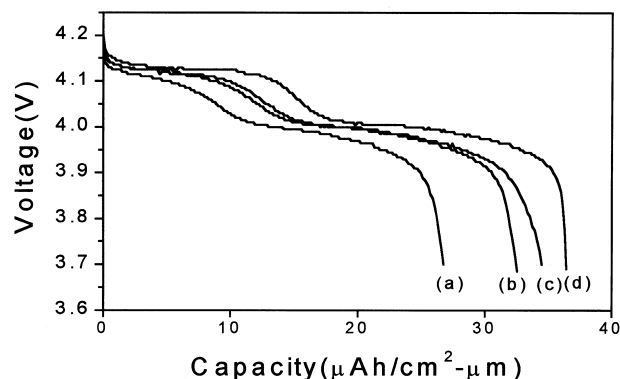


Fig. 3. Discharge curves for Li/1 M LiClO_4 -PC solution/ LiMn_2O_4 thin-film cell. Thin film dried at (a) 230°C for 10 min, (b) 310°C for 10 min, (c) 345°C for 10 min, (d) 380°C for 10 min, and annealed at 750°C for 10 min (current density is 100 $\mu\text{A cm}^{-2}$).

conditions. The films were prepared in the same solution and with the same spin-coating conditions (4000 rpm, eight-layer coating). Thus, the same amount of coating-materials was deposited on the substrate. The larger discharge capacity of the annealed films dried at higher temperature means better ability for intercalation/de-intercalation of Li ions per unit volume.

As the data in Fig. 3 show, two more distinct voltage plateaus are observed in discharge curves of the annealed films dried at higher temperature. This means that $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ has a more distinct two-phase structure in this region, and a more perfect framework with few defects. On the other hand, films with two less-distinct voltage plateaus in the discharge curve may have a relatively perfect spinel framework.

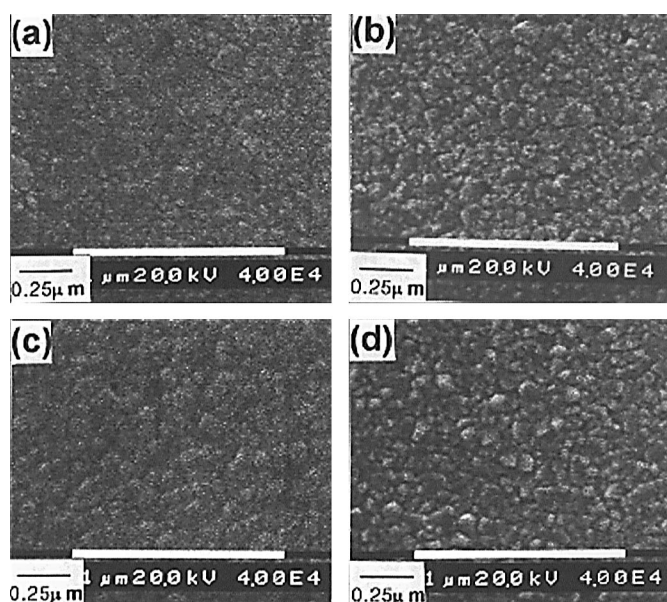


Fig. 2. Electron micrographs of LiMn_2O_4 films dried at (a) 230°C for 10 min, (b) 310°C for 1 min, (c) 345°C for 10 min, (d) 380°C for 10 min, and annealed at 750°C for 10 min.

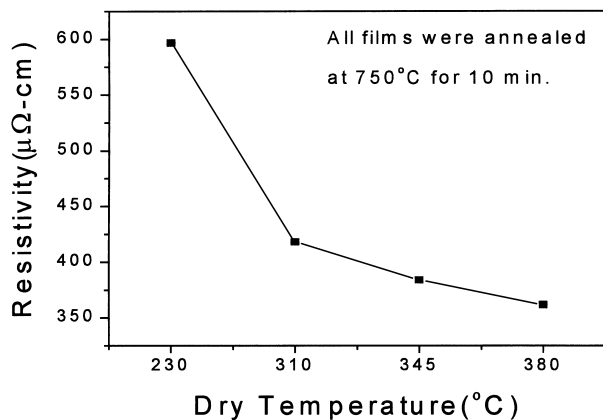


Fig. 4. Resistivity of LiMn_2O_4 thin films dried at different temperature and annealed at 750°C for 10 min.

