Transactions of the Materials Research Society of Japan 28 [4] 1311-1314 (2003)

Effectiveness of SUS cell for preventing the oxidation of Mn evaporant during reactive evaporation process

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Manganese oxide films for lithium secondary batteries were prepared using a reactive evaporation method. The Mn metal in the crucible suffers severe oxidation during the reactive evaporation process, which deteriorates it's deposition rate with increasing deposition run. It is also difficult to maintain the stoichiometry of films from run to run. This paper shows a noble technique which keeps off the Mn evaporant from oxygen atmosphere during the reactive evaporation process. To achieve it a stainless steel cell (SUS cell) has been installed in the bottom of the Mn crucible, which can successfully isolate Mn evaporant from incoming oxygen atoms. It improves the reproducibility of film composition because of stabilizing of the deposition rate. The effect of SUS cell height on the crystal properties was investigated.

KEYWORDS: manganese oxide films, lithium secondary batteries, reactive evaporation, vacuum deposition, hausmannite structure
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1. Introduction

Evolution of electric vehicles depends on the high rate discharge properties of secondary batteries. Lithium (Li) secondary batteries for motorcycles were developed recently. They have been widely used for low energy storage applications like a cellular phone and a camcoder. These devices require energy density more than 100 Wh/kg and power density more than 40 W/kg.[1] There are a lot of potential candidate materials for secondary batteries.[1,2] A combination of manganese (Mn) oxide and Li was considered as the positive and negative electrodes, respectively. An operating voltage of 3～4 V can be obtained by this system.

Structural characteristics and theoretical capacities of defect spinels have been investigated.[3,4] Defect spinel is defined by the Mn_3O_4 - $Li_4Mn_5O_{12}$- λ -MnO_2 triangle in the Li-Mn-O phase diagram. Stoichiometric spinel phase is also defined by the Mn_3O_4- $Li_4Mn_5O_{12}$ line. The λ -MnO_2 has the highest theoretical capacity of 308 mAh/g in the defect spinels. But, 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 mAh/g. Our goal is to prepare defect spinels defined by the $LiMn_2O_4$ - $Li_2Mn_4O_9$ - $Li_4Mn_5O_{12}$ triangle. These defect spinels would have generally a high structural stability upon lithiation. The theoretical capacity of the materials in this triangle scatters between 148 and 213 mAh/g. These materials are appropriate for te batteries of electric vehicles.

Almost all the oxide powders for positive electrodes are prepared by the sintering.[3-13] 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.

Mn oxide films have been prepared by using many deposition methods.[14-32] The Mn_3O_4 films with spinel structure have been successfully prepared using a reactive evaporation method in our early works.[26-31]2They are so called Hausmannite. The Li-Mn-O phase diagrams[3,4] show that defect spinels could be prepared by reacting the Li atoms with Mn_3O_4 as well as with λ -MnO_2.[5,6]

One of the problems is that the Mn metal in the crucible (Mn evaporant) suffers oxidation from oxygen atmosphere during the reactive evaporation process. The oxidation of Mn evaporant increases with deposition run. It deteriorates the deposition rate of films because of higher melting temperature of oxidation layer which covers the metallic Mn. The feasibility of overcoming the oxidation of Mn evaporant has been investigated earlier by a Mo (molybdenum) separator[26-30], a stainless steel (SUS) cell[31] and a quartz ampoule.[32] The effectiveness of SUS cell in these devices was shown in the previous paper.[31] The aim of this study is to evaluate the effect of SUS cell height on the oxidation of Mn evaporant. This SUS cell has a composition of 18 Cr-8 Ni and this is so called SUS304.

The purpose of the present work is to evaluate the ability of SUS cell by which the oxidation of Mn evaporant is successfully prevented during the evaporation process.

2. Experiment

Mn oxide films were prepared on stainless steel sheet by Hotwall epitaxy. Deposition apparatus is shown in Fig. 1. Mn metal was evaporated in the oxygen atmosphere. The oxygen (O_2) flow rate was controlled by a mass flow controller. The O_2 flow rate was fixed at 5 standard cubic centimeter per minute (sccm). The source (T_{source}) and wall (T_{wall}) temperatures of the crucible were kept at 1143 and 1073 K, respectively. The stainless steel crucible was heated by an electric resistance wire.

A SUS cell with a small hole was set in the bottom of the crucible, which contained Mn evaporant. The hole diameter was 6 mm. It acts as a separator which keeps Mn evaporant off the oxygen atoms. The height of SUS cell was varied from 10 to 100 mm. The substrate temperature (T_{sub}) was not controlled during the deposition process.

