

## Synthesis and Characterization of metal (Fe, Al or Mg) doped Li[Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>]O<sub>2</sub> Particle by Ultrasonic Spray Pyrolysis

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Spherical metal (Fe, Al or Mg) doped Li[Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>]O<sub>2</sub> precursor powders were synthesized by ultrasonic spray pyrolysis using aqueous solution of metal nitrate. XRD, SEM and BET analysis were used for determination of the composition, morphology, particle size and surface area. SEM observation showed that the size of as-prepared particles were about 0.9  $\mu\text{m}$  with narrow size distribution. The crystal phase of metal (Fe, Al or Mg) doped Li[Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>]O<sub>2</sub> was resulted in layered rock salt structure with R $\bar{3}m$  space group after calcinations at 1023 K, 10 hrs. No impurity-related peaks are observed from the XRD pattern with various doping metals. Mg and Al doped Li(Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)O<sub>2</sub> showed a very good cycling stability. The Mg substitution for Ni led to the most excellent results. On the other hand, the capacity fading on cycling was observed for Fe(5%, substitution for Mn) and Mg(30%, substitution for Co and Mn) doped Li(Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)O<sub>2</sub>.

Key words: Lithium Secondary Battery, Cathode Materials, Spray Pyrolysis, Cycling Stability, Li(Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>)O<sub>2</sub>

### 1. INTRODUCTION

To date, LiCoO<sub>2</sub> [1,2] has been commercial density lithium secondary battery. Recently, two types of lithium manganates have been noted as alternative cathode active materials because of low cost and high safety compared to LiCoO<sub>2</sub> and LiNiO<sub>2</sub>, LiMnO<sub>2</sub> [3-5] has been proposed as a cathode active material due to higher capacity rather than LiCoO<sub>2</sub>. There are two plateaus regions (3 V and 4 V) in charge and discharge curves because of the phase transition to LiMn<sub>2</sub>O<sub>4</sub> during lithium insertion / extraction. Spinel type LiMn<sub>2</sub>O<sub>4</sub> [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<sub>2</sub>O<sub>4</sub> is much lower than those of layered structures such as LiCoO<sub>2</sub> and LiNiO<sub>2</sub>. There have been many attempts to improve both cycle life and safety by using Co-Ni [10], Mn-Co [11,12], or Mn-Ni [13] mixed oxides. Recently, the combination of Mn, Co and Ni as Li(Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>)O<sub>2</sub> [14] mixed oxide has attracted a great deal of interest from researchers in cathode materials for lithium secondary batteries. It has higher safety as compared to LiCoO<sub>2</sub> with almost the same reversible capacity. [15] Aerosol process (ultrasonic spray pyrolysis etc.) is well known as a useful tool for the rapid production of multi-component powders in a continuous process. In this work, we prepared Li[Ni<sub>(1/3-x)</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>M<sub>x</sub>]O<sub>2</sub>, Li[Ni<sub>1/3</sub>Mn<sub>(1/3-x)</sub>Co<sub>1/3</sub>M<sub>x</sub>]O<sub>2</sub> and Li[Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>(1/3-x)</sub>M<sub>x</sub>]O<sub>2</sub> (M=Fe, Al or Mg) precursor powders [16] with submicron size, good crystallinity, spherical morphology and non-aggregation by ultrasonic spray pyrolysis. Characteristics of as-prepared particles such as crystallinity,

morphology and electrochemical properties were investigated. The electrochemical properties were compared with that of each doping metal.

