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# Synthesis of $LiMn_2O_4$ Cathode Materials by Emulsion Method and Its Electrochemical Properties

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Synthesis of the spinel $LiMn_2O_4$ by emulsion method was investigated. $LiOH \cdot H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ were used as starting materials to prepare mixed aqueous solution (0.5 mol/*l* for the $LiMn_2O_4$). Kerosene, paraffin oil and span 80 were used for organic phase. The aqueous solution and organic phase were mixed in the ratio of 2:1 and emulsified at the speed of 4000 rpm for 5 min. The prepared emulsions were dropped into the petroleum heated at 170°C to evaporate water in the silicon oil bath, dried at 120°C in the oven to remove petroleum and calcined at temperature ranges from 600 to 900°C for 48 hrs. The characteristics of powders were investigated by XRD, SEM, BET and electrochemical properties of synthesized cathode materials were measured with Galvanostatic system. $Li_{1.05}Mn_2O_4$ calcined at 800°C for 48 hrs showed initial discharge capacity of 125.9 mAH/g.

***Key words :*** $LiMn_2O_4$, Cathod Materials, Emulsion Method, Synthesis

## I. Introduction

More than 200 materials have been evaluated for using positive electrodes of secondary batteries over the past two decades. Of these, manganese oxides were found to be the most promising materials from the viewpoint of specific capacity, toxicity, and cost. However, lithium spinel $LiMn_2O_4$ is the most promising candidate for the recently proposed innovative lithium ion batteries.[1-4] Batteries consist of a high voltage intercalation compound as the positive electrode and lithium metal as the negative electrode in electrolyte. The rechargeable capacity of $LiMn_2O_4$ is 100-130 mAh/g which is comparable to that of $LiCoO_2$. $LiMn_2O_4$ is easy to prepare and less expensive than $LiCoO_2$ and $LiNiO_2$. However, various methods for preparing the $LiMn_2O_4$ compound have been reported, such as solid state reaction,[5-6] sol-gel process,[7] ultrasonic spray method and so on. Emulsion method is that organic phase divide mixed metal salt solution into fine droplets by high speed stirrer. All of these divided fine droplets, that is, emulsion is spherical and homogenized composition. It is considered that these emulsions could be easily decomposed, reacted and synthesized to crystalline solid by calcination at proper temperature. This emulsion method will be more preparable to synthesis of spinel $LiMn_2O_4$ powders than any other process. In this study, synthesis of $LiMn_2O_4$ powders by emulsion method and electrochemical properties of it were investigated.

## II. Experimental Procedure

$LiOH \cdot H_2O$(99.95%, Aldrich Chemical Company, Inc.), $Mn(NO_3)_2 \cdot 6H_2O$(98.0% Showa Chemicals Inc.) were used as starting materials to prepare mixed aqueous solution (0.5 mol/*l* for the $LiMn_2O_4$ composition). Aqueous solutions of each starting material were mixed on the magnetic stirrer for 24 hrs. Span 80(5v/v%) for the surfactant, Kerosene(92v/v%) for solvent and paraffin oil(3v/v%) for emulsifying agent were mixed on the magnetic stirrer for 24 hrs to prepare organic phase. The mixed aqueous solution and organic phase were mixed in the ratio of 2:1 and emulsified at the speed of 4000 rpm for 5 min. To evaporate water and petroleum included in the water-in-oil type emulsions, the prepared emulsions were dropped into the petroleum heated at 170°C[8] in the silicon oil bath and dried at 120°C in the oven. Thermal analysis of emulsion derived powders was carried out with heating rate of 10°C/min using DT-TGA.

$Li_xMn_2O_4$(x=0.90 ~ 1.10) cathode material was calcined at temperatures from 600 to 800°C for 48 hrs in air with heating rate of 5°C/min and cooling rate of 1°C/min. The crystalline phase of emulsion derived and calcined powders were examined by X-ray diffraction (XRD: Rigaku, D/MAX-111A) operating at 40 KV, 30 mA, scanning speed of 4°/min with CuKα radiation. The shape of powders and microstructure were observed by scanning electron microscope (SEM: JEOL JSM-6400). Surface area was measured by BET apparatus (Quantachrome, Quantasord). The electrochemical properties of samples were tested at room temperature with half cell in Li metal/electrolyte{1M $LiPF_6$-ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume)}/cathode material at room temperature. The positive material consists of the ratio of $LiMn_2O_4$ pow-

