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Reactively evaporated manganese spinel films for Li secondary batteries

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Abstract Manganese oxide with spinel structure is one of the candidate materials for positive electrode in the Li secondary batteries. Mn_3O_4 films were prepared by the reactive evaporation process. There are two types of crystal structure in the Mn_3O_4 films. One is so called Hausmannite. The other is so called Manganese spinel and could be shown by the chemical formula of $MnO.Mn_2O_3$. These films could be obtained under the restricted deposition condition. The dependence of oxygen flow rate on the film properties was investigated in the present work.

Key words (Li secondary batteries, Manganese oxide film, Spinel structure, Reactive evaporation)

1. Introduction

We can get electric vehicles in these days. The motivation of using the electric vehicles is come from the oil crisis in the middle of 70's and the environmental problems evolved recently. The batteries for them should have a high energy and power density for daily use. For example, we would like to drive more than 200 kilometers for one charge.

There are a lot of potential candidate materials for secondary batteries.[1] A combination of manganese (Mn) oxide and lithium (Li) as the positive and negative electrodes ,respectively, was focussed in this study. Mn oxides are one of the best materials for the positive electrode in the Li secondary batteries.[2] Mn is inexpensive because it is found in abundance on earth. The operating voltage of 3-4V is obtained with this material.

The positive electrode is composed of an oxide film pasted on the metal electrode. Almost all the oxide powders for positive electrodes are prepared by the sintering method.[3-20]

Then they are mixed with some binders and applied to the metal electrode. This application method makes the electric contact insufficient. So some ingredients must be added to improve the electric conductivity. This problem could be overcome by using the vacuum deposition process proposed in this paper.

Lithium atoms are very active in air and in water vapor. Li secondary batteries should be fabricated in high quality vacuum during the fabrication process. From the reason above mentioned, Mn oxide films which involves Li atoms should be carefully prepared in vacuum. One of the best ways is the all solid state batteries which are built up in vacuum at one batch.

Some oxide films were prepared by so called reactive evaporation method.[21-23] No paper has mentioned the Mn oxide films prepared by the reactive evaporation method. The dependence of oxygen (O_2) flow rate on film quality was investigated.

The purpose of the present work is to investigate the crystallinity of the films with varying the O_2 flow rate.

2. EXPERIMENT

Manganese oxide films were prepared on a stainless steal substrate by Hotwall epitaxy. Deposition apparatus is shown in Fig. 1. Mn was evaporated in the oxygen atmosphere. The O_2 flow rate up to 10 sccm was controlled by a mass flow controller. The O_2 nominal flow rate above 10 sccm was obtained by partly closing the main valve of the evaporator with maintaining the O_2 flow rate at 10 sccm. The vacuum pressure reaches at an equilibrium pressure under the O_2 introduction and evacuation of the vacuum chamber.

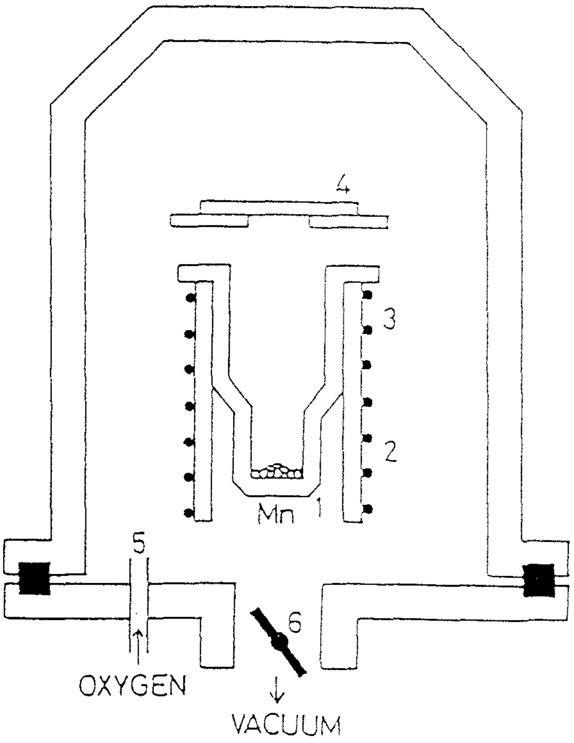

FIG. 1. Schematic of the apparatus. 1: Quartz crucible. 2: Hotwall heater for Mn source material. Quartz tube wound with W heater wire. 3: Hotwall heater for wall area. 4: Stainless steel substrate. 5: O_2 inlet. 6: Main valve to control the O_2 atmosphere.