The resistivities of LiMn_2O_4 thin films with different drying temperatures are given in Fig. 4. (All films were annealed at 750°C for 10 min.) The annealed films dried at lower temperatures have relatively larger resistivity, which may be due to structural imperfections and defects contained in the films. The resistivity decreases as the drying temperature increases. This probably indicates an increase in the structural perfection by a decrease in defects.

In summary, it can be inferred that as the dry temperature increases, the perfection of the spinel framework is increased, which may cause an increase in the discharge capacity per unit volume.

The discharge capacity is dependent on the grain size [8,9] and the crystallinity of the films. The grain size and crystallinity of the films do not have a special dependence on the drying temperature, as confirmed by SEM images and rocking curves of the films. This indicates that the possibility of a change in the discharge capacity with changes in the grain size and the crystallinity of the film can be excluded.

The cycling performance of the LiMn_2O_4 thin film was measured galvanostatically between 4.3 and 3.7 V with LiMn_2O_4 thin film/PC + LiClO_4/Li cells. The rechargeabilities of films annealed at different drying temperatures are exhibited in Fig. 5. Films dried at 230°C (Fig. 5(a)) and 310°C (Fig. 5(b)) exhibit good rechargeability. No appreciable degradation is observed after 100 cycles at room temperature. The rechargeability of a LiMn_2O_4 film dried at 345°C is given in Fig. 5(c). The solid line represents the discharge curve after one cycle, and the dotted line is the curve after 100 cycles. A small degradation in capacity is observed after 100 cycles at room temperature, a finding which differs from that of films dried at 230°C and 310°C .