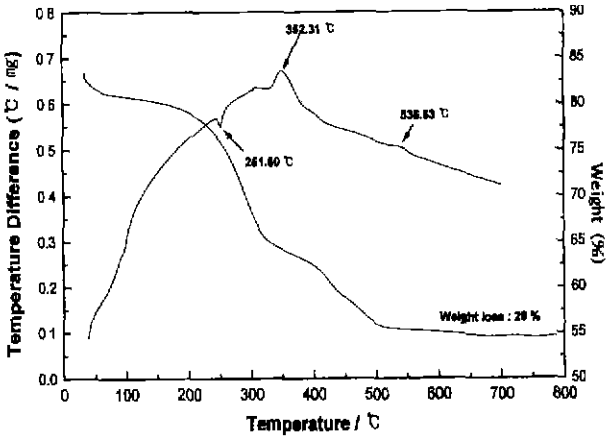


**Fig. 1.** DTA-TGA curves of precursor powder dried at 170°C.

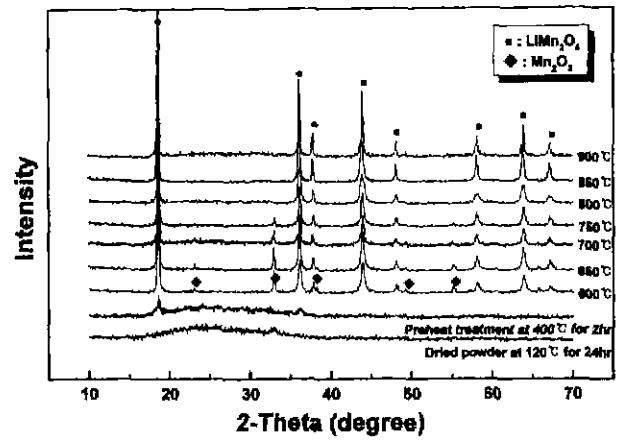


**Fig. 3.** XRD patterns of powders calcined at various temperatures.

der, acetylene black as conductor and PTFE as binder at the ratio of 89:10:1 by weight. The cathode material (45 $mg/cm^2$) was pressed onto an Al mesh current collector with pressure of 3 $ton/cm^2$ to disk with 12 mm in diameter. Lithium foil and glass microfibre filters (GF/A, Whatman) were used for anode and separator respectively. The cells were automatically charged and discharged between 2.8 and 4.2 V at 1 $mA/cm^2$ for 30 cycles.

## III. Results and Discussion

### *1. Characteristics of dried precursor powders*

Fig. 1 shows the simultaneous DT-TGA traces obtained from dried precursor powders. Endothermic peak at 251°C is considered due to the decomposition of lithium salt. Two exothermic peaks were observed. It is considered that one of exothermic peak was the decomposition of manganese salt and oxidation of organic substances such as surfactant, kerosene and paraffin oil at 352°C and the other was due to formation of $LiMn_2O_4$ at 536°C. The SEM images of dried precursor powders is Fig. 2. The shape of powders was sphere and average particles size was 0.21 μm from

**Fig. 2.** SEM photograph of dried precursor powders.

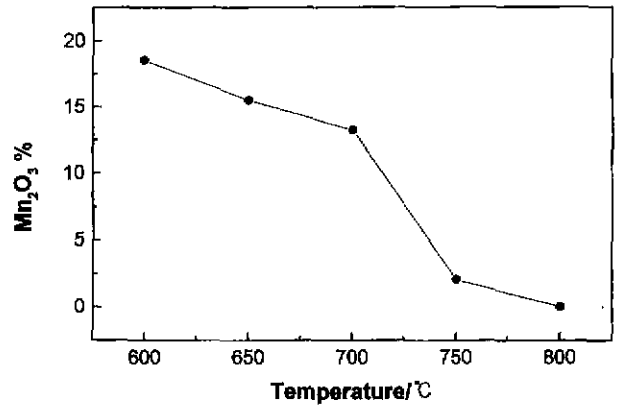


**Fig. 4.** Content of $Mn_2O_3$ phase of powders calcined at various temperatures.

SEM photographs. Specific surface area was 6.95 $m^2/g$.

