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Oxidation process in the Mn crucible during the reactive evaporation

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Abstract Manganese oxide films for lithium secondary batteries were prepared using reactive evaporation method. One of the problems is that the manganese (Mn) evaporant suffers oxidation from oxygen atmosphere. This deteriorates the deposition rate as increasing the deposition run. A separator was introduced in the bottom of the Mn crucible. It can successfully isolate Mn evaporant from incoming oxygen atoms. The oxidation process in the Mn crucible was investigated by inserting a stainless steel sheet in the crucible. It was found that the composition of the deposited film on this sheet depended on the position in the crucible. X-ray diffraction analyses showed that the Mn_3O_4 films, so called Hausmannite, can be deposited on the position over the crucible top. On the other hand, the films in the crucible have strong MnO and weak Mn_3O_4 structures. This study helps us understanding the reactive evaporation process of Mn oxide films.

Key words (Li secondary batteries, Reactive evaporation, Manganese oxide films, Hausmannite)

I. INTRODUCTION

The environmental pollution problems as well as the oil exhaustion have advanced the development of electric vehicles. We can get some hybrid cars in these days. The power sources recently focused are lithium secondary batteries, fuel cells and so on.[1,2] A tight race (A hot competition) of the development of power sources has continued for a long time. A combination of manganese (Mn) oxide and lithium (Li) was focused in this study as the positive and negative electrodes, respectively. Mn oxide is one of the best materials for the positive electrode in the Li secondary batteries.[3] Mn is more abundant and less expensive than cobalt (Co), so that the overall cost would be minimized if $LiMn_2O_4$ is used as the positive electrode. Toxicity (if any) or recycling are already well known. The operating voltage of 3～5V could be obtained with this material.

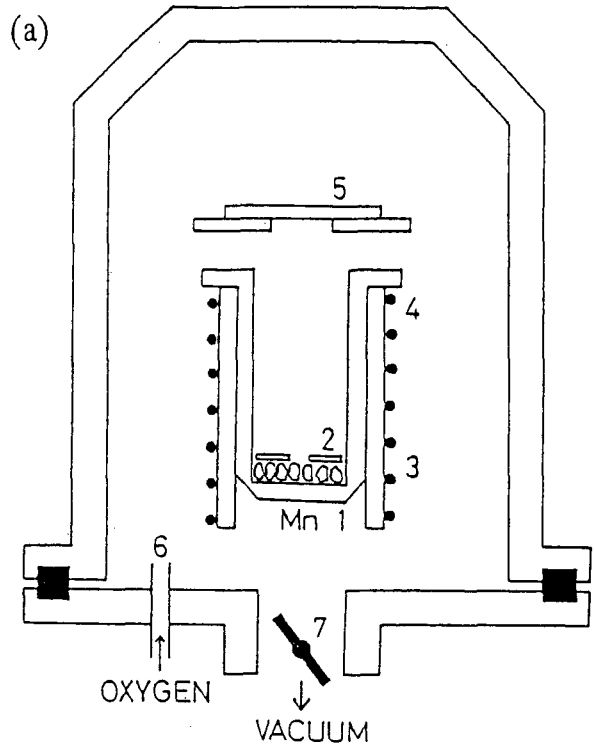
Almost all the oxide powders for positive electrodes are prepared by the sintering method.[4-15] They have inferior of electric conductivity. So we focused on the thin film technology, so called Hotwall epitaxy, to improve the electric conductivity. Mn oxide films were prepared by using reactive evaporation method.[16-24] One of the problems is that the Mn evaporant suffers oxidation from oxygen atmosphere during the reactive evaporation process. A separator was introduced in the bottom of the Mn crucible. The oxidation of the Mn evaporant was successfully prevented by this method.

The oxidation process in the Mn crucible was investigated by inserting a stainless steel sheet parallel to the crucible axis. The film composition on this sheet could be varied as a function of the distance from Mn evaporant. This study could help clarifying the reactive evaporation process of Mn oxide films.