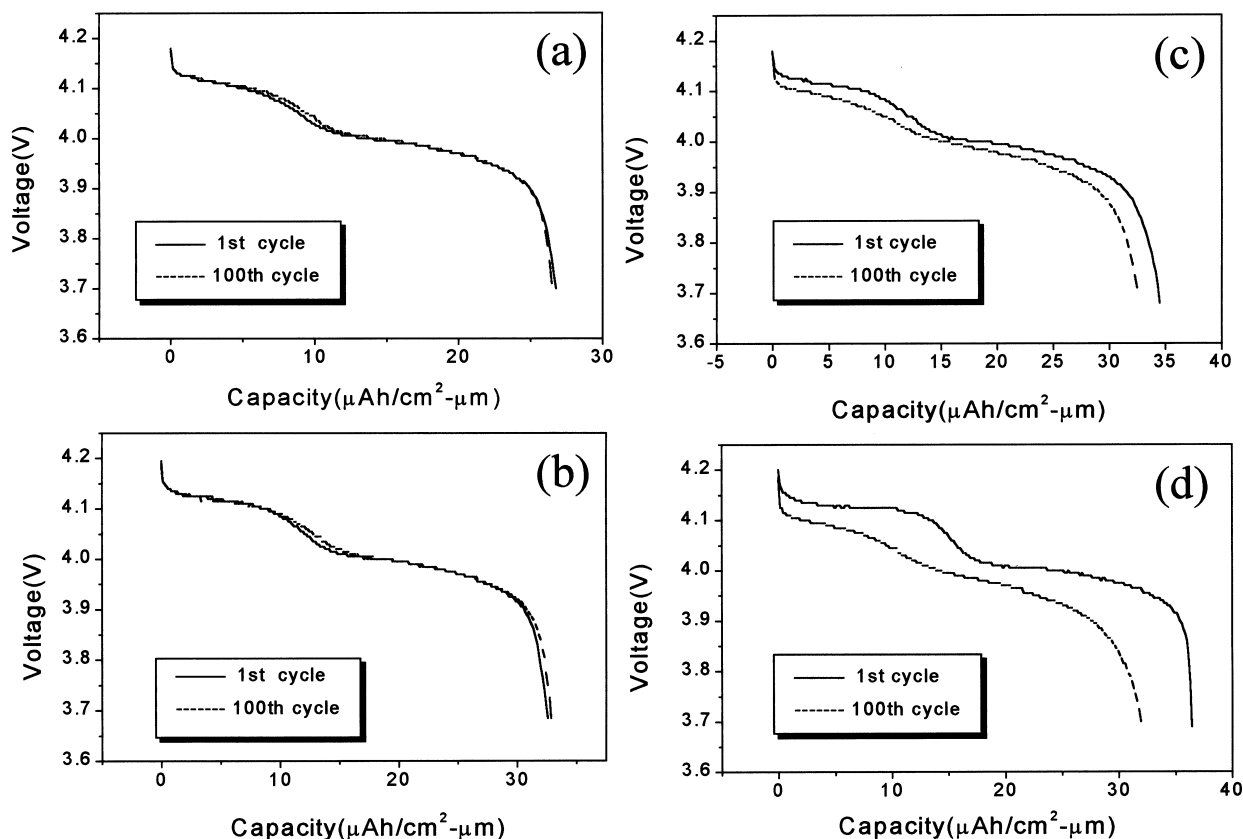


Fig. 5. Comparison of discharge curves between 1st and 100th cycles for the cell of $\text{Li}/1\text{ M LiClO}_4\text{-PC solution}/\text{LiMn}_2\text{O}_4$ thin film dried at (a) 230°C for 10 min, (b) 310°C for 10 min, (c) 345°C for 10 min, (d) 380°C for 10 min, and annealed at 750°C for 10 min (current density is $100\ \mu\text{A}/\text{cm}^2$).

The change in the discharge curve of an annealed film dried at 380°C after 100 cycles is shown in Fig. 5(d). A relatively large fading in capacity is observed compared with the above observations for annealed films dried at lower temperatures.

From these data, it is clear that capacity fading increases as the drying temperature is increased. It is concluded that this phenomenon is associated with the degree of structural perfection of the spinel framework.

Chen and Schoonman [12] examined the influence of sintering temperature on the formation and phase purity of LiMn_2O_4 . It was reported that samples sintered at high temperatures had a more perfect spinel phase, but showed less reversibility. Given this behaviour, it is concluded that an increase in the perfection of the structure may result in a decrease in reversibility.

Films dried at lower temperatures (230°C, 310°C) have less-perfect lattice structures. Small defects such as micropores and vacancies contained in the film can offer ‘vacant room’ for a small flexible shift in the lattice during lithium intercalation/de-intercalation process. Thus, the spinel structure can be protected from any strain which may be generated during cycling.

On the other hand, films dried at higher temperatures (345°C, 380°C) have more perfect structure, which means that fewer defects are present in the film. The small defects may suppress the effects of ‘several factors’ which are considered to be causes for capacity loss during cycling. Therefore, reduction of these defects may lead to poor reversibility. Hence, the rechargeability of films dried at higher temperatures is inferior to that of films dried at low temperature.

3.2. Survey of causes of capacity loss of LiMn_2O_4

The change in the charge–discharge curves after 1000 cycles for a LiMn_2O_4 thin film dried at 310°C and annealed at 750°C is shown in Fig. 6. The discharge capacity

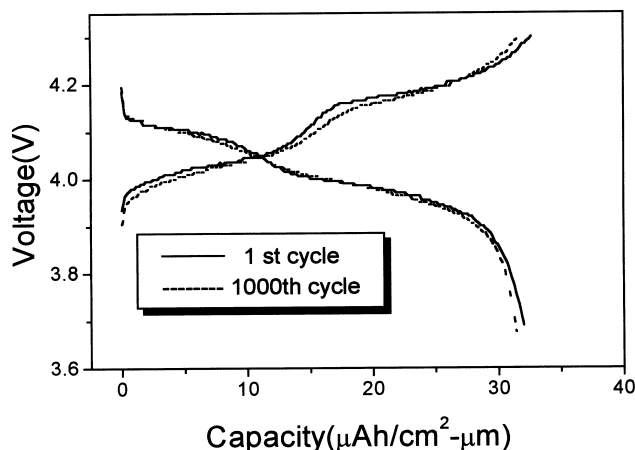


Fig. 6. Comparison of discharge curves between 1st and 1000th cycles for $\text{Li}/1\text{ M LiClO}_4\text{-PC solution}/\text{LiMn}_2\text{O}_4$ thin-film cell.

