Fabrication and characterization of an Li–Mn–O thin-film cathode for rechargeable lithium microbatteries

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Abstract

Thin films of $LiMn_2O_4$ spinel were fabricated by r.f. magnetron sputtering. The fresh films were amorphous but could be crystallized into a spinel structure by rapid thermal annealing in an oxygen ambient. The electrochemical performance of $LiMn_2O_4$ thin-film cathode was tested in $LiMn_2O_4$ thin-film (2000 Å)/1 M $LiClO_4$ in propylene carbonate + dimethoxyethane/ Li metal arrangements. $LiMn_2O_4$ spinel films prepared at 750 °C had a favorable structure and grains for lithium-ion intercalation. Room temperature cycling of these films showed good intercalation kinetics and very promising cycling behavior.

Keywords: Rechargeable lithium batteries; Thin-film cathodes; Lithium; Manganese dioxide

1. Introduction

All solid-state systems have several advantages such as simple design, no gas generation during operation, natural seal, and so on. Most important of all, solid-state devices can be miniaturized. These capabilities and the reduction in scale and power requirements of electronic devices prompted work on developing all solid-state thin-film microbatteries for microelectronic applications. To date, an attempt to integrate lithium microbatteries on CMOS memory chip as a noise-free stand-by power source has been made [1]. In addition to low-power applications, multicell thin-film batteries might be fabricated to obtain high capacities and/or voltages. Another possible application of thin-film microbatteries is to couple them with microsensors and microactuators. Rechargeable lithium systems are considered to be most promising for an all solid-state thin-film battery because of the following reasons. Lithium batteries which are commercially available show relatively high cell voltages, large discharge capacities, and small self-discharge rates and thus satisfy the need for a high energy density, long-lasting power source. Moreover, many fast ionic conductors for lithium have been known which is essential to fabricate solid-state batteries. In recent years, much interest has been centered on the development of lithium insertion electrodes for rechargeable lithium batteries. Particularly, it is essential to fabricate the cathode materials into a thin-film form for microbatteries. Several lithium-intercalation compounds such as TiS_2 [2,3], V_2O_5 [4], $LiMn_2O_4$ [5,6]

have been made in thin-film forms. Unlike the other intercalation compounds, $Li_xMn_2O_4$ spinel has been known to provide an almost constant potential of 4 V over the lithium composition range of $0 < x < 1$. High cell voltage, long shelf life, wide operating temperature range, low cost and the use of non-toxic electrode materials are thought to be advantageous over other intercalation compounds [7]. Therefore, many research works have been concentrated on $LiMn_2O_4$ [8–12] and the development of its thin-film fabrication process. Among these, the report by Shokoohi et al. [6] where the $LiMn_2O_4$ spinel films were made by reactive electron beam evaporation is of particular interest because the films showed reasonable cycling performance.

Manganese oxides, especially MnO_2 which has been widely used as a cathode material in lithium primary batteries cannot be used for the rechargeable batteries because of an irreversible reaction with lithium. However, by reacting manganese oxides with lithium salts, spinel $Li_xMn_2O_4$ ($x \approx 1$) is known to be formed [8–12], where a three-dimensional interstitial space for Li^+-ion transport is available through the framework of Mn_2O_4. Hence, in the fabrication of $Li_xMn_2O_4$ thin films, the formation of spinel structure is very important and the spinel structure should be maintained along the cycling of lithium to provide good rechargeability and to prevent loss of capacity at high current levels.

In this work, lithium manganese oxide thin films were deposited by r.f. magnetron sputtering and spinel-phase $LiMn_2O_4$ films were obtained through a rapid thermal annealing (RTA) process. We have intended to improve

the cycling performance of the $LiMn_2O_4$ thin-film cathode by controlling the RTA temperature.

