Improvement of battery properties of LiMn_2O_4 thin films

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Abstract The LiMn_2O_4 thin films for Li secondary batteries have been prepared by a RF magnetron sputtering method. In this research, we have prepared LiMn_2O_4 films under various preparation conditions. The charge-discharge characteristics of these films were evaluated. Several films showed good charge-discharge curve and good voltage, but charge-discharge efficiency was not so good. It was shown that the capacity of a film was approximately half of the theoretical value.

Keyword LiMn_2O_4 thin film, RF magnetron sputtering, Li secondary batteries

1. INTRODUCTION

Recently, an attention has been paid to the cars that run by using clean energy such as electric cells, fuel cells, and hybrid-power cells. They are intended to decrease the exhaust gases. However, there are a lot of problems of these cars. For example, the distance that they can run for one charge is short. It takes long time to charge the batteries. The place of charging batteries is few, etc.

The Li secondary battery has a high energetic density and a high voltage that exceeds the electrolysis voltage of water. So non-water electrolyte should be used. These contribute to the miniaturization of the battery size.

For a lithium secondary battery, the manganese based materials were paid attention for cathode.^[1-30] They could have high voltage, for example 4 to 5V, and high theoretical capacity of 148 mAh/g. The LiMn_2O_4 films were prepared by a RF magnetron sputtering method and the battery properties were evaluated.^[26-30]

As a result, we confirmed that films worked as an active material, but the film capacity was extremely small. The reason is as follows. The crystalline size of the films was small. The composition of films deviated from stoichiometry of LiMn_2O_4 . The Mn deficiency was observed in the former study.^[29]

In this research, the manganese dioxide (MnO_2) was added to the target material of LiMn_2O_4 to compensate Mn deficiency.^[29] The crystalline and battery properties were evaluated through this study.

2. EXPERIMENT

Figure 1 shows a RF magnetron sputtering apparatus. As this apparatus has three targets, three materials could be sputter deposited. The Ar and O_2 gases are introduced through flow meters. The total flow rate was fixed at 4 sccm (standard cubic centimeter per minute) through this study. The Ar: O_2 flow ratio was varied from 4:0 to 1:3. The Ar ions collide on the surface of the LiMn_2O_4 target by applying a RF power of 13.56 MHz and the films are deposited. The distance between substrate and target is 40 mm and the shutter is installed between them. The distance between shutter and target is 25 mm. The doughnut-type plate was put on the shutter through this work.^[25, 26] This plate has a hole of 30 mm ϕ . The potential of this plate is grounded and equal to the shutter potential.

Table 1 shows the deposition condition. The Al substrates with 0.2 mm in thickness and size of 40×40 mm were used. The Ar and O_2 gas-flow rate and the sputtering pressure were controlled. The RF power, sputtering time, sputtering pressure, and sputtering atmosphere (the Ar to O_2 gas ratio) were varied as a parameter. The crystal properties of the prepared films were evaluated by X-ray diffraction (XRD). The accelerating voltage and current were 30keV and 16mA, respectively.

The LiMn_2O_4 films were prepared with the deposition condition as shown in Table 1. The XRD pattern of films was

compared with that of the LiMn_2O_4 film powder.

Fig. 1 Schematic of a RF magnetron sputtering apparatus

Table 1 A typical film preparation condition

type	value	unit
sputtering target	LiMn_2O_4	
substrate	aluminum	
RF power	30, 90	[W]
Ar/ O_2 flow ratio	4:0, 3:1, 2:2, 1:3	
sputtering pressure	5	[Pa]
aperture of doughnut-type plate	30	[mm]

We performed an experiment to make the film-composition close to LiMn_2O_4 by using a mixture of LiMn_2O_4 and MnO_2 for a target. Table 2 shows the mixture ratio of LiMn_2O_4 and MnO_2 and the deposition condition.

Table 2 Preparation condition of films

Type	value	unit
sputtering target	$\text{LiMn}_2\text{O}_4 + x\text{MnO}_2$ ($x=1/4, 1/2, 3/4, 1$)	
substrate	aluminum	
RF power	150	[W]
sputtering time	2	[hour]
Ar/ O_2 flow ratio	4:0, 3:1	
sputtering pressure	5	[Pa]
aperture of doughnut-type plate	30	[mm]

Thin films were prepared with varying the target material and annealing condition. Table 3 shows preparation condition and annealing condition of each films.

Table 3 Preparation condition and annealing conditions of films

sample number	1	2	3	4
RF power [W]	150			
sputtering pressure [Pa]	5			
Ar flow rate [sccm]	3			
O ₂ flow rate [sccm]	1			
sputtering time [h]	3			
target material	LiMn_2O_4 +1/4 MnO_2		LiMn_2O_4	
annealing temperature [°C]	800		800	
annealing time [h]	10		10	

The performance of batteries was examined as follows. The positive electrode is LiMn_2O_4 films. The negative electrode is Li metal-foil. The battery cells were assembled in an Ar-filled glove box. The electrolytic solution is the 1Mol/L LiPF₆ in a mixture (1:1 in volume) of ethylene carbonate (EC)/diethylene carbonate (DEC). The cycling test of the cells was carried out at a current of 1 or 10 μA between 3 and 4.3V.