### *2. Characteristics of calcined powders*

The emulsion derived powders were calcined at the temperatures of 600~900°C for 48 hrs. The XRD patterns of calcined powders are shown in Fig. 3. The relative amount of $Mn_2O_3$ and spinel $LiMn_2O_4$ were determined with the 100% intensity peaks of (222) for $Mn_2O_3$ $I_{Mn}$ and (111) for spinel $LiMn_2O_4$ $I_{sp}$. The percentage of $Mn_2O_3$ phase was calculated using the following equation (1) and si shown in Fig. 4.

$$\% \ Mn_2O_3 = \{I_{Mn}/(I_{Mn}+I_{sp})\} \times 100 \quad (1)$$

$Mn_2O_3$ phase and $LiMn_2O_4$ phase were formed at 600°C. The amount of $Mn_2O_3$ decreased gradually at 700°C, but rapidly at 750°C and disappeared at 800°C. These suggest that $Mn_2O_3$ and lithium compound reacted each other to form $LiMn_2O_4$ rapidly at 750°C. Crystallite size by FWHM and surface area by BET are shown in Fig. 5. Crystal grew gradually up to 700°C, but rapidly at 750°C. Single phase of $LiMn_2O_4$ was formed from 800°C. Surface area decreased with crystallite size increasing. Fig. 6 shows the lattice constant changes of $LiMn_2O_4$ powders calcined at various tem-

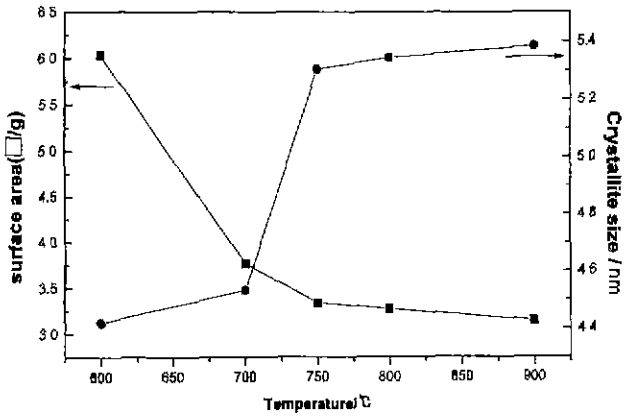


**Fig. 5.** Crystallite size by FWHM and surface area by BET of powder calcined at various temperatures.

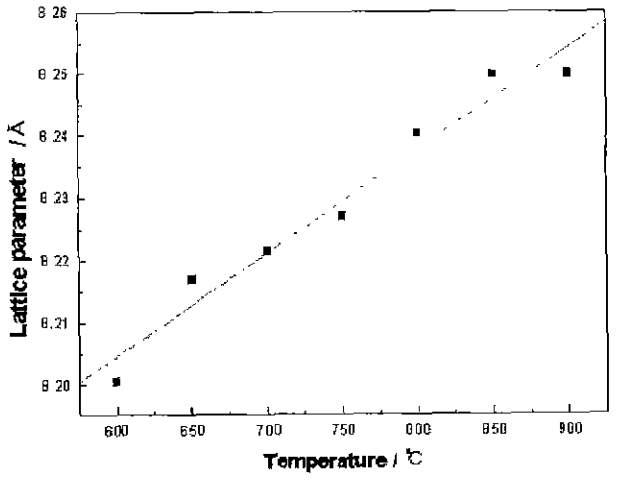


**Fig. 6.** The lattice constant of powders calcined at various temperatures.

peratures. Lattice constant increased with elevating temperature. It is considered that valence of Mn was changed from 4+ to 3+ with increasing temperature.[10] $Mn^{3+}$ is stable at high temperature and occupied Mn site more than $Mn^{4+}$. So the lattice constant was increased.

Fig. 7 shows SEM image of calcined powder at 800°C. The shape of particles was sphere. Average particle size was 0.18 μm from SEM photograph. Specific surface area was 3.34 $m^2/g$.

### *3. Effect of lithium content in $Li_xMn_2O_4$*

The XRD patterns of powders with various lithium content calcined at 800°C are shown in Fig. 8. All of XRD powders shows single phase of spinel structure. Fig. 9 shows the lattice constant changes of $Li_xMn_2O_4$ with various x calculated from XRD patterns. Lattice constant increased from x=0.90 to 1.0 and decreased from x=1.00 to 1.10. Increment of lattice constant was due to the occupation of deficient lithium eite with lithium in the range of x=0.9~1.00 in $Li_xMn_2O_4$ composition as the lithium added.

