

# Preparation of manganese oxide films for Li secondary batteries

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**Abstract** Manganese oxides have been focused as a cathode material in the Li secondary batteries. These films are prepared by a reactive evaporation method. There is a problem that manganese metal is drastically oxidized through the first deposition run. A SUS cell was installed in the crucible to keep the manganese metal off the oxygen atmosphere. The  $Mn_3O_4$  films were successfully prepared under the deposition rate of  $15 \text{ \AA/s}$  in the first deposition run. Preparation of  $LiMn_2O_4$  films has been tried through this study.

**Keyword** Li secondary batteries, Manganese oxide films, Li-Mn spinel structure, Reactive evaporation

## 1. Introduction

The lithium (Li) secondary batteries are so familiar that they are used for mobile phones or video cameras, etc. Recently, they have been using in bicycles, under the development of high-power batteries. These devices require energy density more than  $100 \text{ Wh/kg}$  and power density more than  $40 \text{ Wh/kg}$ , which used for electric vehicle.<sup>1</sup>

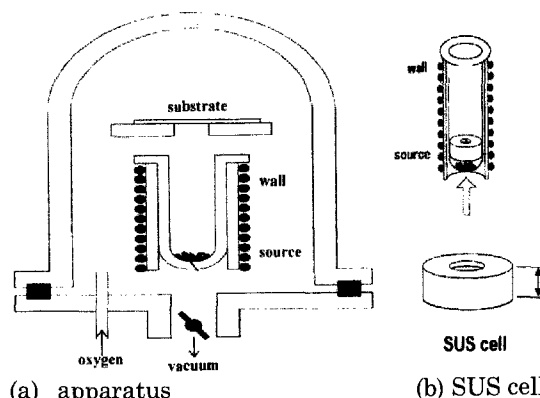
Various materials have been used as the positive electrode for Li secondary batteries.<sup>1,2</sup> Recently, various manganese oxides have been investigated as the positive electrode materials. They are especially recognized as a Li-Mn-defect-spinel-structure.<sup>3,16</sup> In this article, they are simply called as a defect-spinel-structure. The operating voltage of 3-4V would be obtained, by using a defect-spinel.<sup>3,4</sup> Crystalline structure of defect-spinel and theoretical capacity were investigated. Defect-spinel-structure is defined by the  $Mn_3O_4$ - $Li_4Mn_5O_{12}$ - $\lambda$ - $MnO_2$  triangle in the Li-Mn-O. Stoichiometric spinel phase is also defined by the  $Mn_3O_4$ - $Li_4Mn_5O_{12}$  line. The  $\lambda$ - $MnO_2$  has the highest theoretical capacity of  $308 \text{ mAh/g}$  in the defect spinels. However, it has highly oxidizing character over the compositional range  $0 \leq x \leq 1$  in  $Li_x[Mn_2]O_4$ .  $Mn_3O_4$  has the theoretical capacity of  $117 \text{ mAh/g}$ . Our goal is to prepare defect-spinels defined by the  $Mn_3O_4$ - $Li_4Mn_5O_{12}$ - $\lambda$ - $MnO_2$  triangle. These defect spinels would have generally a high structural stability upon insertion and desorption of Li. The theoretical capacity of the materials in this triangle scatters between  $148$  and  $213 \text{ mAh/g}$ .

All the materials for positive electrode used for secondary batteries have been prepared by the sintering method.<sup>3-16</sup> They are applied electric conductive materials like carbon or

pastes because they are powdery and inferior electric conductivity, but poor mass energy. In order to improve these problems, manganese oxide films have been prepared using various techniques.<sup>7-33</sup> Defect spinel structure described above could be obtained through the reaction between Li and  $\lambda$ - $MnO_2$  or  $Mn_3O_4$ .

One of the problems using reactive evaporation method is the metallic Mn as an evaporant is oxidized while it evaporates. In early studies, the superior protection against oxidation is obtained by using molybdenum (Mo) separator, stainless steel cell (SUS cell), and quartz ampoule.