2. Experimental

Films about 2000 Å thick were prepared by r.f. magnetron sputtering of two-inch diameter $LiMn_2O_4$ target in Ar–O_2 mixtures. All films were deposited on M(1500 Å)/Ti(300 Å)/SiO_2(5000 Å)/Si wafer substrates (M = Au, Pd, Pt). The titanium layer was deposited for good adhesion between the M layer and the silicon oxide layer. The M layer worked as both a current collector in the electrochemical test cell and the reaction barrier of $LiMn_2O_4$ with the silicon substrate at elevated temperatures. Targets for r.f. magnetron sputtering were made by cold pressing of $LiMn_2O_4$ powder prepared by the solid-state reaction of stoichiometric amounts of lithium hydroxide monohydrate (LiOH·H_2O) and electrolytic manganese dioxide (EMD) at 800 °C in air for 24 h. For cold pressing, 1 w/o (poly(vinyl alcohol)) PVA was used as a binder. Quite robust targets could be obtained by a second sintering at 900 °C for 12 h. X-ray diffraction data of the fresh films indicated no crystallinity. For crystallization, RTA process was performed at 400 to 800 °C in oxygen ambient for 60 s. Surface morphologies were examined with the scanning electron microscope (SEM). To evaluate the electrochemical properties, glass beaker-type test cells were used. The cell of the spinel cathode consisted of $Li_xMn_2O_4$ film as the positive electrode, lithium metal foil as the negative electrode, and 1 M $LiClO_4$ in propylene carbonate (PC) + 1,2-dimethoxyethane (DME) (50/50 by volume) as the electrolyte. The electrochemical cells were discharged and charged at constant current between preset voltage limits using a current source (Keithley 220) and volt meter (Keithley 192). All electrochemical measurements were undertaken in an argon-filled glove box at room temperature.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction patterns of 2000 Å lithium manganese oxide films prepared by sputtering and post-annealing by RTA at various temperatures. The $LiMn_2O_4$ spinel phase could be obtained after 60 s RTA at temperatures above 650 °C. The crystallinity of the films improved as the RTA temperature increased and was saturated at 750 °C. As shown in Fig. 1(a), peaks at $2\theta = 18.61°$, 36.09°, 43.87° and 58.06° corresponding to the (111), (311), (400), (511) reflections of $LiMn_2O_4$ spinel phase, respectively, can be distinguished. For comparison, an X-ray diffraction pattern of bulk $LiMn_2O_4$ spinel phase used as a target material is shown in Fig. 1(b). Peaks at $2\theta = 32.98°$ and 39.67° marked as 'S' correspond to the diffraction lines of the
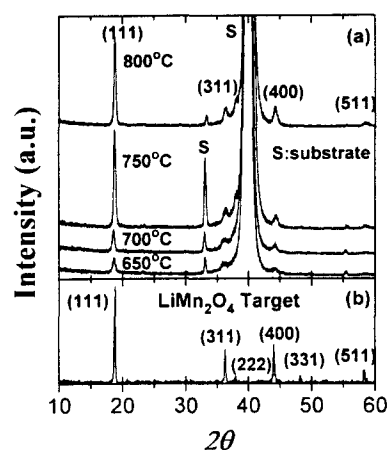

Fig. 1. (a) X-ray diffraction patterns of 0.2 μm thin films of $LiMn_2O_4$ spinel after rapid thermal annealing at various temperatures. (b) For comparison, X-ray diffraction patterns of the target material is shown.
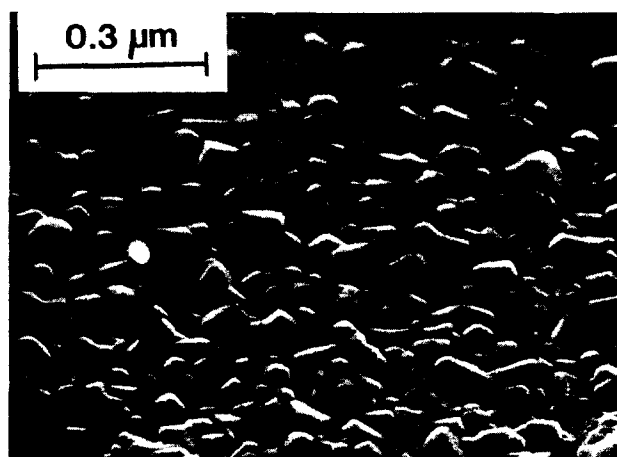

Fig. 2. Scanning electron micrograph of an $LiMn_2O_4$ spinel film after rapid thermal annealing at 750 °C in oxygen ambient for 60 s.

silicon wafer and the platinum layer of the substrate, respectively. Peaks corresponding to Mn_2O_3 or Mn_3O_4 could not be observed in these films, which might indicate the full reaction of lithium with manganese oxides.

Fig. 2 shows the surface morphology of an $LiMn_2O_4$ spinel film annealed at 750 °C for 60 s by RTA. The heat-treated films showed uniform thickness, grain size, and smooth surface. This is very important for preventing short circuits in thin-film batteries. There was a trend that the grain size of the films increased with increasing RTA temperature. But the short-time annealing process produced significantly smaller grains (< 0.05 μm) than those of the bulk materials (1–2 μm). The grain size plays a fundamental role in terms of charge-transfer rate capability and cycle life because small grains increase the effective surface area of the cathode and then facilitate lithium diffusion into and out of the three-dimensional channels of the crystal structure [5,6,8].