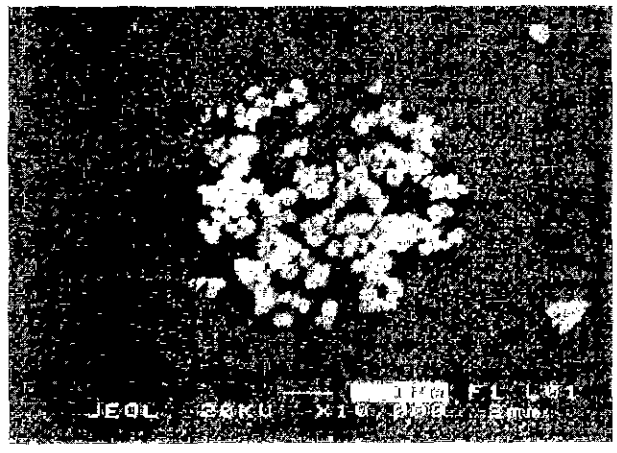


**Fig. 7.** SEM image of powders calcined at 800°C for 48 hrs.

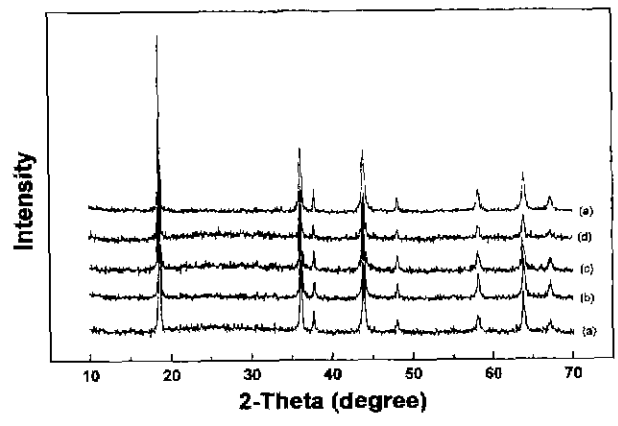


**Fig. 8.** XRD patterns of $Li_xMn_2O_4$ powder with various x calcined at 800°C for 48 hrs. (a) 0.9, (b) 0.95, (c) 1.0, (d) 1.05 and (e) 1.1.

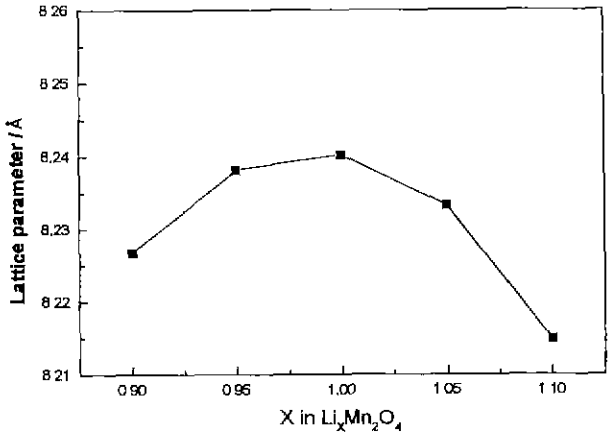


**Fig. 9.** The lattice constant of $Li_xMn_2O_4$ powders with various x content.

But in the range of x=1.00~1.10 with excess lithium, manganese ion charge was changed from $Mn^{3+}$ to $Mn^{4+}$ to compensate electrical neutrality and lattice constant decreased.

