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Review Paper

Research on Reactively Evaporated Mn Oxide Films

Masaaki Isai
Department of Electrical and Electronic Engineering, Shizuoka
University, 3-5-1 Johoku, Hamamatsu, Shizuoka, Japan 432-8561
Electronic mail: temisai@ipc.shizuoka.ac.jp

Manganese oxide films for lithium secondary batteries have been prepared using a reactive evaporation method. The metallic Mn in the crucible suffers oxidation since it is evaporated in the oxygen atmosphere. So the deposition rate is deteriorated with increasing deposition run. This paper shows a technique which keeps off the Mn evaporant from oxygen atmosphere during the reactive evaporation process. Three types of separators have been developed through our studies: a Mo separator, a stainless steel cell (SUS cell), and a quartz ampoule. They have been installed in the bottom of the Mn crucible. The Mn_3O_4 films could be prepared with high reproducibility with these devices. The preparation procedure of manganes oxide films were reviewed.

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

1. Introduction

Revolution of energy sources for electric vehicles has been started by using fuel cells and Lithium (Li) secondary batteries. Its success depends on high rate discharge properties of secondary batteries. These devices require in energy density higher than 100 Wh/kg and a power density higher than 40 W/kg.[1] There are a lot of potential candidate materials for the 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.

Defect spinels are appropriate materials for the batteries of electric vehicles and scooters. Structural characteristics and theoretical capacities of defect spinels have been investigated.[3,4] 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 ranges between 148 and 213 mAh/g.

Almost all the oxide powders for positive electrodes have been prepared by sintering methods.[3-13] These powders are mixed with binders and highly conductive materials like carbon black to apply the metal electrode. This process is complex and results in 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 many deposition methods.[14-33] Mn_3O_4 films with spinel structure have been successfully prepared using a reactive evaporation method in our early work.[26-33] They are so called Hausmannite. The Li- Mn- O phase diagrams[3,4] show that defect spinels could be prepared by the reduction between Li and Mn_3O_4 or λ-MnO_2.[5,6]

The reactive evaporation brings about the oxidation of metallic Mn in the crucible (Mn evaporant) in an oxygen (O_2) atmosphere. The deposition rate is decreased run by run because of the growing thickness of oxidation layer which covers the metallic Mn. Three methods which overcome the oxidation of Mn evaporant have been invented, for example, a Mo (molybdenum) separator[26-30], a stainless steel (SUS) cell[32] and a quartz ampoule.[32] The purpose of the present work is to review the trajectory of developed three devices by which the oxidation of Mn evaporant is successfully prevented during the evaporation process.

2. Experiment

Mn oxide films were prepared on glass slide substrates by a reactive evaporation method as shown in Fig. 1.[23] A Mo sheet was used as a source heater.

Figure 2 shows the source current dependence of the vacuum pressure using the O_2- flow rate as a parameter.[23] This data suggest an oxygen gettering effect of manganese. The mechanism of reactive evaporation could be successfully explained by this gettring effect. It is shown that manganese oxide films could be prepared on the substrate through this reactive evaporation process.

A new deposition technique was introduced. It is Hotwall epitaxy. Hereafter Mn oxide films have been prepared on stainless steel substrates. Deposition apparatus is shown in Fig. 3.[24] Metallic Mn was evaporated in an oxygen atmosphere. The oxygen flow rate was controlled by a mass flow controller. The O_2-flow rate was varied from 5 to 20 standard cubic centimeter per minute (sccm). The wall (T_{wall}) and the source (T_{source}) temperatures were varied from 800 to 960 ℃. The stainless steel crucible was heated by an electric resistance wire.

A Mo separator[26-30], SUS cell[31,32] and quartz ampoule[33] were set in the bottom of the crucible, which contained Mn evaporant. They work as a separator which keep Mn evaporant off the oxygen atoms. They have small holes on top as shown in Fig. 4 (a),(b) and (c). The diameter of the hole is 6mm Φ.

The substrate temperature (T_{sub}) was not controlled during the deposition process.

In order to obtain crystallographic data, X- ray diffraction (XRD) measurements were performed with a RIGAKU Rotaflex 12 kW with a CN2173D6 goniometer. The film thickness was measured by the gravimetric method.

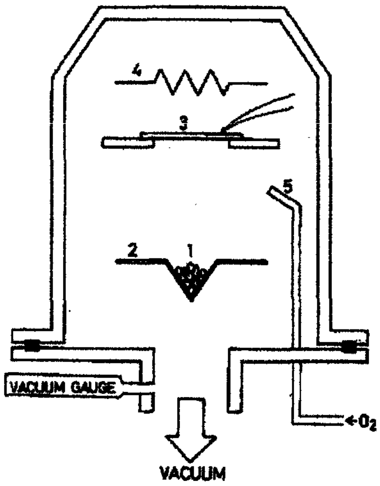


Fig. 1 Schematic of the apparatus that was used to investigate O_2 gettering effect of manganese. 1. Mn, 2. Mo crucible, 3. substrate, 4. substrate heater.

