Electrochemical Properties and Estimation on Active Material $LiMnO_2$ Synthesis for Secondary

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This paper is contents on the orthorhombic crystalline calcined by the solid phase method with $LiMnO_2$ thin film structured as the result which an average pore diameter of power was 132.3Å in porosity analysis. Voltage ranges are able to get the properties of charge and discharge for experimental results of $LiMnO_2$ thin film were 2.2V 4.3V. The current density and scan speed were 0.1mA/cm^2 and 0.2mV/sec respectively. Properties of the charge and discharge are obtained by optimum experiment condition parameters. Li dense ratio of the $LiMnO_2$ thin film that discharged capacities were 87mAh/g have been 96.9[ppm] at 670.784[nm] wavelength. The dense ratio of Mn analyzed to 837[ppm] at 257.610[nm] wavelength. It can be estimated the quality of the $LiMnO_2$ thin film as that the wrong $LiMnO_2$ thin film pulled up from cell of electrolyte and became dry it at 800℃. The results of SEM and XRD were the same as that of original researchers

Keywords : Lithium Batteries, 925℃ Calcination

1. INTRODUCTION

An existing lithium secondary batteries of a cathode active material $LiNiO_2$ and $LiCoO_2$ is used with the layered structure of chemical compound. But they are difficult for the fabrication with having the high price and a nontoxicity for the human health and so on. Therefore $LiMnO_2$ is developed to improve the reason of these problem, but the properties of $LiMnO_2$ had a rapid capacity decrease and moreover short cycles life. For improving of these weak points, early these are proposed by Johnston in 1956, and an information of detail structure is known by Hoppe. Accordingly a study on the orthorhombic structure of $LiMnO_2$ in high capacity is researched recently very hard. In Japan the experiment of the synthesis and crystallization is prepared by the hydrothermal method at 925℃. Three voltages level theoretical capacitances of $LiMnO_2$ on this study had a more merit of double capacities than the four voltages level of $LiMn_2O_4$. The method of synthesis and crystallization of $LiMnO_2$ thin film to be taken by emulsion dry, hydrothermal, sol-gel and ion exchange etc are used. However, it is a aim to estimate a quality of thin film about the experimental values of powder and the values of electrochemical reaction to be got by the cell using 1M PC $LiClO_4$ of liquid electrolyte. With result, a cathode active material $LiMnO_2$ of lithium ion secondary batteries is synthesised and crystallized by a solid phase method in the first at 450℃ and secondary at 925℃. The average pore diameters of particles was the values of 132.3Å . Analytic density ratio of the metal property structured of the thin film are analyzed to 96.90 of Li [ppm] and 837[ppm] of Mn respectively. It was found by method to be able to estimate a wrong thin film

as that it pull up from the cell of liquid electrolyte ad became dry it at about 80℃. [1-3]

2. PREPARATION OF CATHODE ACTIVE MATERIAL $LiMnO_2$ THIN FILM

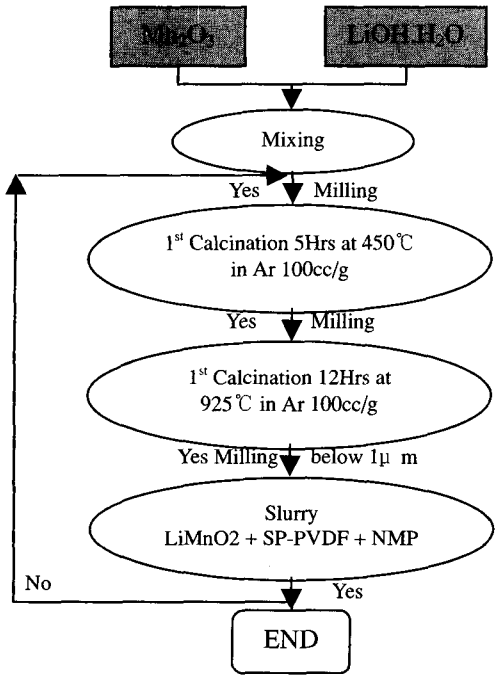

Fig. 1. Flow chart of synthesis and crystallization of $iMnO_2$.

2.1 Cathode material production and synthesis and crystalization of $LiMnO_2$

Shrinking word together of synthesis and crystallization of $LiMnO_2$ will be written a synthesis crystallization in this thesis. The preparation of $LiMnO_2$ with the layer and orthorhombic structure is shown by the flow chart of Fig. 1 The detailed treatment to be synthesised and crystallized is calcined at 450℃ and 925℃ with mixing a ratio of 1.1 : 1 of $LiOH.H_2O$ and precurse Mn_2O_3 as the following figuration[5].

