

Preparation of lithium manganese oxide films for Li secondary batteries

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The manganese oxides have been focused as a cathode material in the Li secondary batteries. These films have been prepared by a reactive evaporation method under the oxygen flow rate of 5 sccm. The Mn_3O_4 films were successfully prepared under the deposition rate of 15 \AA/s . The preparation procedure of $LiMn_2O_4$ films was investigated through this study.

Key words: Li secondary batteries, manganese oxide films, Li-Mn defect spinel structure, reactive evaporation

1. Introduction

The lithium (Li) secondary batteries have been used for the batteries of cell phones, video cameras, etc. The revolution of energy sources for electric vehicles has been started by using fuel cells and Li secondary batteries. These devices require the specific energy density more than 100 Wh/kg and the power density 40 W/kg.¹

Various materials have been used for the positive electrodes of Li secondary batteries.^{1,2} Recently, various manganese oxides have been investigated as the positive electrode materials. We have been focusing especially on the Li-Mn-defect-spinel-structure (so called defect-spinel-structure).^{3,16} If this structure is adopted as a positive electrode, the operating voltage of 3-4 V could be obtained.

The crystalline structure and theoretical capacity were investigated.^{3,4} The defect-spinel-structure is defined by Mn_3O_4 , $Li_4Mn_5O_{12}$, and $\lambda\text{-MnO}_2$ triangle in the Li-Mn-O phase diagram⁴ as shown in Fig. 1 and 2. The stoichiometric spinel phase is also defined by the Mn_3O_4 - $Li_4Mn_5O_{12}$ line. The $\lambda\text{-MnO}_2$ has the highest theoretical capacity of 308 mAh/g in the defect spinels. However, it has highly oxidizing character over the compositional range $0 \leq x \leq 1$ in $Li_x[Mn_2]O_4$. The Mn_3O_4 structure has the theoretical capacity of 117 mAh/kg. Our goal is to prepare the defect-spinels defined by the Mn_3O_4 , $Li_4Mn_5O_{12}$, and $\lambda\text{-MnO}_2$ triangle. These defect-spinels are considered to have high structural stability upon insertion and desorption of Li ions. The theoretical capacity of them is 148-213 mAh/kg.

All of the materials for the positive electrodes have been prepared by sintering method.³⁻¹⁶ These powders have to be mixed with some binders and high electric conductivity materials like carbon black to apply the metal electrode. This process has complex procedures and induces thick films. This is less attractive in the point of energy density than the deposition process proposed in this paper. In order to improve these problems, we have focused on the reactive evaporation method.

The manganese oxide films have been prepared using various techniques.¹⁷⁻³³ The defect spinel structure described above could be obtained through the reaction

between Li and $\lambda\text{-MnO}_2$ or Mn_3O_4 .^{5, 6, 24-33}

One of the problems encountered in the reactive evaporation method is that the metallic Mn as an evaporant is oxidized during evaporation. In early studies, the superior protection against oxidation was obtained by using a molybdenum (Mo) separator²⁶⁻³⁰, a stainless steel cell (SUS cell)^{31, 32}, and a quartz ampoule.³³

In this study, the preparation procedure of manganese oxide thin films including Li was tried. The results are shown in this article.

Thermal annealing was proceeded in our early study.¹¹ The deposited films were succeedingly annealed without breaking vacuum. It takes long time to increase and decrease the annealing temperature. It is easy for sulfur to reevaporate from SrS matrix during high temperature annealing process. The EL elements have been damaged after annealing of 700°C. It could be overcome with compensating sulfur or applying a rapid thermal annealing process proposed in this paper.

In this study, a rapid thermal annealing process was applied to the EL elements. It was intended to improve the crystal properties of SrS:Cu films.