Preparation of manganese oxide thin films including Li was tried. The results are shown in this article.



(a) apparatus (b) SUS cell  
Fig. 1 Schematic of apparatus. A stainless steel crucible was used. The wall ( $T_{wall}$ ) and source ( $T_{source}$ ) temperatures could be controlled independently.

## 2. Experiment

Manganese (Mn) oxide films were prepared on Aluminum (Al) substrates ( $0.2\text{mm}$

in thickness) by Hotwall epitaxy.

Deposition apparatus is shown in Fig. 1 (a). Metallic Mn as an evaporant was evaporated in the oxygen (O<sub>2</sub>) atmosphere. The O<sub>2</sub> flow rate was controlled by a mass flow controller. It was fixed at 5 standard cubic centimeter per minute (sccm). The temperatures of the upper and lower part of the crucible are referred as T<sub>wall</sub> and T<sub>source</sub>, respectively. The temperatures of both T<sub>wall</sub> and T<sub>source</sub> were set at the same temperature and varied from 930 to 990°C. The stainless steel crucible was heated by an electric resistance wire.

SUS cell is shown in Fig. 1 (b). The metallic Mn was set in it. The SUS cell has an aperture size of 6mm φ and the cell length of 20mm. In order to obtain crystallographic characteristics, X-ray diffraction (XRD) measurements were performed with a RIGAKU Rotaflex 12 kW with CN2173D6 goniometer. The film thickness was measured by the optical method (interference fringes) and gravimetric method. The micro interferometer (Olympus) was used.

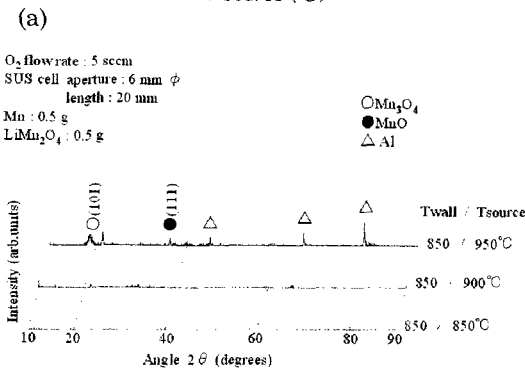
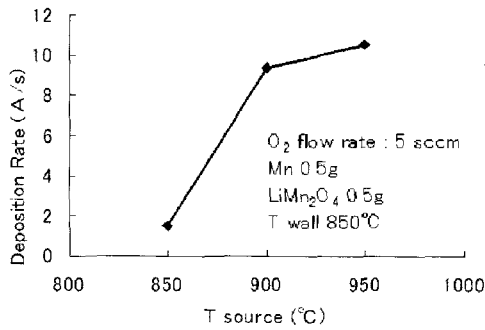


Fig. 2 (a) Dependence of T<sub>source</sub> of deposition rate no T<sub>source</sub>. T<sub>wall</sub> was set at 850 °C. (b) XRD patterns of these samples.

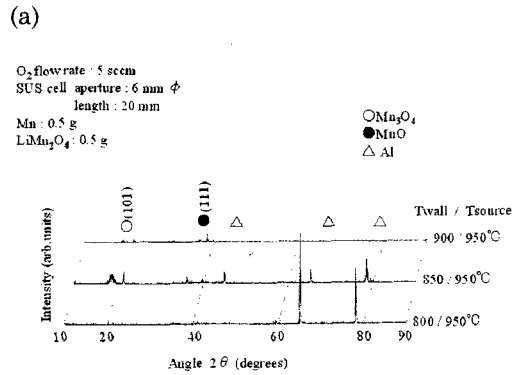
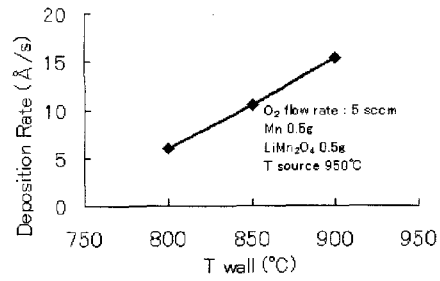