### 2. EXPERIMENTAL

A stoichiometric amount of metal nitrates were used as starting materials for the synthesis of Li[Ni<sub>(1/3-x)</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>M<sub>x</sub>]O<sub>2</sub>, Li[Ni<sub>1/3</sub>Mn<sub>(1/3-x)</sub>Co<sub>1/3</sub>M<sub>x</sub>]O<sub>2</sub> and Li[Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>(1/3-x)</sub>M<sub>x</sub>]O<sub>2</sub> (M=Fe, Al or Mg) powders and they were dissolved in distilled water with nitric acid. The concentration of the total metal nitrate was 0.5 M. The concentration of Fe, Mg and Al nitrates were 5 mol% for target metal nitrate. A spray pyrolysis system was used in this study, consisting of ultrasonic generator, furnace with two different thermal zones and cyclone for produced powders capture. The starting solution was misted at a frequency of 2.4 MHz by an ultrasonic atomizer (HM-2412, Honda Electronics). The generated mist was carried to an electric furnace by air carrier gas with a rate of 7 dm<sup>3</sup>/min and then pyrolyzed at 1173 K. Structural properties of the products were investigated by XRD (XRD-6100, shimadzu), observed intensities were measured by both scanning and counting techniques with silicon as an internal standard. Surface morphology was investigated by SEM (S-2300, Hitachi) and specific surface area (SSA) by the BET method (Trystar3000, Shimadzu). The lithium secondary battery consisted of cathode materials, an Li sheet as the anode, a cellgard microporous membrane as the separator. The electrolyte solution was 1 mol/dm<sup>3</sup> LiPF<sub>6</sub> in DC/DME. Cathode materials were prepared using 80 wt.% calcined powders, 6 wt.% polyvinylidene fluoride (PVdF) as a binder and 6wt.% as acetylene black in 1-methyl-2-pyrrolidi-

none (NMP). The slurry was then coated onto an aluminum foil. The coated aluminum foil was dried at 393 K for 24h in a vacuum oven. The experimental battery was fabricated using stainless steel case and assembled in a glove box filled with argon gas. The charge/discharge capacity was measured galvanostatically between 2.5 and 4.2 V at a current density from 0.5  $\text{mA}/\text{cm}^2$ . All electrochemical measurements were carried out at room temperature on a battery tester (BTS-2004, Nagano).

### 3. RESULTS AND DISCUSSION

#### 3.1 Powder characteristics

Figure 1 shows typical particle morphology of as-prepared metal doped  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  powders by SEM photographs. As-prepared powders have a spherical particle shape with a mean diameter of about 0.9  $\mu\text{m}$ . The particle size ranged 0.4 to 3.4  $\mu\text{m}$ . The value of geometrical standard deviation calculated from the particle size distribution was 1.36, suggesting that the particle size distribution was narrow. Such morphology is sometimes observed when an ultrasonic spray pyrolysis was employed. SSA of as-prepared powders determined by BET method was less than 11.7  $\text{m}^2/\text{g}$ . After the calcinations at 1023 K, SSA decreased to 2.4  $\text{m}^2/\text{g}$ . Figure 2

shows X-ray diffraction patterns of metal doped  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  powders calcined for 10 hrs at 1023 K. The crystal phases of all samples were resulted in layered rock salt structure with  $R\bar{3}m$  space group. No impurity-related peaks are observed from the XRD pattern with various doping metals. However, the crystallinity of metal (Fe, Al or Mg) doped powders were lower than pure  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  powder. The lattice parameters were also calculated from the XRD patterns in Fig. 2. The a- and c-axes slightly

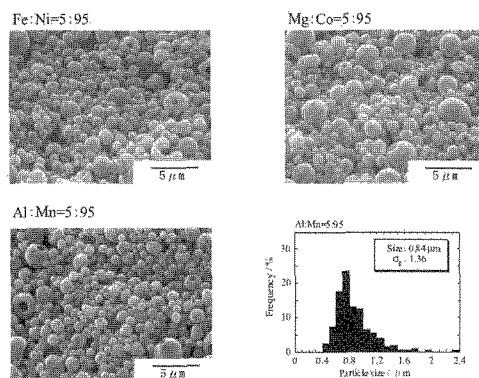


Fig. 1 SEM photographs of as-prepared metal doped  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  powders.