is about $32\ \mu\text{A h cm}^{-2}\ \mu\text{m}$. Taking the theoretical density of LiMn_2O_4 ($4.281\ \text{g cm}^{-3}$), the discharge capacity becomes about $75\ \text{mA h g}^{-1}$, which is similar to the value reported by Bates [5–7]. The value of the discharge capacity is lower than that of the bulk electrode (over $100\ \text{mA h g}^{-1}$). A direct comparison of the value of discharge capacity between the film electrode and bulk electrode is not appropriate, however, because the density of the film is lower than that of the bulk.

Though a slight degradation in capacity is observed, it is a negligible amount. This result confirms the excellent rechargeability of the thin film of LiMn_2O_4 fabricated by the sol–gel method. On the other hand, it is still reported by many researchers that slow capacity fading is observed for bulk electrodes on repeated charge–discharge cycling.

As mentioned earlier, several factors have been suggested by many research groups as the causes for the cycling loss. Among these, the instability of organic-based electrolytes has already been solved [3,4] by the development of an electrolyte which is stable at high voltage.

The effects of dissolution of the $\text{Li}_x\text{Mn}_2\text{O}_4$ electrode into the electrolyte has been suggested as a cause for the capacity loss by Tarascon et al. [13]. They reported that the cause of the capacity loss is a slow dissolution of spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ according to this reaction:



According to the study by Xia et al. [14–16], the capacity loss of LiMn_2O_4 is not simply caused by the dissolution of Mn ions into the solution. It suggested that the main factor responsible for the capacity loss of a LiMn_2O_4 spinel is the repeated removal/insertion of lithium from the spinel framework, which requires higher energy compared with the first cycle. In particular, the authors focused on the inhomogeneous local structure of LiMn_2O_4 as the main cause of capacity loss. In this respect, most of the analysts have suggested that the main factor is not dissolution of manganese into the electrolyte but Jahn–Teller distortion and the inhomogeneous structure of $\text{Li}_x\text{Mn}_2\text{O}_4$ material. In addition, several researchers have ignored the effect of the instability of the organic-based electrode [17].

At this stage, it is difficult to accept that large a portion of the capacity loss is caused by manganese dissolution, moreover it can be said that it is not a major effect. Therefore, in this work, we examine mainly consider the Jahn–Teller effect and the inhomogeneous local structure of $\text{Li}_x\text{Mn}_2\text{O}_4$ materials.

3.2.1. Jahn–Teller effect

The onset of the Jahn–Teller effect in deeply discharged $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes has been suggested as a major cause of capacity fading after cycling [1,18]. The insertion of lithium in LiMn_2O_4 to give $\text{Li}_2\text{Mn}_2\text{O}_4$ is accompanied by a reduction in the average oxidation state of manganese from 3.5 to 3. The presence of more than 50% of Jahn–Teller ions (Mn^{3+}) in the host structure

introduces a cubic to tetragonal distortion (from $c/a = 1$ to $c/a = 1.16$, $\Delta V/V = 6\%$). Upon repeated cycling, it is believed that this distortion results in either deterioration of the electrical contact between the surface of the insertion-material particles or in a collapse of the spinel framework and, hence, a decrease in the capacity of the cathode.