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.

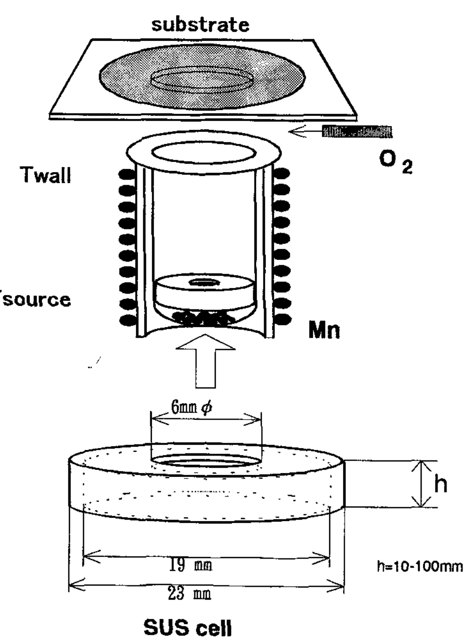
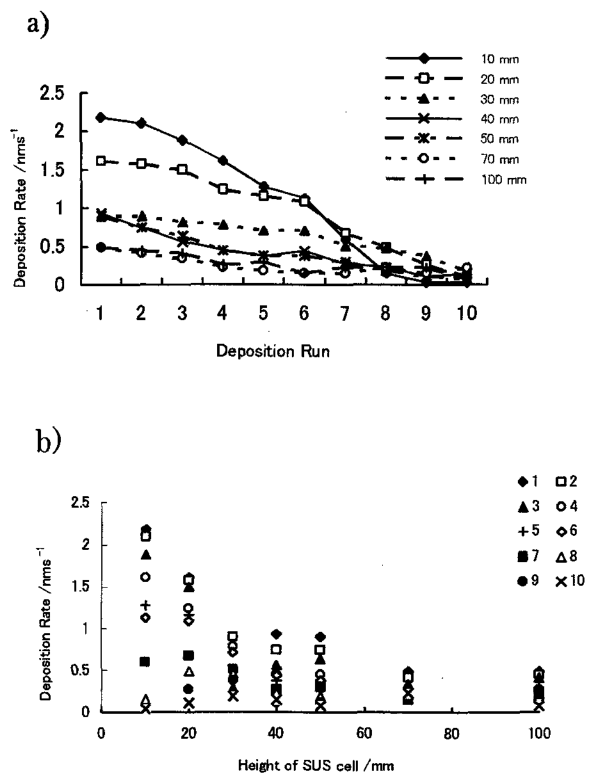


Fig. 1 Schematic of a SUS cell. The stainless steel (SUS) cell with a hole is set in the bottom of the crucible.

3. Results and Discussion

Figure 2(a) shows the dependence of deposition rate on the deposition run with SUS cells which have different height. The height of SUS cell was varied from 10 to 100 mm. They show several curves which could be identified each with a different symbol. One curve involves 10 data of consecutive deposition runs. In the case with a height more than 20 mm, the deposition rate is still stable after several deposition runs. These SUS cells work very well. In the case of 10 mm, the deposition rate is too high to get a hausmannite structure until sixth deposition run.

Figure 2(b) shows the dependence of deposition rate on the height of SUS cell. In the case of first run (run 1), the deposition rate was drastically decreased with increasing the height of SUS cell from 10 to 30 mm. It means that the deposition rate depends on the height of SUS cell. After run 2, the oxidation of Mn evaporant also effects the degradation of deposition rate.



Figures 2 (a) The dependence of deposition rate on the deposition run with SUS cells which have different height. The height of SUS cell was varied from 10 to 100 mm. (b) The dependence of deposition rate on the height of SUS cell.

Figure 3(a) shows a XRD pattern of a film prepared with SUS cell height of 20 mm. This film has Mn_3O_4-rich structure which is so called a Hausmannite. The preferred orientation is (103).

Figure 3(b) shows the variation of XRD peak strength with increasing deposition run. The parameter is the height of SUS cell. Large (103) peaks were obtained in the case of SUS cell height of 20 and 30 mm. The Fig. 2(a) shows that the deposition rate between 1.0 to 1.5 nm/s results in the preparation of (103) oriented films.

Figure 4 shows the variation of substrate temperature (T_{sub}) on the height of SUS cell. Mn_3O_4 films could be prepared in the T_{sub} range between 633 to 683 K. The value of T_{sub} ranged from 703 to 740 K in the case of a Mo separator. [27] T_{sub} range in the case of SUS cell is about 60 K lower than that with a Mo separator.