This value means the attainable vapor pressure. If the main valve is slightly closed under the O_2 pressure of 10 sccm, this attainable vacuum pressure in the chamber could be increased as shown in Fig. 2. This method brings the same effect as if the O_2 flow rate is increased. These O_2 flow rates were estimated by detecting the vacuum pressure during the deposition process as shown in Fig. 2. These estimated O_2 flow rates were used hereafter. A quartz crucible was resistively heated. The substrate temperature was not controlled in the present study. The substrate temperature rises through the deposition process because of getting heat from the wall heater and Mn source material. The substrate temperature was measured at the rear side of the substrate surface.

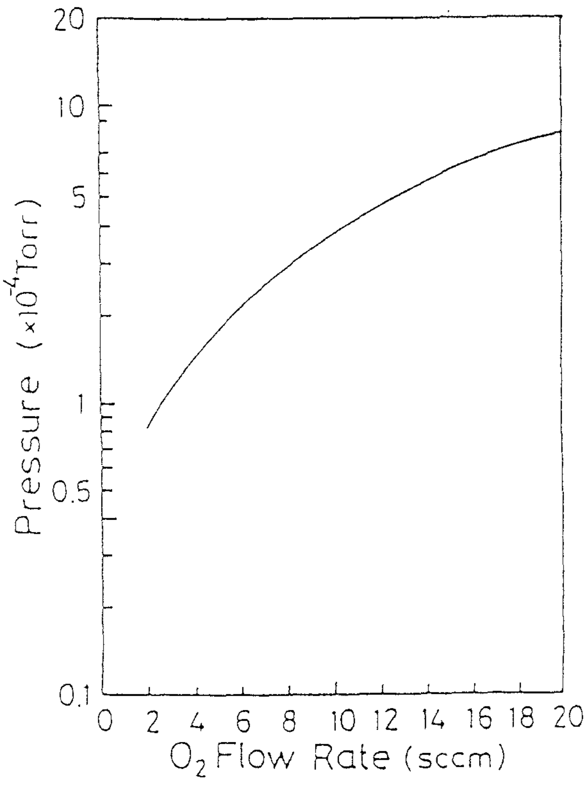

FIG. 2. The dependence of attainable vacuum pressure on the O_2 flow rate. The O_2 flow rate was estimated by this figure. The estimated O_2 flow rates were used hereafter.

In order to obtain crystallographic information, some films were analyzed by X-ray photo electron spectroscopy (XPS) carried out in a KRATOS XSAM-800 pci, using a 15-keV Mg Kα radiation. A spot size on the sample for collecting photoelectrons was ellipsoid of 4 × 8mm. The sputtering gun was set to 3 kV Ar^+ ions. The X-ray Diffraction (XRD) measurements were also carried out by a RIGAKU Rotaflex 12kW with CN2173-D6 goniometer. A film thickness was measured by the optical method (interference fringes). The micro-interferometer (Olympus) was used.

3. RESULTS AND DISCUSSION

Figure 3 shows the XRD patterns of the films prepared with varying the O_2 flow rate from 2 to 19.4 sccm. It was revealed that the manganese oxide films with spinel structure could be obtained at the restricted O_2 flow rate area. The (211) oriented Mn_3O_4 (Hausmannite) films were prepared at the O_2 flow rate of 10.5 sccm. The (311) oriented $MnO.Mn_2O_3$ (Manganese spinel) films were prepared at the O_2 flow rate of 14.8 sccm. The (200) oriented MnO films were prepared at the O_2 flow rate area under 10.5 and over 17 sccm.