3. RESULTS OF THE EXPERIMENT AND DISCUSSION

3.1. The thin film evaluation by changing the preparation condition

Figure 2 shows the dependence of XRD intensity on the RF power. The sputtering pressure was fixed at 5 Pa. The Ar flow rate was 3 sccm. The O₂ flow rate was 1 sccm. The RF power was 30 and 90 W, and each deposition time was 9 and 3 hours, respectively. It was found from the former study that the film thickness increases in proportion to the RF power.^[29] The peak at around 19 degrees cannot be recognized at RF power of 30 W. This peak was recognized in the case of RF power of 90 W. This shows that the crystallinity of the film prepared at RF power of 90 W is superior to that prepared at 30 W.

Fig. 2 Comparison of XRD data (parameter : RF power)

Figure 3 shows the dependence of XRD intensity on Ar:O₂ flow ratio. The sputtering pressure was fixed at 5 Pa. The Ar to O₂ flow ratio varied from 1:3, 2:2, 3:1 and 4:0 as a parameter. It is thought that a composition change is hard to occur when the Ar:O₂ flow rate is 3:1.

Fig. 3 Comparison of XRD data (parameter : Ar:O₂ flow ratio)

3.2. Mixture of MnO_2

Figure 4 shows the XRD data with varying the ratio of LiMn_2O_4 to MnO_2 . The Ar:O₂ flow ratio was fixed at 3:1.

As a result of XRD measurement, it is thought that the XRD pattern and film composition are similar to the LiMn_2O_4 under the deposition condition of Ar:O₂ flow ratio of 3:1 with using LiMn_2O_4 +1/4 MnO_2 powder.

Fig. 4 Comparison of XRD data at Ar:O₂ = 3:1
(parameter : LiMn_2O_4 : MnO_2 rate in sputtering target)

3.3. Measurement of charge-discharge characteristics

Figures 5 and 6 show the representative charge-discharge characteristics of the test cells shown in Table 3. A Li metal-foil is used as a negative electrode. An electrolyte is the LiPF₆ EC+DEC(1:1 Vol.) solution of 1Mol/L as described in the previous section.

The charge-discharge characteristics were measured between 3 to 4.3V at a constant current. At first, the test cell was charged under the constant current (CC) mode. After starting charging process, the cell voltage gradually increases and saturates at 4.3V. After this point, the cell is still charged in a constant voltage (CV) mode. After the voltage plateau is created, the charging process is stopped. Then, the discharge process starts.

The discharge process starts from the cell voltage of 4.3V. The constant current flows through the cell. The cell voltage gradually decreases during the discharge process. The discharge process is stopped when the cell voltage decreases to 3.0V.

The charge capacity is defined as the value when the cell voltage reaches to 4.3V. The discharge capacity is also defined as the value when the cell voltage decreases to 3.0V.

The figures on the curves show the charge and discharge cycle-numbers. For example, 1, 2 and 3 show the first, the second and the third charging or discharging processes, respectively.

Sample 2

Figure 5 shows the result of charge-discharge characteristics of sample 2. The constant current of $10\ \mu\text{A}$ was used in the charge and discharge process. It was shown that a typical charge-discharge curve was observed at the third cycle. The capacity was approximately 55 mAh/g. The theoretical capacity of LiMn_2O_4 was 148 mAh/g and the effective capacity was approximately 110 mAh/g. The capacity of sample 2 was half of the effective capacity.

This figure shows that the charge and discharge capacities are 100 and 55 mAh/g, respectively. The charge-discharge efficiency is not so good as the difference between charge and discharge capacities was large. However, the shape of charge-discharge curves was very good.

Fig. 5 Measurement of charge-discharge characteristic (sample 2)

Sample 4

Figure 6 shows the result of charge-discharge characteristics of sample 4. In this case, the constant current of $1\ \mu\text{A}$ was used in the charge and discharge process. Unlike sample 2, the first discharge curve is not so good. An ambiguous reaction between the positive, negative electrodes and electrolyte solution occurs during this first charging process. A stabilized charging curve was observed after the second charging process. The shape of discharge curves was very good from the first discharge process.

Fig. 6 Measurement of charge-discharge characteristic (sample 4)

It was shown that a typical charge-discharge curve was observed after the second cycle. This figure shows that the charge and discharge capacities are 75 and 40 mAh/g, respectively.

Unfortunately, in this sample, it was not possible to discharge at the current value at $10\ \mu\text{A}$.

As a result of measurement of charge-discharge characteristic, only un-annealed samples of 2 and 4 could be measured. The capacities of samples of 2 and 4 were approximately 55 and 40 mAh/g, respectively. These values are about a half of the effective capacity of 110 mAh/g. The performance of the batteries has been improving by optimizing the deposition condition. For example, the cell capacity of prepared films in the former studies was 10 mAh/g. [27-28]

It was reported that the charge-discharge characteristics was improved by annealing in other papers. [17] However, the charge-discharge characteristics of the annealed samples could not be measured in this research. The investigation of annealing conditions is now under study.

4. Conclusion

The LiMn_2O_4 films were successfully prepared by using a RF magnetron sputtering method. The target materials were contrived to improve the stoichiometry of the LiMn_2O_4 films. It was found that an optimum composition of target material was $\text{LiMn}_2\text{O}_4 + 1/4\text{MnO}_2$.

It was also found that an optimum $\text{Ar}:\text{O}_2$ flow ratio was 3:1. The battery capacity of 55 mAh/g was observed.

5. Acknowledgment

We wish sincerely express our gratitude to everyone in Tomita's laboratory for measuring the battery properties and giving fruitful advices.

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(Received December 18, 2013; Accepted September 9, 2014)