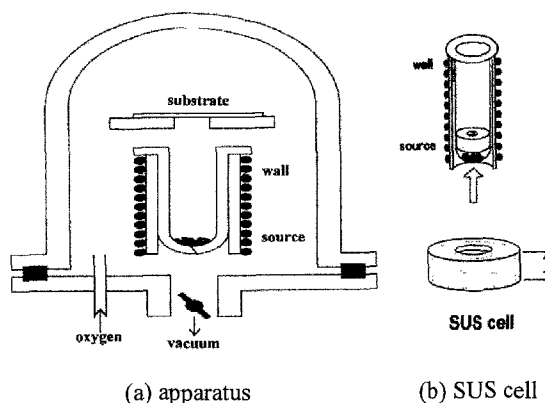


Fig. 1 Schematic of apparatus

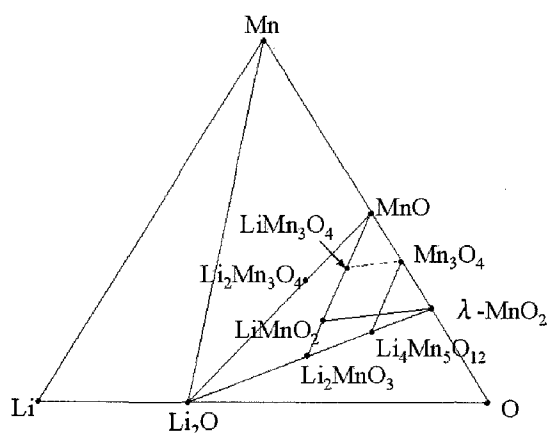
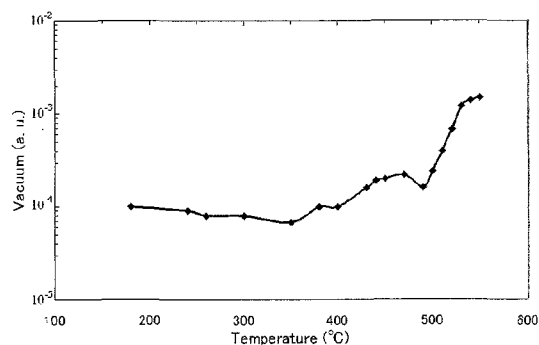


Fig. 2 Phase diagram

Fig. 3 Relation between vacuum and temperature of LiNO_3

2. Experiment

The manganese (Mn) oxide thin films were prepared on aluminum (Al) substrates which have the thicknesses of 0.2 mm by a Hotwall epitaxy. The deposition apparatus is shown in Fig. 1 (a). The metallic Mn as an evaporant was evaporated in the oxygen (O_2) atmosphere. The O_2 flow rate was controlled by a mass flow controller. It was fixed at 5 standard cubic centimeter per minute (sccm). Two crucibles for Mn and Li, which were made from stainless steel, were set and heated by electric resistance wires.

The SUS cell is shown in Fig. 1 (b). It was set in the crucible for Mn in order to prevent oxidization of metallic Mn. The aperture size and cell length are 6mm and 20mm, respectively. The substrate heater was not used in this study.

3. Results and discussion

The relation between source temperature of LiNO_3 and the pressure of vacuum chamber is shown in Fig. 3. The LiNO_3 has a melting point of 255°C and a boiling point of 600°C. The deposition temperature was set at 400°C. The deposition time of 10 minutes was used because, for more than 10 minutes, all the LiNO_3 could be evaporated.

Figure 4 shows the cross-section view of the deposited films on the Al substrate. The film shown in Fig. 4(a) was prepared by evaporating Mn for 10 minutes at 900°C, and LiNO_3 for 10 minutes at 400°C. When the prepared film was extracted from the chamber, a deliquescence was occurred because the Li layer was exposed to the air. The XRD measurements were not proceeded due to the deliquescence.

Based on the result described above, the LiNO_3 films were tried to be sandwiched with Mn layers as shown in Fig. 4(b) in order to prevent deliquescence. When the films shown in Fig. 4(b) were prepared, the deposition time was varied as 5, 10, 15 and 20 minutes to obtain the optimum thickness of the top Mn layer. There was no oxygen gas (O_2) flow. The difference of film properties was evaluated.

The XRD patterns of these films were shown in Fig. 5. In any case, the peaks of (111) and (200) for MnO and those of (103), (224) and (305) for Mn_3O_4 were found. However, the peaks of (111), (311) and (400) for LiMn_2O_4 were not found. As shown in Fig. 5, when the deposition time of Mn layer was set at 15 and 20 minutes, the crystalline characteristics of MnO and Mn_3O_4 were improved. It may be supposed that Li component was reevaporated because of the difference of the deposition temperature between Mn and LiNO_3 .