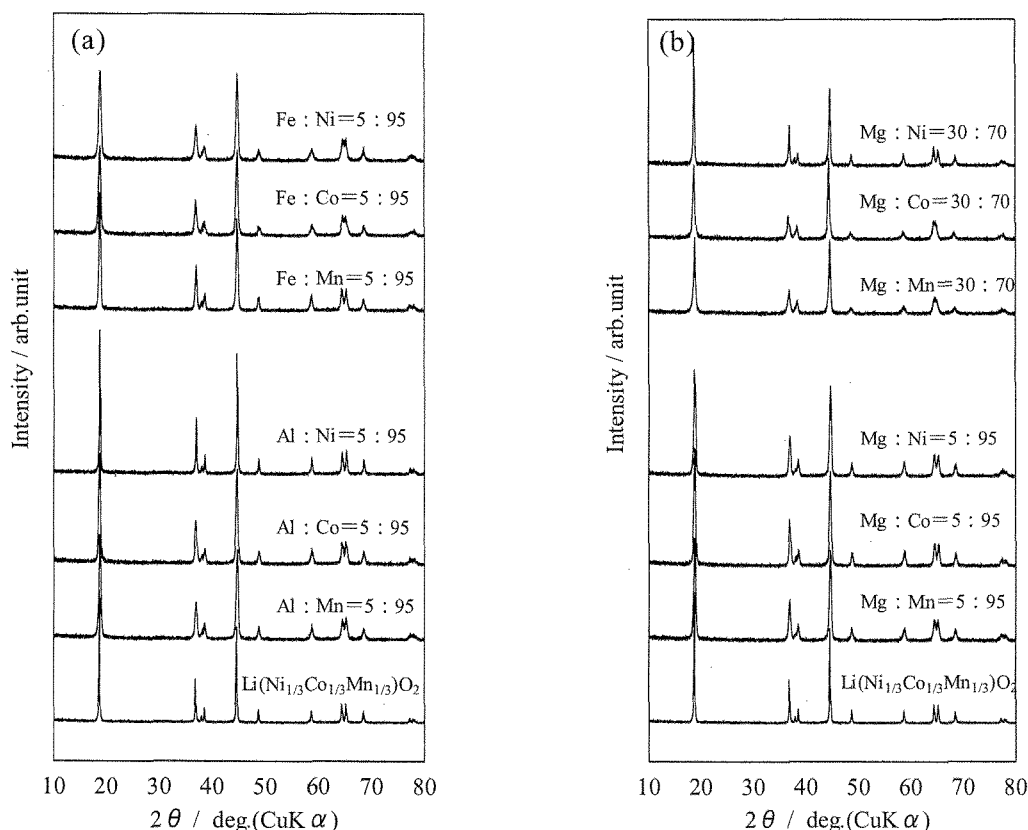


Fig. 2 XRD patterns of metal doped  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  powders calcinations at 1023 K for 10 hrs. (a):Fe or Al doped 5% (b):Mg doped 5% or 30%

Table I  
Lattice parameters of metal doped  
 $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  powders

Chemical composition	<i>a</i> (Å)	<i>c</i> (Å)
$\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$	2.862	14.260
Fe:Ni=5:95	2.858	14.179
Fe:Co=5:95	2.858	14.197
Fe:Mn=5:95	2.860	14.225
Al:Ni=5:95	2.856	14.209
Al:Co=5:95	2.858	14.217
Al:Mn=5:95	2.859	14.212
Mg:Ni=5:95	2.858	14.219
Mg:Co=5:95	2.858	14.217
Mg:Mn=5:95	2.860	14.209
Mg:Ni=30:70	2.858	14.245
Mg:Co=30:70	2.936	14.311
Mg:Mn=30:70	2.868	14.160

decreased when 5% Fe, Al or Mg are doped in Table I. However, the calculated parameters were slightly increased for 30% doping Mg because the ionic radius of  $\text{Mg}^{2+}$  is greater than those of  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{Mn}^{4+}$ . These results clearly confirm that various metals substitutions for Ni, Co and Mn sites were successful and the single phase was formed in the final product of  $\text{Li}[\text{Ni}_{(1/3-x)}\text{Mn}_{1/3}\text{Co}_{1/3}\text{M}_x]\text{O}_2$ ,  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{(1/3-x)}\text{Co}_{1/3}\text{M}_x]\text{O}_2$ ,  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{(1/3-x)}\text{M}_x]\text{O}_2$  (M=Fe, Al or Mg).

