— Technical Paper —

Electrochemical Properties of Spherical, Porous $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ Powders Prepared by Ultrasonic Spray Pyrolysis

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Spherical $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders were prepared by the ultrasonic spray pyrolysis. As-prepared particles had a porous microstructure and were nonagglomerated, which had an average diameter of about 1 μm with narrow size distribution. XRD showed that as-prepared powders were well crystallized to spinel structure with Fd3m space group. ICP analysis revealed that Mg ions were homogeneously doped to LiMn_2O_4 . As-prepared powders were used as cathode active material for lithium secondary battery and its electrochemical properties were investigated between 3.5 and 4.3 V. The first charge/discharge capacity of LiMn_2O_4 was 145 and 141 mAh g^{-1} at 0.1 mA cm^{-2} , respectively. The discharge capacity of LiMn_2O_4 decreased with increasing cycle number. The first charge/discharge capacity of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ was less than that of LiMn_2O_4 . However, the cycle performance of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ was superior to that of LiMn_2O_4 .

Key Words : Lithium Secondary Battery, Cathode Materials, Spray Pyrolysis, LiMn_2O_4

1 Introduction

To date, LiCoO_2 ^{1,2)} has been commercially used as a cathode active material in high energy density lithium secondary battery. Recently, two types of lithium manganate has been noted as an alternative cathode active material because of low cost and high safety compared to an LiCoO_2 and LiNiO_2 . LiMn_2O_4 ³⁻⁵⁾ has been proposed as a cathode active material due to higher capacity than LiCoO_2 . There are two plateaus region (3 V and 4 V) in charge and discharge curves because of the phase transition to LiMn_2O_4 during lithium insertion/extraction. Spinel type LiMn_2O_4 ⁶⁻⁹⁾ has been investigated for its possible use as an alternative cathode active material in rechargeable lithium batteries. Although the theoretical capacity of spinel LiMn_2O_4 is much lower than that of layered structures such as LiCoO_2 and LiNiO_2 , LiMn_2O_4 shows superior cycle performance to that of layered structure. However, the capacity fading on cycling is still observed for stoichiometric LiMn_2O_4 compound.¹⁰⁻¹²⁾ It has been reported that the substitution of other elements such as Al, Co, Cr, V, Ga, Mg, Zn to the Mn site leads to the stabilization of the spinel structure during lithium insertion/extraction and shows marked improvement in the cycling performance.¹³⁻²⁰⁾

A homogeneous doping process must be developed to achieve the molecular scale blending. It is already well known that the liquid phase reaction such as the sol-gel method is a production technique capable of supplying stoichiometric precursor. However, sol-gel method for preparing LiMn_2O_4 is not economical because of long reaction time and complex synthesis route. We have noted

the spray pyrolysis process as an alternative solution technique. Spray pyrolysis is simple process and then leads to short production time compared with sol-gel method. It has been reported from many researches in spray pyrolysis²¹⁾ that the droplet size generated from ultrasonic atomizer is much smaller than that obtained from two fluid nozzle and the use of ultrasonic atomizer often leads to the formation of fine, spherical particles with narrow size distribution. We expected that use of powders with above particle characteristics as cathode active material resulted in higher charge/discharge capacity because of higher packing density and specific surface area. LiCoO_2 and LiNiO_2 powders have been already prepared by ultrasonic spray pyrolysis and their electrochemical properties have been also investigated.^{22,23)} Furthermore, we have also reported that ultrasonic spray pyrolysis makes it possible for LiNiO_2 to homogeneously dope and then the electrochemical property led to a superior discharge capacity and cycling performance compared to LiNiO_2 .²⁴⁾ A similar effect can be expected for homogeneous doping of foreign metal in LiMn_2O_4 .

In this paper, LiMn_2O_4 and Mg doped LiMn_2O_4 powders were prepared by the ultrasonic spray pyrolysis. The physical and chemical properties of these powders were characterized and then the battery performance was also investigated.

2 Experimental Procedure

2.1 Preparation and characterization of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders

$\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders were prepared by ultrasonic spray pyrolysis using metal nitrates as starting materials. Metal nitrates with atomic ratio ($\text{Li}:\text{Mn}=1:2$) were weighed and dissolved in a water. The concentration of metal nitrate was 0.5 mol dm^{-3} . The concentration of Mg nitrates ranged from 5–20 mol% for Mn nitrate. The detail on ultrasonic spray pyrolysis apparatus was described elsewhere.²⁵⁾ The mist of aqueous nitrate solution was generated with an ultrasonic vibrator (1.6 MHz). The average droplet size of the mist was about $3 \mu\text{m}$ by the equation of Lang.²⁶⁾ The mist was introduced into two electrical furnaces (drying and pyrolysis) using the air carrier gas at a flow rate of $0.083 \text{ dm}^3 \text{ s}^{-1}$ and then pyrolyzed at 900°C . As-prepared powders were collected using the cyclone.