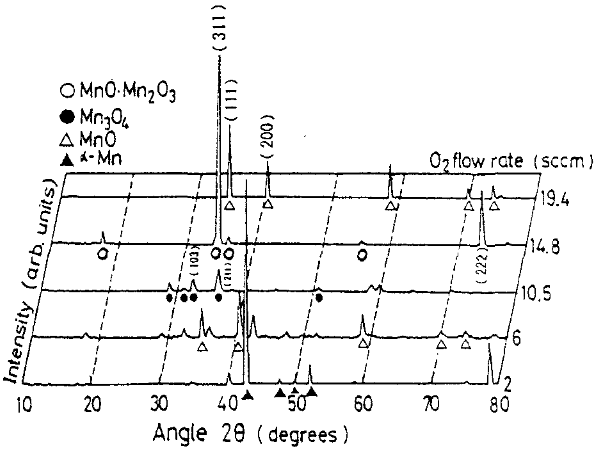

FIG. 3. The XRD patterns of the films prepared with varying the O_2 flow rate from 2 to 19.4 sccm. Manganese oxide films with spinel structure were prepared in the restricted deposition condition.

The α-Mn films were prepared at the O_2 flow rate of 2 sccm. It is the first time in the world to prepare these manganese oxide films with spinel structure by the reactive evaporation method. It is also amazing that nearly single phase $MnO.Mn_2O_3$ films were prepared at the restricted oxygen flow rate area.

The dependence of relative heights of XRD peaks of the films on the O_2 flow rate is shown in Fig.4. The relative heights of XRD peaks, (200)/(111) and (211)/(103), were investigated for MnO and Mn_3O_4 films ,respectively.

It was found that the relative intensity of (211)/(103) for Mn_3O_4 films was increased gradually as increasing the O_2 flow rate up to 10 sccm. The (211) peak is the preferred orientation of the Mn_3O_4 films. This peak height is increased as increasing the constituent and crystallinity of Mn_3O_4 structure in the film. The O/Mn ratio is large in the Mn_3O_4 film than the MnO film.

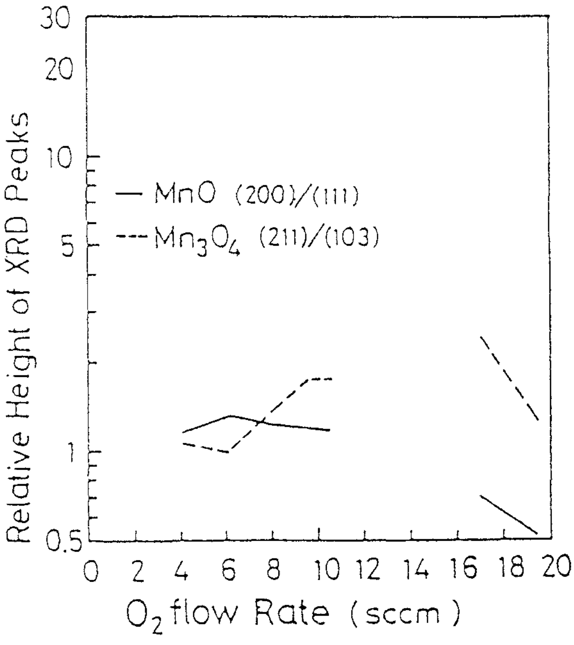

FIG. 4. The dependence of relative heights of XRD peaks of the films on the O_2 flow rate. The relative heights of XRD peaks, (200)/(111) and (211)/(103), are investigated for MnO and Mn_3O_4 films, respectively.

The O_2 content in the film is increased as increasing the constituent and crystallinity of Mn_3O_4 in the MnO matrix. This explains well the increase of O_2 content in this area. But it was decreased at the O_2 flow rate above 16.5 sccm. In the case of the MnO films ,the relative intensity of (200)/(111) was stable at the O_2 flow rate up to 10 sccm. But, it was drastically changed at the O_2 flow rate larger than 16.5 sccm. The (200) peak is the preferred orientation in the MnO films. It is seemed that the crystallinity of MnO films is deteriorated in the large O_2 flow area.

The XPS analysis was carried out for the Mn_3O_4 and $MnO.Mn_2O_3$. The stoichiometry of these oxides was investigated. The atomic concentration was measured after sputtering the surface of the film for 40min.