Charge/discharge curve (V versus x) and differential capacity plot (dx/dV versus V) of a film prepared at RTA temperature of 750 °C were obtained for electrochemical identification of $LiMn_2O_4$ spinel and they are shown in Fig. 3(a) and (b), respectively. Peaks in Fig. 3(b) reveals the electrochemical fingerprints of $Li_xMn_2O_4$ spinel phase ($0<x<2$) and correspond to the voltage plateaus in Fig. 3(a). It is known that the discharge process of a $Li_xMn_2O_4$ spinel occurs in three steps. First, discharge proceeds in a mixture of two cubic phases which can be characterized by the first plateau (peak I), and then in a homogeneous phase which can be characterized by the second S-shaped plateau (peak II) and finally, in the coexistence of a cubic and a tetragonal phase which leads to the third L-shaped plateau (peak III) [13]. In the calculation of x in $Li_xMn_2O_4$, crystalline density 4.281 g/cm^3 was assumed since the density of the $LiMn_2O_4$ thin film has not been determined, although the actual density of the thin film might be slightly lower than that.

The effect of RTA temperature on the cycle life is shown in Fig. 4. The samples prepared at 700, 750, and 800 °C were cycled more than 95 times in an $LiMn_2O_4$(2000 Å)/1 M $LiClO_4$+PC+DME/Li cell at 100 $\mu A/cm^2$ at room temperature. It can be seen in this Figure that the film annealed at 700 °C shows significant degradation upon cycling, while no appreciable degradation can be noticed for the films annealed above 750 °C. Referring to X-ray analysis, it can be said that the framework of Mn_2O_4 in the film annealed at 700 °C is not stable enough for lithium cycling, while the films annealed above 750 °C have a stable framework of Mn_2O_4 necessary for reversible lithium intercalation.
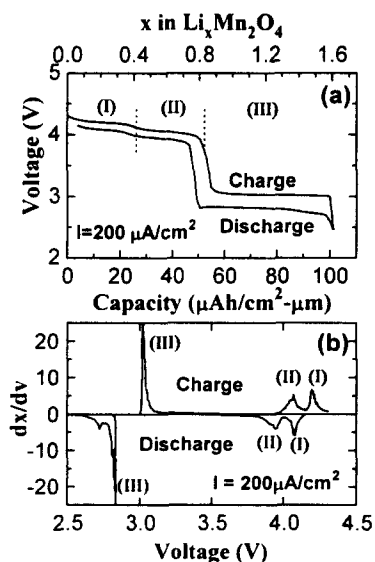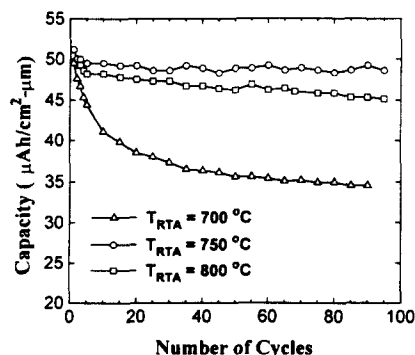

Fig. 4. The effect of rapid thermal annealing temperature on the cycling behavior of $LiMn_2O_4$ films. Li/1 M $LiClO_4$+PC+DME/$Li_xMn_2O_4$ cells were cycled at 100 $\mu A/cm^2$ at room temperature.
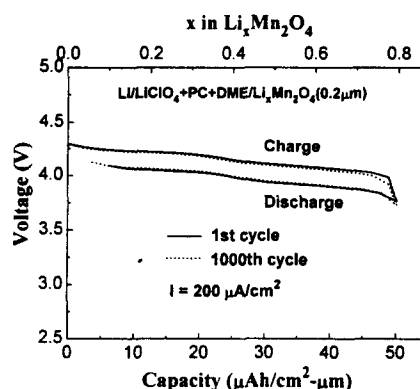

Fig. 5. Typical electrochemical behavior of a 0.2 μm $LiMn_2O_4$ spinel structured thin film prepared at a rapid thermal annealing temperature of 750 °C.

The increase in grain size which is supposed to increase with annealing temperature might be responsible for the decrease in the capacity of the film annealed at 800 °C compared with that at 750 °C. Therefore, the stability of spinel structure and grain size are important for good cycling performance. Stable structure and fine grains for Li^+-ion intercalation could be obtained by RTA at 750 °C.