2.2 Cathode thin film preparation and reference electrode

Preparation of cathode $LiMnO_2$ thin film is treated like a Fig. 2 The ratios of an active material $LiMnO_2$ of 75wt%, a conductive material of SP-270 20wt% and a combine material of PVDF 5wt% are mixed equally to melt at the NMP aqueous solution. The reversible reaction of intercalation and deintercalation between a cathode electrode and an anode electrode of reference was due to a theory of the Rocking Chair Battery by Armond. When the lithium foil used an anode of the half cell, some problems of dendrite is known by Herold in 1955. But it should be used the reference electrode for an experiment of electrochemical reaction of active material $LiMnO_2$[5-6].

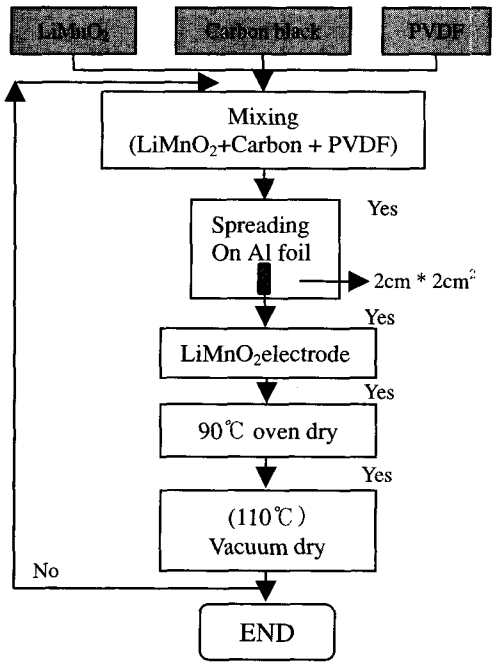

Fig. 2. Flow chart of cathode electrode preparation of $LiMnO_2$.

3. EXPERIMENTAL METHOD

3.1 Cyclic voltammogram and charge/discharge

An analysis of the reversibility of reaction of oxidation and reduction on the experimental result of the $LiMnO_2$ cell to be taken in PC 1M $LiClO_4$ of liquid electrolyte is obtained by using an WSC-3000 apparatus. The experimental system of the thin film of Fig. 3 are structured by a XRD/SEM, an amounts of charge/ discharge and the cyclic voltammogram of $LiMnO_2$/Li cell in the PC 1M $LiClO_4$ and the flow chart of particles analytic process on the measurement of the pore diagram. The ranges of the voltage were 2.2V~4.3V and the current density was 0.1mA/cm^2 and the scanning speed was 0.2mV/sec and the Open Circuit Voltage wrote the checked value after thirty minutes since connecting the electrodes of positive and negative. The parameters of condition files tables of charge /discharge and cyclic voltammogram are set at optimum condition. When the reversible reaction of intercalation and deintercalation between the cathode and reference electrode was due to a theory of the Rocking Chair Battery by Armond, some problems on the dendrite of lithium foil used to a half cell is proposed by Herold in 1955, but it should be used the reference electrode for an experiment of electrochemical reaction of the $LiMnO_2$.

3.2 SEM of $LiMnO_2$

SEM photograph of $LiMnO_2$ thin film is surveyed by a gap of 12.2mm between the sample and prove with 5KV of an accelerative voltage of FE-SEM. The $LiMnO_2$ thin film is surveyed by JSM-5400 of the other experimental apparatusis with setting parameters of 5 m, 10μ m scales with 20KV of the accelerative voltage.

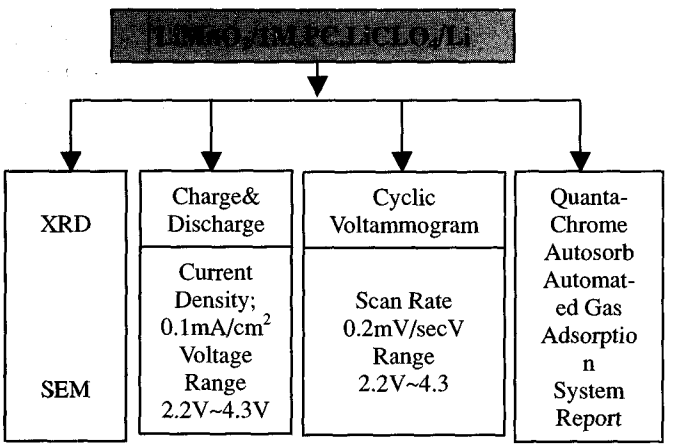

Fig. 3. Flow chart of test measurement of XRD/SEM, charge/discharge, cyclic voltammogram and pore size measurement.