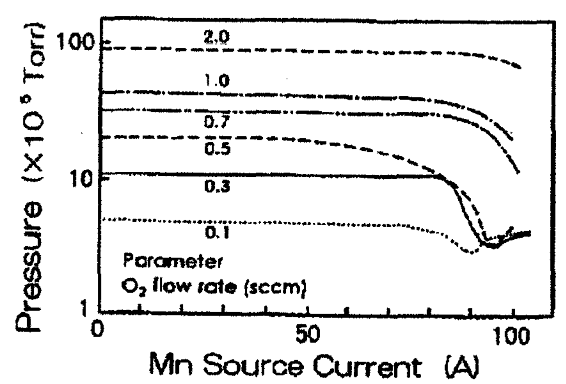


Fig. 2 Source current dependence of the vacuum pressure with oxygen flow rate as a parameter.

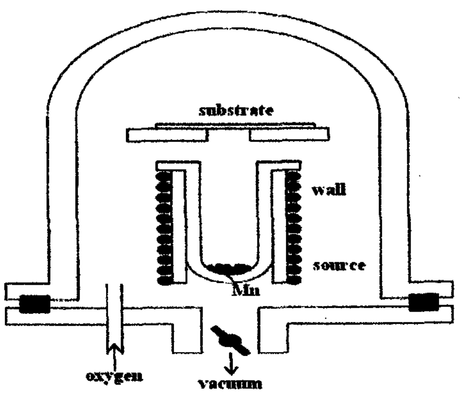


Fig. 3 Schematic of the apparatus. A stainless steel crucible was used. The wall (T_{wall}) and source (T_{source}) temperatures were controlled independently.

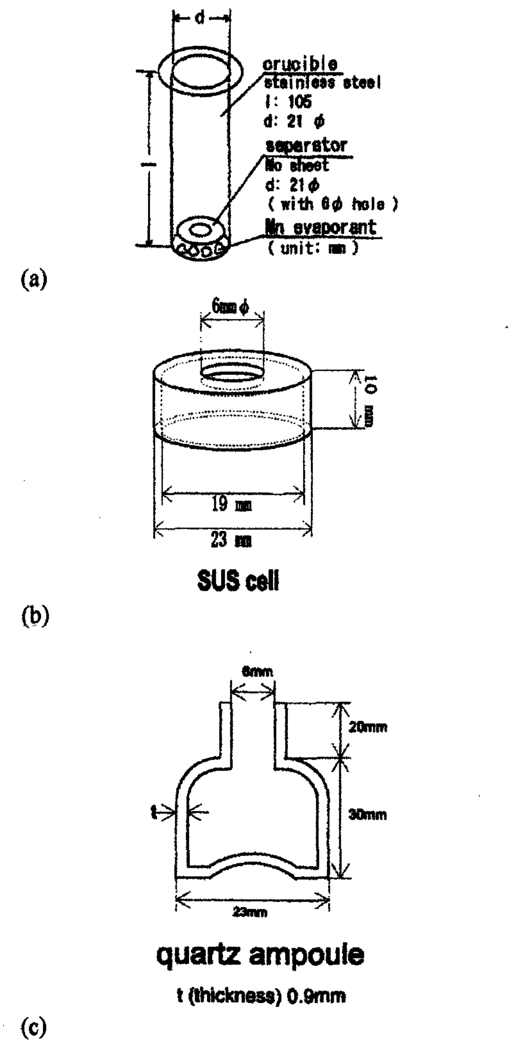


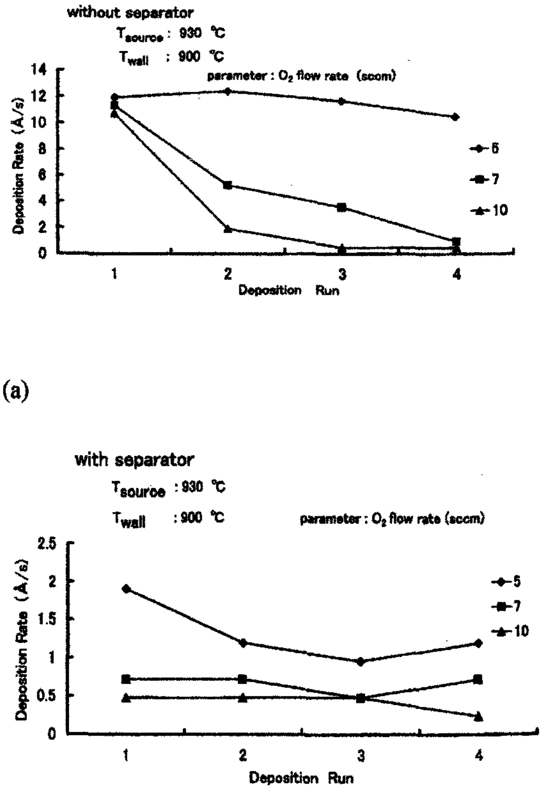
Fig. 4 (a) Mo separator, (b) SUS cell and (c) quartz ampoule. These three devices were installed in the crucible as shown in Fig. 3. The SUS cell has a composition of 18 Cr- 8 Ni (SUS304).