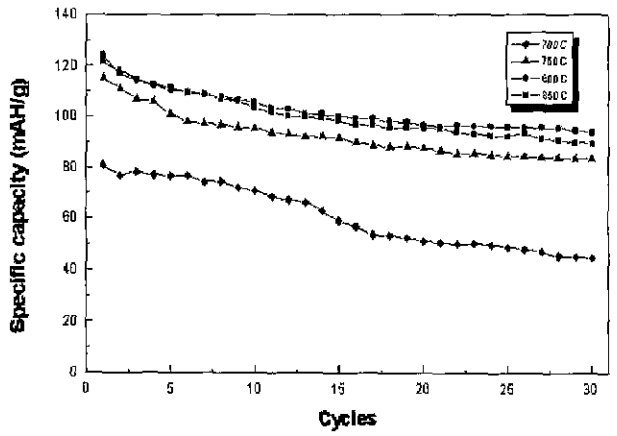


**Fig. 10.** The discharge capacity of $Li_xMn_2O_4$ powders calcined at various temperatures.

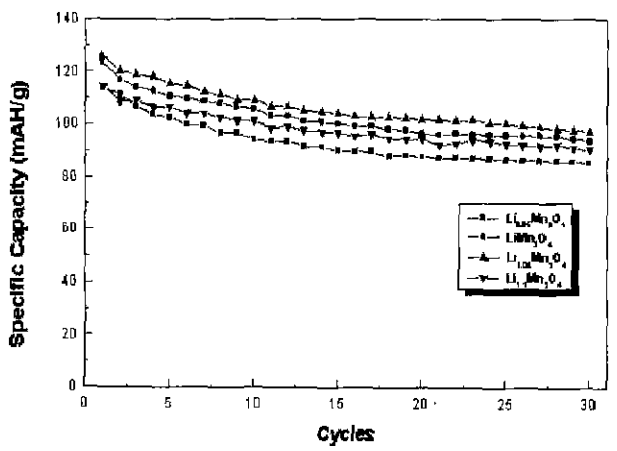


**Fig. 11.** The discharge capacity of $Li_xMn_2O_4$ powders with various x content.

### *4. Electrochemical properties of $Li_xMn_2O_4$ Powders*

The discharge capacity of $LiMn_2O_4$ powders calcined at various temperatures at I=1 mA/cm$^2$ is shown in Fig. 10. As the amount of $Mn_2O_3$ phase decreased, the initial discharge capacity increased. The Mn site in $LiMn_2O_4$ powder calcined at low temperature under 800°C was occupied by $Mn^{4+}$ more than $Mn^{3+}$. It accorded with lattice constant change in Fig. 6. If the powder calcined at low temperature was tested above 4 V continuously, average manganese oxidation state increased by partial overdischarge. Then, the discharge capacity was faded fast by Jahn-Teller distortion.[5] This was shown in discharge capacity of $LiMn_2O_4$ powder calcined at 700°C with testing 30 cycles. Maximum discharge capacity was obtained in the $LiMn_2O_4$ powder calcined at 800°C. The initial discharge capacity was 123.7 mAh/g and the final discharge capacity was 93.63 mAh/g, after 30 cycling.

The discharge capacity of $Li_xMn_2O_4$ powders with various lithium contents is shown in Fig. 11. Discharge capacity was improved in $Li_{1.05}Mn_2O_4$ but reduced in $Li_{0.9}Mn_2O_4$ and $Li_{1.1}Mn_2O_4$. Reduction of discharge capacity in $Li_{0.9}Mn_2O_4$ was caused by deficient lithium site of $LiMn_2O_4$ spinel structure. In $Li_{1.10}Mn_2O_4$ with excess lithium above 10 mol%, it is most probably associated with the fact that under these condition the Li rich spinel $Li_4Mn_5O_{12}$[11] was obtained together spinel $LiMn_2O_4$. But Thackeray et al. have shown that the XRD diagram of $Li_4Mn_5O_{12}$ phase can hardly be distinguished from that of $LiMn_2O_4$ phase. Then, the reduction of discharge capacity was due to Li rich spinel $Li_4Mn_5O_{12}$ phase. Maximum initial discharge capacity was 125.9 mAh/g and the final discharge capacity was 96.95 mAh/g after 30 cycling in $Li_{1.05}Mn_2O_4$ powder calcined at 800°C.

## IV. Conclusions

The results of this study are summarized as follows.

1. Aqueous solution of metal salts, and the organic substances were used to prepare emulsions.
2. The amount of $Mn_2O_3$ phase was decreased with increasing calcination temperature. Single phase of spinel $LiMn_2O_4$ was obtained above 800°C for 48 hrs.
3. Single phase of spinel structure was obtained at 800°C in $Li_xMn_2O_4$ (x=0.90~1.10).
4. Maximum initial discharge capacity was 123.7 mAh/g, and the final discharge was 93.63 mAh/g after 30 cycling in $LiMn_2O_4$ powders calcined at 800°C.
5. Maximum initial discharge capacity was 125.9 mAh/g and the final discharge was 96.5 mAh/g after 30 cycling in $Li_{1.05}Mn_2O_4$ powders.

## Acknowledgment

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