3.3 ICP and pore diagram of $LiMnO_2$ thin film

The experiment of ICP(Atomic Emission Spectrometer) treated the dense ratios of lithium and manganese by melting as a ratio of solution of three versus one of the nitrogen and hydrochloride acid with using the remain materials after that $LiMnO_2$ powder are fired at 800℃. They are analysed by setting the parameters of the wavelengths 670, 784[nm] of the lithium material and the wavelengths 257, 610[nm] of the manganese material by using OPTIMA 4300DV. The experimental apparatus whose the pore diagram measurement is structured with a $LiMnO_2$ thin film by using the isotherm due to adsorption and desorption of the nitrogen in liquid nitrogen temperature is used by the Quantachrome Autosorb Automated Gas Adsorption system Reporter Version 1 05.

4. RESULTS AND ESTIMATION

4.1 Scanning electron microscopic analysis of $LiMnO_2$

SEM photograph is shown a wrong thin film by the Fig. 4 meaning the relation of particle magnitude, a viscosity and the pasting place of between a foil and slurry.

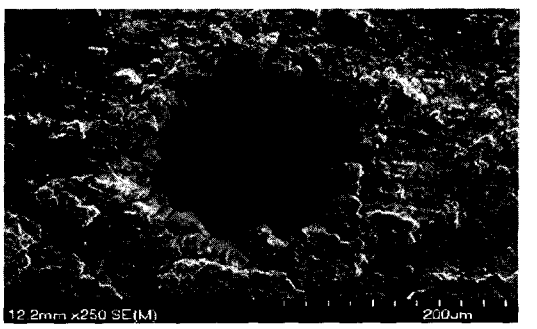

Fig. 4. Air ball phenomenon of wrong $LiMnO_2$ thin film of SEM.

The role of roll-press symbolized the generative suppression of the very small air balls to be appeared on the surface of $LiMnO_2$ thin film. In result, the synthesis-crystallization of the thin film means the quality to be grown by the $LiMnO_2$ thin film related only the single crystal with the properties of a viscosity of slurry and the process of a milling and only one calcining among an amorphous, a poly crystal and single crystal.

4.2 Cyclic voltammogram of $LiMnO_2$/PC 1M $LiClO_4$Li cell

The type of Fig. 5 is shown by the properties of cyclic voltammogram of which the electrochemical reaction displayed a phenomenon to change a battery energy as a behavior when Li ion are intercalated and deintercalated in electrolyte of the PC 1M $LiClO_4$.

$$\text{Cathode : } LiMnO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li1MnO_2 + Li+ + e^-$$

$$\text{Refference : } Li \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li+ + e^-$$

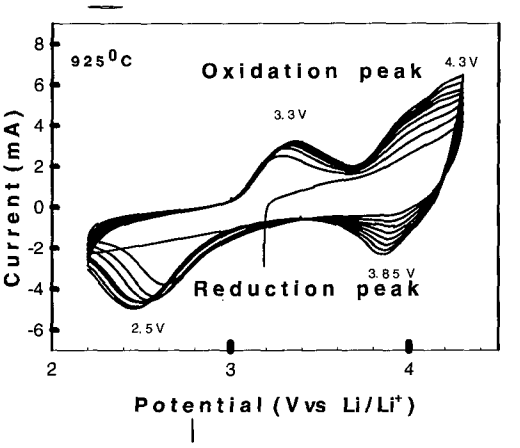

Fig. 5. Cyclic voltammogram of LiMnO2 cell (Ar flow at 100cc/min)

4.3 Charge/discharge properties of cathode active material

The initial discharged capacity of an experiment of charge/discharge of the thin film synthesised and crystallized at 925℃ are increased according to proceed the cycles at 9cycles, but it decreased oppositely after 9 cycles as follow the proceeding cycles. Though it will be increased over 100mAh/g, because the cell stopped at the time that it was proceeding from the start. Discharged capacities of 87mAh/g got after restarting for measure values of the experimental data. The results of Fig. 5 are shown by an energy efficiency over 90% at Fig. 6.

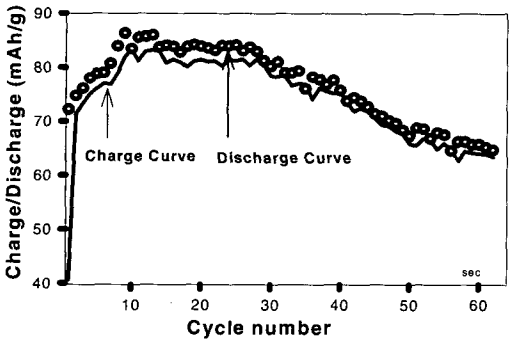

Fig. 6. Capacity of charge and discharge.