Fig. 3 (a) Dependence of deposition rate of T<sub>wall</sub>. T<sub>source</sub> was set at 850 °C. (b) XRD patterns

3. Results and discussion

Figure 2 (a) shows the dependence of deposition rate on T<sub>source</sub> when T<sub>wall</sub> was set at 850 °C. It was found that the deposition rate was saturated when T<sub>source</sub> was increased over 900 °C. Figure 2 (b) shows the XRD patterns of samples as shown in Fig. 2 (a). It was found that the deposition rate was decreased at the temperature of T<sub>source</sub> below 900 °C.

Figure 3 (a) shows the dependence of deposition rate on T<sub>wall</sub> when T<sub>source</sub> was set at 950 °C. The deposition rate proportional to T<sub>wall</sub> in the range between 800 and 900 °C. Figure 3 (b) shows the XRD patterns of these samples. The peaks of Mn<sub>3</sub>O<sub>4</sub> were appeared at the temperature of T<sub>wall</sub> over 850 °C.

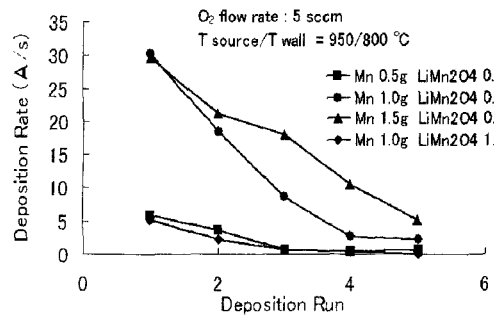


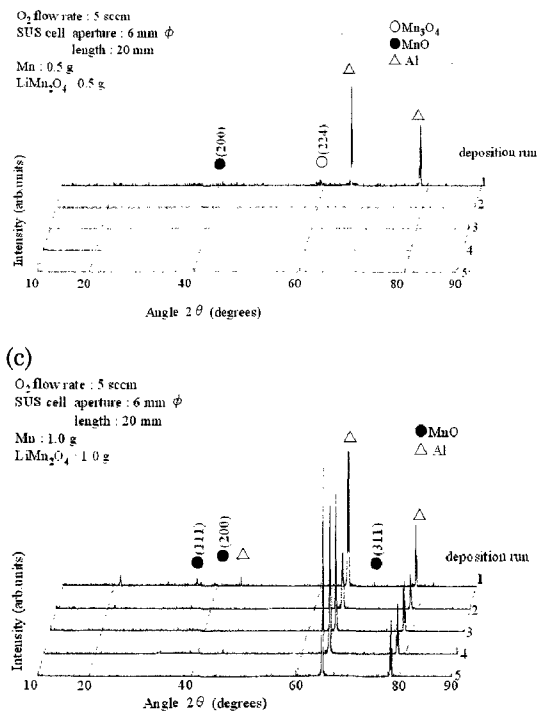
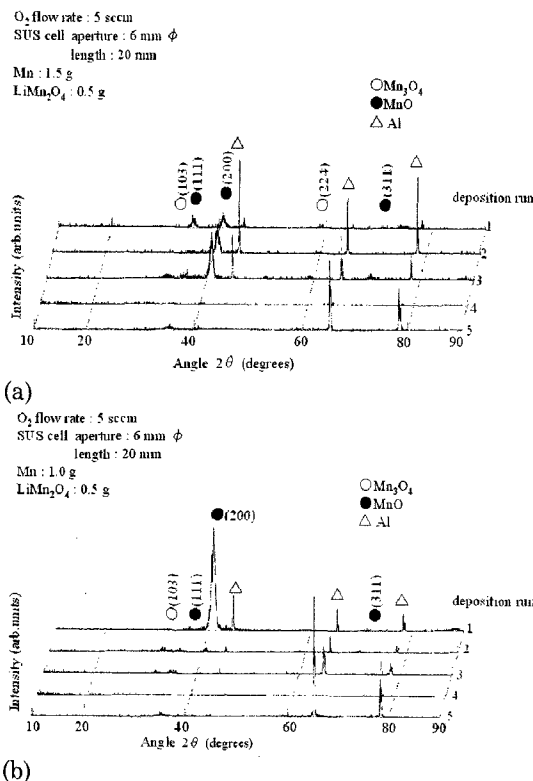
Fig. 4 Dependence of deposition rate on deposition run with varying ratio Mn and LiMn<sub>2</sub>O<sub>4</sub>.