Thackeray [19] have placed the onset of the critical Jahn–Teller effect at $x = 1.08$ in $\text{Li}_x\text{Mn}_2\text{O}_4$. In a multi-phase system, however, when phase changes occur during the discharge near the transition points, more phases occur than are allowed by true thermodynamic equilibrium. Under non-equilibrium conditions, it is therefore expected that there will always be spinel particles which are more extensively lithiated than others. It is also likely that beyond this stage of discharge, when the cell voltage is falling sharply and has a value between 4 and 3 V, and while most of spinel particles will have an average composition of $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ (i.e., a slightly lithium-deficient spinel), the Jahn–Teller effect may start to occur on the surface of a few particles that have already reached the stoichiometric spinel composition (LiMn_2O_4). It therefore seems plausible that below the knee of the discharge curve, i.e., between 4 and 3 V, a few spinel particles may reach an overall composition, $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$. This is a state in which the average manganese oxidation falls below 3.5. Hence, the Jahn–Teller effect is practically observed in the range of the 4-V plateau. It is still to be determined, however, whether or not the Jahn–Teller effect is responsible for the capacity loss after cycling in the 4-V plateau.

To investigate the voltage region which is critically affected by the Jahn–Teller effect during cycling, charge–discharge curves for 100 cycles were recorded in the voltage ranges 4.3 to 3.0 V (Fig. 7) and 4.3 to 2.5 V (Fig. 8). When the film is cycled in the former region, a slight capacity loss is observed (Fig. 7). Nevertheless, the degree of the capacity loss is still very small compared with the capacity loss of the bulk electrode. After being cycled 100 times in the voltage range 4.3 to 2.5 V, a large loss of

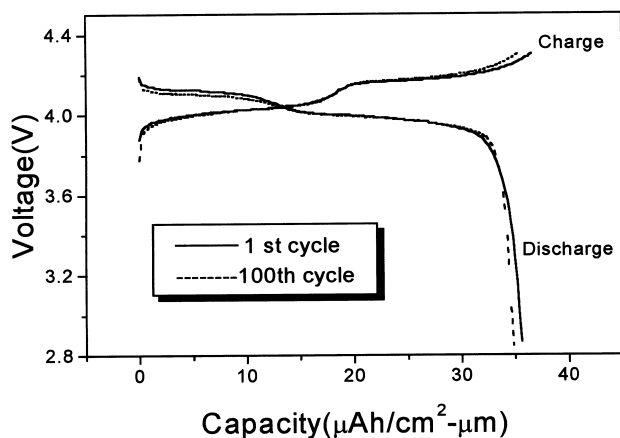


Fig. 7. Comparison of charge–discharge curves between 1st and 100th cycles for Li/1 M LiClO_4 –PC solution/ LiMn_2O_4 thin-film cell in voltage range 4.3 to 3.0 V.

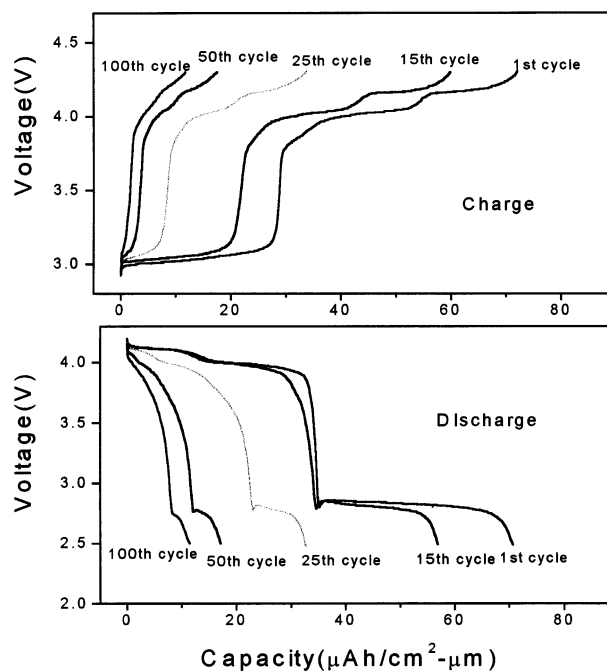


Fig. 8. Degradation of charge–discharge curves for Li/1 M LiClO_4 –PC solution/ LiMn_2O_4 thin-film cell during cycling in voltage range 4.3 to 2.5 V.

capacity is observed (Fig. 8), which is caused by the strain due to the Jahn–Teller effect.