The purpose of the present work is to investigate the compositional variation in the Mn crucible during the deposition process.

II. EXPERIMENT

Deposition apparatus is shown in Fig. 1 (a). Mn was evaporated in the oxygen atmosphere. The oxygen (O_2) flow rate was controlled by a mass flow controller. The flow rate was varied up to 10 sccm. Mn oxide film was deposited on a stainless steel sheet settled in the Mn crucible by Hotwall epitaxy. The stainless steel crucible was resistively heated. A molybdenum (Mo) sheet with a small hole was settled just over the Mn evaporant as shown in Fig. 1 (b). It is called as a separator hereafter. It acts as a separator which keeps Mn evaporant off the oxygen atoms. During the deposition



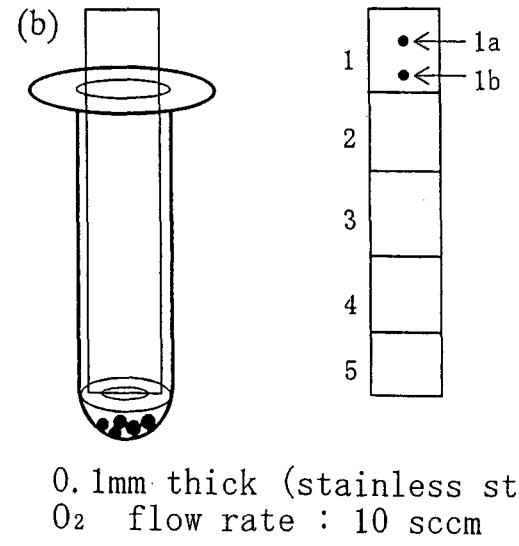


Fig. 1(a). Schematic of the apparatus. 1: Stainless steel crucible for Mn evaporation. 2: A molybdenum (Mo) sheet with a hole is settled in the bottom of the crucible. 3: W wire heater for Mn evaporant. The temperature of this area is shown as T_{source}. 4: W wire heater for wall area. The temperature of this area is shown as T_{wall}. 5: Stainless steel substrate. 6: O_2 inlet. 7: Main valve to control the O_2 atmosphere. (b) Schematic of the Mn crucible. A Mo sheet with a hole is set in the bottom of the crucible. It is called as a separator in the text. A stainless sheet of 0.1 mm thickness was inserted parallel to the crucible axis.

process, the substrate temperature (T_{sub}) was kept at room temperature. The film composition on this sheet was evaluated as a function of the distance from Mn evaporant. The stainless sheet was divided into 5 pieces for x-ray diffraction (XRD) and x-ray photo electron spectroscopy (XPS) evaluations. These 5 pieces of specimen were denoted as sample 1 to sample 5 as shown in Fig.1(b).

In order to obtain crystallographic information, some films were analyzed by a XPS carried out in a KRATOS XSAM-800pci, using a 15-keV Mg K_α ray. The spot size on the sample for collecting photoelectrons was ellipsoid of 4 $\times 8mm^2$. The sputter gun was set to 3 kV Ar^+ ions. XRD measurements for same samples were also performed on a RIGAKU Rotaflex 12kW system with a CN2173D6 goniometer. The film thickness was measured by the optical method (interference fringes) and gravimetric method. The micro-interferometer (Olympus) was used.

III. RESULTS AND DISCUSSION

Figure 2 shows the dependence of deposition rate on the deposition run under the O_2 flow rate of 10 sccm. The deposition rate did not deteriorate after four deposition runs. It means that the Mn evaporant was not oxidized under the oxygen atmosphere. This shows the effectiveness of a separator. A separator can effectively keep oxygen off the Mn evaporant.