The average particle size, size distribution, morphology and microstructure of particles were determined with a scanning electron microscope (SEM, Hitachi S-800). The crystalline phase of as-prepared powders was identified using powder X-ray diffraction (XRD, Mac science M3X). The thermal behavior of as-prepared powders was observed by differential thermal analysis and thermogravimetry (DTA-TG, Rigaku PTC-10). The chemical composition of as-prepared powders was determined by inductively coupled plasma spectroscopy (ICP, Seiko SPS-4000).

2.2 Electrochemical measurement

Lithium secondary battery consisted of cathode materials, Li sheet as an anode, cellgard microporous membrane as the separator, and $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ in propylene carbonate/1,2-dimethoxyethane (1:1 in volume) as the electrolyte. Cathode materials were prepared using 85 wt% $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders, 10 wt% acetylene black and 5 wt% fluorine resin. LiMn_2O_4 powders were mixed with acetylene black and fluorine resin and pressed on either side of a Ti mesh (3 cm^2). An experimental battery was fabricated by a stainless steel case ($2 \text{ cm} \times 3 \text{ cm} \times 3 \text{ cm}$) and assembled in a glove box filled with argon. The charge/discharge capacity of battery was measured with a potentiostat (Hokutodenko HJ-201 B) between 3.5 V and 4.3 V at a current density from 0.1 to 0.5 mA cm^{-2} . All electrochemical measurement was carried out at 25°C .

3 Results and Discussion

A typical SEM photographs and particle size distributions of LiMn_2O_4 and $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$ powders prepared by the ultrasonic spray pyrolysis were shown in Fig. 1. Both of as-prepared particles had spherical morphology and were non-agglomerated, which had a porous microstructure. The average particle size of LiMn_2O_4 and $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$ powders estimated from SEM photographs was $1.15 \mu\text{m}$ and $1.24 \mu\text{m}$, respectively. The geometrical standard deviation (σ_g) of them was 1.34 and 1.31, respectively. It is clear that the powder characteristics of LiMn_2O_4 are the same as that of $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$.

Fig. 1 SEM photographs and particle size distributions of LiMn_2O_4 and $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$.

This finding indicates that the particle morphology, size and size distribution of as-prepared powders are not influenced by the addition of Mg^{2+} ion. Specific surface areas of as-prepared powders determined by BET method were listed in Table 1. Specific surface areas of as-prepared powders were about $10\text{--}20\text{ m}^2\text{ g}^{-1}$, regardless of Mg contents. This finding indicates that as-prepared powders have porous particles. Table 2 shows the chemical composition of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders determined by ICP analysis. The chemical composition of them listed in Table 2 was in good agreement with the starting solution composition. This suggests that Mg^{2+} ions are homogeneously doped to the LiMn_2O_4 powders by the ultrasonic spray pyrolysis, *i. e.*, the droplet composition obtained by ultrasonic vibrator is homogeneous. DTA-TG analysis revealed a broad endothermic peak from room temperature to 250°C due to the dehydration in all samples. The weight loss of as-prepared powders was less than 1 wt%.

Figure 2 shows XRD patterns of LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders prepared by the ultrasonic spray pyrolysis. XRD patterns revealed that LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders prepared at 900°C were well crystallized to spinel structure with a space group (Fd3m). The single phase of LiMn_2O_4 was also observed at the pyrolysis temperature less than 900°C , but the crystallinity was much lower than that prepared at 900°C . The crystallinity of LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders gradually increased with increasing the pyrolysis temperature. The other oxide phases such as Mn_2O_3 and MgO were not observed up to $x = 0.2$ in XRD patterns. A single LiMn_2O_4 phase was retained at up to $x = 0.2$ in $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$. Spinel structure was still kept when a part of Mn site (16d) in LiMn_2O_4 was substituted by Mg ion. Figure 3 shows the change of cubic lattice parameter a_0 as a function of Mg contents in $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$. The a_0 of LiMn_2O_4 powders was 0.8241 nm . The a_0 linearly decreased from 0.8241 to 0.8227 with increasing Mg contents. This tendency can be also observed in Mg or other cation doped LiMn_2O_4 obtained by the conventional solid state reaction.^{17,27)} Idemoto *et al.* examined the change of Mn valence by doping Mg^{2+} ion from chemi-

Table 1 Specific surface area of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders determined by BET method.

$\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$	m^2/g
$x = 0$	15
$x = 0.05$	18
$x = 0.1$	19
$x = 0.2$	16

Table 2 Chemical composition of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders determined by ICP analysis.

$\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$	Atomic concentration/mol%		
	Li	Mn	Mg
$x = 0$	33.5	66.5	
$x = 0.05$	33.4	61.8	4.8
$x = 0.1$	33.5	56.6	9.9
$x = 0.2$	33.4	47.1	19.5

Fig. 2 XRD patterns of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders.

Fig. 3 Relation between lattice parameter and Mg contents in $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$.

cal analysis such as chelate titration and iodometry.¹⁷⁾ They have reported that the addition of Mg led to the increase of Mn valence. Similarly, it is predicted from the results in Figs. 2 and 3 that the valence of Mn at 16d site gradually increases with increasing Mg contents, *i. e.*, the number of Mn^{4+} ion is likely to be increased at 16d site.