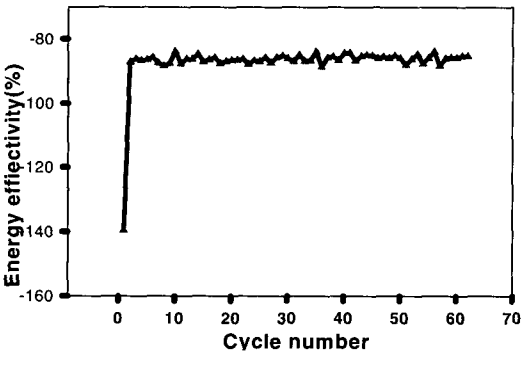

Fig. 7. Energy efficiency.

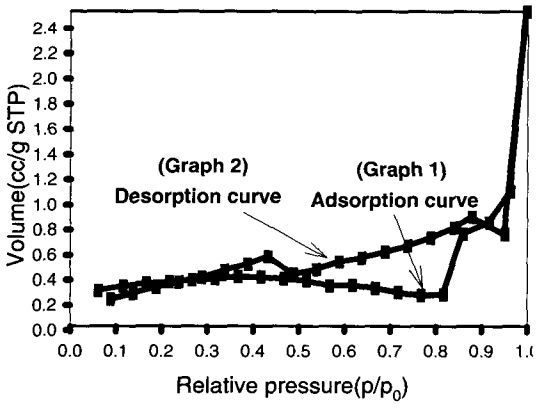

Fig. 8. Isotherm of powder particles of $LiMnO_2$ thin film.

4.4 ICP and measurement analysis of pore diagram

The experimental thin film are synthesised and crystallized by the solid state method with that start materials of $LiOH.H_2O$ 4.616g and Mn_2O_3 7.894g are mixed together to prepare the properties of $LiMnO_2$ thin film. The $LiMnO_2$ thin film is structured with 96.9 [ppm] and 837[ppm] of density ratios of Li and Mn respectively. The results of $LiMnO_2$ powder pore diagrams are analysed by showing only graphs data of the isotherm and a pore size distribution of the adsorption and desorption. The magnitude of pore diagram for the preparation of $LiMnO_2$ thin film indicated the effective that the magnitude of powder particles forced to the thin film. And the values of isotherm to analyse the relation of particles were the values of 0.0609~0.9945 that is shown by graph 1 of Fig. 8, when the nitrogen gas adsobed at the input of p/p. And values of 0.9400~0.0869 in the vacuum indicated the volume [volume cc/g STP] at graph 2 when the nitrogen gas desorbed from the pore.

4.5 Estimation of $LiMnO_2$ thin film

1. Powder of $LiMnO_2$ for a preparation of $LiMnO_2$ thin film must be milled at the least to become below 1 m.
2. The viscosity of slurry should be suitable the press scale of role press should fix at range that the air balls of thin film must be not formed between an aluminum foil and a slurry.
3. The phenomenon of air bolls of $LiMnO_2$ thin film quality is estinated by the preparing $LiMnO_2$thin film let reject from the liquid electrolyte when a discharged amount is less, and became dry it in oven at about 80℃ .
4. magnifying distribution of adsorption and desorption pore can know to be shown the effectivity that the thin film forced with analysis according to the values of the differential volume[cc/g] of the diameter of pore[Å].
5. The average pore diameter of powder particles of $LiMnO_2$ thin film estimated that the $LiMnO_2$ thin film were prepared with very tiny powder with 132.3Å of it.

5. CONCLUSION

1. Dense ratios of Li and Mn of ICP analysis for an estimating of a cathode active material $LiMnO_2$ thin film quality were 96.9[ppm] at the wavelengths 670.784[nm] and 257.610[ppm] at the wavelengths 257[nm] respectively.
2. The average pore diameter of $LiMnO_2$ thin film powder was 132.3Å being very tiny particles, but the $LiMnO_2$ cell didn't get a good discharged capacity.
3. The energetic efficiency of the $LiMnO_2$ cell was over 90% as the amount of the discharged capacities of 87mAh/g.

4. The particles component, the density analysis of metal materials and the magnitude of average pore diameter are analyzed by the measurements of the ICP and porosity.
5. The energetic efficiency and the discharged capacity thought to the matter to be depended by a distance between anode electrode and cathode electrode in electrolyte of the cell.

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