Figure 4 shows the dependence of deposition rate on deposition run with varying the ratio of Mn and  $\text{LiMn}_2\text{O}_4$ .

The more the Mn to  $\text{LiMn}_2\text{O}_4$  ratio was increased, the more deposition rate was increased, as shown in Fig. 4. The comparison of the ratio between 3 and 2 showed that the ratio of 3 was better than that of 2. It means that the deposition rate was gradually decreased as increasing the deposition run. It is due to the fact that it is much easier to evaporate Mn than  $\text{LiMn}_2\text{O}_4$ .

In the case of comparison ratio between 2 and 3, the initial deposition rate stayed  $30 \text{ \AA/s}$ . When the ratio was 1, however, it was decreased to  $5 \text{ \AA/s}$ .

At the same composition ratio of 1, two types of evaporant (0.5 and 1.0 g) weight were tested. There was no difference between the deposition rates of them. Therefore the deposition rate is independent on the evaporant mass, but depends on the comparison ratio.



(d) Fig. 5 XRD patterns of prepared films.

Figure 5 (a)-(d) show the XRD patterns of the samples as shown in Fig. 4. The composition ratio was varied from 1 to 3.

Figure 5 (a)-(c) show that there were  $\text{MnO}$  and  $\text{Mn}_3\text{O}_4$  peaks in these samples. There were  $\text{MnO}$  peaks in the case of composition ratio of 3 as shown in Fig. 5 (b). Figure 5 (d) shows that the sample also gives  $\text{MnO}$  peaks. There are no XRD peaks related to  $\text{LiMn}_2\text{O}_4$ .

It was found that  $\text{MnO}$  films were prepared as shown in Fig. 5 (d).

These data showed that  $\text{MnO}$  and  $\text{Mn}_3\text{O}_4$  films which have orientation of (200) and (111) and that of (103) and (224) were prepared, respectively.  $\text{LiMn}_2\text{O}_4$  films unfortunately have not been recognized yet.

From these results described above, it was supposed that Mn in the crucible was somewhat evaporated, but  $\text{LiMn}_2\text{O}_4$  was not prepared. And it seemed that  $\text{LiMn}_2\text{O}_4$  was decomposed and Li was reevaporated from the deposited films.

In our early works, it was found that  $\text{Mn}_3\text{O}_4$  films could be successfully prepared at the condition of the initial deposition rate of below  $15 \text{ \AA/s}$ .

The insertion technique of Li atoms in the matrix of manganese oxide could be improved in the future work.

#### 4. Conclusion

Manganese oxide films were prepared using reactive evaporation method.  $\text{LiMn}_2\text{O}_4$

have not been prepared yet.

In the case of  $T_{\text{wall}}$  of 850 °C, the deposition rate was saturated as increasing  $T_{\text{source}}$  more than 900 °C.

The deposition rate was increased as increasing  $T_{\text{wall}}$  between 800 °C and 900 °C when  $T_{\text{source}}$  was fixed at 950 °C.

It was found that the deposition rate was greatly influenced by the composition ratio of Mn to  $\text{LiMn}_2\text{O}_4$  in the case of that of 3 and 2, it was decreased to 5 Å/s in the case of that of 1.

#### 5. Acknowledgment

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