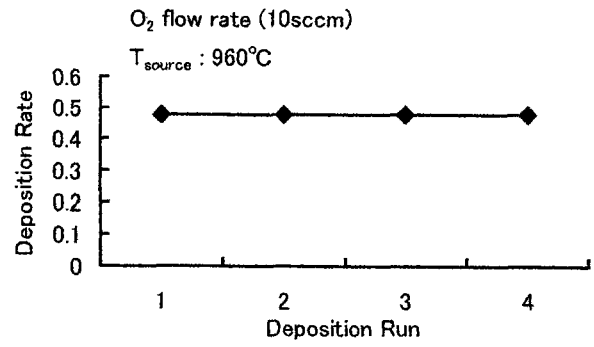


FIG. 2 Dependence of deposition rate on the deposition run under the O_2 flow rate of 10 sccm.

Figure 3 shows the variation of XRD data for the films prepared at the oxygen (O_2) flow rate of 10 sccm. The stainless sheet was divided into 5 pieces for XRD and XPS evaluations. These 5 pieces of specimen were denoted as sample 1 to sample 5 as shown in Fig.1(b). Films deposited over the crucible top only have the composition of Mn_3O_4. These films are so called Hausmannite.[23] All the films in the crucible have different colors. They have more than two structures, for example, MnO, Mn_3O_4 and etc..

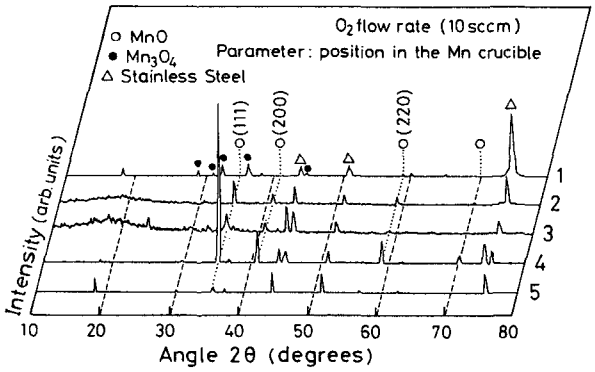


Fig. 3 XRD data for the films prepared at the O_2 flow rate of 10 sccm.

Figure 4 shows the dependence of relative heights of XRD peaks on the position of samples. The values of (111)/(200) and (111)/(220) were examined in this study. They are quite similar in shape in their curves except a slight difference between the values in the sample 4. It means that highly (111) oriented MnO films were prepared at the area of sample 4. The MnO films of (111) preferred orientation have been prepared.[23] It was found that the MnO films prepared in the crucible have the same (111) preferred orientation.

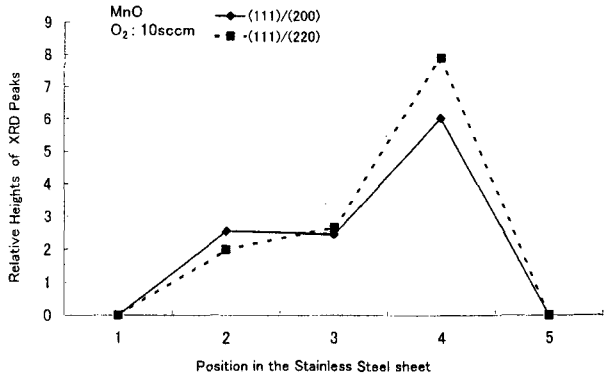


Fig. 4 The dependence of relative heights of XRD peaks on the position of samples.

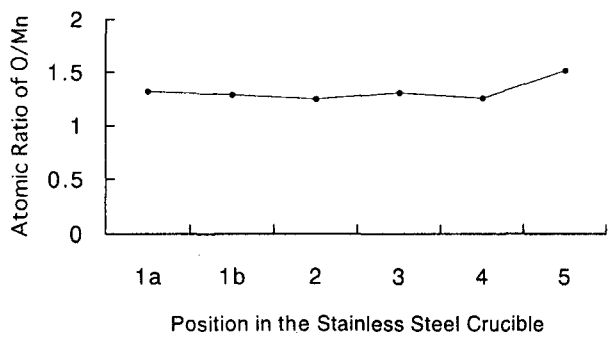


Fig. 5. XPS analysis was proceeded for the films shown in the Fig. 4.