From these analyses, it is concluded that the Jahn–Teller effect critically affects the capacity loss of a cell with a $\text{Li}_x\text{Mn}_2\text{O}_4$ thin-film electrode when $x > 1$. When the cell is cycled to the adjacent region of $x \approx 1$ in $\text{Li}_x\text{Mn}_2\text{O}_4$, only a slight capacity loss may be caused by the Jahn–Teller effect. When the cell is cycled in the region of $x < 1$ in $\text{Li}_x\text{Mn}_2\text{O}_4$ (4-V plateau region), a capacity loss was not observed.

If the Jahn–Teller effect is responsible for the capacity loss after cycling in the 4-V plateau, how can the excellent rechargeability of the LiMn_2O_4 thin film in the plateau region be explained?

It is difficult to say clearly whether the Jahn–Teller effect is the main cause for capacity fading after cycling at $x < 1$ in $\text{Li}_x\text{Mn}_2\text{O}_4$. If it is true, however, it can be inferred that the effect can be successfully suppressed in the thin-film electrode, i.e., thin film can relax the strain generated from the lattice mismatch between the cubic and tetragonal phases.

3.2.2. Inhomogeneous local structure

The discharge curve of $\text{Li}_x\text{Mn}_2\text{O}_4$ shows two distinct regions in the region of $x < 1$ [20]. In the high-voltage region ($x < 0.45$), two cubic lattices with $a_c = 8.045 \text{ \AA}$ and $a_c = 8.142 \text{ \AA}$ coexist. During the intercalation of lithium ions into the spinel structure, a cubic lattice with $a_c = 8.045 \text{ \AA}$ is inhomogeneously converted into a cubic lattice with $a_c = 8.142 \text{ \AA}$, because no intermediate cubic lattice exists. Therefore, the spinel framework expands/

contracts inhomogeneously during the intercalation/de-intercalation, which is suggested to be the main cause for loss after cycling.

According to several researchers, a decrease in the firing temperature during fabrication of LiMn_2O_4 produces a weak enhancement in cycling ability with some sacrifice of capacity [12,21]. According to Liu et al. [21], a decrease in firing temperature results in a lower degree of crystallinity. This results in a less-distinct two-step electrochemical oxidation and reduction, and gives rise to more reversible lithium intercalation. Although the authors did not explain the good rechargeability of powder with a lower degree of crystallinity, we consider that it may be caused by a decrease in the strain generated from volume expansion/contraction. This is due to a less-distinct two-step electrochemical reaction. In view of the above findings, it is considered that the excellent rechargeability was associated with a locally disordered and imperfect crystalline structure.

3.3. Factors for excellent rechargeability of LiMn_2O_4 thin-film electrodes

As stated earlier, the main criterion for excellent rechargeability is suppression of the ‘effects’ of strain generated from volume expansion/contraction or mismatch of two phases during the lithium intercalation/de-intercalation process. The strain may arise from the Jahn–Teller effect, inhomogeneous local structure, or other effects during cycling.

Methods to suppress the ‘effects’ may be approached in two ways. One is to reduce directly the amount of strain to a lower level, to make the structure sustainable without collapse during the lengthy cycling. The other method is an effective relaxation of the newly generated strain, so as not to damage the structure integrity and not to decrease the number of intercalation sites.

The doping of cations with low valences [15–18,22–24] and treatment at low firing temperatures [12,24] are attempts to reduce the amount of strain through decreasing the inhomogeneous expansion/contraction of volume during cycling or through suppressing the Jahn–Teller effect. A sample with good rechargeability had a relatively small lattice constant and showed a less-distinct two-voltage plateaus in discharge curves. This suggests the presence of imperfection in the lattice sites.

In general, thin films with excellent rechargeability have a lower degree of structural perfection than bulk electrodes because, in fabrication steps, atomic defects such as vacancies in the structure are easily generated and, generally, an amorphous phase is contained inside the films. In particular, vacancies in the lattice structure may reduce the inhomogeneous expansion/contraction in volume during cycling. Therefore, it can be inferred that the reason for excellent rechargeability is a decrease in strain generated from the expansion/contraction of volume because of a lower degree of structural perfection.

In our work, films with a lower degree of structural perfection display better rechargeability than those with a higher degree of structural perfection (Fig. 5). This result is consistent with above the conclusion.