Figures 6 (a) and 6 (b) show the XRD patterns of the films prepared as shown in Fig. 4(b). In Fig. 6(a), the films were prepared without O_2 flow and in Fig. 6(b) with O_2 flow during the deposition process of middle and top layer, respectively. In Fig. 6(b), the reason why O_2 was not flown is to evaporate Mn firmly on the substrate. The estimated deposition rate of the film (a) was 15.5 Å/s and that of (b) was 5.67 Å/s, respectively. It was found that if the deposition rate was low, the crystalline characteristics of manganese oxide films could be improved. In any samples, the peaks of (111) and (200) for MnO and those of (103), (224) and (305) for Mn_3O_4 were found. However, the peaks of (111), (311) and (400) for LiMn_2O_4 were not observed. So the evaporation of LiMn_2O_4 has not been confirmed yet. This is seemed to be due to the difference between the evaporation temperatures of Mn and LiNO_3 is extremely high. The Li constituent in the LiNO_3 was reevaporated during succeeding deposition of Mn top layer.

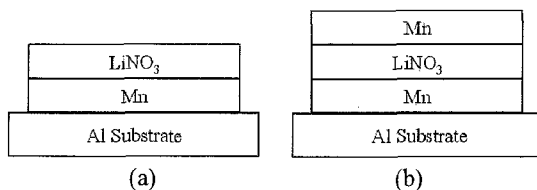


Fig. 4 Schematic of prepared film

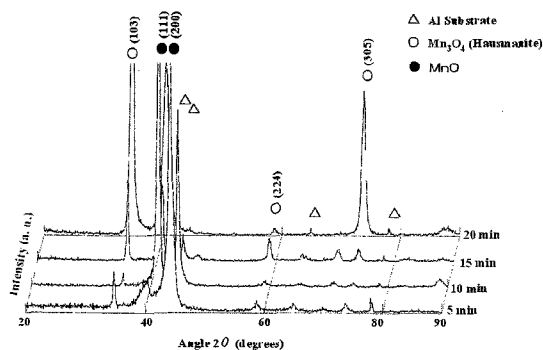


Fig. 5 XRD patterns with varying the deposition time of the Mn top layer

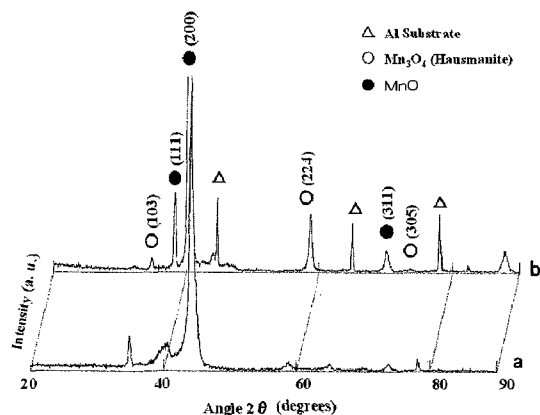


Fig. 6 XRD patterns prepared without O₂ and with O₂

In Fig. 5 and Fig. 6, the peaks of (200) plane for MnO was appeared notably compared to that for other Manganese oxides. This is supposed that the deposition rate of Mn was too high.

In the research we have tried, the Mn₂O₄ films could be successfully prepared under the deposition rate of 15 Å/s in the first deposition run.²⁶⁻³³

The preparation method of lithiated manganese oxide thin films has to be examined with considering the deposition rate and varying the deposition temperature. One of the problems is how to keep the Li layer on the first Mn layer during succeeding deposition of the Mn top layer. Another candidates of Li compounds as well as the LiNO₃ should be found in the future.

4. Conclusion

It was found that the manganese oxide films were successfully prepared by a reactive evaporation method under the oxygen flow rate of 5 sccm. The LiNO₃ was used as a Li source. The LiMn₂O₄ films have not been prepared yet. It was supposed that the Li component was reevaporated because of the difference of the deposition temperature between Mn and LiNO₃.

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