The XPS analysis was proceeded for the samples shown in Fig. 4. Figure 5 shows the dependence of atomic ratio of O to Mn on the position of samples. The stoichiometry of these samples was investigated. The atomic concentration of the films was measured after sputtering the surface of the film for 30min. The sensitivity coefficients of 0.669 for O 1s and 3.197 for Mn 2p were used to estimate the chemical composition. The atomic ratio of O to Mn is 1.32 at the position of 1a. It means that this film is constructed with almost Mn_3O_4 structure. The sample of 1b has a weak MnO structure as well as a Mn_3O_4 structure. In the crucible, the atomic ratio of O to Mn varies from 1.25 to 1.31 except the bottom area (sample 5). These data show that they are constructed with the mixture of strong MnO and weak Mn_3O_4 structures. Especially, a weak Mn_3O_4 structure can be identified in the sample 3 as shown in Fig. 3. The atomic ratio of 1.52 in the sample 5 could be explained as follows. The atomic ratio in the bottom area depends on the analyzed point in the sample 5. The composition varies as a function of the distance from hole of the separator. In this case, It is seemed that the analyzed point was far from the hole. The Mn evaporation rate is highest just over the hole as shown in Fig. 1 (b). The deposition rate of Mn is drastically decreased with leaving from the hole. So, the atomic ratio of O to Mn has a large value, for example, in the sample 5 provided that the O_2 pressure is maintained at a same condition near the hole of the separator.

The oxygen molecules react with the evaporating manganese atoms on the stainless sheet. The MnO structure is the most stable form in the Mn oxides. So, it is the most dominant phase especially in the high temperature area, for example, in the crucible. The color of the deposited films depends both on the distance from the Mn evaporant and on the Mn source temperature (T_{source}). It means that the atomic ratio of O to Mn is not same in the whole crucible area. One of the reasons is seemed to be due to the temperature distribution in the crucible. The Mn partial pressure is gradually decreased as leaving the Mn evaporant. The value of O/Mn is increased as reaching the crucible top if the O_2 partial pressure is considered as a fixed value. But the O_2 partial pressure could be varied as reaching the bottom of the crucible because the Mn vapor keeps O_2 atoms off the Mn evaporant.

It is found that the separator contributes to the successes of controlling the stoichiometry as well as of protecting the oxidation of Mn evaporant. The usage of this separator increases the atomic ratio of O to Mn in the films. The reason for this behavior is as follows. The Mn deposition rate is decreased as introducing the separator because of decreasing the effective aperture size of Mn crucible. If the oxygen flow rate is fixed at a value, the atomic ratio of O to Mn is increased.

These circumstances could be changed as varying the Mn source temperature (i.e. deposition rate). The complexity is increased as adding extra parameters, for

example, Mn source temperature and wall temperature (T_{wall}). The exact explanation is in the future work.

A deep insight into the reactive evaporation process could improve the reproducibility of preparing Hausmannite structure. The present work contributes to this problem.

Our goal is to prepare Mn spinel (λ -MnO_2) films.[4-6] They have generally a high structural stability upon lithiation. One of the problems to be solved is to maintain high vapor pressure of Mn with keeping O_2 off the Mn evaporant. We hope we will report on them somewhere. It is convinced that the idea shown in the present work could be equally applicable for the preparation of other oxide films.

IV. CONCLUSION

The oxidation process in the Mn crucible was investigated by inserting a stainless steel sheet in the crucible. It was found that the film composition depended on the position in the crucible. The Hausmannite (Mn_3O_4) films can be deposited on the position over the crucible top. The films in the crucible have strong MnO and weak Mn_3O_4 structures. This study helps us understanding the reactive evaporation process of Mn oxide films. This method could also improve the reproducibility of Mn oxide films for Li secondary batteries.

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