3. Results and Discussion

Figure 5(a) shows the variation of deposition rate in each deposition run in the absence of the Mo separator.[27] It was shown that the deposition rate was drastically decreased with increasing deposition run especially at O_2- flow rates of 7 and 10 sccm.

Figure 5(b) shows the variation of deposition rate for the deposition run using the Mo separator.[27] The deposition rate was gradually decreased with increasing depositon run for all O_2- flow rates. In the case with a Mo separator, the deposition rate is still stable after several deposition run even in the case of large O_2- flow rate condition. It means that the oxidation of Mn evaporant could be successfully prevented by this Mo separator.

Figure 6 shows the dependence of deposition rates for the deposition run with the three devices.[33] The three curves are representative of three types of device. In the cases of the Mo separator and SUS cell, the average deposition rates in each run was used in this figure. The degradation of depositon rate with increasing deposition run is the smallest in the case of quartz ampoule.[33] The quartz ampoule contributes to the success of controlling the stoichiometry and of protecting the oxidation of Mn evaporant.



(a)

(b)

Fig. 5 The dependence of deposition rate on the deposition run (a) without and (b) with Mo separator, respectively.

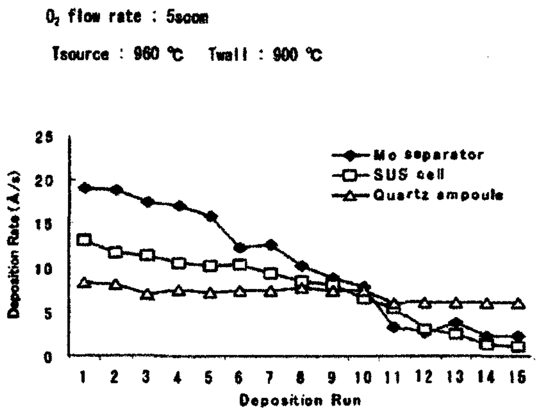


Fig. 6 Dependence of deposition rate on the deposition run with a Mo separator, SUS cell and quartz ampoule.

In the case of Mo separator, many studies have been proceeded as follows. The dependence of the O_2-flow rate on the film properties was investigated. Mn_3O_4 films could be prepared in the O_2- flow rate ranges of 4 to 10 and 17 to 20 sccm.[24]

The XPS (X-ray Photoelectron Spectroscopy) analysis was proceeded for the Mn oxide films.[27,28,30] It was found that the atomic ratio of O to Mn is 1.33,[27] that is, film consists of Mn_3O_4.

A stainless sheet of 0.1 mm thickness was installed parallel to the crucible axis. The composition of films deposited on the sheet was evaluated by the XPS analysis. In the crucible, the atomic rate of O to Mn varies from 1.25 to 1.51 except for the bottom area. These data suggested that they are the mixture of MnO and Mn_3O_4 structure.[28] It means that the reaction between oxygen and Mn evaporant could be successfully decreased at the bottom of the crucible.

The effect of the distance between the crucible top and the substrate on the film properties was investigated. The Mn_3O_4 films can be successfully prepared under a distance of 30 mm.[29]

In the case of SUS cell, the dependence of neck length on the film properties was investigated. The neck of the SUS cell is shown in Fig. 4(b). The optimum necklength was from 20 to 30 mm for T_{wall} of 800 ℃ and T_{source} of 870 ℃.[32]

The quartz ampoule successfully protects oxidation of Mn evaporant in the crucible.[33] The Mn deposition rate could accordingly be maintained at appropriate values. The reproducibility of film composition is improved by using the quartz ampoule. It was found that the quartz ampoule was superioir to the Mo separater and SUS cell as shown in Fig. 6. This ability depends on the shape of devices and not on the materials used.

There are three parameters that govern the composition and crystallinity of the films. They are O_2-flow rate, Mn deposition rate, and T_{sub}. The O_2-flow rate was varied from 5 to 20 sccm and T_{sub} was not controlled through these studies. For the reason the film properties depend on the combination of O_2- flow rate and the Mn-deposition rate. If the O_2- flow rate is fixed at 5 sccm, a desired composition, for example Mn_3O_4 in this work, could be obtained with a restricted range of the deposition rate, for example, below around 12 Å/s.[31] It is crucial to maintain the deposition rate in this restricted range to prepare the Mn_3O_4 films.

One of the problems to be solved is how the $LiMn_2O_4$ 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

A Mo separator, SUS cell, and quartz ampoule were installed in the bottom of Mn crucible, which successfully protected Mn evaporant being oxidized during the reactive evaporation process. The properties of these three devices which overcome the oxidation of metallic Mn in the crucible were reviewed.

It was found that the quartz ampoule had superior performance of controlling the stoichiometry and of protecting the oxidation of Mn evaporant.

The Mn_3O_4 structure could be prepared at a Mn-deposition rate below around 12 Å/s and a O_2- flow rate of 5 sccm.

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

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