A decrease in volume expansion/contraction cannot, however, totally explain the excellent rechargeability of LiMn_2O_4 thin films because all of the strain generated during cycling cannot be decreased by the imperfection of the structure. The generation of strain may have other causes such as the Jahn–Teller distortion, etc. Hence, it can be inferred that a thin film of LiMn_2O_4 can easily relax the strain generated during cycling.

We can suggest that the effects of ‘vacant room’ such as micropores, microvoids, vacancies, and amorphous phases are factors which relax the strain. Thin films have lower density than bulk electrodes because micropores and microvoids can be easily created during the deposition and crystallization process. Also, an amorphous phase can be retained after the annealing treatment. These micro-defects may be homogeneously mixed with the crystalline structure and can relax the strain, i.e., micropores and amorphous phases offer ‘vacant room’ with a little shift of the lattice during cycling and relax the strain generated in the intercalation/de-intercalation process. The models of stress relaxation through vacancies and micropores are suggested in Figs. 9 and 10, respectively. In this manner, the effects of the Jahn–Teller distortion or inhomogeneous local structure on capacity loss after cycling can be successfully suppressed.

The effect of low density on rechargeability has been reported. The EBC (Eveready Battery) microbattery containing a TiS_2 thin film has exhibited excellent rechargeability [25–28]. The Company stated that the low density of the TiS_2 thin film reduced the volume expansion of the

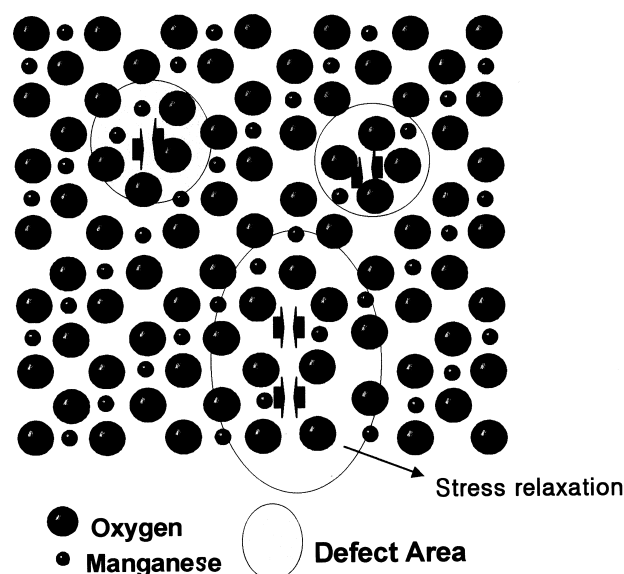


Fig. 9. Model of stress relaxation through vacancies in lattice structure of LiMn_2O_4 thin films.

cathode during intercalation and enabled the EBC micro-battery to be cycled thousands of times, which is analogous to the explanation made earlier in this paper.

Another possible factor which may suppress the Jahn–Teller effect can be deduced from analysis of impedance plots. Fig. 11 shows typical Nyquist plots for a bulk and thin-film LiMn_2O_4 electrode. The impedance spectrum for the bulk electrode consists of two separated arcs in the high and intermediate frequency range. According to a previous study [29], the high frequency arc represents particle-to-particle contact resistance and capacitance among the oxide particles. The intermediate frequency arc is related closely to the absorption of lithium ions, which are adsorbed on the oxide surface and into the oxide. The Nyquist plot obtained from a LiMn_2O_4 thin film shows only one arc in the high frequency range. This means that contact resistance and capacitance among the oxide particles do not exist in thin-film electrodes. These electrodes are homogeneously deposited on the current-collectors. It can be said that the particles of a thin-film electrode are in continuous contact with the current-collector. Thus, there is no contact impedance between particles in a thin-film electrode.