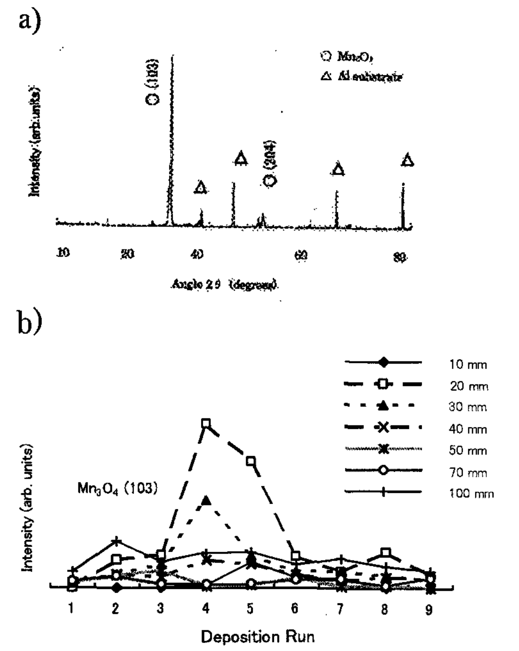


Fig. 3 (a) A XRD pattern of a film prepared with SUS cell height of 20 mm. (b) The variation of XRD peak strength with increasing deposition run. The parameter is the height of SUS cell.

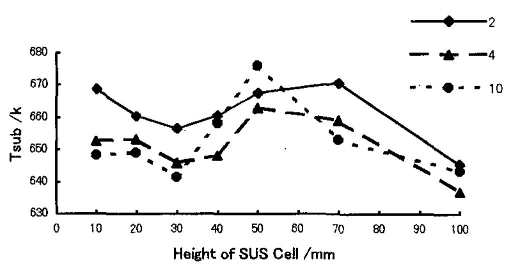


Fig. 4 The dependence of substrate temperature (T_{sub}) on the height of SUS cell.

The oxygen molecules react with the manganese atoms deposited on the substrate. There are three parameters that govern the film properties, for example, composition and crystallinity. They are O_2 flow rate, Mn deposition rate, and T_{sub}. O_2 flow rate was fixed at 5 sccm but T_{sub} was not controlled through this study. So the correlation between O_2 flow rate and Mn deposition rate is the most important parameter which determines the film composition. A desired composition, for example Mn_3O_4 in this work, could be obtained with a restricted range of deposition rate. So it is the most important issue to maintain the deposition rate at a restricted range.

The SUS cell successfully protects oxidation of Mn evaporant in the crucible. So the Mn deposition rate could be maintained at an restricted value. The reproducibility of film composition is improved by using the SUS cell. The deposition rate depends on the height of SUS cell. The optimum height of SUS cell is from 20 to 30 mm under the condition of T_{wall} and T_{source} of 1073 and 1143 K, respectively. These values are about 100 K lower than those obtained former cases. [31] This is due to quartz caps which cover the thermocouples. These caps could be attached to the crucible surface with the same geometry even after changing SUS cell. It contributes to improve the reproducibility of temperature measurement of T_{wall} and T_{source}.

The Mn_3O_4 structure could be prepared at the deposition rate under 1.2 nm/s. T_{sub} scatters between 633 to 683 K during these evaporation conditions. The SUS cell can help us to prepare Mn_3O_4 films under a low temperature range. It seems that this SUS cell shields latent heat from the Mn evaporant and undesirable temperature rise of T_{sub} is prevented.

One of the problems to be solved is how $LiMn_2O_4$ structure should be prepared from our Mn_3O_4 films. We hope we will report on that aspect later. We are convinced that the idea shown in the present work could be applicable to the preparation of other oxide films.

4. Conclusion

The feasibility of overcoming the oxidation of Mn metal in the crucible was examined. A SUS cell was introduced in the bottom of the Mn crucible, which successfully protected Mn evaporant from being oxidized during the reactive evaporation process. This SUS cell contributes to the successes of controlling the stoichiometry as well as of protecting the oxidation of Mn evaporant.

The Mn_3O_4 structure could be prepared under the conditions of Mn deposition rate below 1.2 nm/s and O_2 flow rate of 5 sccm. The optimum height of SUS cell is from 20 to 30 mm under the condition of T_{wall} and T_{source} of 1073 and 1143 K, respectively.

This method could improve the reproducibility of Mn oxide films for Li secondary batteries.

Ackowledgments

This work was supported in part by Shizuoka Research Institute.

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(Received December 20, 2002; Accepted January 31, 2003)