Figure 5 shows an XPS spectrum of the Mn_3O_4 film prepared at O_2 flow rate of 10.5 sccm. This data shows that this film is constituted with Mn and O_2 atoms. This means that manganese oxide film could be prepared by our reactive evaporation method. The C and Cl peaks in the figure seem to be due to contamination in the deposition chamber. In order to investigate the stoichiometry of the Mn_3O_4 and $MnO.Mn_2O_3$ films, the sensitivity coefficients of 0.669 for O 1s and 3.197 for Mn 2p were used to estimate the chemical composition.

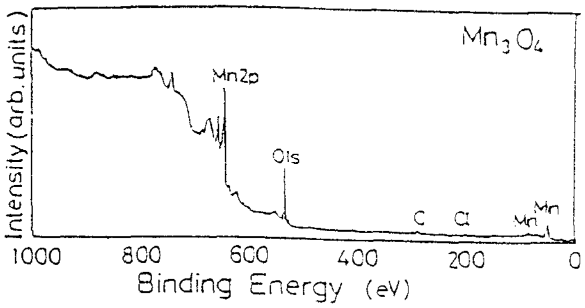

FIG. 5. An XPS spectrum of the Mn_3O_4 film preferred at O_2 flow rate of 10.5 sccm..

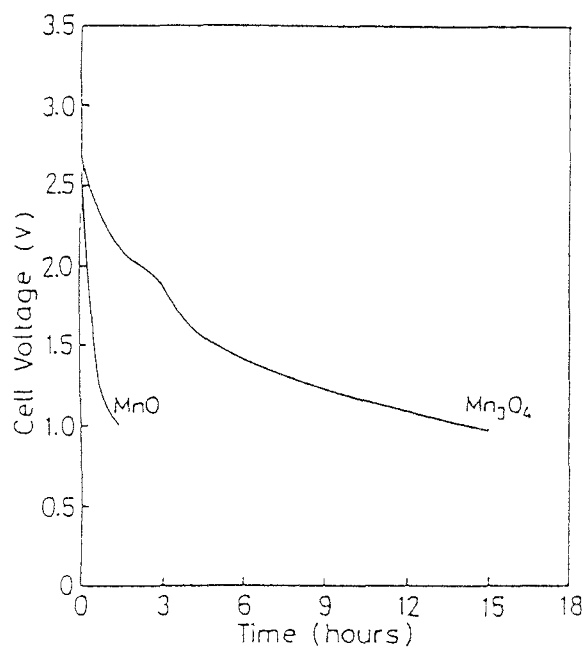

FIG. 6. The discharge characteristics of the two test cells. The MnO and Mn_3O_4 films ,preferred at the O_2 flow rate of 19.4 and 14.8, were used as the positive electrode in each cell ,respectively.

It was found that the Mn_3O_4 and $MnO.Mn_2O_3$ films have the atomic ratio (O/Mn) of 1.33 and 1.2,respectively. The quantitative measurement was carried out with using a standard sample. It means that the data of XRD analysis coincide with that of XPS analysis.

Fig. 6 shows the discharge characteristics of the two test cells. The MnO and Mn_3O_4 films, prepared at the O_2 flow rate of 19.4 and 14.8, were used as the positive electrode in each cell, respectively. It was found that the cell using Mn_3O_4 films has superior discharge characteristics than that of using the MnO films.

Manganese oxide films of spinel structure were prepared in the restricted O_2 flow rate area as shown in Fig. 3. Our goal is to prepare the λ-MnO_2 films [4-8] with spinel structure. One of the problems to be solved is to increase the atomic ratio (O/Mn) in the manganese oxide films. The oxygen molecules are reacted with the evaporating manganese atoms on the substrate. It is convinced that the higher substrate temperature can activate more oxygen atoms which react with evaporating Mn atoms. Further studies are now in progress.

4. CONCLUSION

Manganese oxide films of spinel structure were successfully prepared by using reactive evaporation process. The crystal structure of these films was identified by the XRD and XPS examinations. It was found that the data of XRD analysis coincide with that of XPS analysis.

Mn_3O_4 (Hausmannite) and $MnO.Mn_2O_3$ (Manganese spinel) films were prepared in the present study. These films could be obtained at the restricted deposition condition. The crystallinity of these films was increased as increasing the O_2 flow rate up to 10 sccm.

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