The absence of contact impedance may be responsible for the suppression of the Jahn–Teller effect in thin-film electrodes. As stated earlier, the Jahn–Teller effect would damage not only the structural integrity but also the particle-to-particle contacts in bulk electrodes. In the cases of a thin film, however, the electrical contact between the particles is not affected because of the continuous contact with the current-collector. Hence, the loss of contact be-

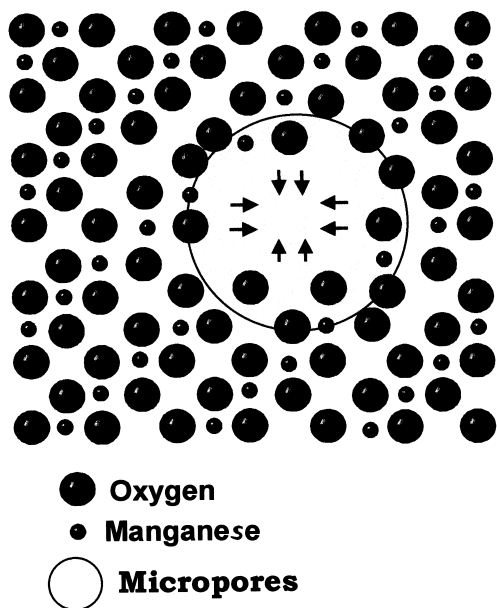


Fig. 10. Model of stress relaxation through micropores in LiMn_2O_4 thin films.

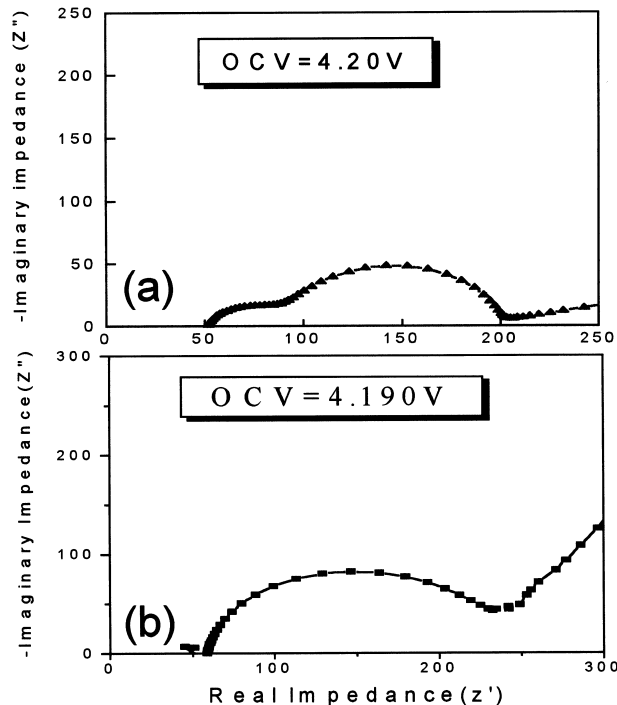


Fig. 11. Comparison of typical Nyquist plots for (a) LiMn_2O_4 bulk electrode and (b) LiMn_2O_4 thin-film electrode.

tween particles is not a cause of discharge capacity loss in LiMn_2O_4 thin films after cycling.

4. Conclusion

The films of LiMn_2O_4 fabricated by sol–gel method have been investigated. The electrochemical properties of the annealed films are changed according to the condition of the drying temperature. Annealed films dried at a high temperature display larger discharge capacity and have a more perfect structure. The capacity loss after cycling is, however, larger than that of annealed films dried at lower temperatures.

LiMn_2O_4 films prepared under optimum fabrication conditions show excellent rechargeability. This means that the possible causes for capacity loss during cycling, as suggested by other workers, are successfully suppressed in the film electrode.

From the analysis of our results and those of earlier reports, we suggest the following ‘possible factors’ which may be responsible for the excellent rechargeability of LiMn_2O_4 thin films:

- (i) a lower degree of structural perfection, which reduces the inhomogeneous expansion/contraction in volume during cycling;
- (ii) micro-defects in the film and these can offer ‘vacant room’ for a shift in lattice during cycling and relax the strain generated during the intercalation/de-intercalation process;

(iii) no contact impedance between particles, i.e., the particles contact homogeneously with the current-collector, which can suppress the effect of strain due to Jahn–Teller distortion.

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