### 3.2 Electrochemical characteristics

Figure 3 shows the relation between discharge capacity and cycle number at rate of  $0.5 \text{ mA/cm}^2$  [(a) - (c)] or  $1.0 \text{ mA/cm}^2$  [(d)], which indicate an initial capacity of 143.1 mAh/g (non-dope), 142.4 mAh/g (Fe substitution for Co), 148.5 mAh/g (Mg substitution for Ni) and 144.6 mAh/g (Al substitution for Ni). The discharge capacity of  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  gradually decreased with increasing cycle number. Mg and Al doped  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  showed a very good cycling stability. The Mg substitution for Ni led to the most excellent results and then the discharge capacity was maintained at about 130 mAh/g after the 60th cycle. On the other hand, the capacity fading on cycling were observed for Fe(5%, substitution for Mn) and Mg(30%, substitution for Co and Mn) doped  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ . It thought that this result was caused by the crystallinity of powders obtained from Fe(5%, substitution for Mn) and Mg(30%, substitution for Co and Mn) were lower than the others.

## 4. CONCLUSION

Spherical metal (Fe, Al or Mg) doped  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$  precursor powders were synthesized by ultrasonic spray pyrolysis using aqueous solution of metal nitrate. As-prepared particles were spherical which have the average

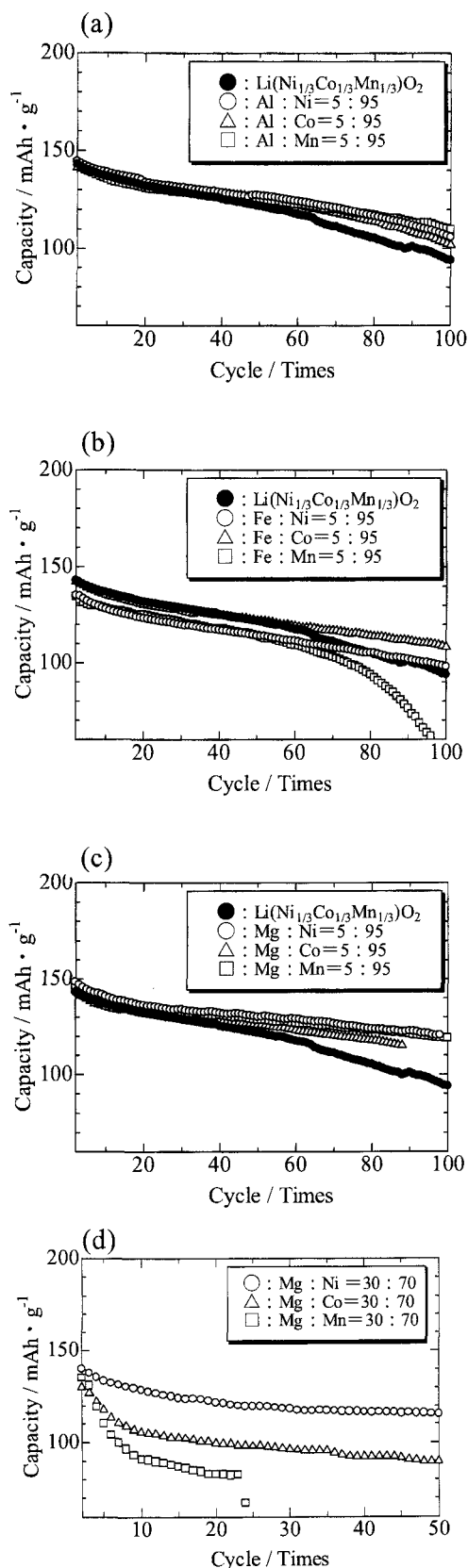


Fig.3 Cycle performance of lithium secondary batteries fabricated from metal doped  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  powders. (a)Al, (b)Fe and (c)Mg doped 5%, (d)Mg doped 30%

diameter of about 0.9  $\mu\text{m}$  with narrow size distribution of 1.4. The crystal phase of metal (Fe, Al or Mg) doped  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$  was resulted in layered rock salt structure with  $\overline{\text{R}3\text{m}}$  space group after calcinations at 1023 K, 10 hrs. No impurity-related peaks are observed from the XRD pattern with various doping metals. Mg and Al doped  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  showed a very good cycling stability. The Mg substitution for Ni led to the most excellent results and then the discharge capacity was maintained at about 130 mAh/g after the 60th cycle. On the other hand, the capacity fading on cycling was observed for Fe(5%, substitution for Mn) and Mg(30%, substitution for Co and Mn) doped  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ .

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