Figure 4 shows the typical first charge/discharge curves of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ at 0.1 mA cm^{-2} . The first charge/discharge capacity of LiMn_2O_4 was about 145 and 141 mAh g^{-1} , respectively. It was found that the charge/discharge capacity was closed to the theoretical value (148 mAh g^{-1}). The charge/discharge curves of LiMn_2O_4 had two plateaus with a clear voltage jump at about 4.1 V. The charge/discharge of $\text{Li}_{1-y}\text{Mn}_2\text{O}_4$ was reversible in a

Fig. 4 First charge/discharge curves of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ at 0.1 mA cm^{-2} .

range of $0.026 \leq y \leq 0.979$ between 3.5 and 4.3 V. The irreversible capacity (Δx) which Li^+ ion could not return to the cathode on discharge was 0.026. However, the first charge/discharge capacity of LiMn_2O_4 was decreased by the addition of Mg^{2+} ion. The first charge/discharge capacity of $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$ was 141 and 138 mAh g^{-1} , respectively and the first charge/discharge capacity of $\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$ was 125 and 122 mAh g^{-1} , respectively. The value of Δx in $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$ and $\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$ was 0.012 and 0.02, respectively, which was less than that of LiMn_2O_4 ($\Delta x = 0.026$). It was found that the addition of Mg^{2+} ion led to the improved efficiency of charge/discharge. The voltage jump in the charge and discharge curves of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ at $x = 0.05$ was also observed at about 4.1 V, but a clear voltage jump was not observed at $x = 0.2$. The phenomena on the disappearance of voltage jump by doping excess foreign metal have been already reported.^{17, 27)} It appears that the electrochemical behavior of $\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$ is close to that of nonstoichiometric LiMn_2O_4 compound reported by Yoshio *et al.*^{9, 10)} This may be resulted in the reduction of charge/discharge capacity at $x = 0.2$. It was concluded that the optimum Mg contents in $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ was ranged from 5 to 10 mol%.

Figure 5 shows the relation between cycle number and discharge capacity of LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ at 0.1 and 0.3 mA cm^{-2} , respectively. The discharge capacity of LiMn_2O_4 decreased to 127 and 123 mAh g^{-1} with increasing cycle number at 0.1 and 0.3 mA cm^{-2} , respectively. This result is similar to that of stoichiometric LiMn_2O_4 compound obtained by the previous works.^{9–11)} The discharge capacity of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ also gradually decreased up to 100 cycles without the dependence of Mg contents at 0.1 and 0.3 mA cm^{-2} , respectively. The reduction in discharge capacity of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ was less than that of LiMn_2O_4 . It was found that $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ showed more stable cycling performance than LiMn_2O_4 . When the current density was 0.1 mA cm^{-2} , the addition of 5 mol% Mg led to the most excellent results and then the discharge capacity was maintained at 135 mAh g^{-1} , but decreased to 118 mAh g^{-1} by the addition of 20 mol% Mg. Since the composition of $\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$ is closed to nonstoichiometric LiMn_2O_4 , the rechargeable capacity decreased, but exhibited the stable cycle performance more than that of LiMn_2O_4 . On the other hand,

the discharge capacity of $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$ and $\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$ at 0.3 mA cm^{-2} decreased to 131 and 112 mAh g^{-1} , respectively. However, even at a higher current density, the cycle performance of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ is excellent more than that of LiMn_2O_4 . Those results also showed superior cycle performance to that of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ reported by the previous work.¹⁷⁾ It is clear that the porous structure in cathode active materials is most effective for the diffusion of Li^+ ion from the particle. This suggests that the electrochemical behavior of cathode active materials for rechargeable capacity and cycle performance is also influenced by the particle characteristics such as particle morphology, particle size and porous structure. Porous structure increases the activity of diffusion species (Li^+ ion) at particles/electrolyte interface. Thus, the porous particles lead to higher rechargeable capacity and cycle performance.

4 Conclusion

LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ particles were prepared by the ultrasonic spray pyrolysis. LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ particles were spherical and porous which have a diameter of about 1 μm with narrow size distribution. As-prepared powders were well crystallized to spinel structure with Fd3m space group. The cubic lattice parameter a_0 decreased with increasing Mg contents. ICP analysis revealed that the powder composition was good agreement with the starting solution composition. The first discharge capacity of LiMn_2O_4 was 141 mAh g^{-1} at 0.1 mA cm^{-2} . The discharge capacity of LiMn_2O_4 decreased with increasing cycle number. Although the first discharge capacity of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ decreased to 125 mAh g^{-1} by the addition of 20 mol% Mg^{2+} ion, the addition of Mg to LiMn_2O_4 led to improved cycle performance. $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$ offered superior cycle performance to LiMn_2O_4 . It was found that the addition of Mg is effective for the stabilization of electrochemical cycling.

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Fig. 5 Cycle characteristics of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ at 0.1 (a) and 0.3 (b) mA cm^{-2} .

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