To demonstrate the rechargeability of these films annealed at 750 °C, test cells were cycled more than 1000 times at a current density of 200 $\mu A/cm^2$ between 3.7 and 4.3 V at room temperature. Charge and discharge curves of 2000 Å $LiMn_2O_4$ film at the first (solid line) and after the 1000th (dotted line) cycle are shown in Fig. 5. The discharge capacity was about 50 $\mu Ah/(cm^2$ $\mu m)$ which corresponds to 0.8 Li per mole of Mn_2O_4. The discharge occurred at a nearly constant potential of 4 V. The capacity loss was less than 2% of their original capacity even after 1000 cycles. It is therefore believed that films annealed at 750 °C have the most favorable Mn_2O_4 framework which remains intact within the composition range of $0<x<1$ in $Li_xMn_2O_4$, and thus showed excellent reversibility. Shokoohi et al. [6]

Fig. 3. Electrochemical identification of a 0.2 μm $LiMn_2O_4$ spinel film prepared at 750 °C by rapid thermal annealing: (a) charge/discharge curve, and (b) differential capacity plot were obtained using an Li/1 M $LiClO_4$+PC+DME/$Li_xMn_2O_4$ cell at 200 $\mu A/cm^2$ at room temperature.

prepared thin films of $LiMn_2O_4$ by reactive electron beam evaporation followed by in situ annealing at 400 °C. Then the results are compared with our data in Fig. 6. The capacity unit mAh/g used by Shokoohi et al. [6] was converted into $\mu Ah/(cm^2 \, \mu m)$ using the crystalline density of $LiMn_2O_4$. It can be noticed that our films show no appreciable degradation after more than 220 cycles, while about 30% capacity loss occurred in Shokoohi's observations. Fig. 7 shows the room temperature electrochemical behavior of 2000 Å $LiMn_2O_4$ film annealed at 750 °C as a function of current densities up to 1 mA/cm^2. The slow decrease in capacity with increasing current densities can be noticed which can be attributed to the ohmic voltage drop and the cathode overpotential related to lithium diffusion kinetics. The discharge capacity obtained at 1 mA/cm^2 was 45.5 $\mu Ah/(cm^2 \, \mu m)$, which was more than 90% of the capacity obtained at 50 $\mu A/cm^2$, indicating that fast lithium intercalation kinetics resulted from the fine grains produced by RTA process.

4. Conclusions
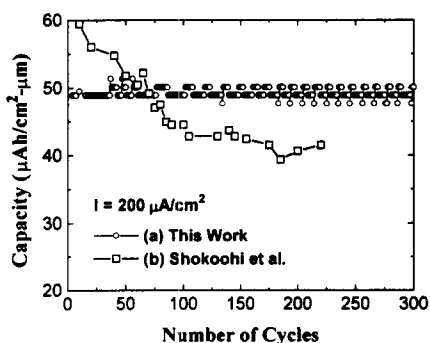
$LiMn_2O_4$ spinel structured thin films could be fabricated by r.f. magnetron sputtering followed by RTA above 650 °C in an oxygen ambient. By controlling the RTA temperature, $LiMn_2O_4$ spinel films with stable structure and fine grains could be obtained at 750 °C and this resulted in an enhanced cycling performance. No appreciable degradation could be observed even after 1000 cycles at a current density of 200 $\mu A/cm^2$ at room temperature. Good intercalation kinetics could be maintained even at a current density of 1 mA/cm^2. These electrochemical properties are thought to be very promising for a new generation of rechargeable thin-film lithium microbatteries.

Acknowledgements

Fig. 6. Comparison of cycling behavior. (a) Li/1 M $LiClO_4$ + PC + DME/ $Li_xMn_2O_4$ (0.2 μm) at room temperature. (b) Li/1 M $LiClO_4$ + EC + DEE/$Li_xMn_2O_4$ (1.2 μm) at 55 °C, Ref. [6].
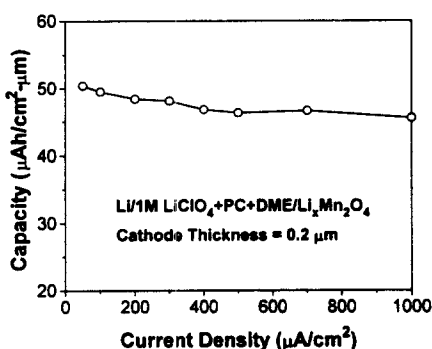
Fig. 7. Capacity change with discharging current density at room temperature.

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