

Synthesis and Characterization of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Particle by Internal Combustion Type Spray Pyrolysis and Spray Drying

Kenichi MYOUJIN, Masayuki KOJIMA, Takashi OGIHARA,
Koji NAKANE and Nobuo OGATA

University of Fukui, 9-1 Bunkyo 3, Fukui-shi, Fukui, 910-8507 Japan

Fax: 81-0776-27-8624, e-mail: ogihara@matse.fukui-u.ac.jp

Spherical $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ precursor powders were synthesized different heating method by internal combustion type spray pyrolysis apparatus using gas burner. After calcinations of as-prepared powders contained Ni at different temperatures from 800 to 1200 °C in air for 10h, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were obtained. As-prepared particles have a porous microstructure with an average diameter of about 5 μm (spray pyrolysis) and 2 μm (spray drying) with narrow size distribution. The powder production capacity was 1 kg/h by this equipment. XRD showed that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were well crystallized to a spinel structure with Fd3m space group. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders calcined at 1000 °C shows good cycle performance with initial discharge capacity of 130 mAh/g and 93 % retention after 300 cycles between 3.5 V and 5.0 V. The most of electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders that spray drying method offered superior performance to spray pyrolysis method.

Key words: Lithium Manganese Oxides, Lithium Secondary Battery, Spinel, Spray Pyrolysis, Spray Drying

1. INTRODUCTION

Lithium ion secondary batteries are well regard as the power sources for the hybrid-type electric vehicles (HEV) and zero emission vehicles (ZEV) demand in the near future. It is also well known that LiCoO_2 , LiNiO_2 , and LiMn_2O_4 have great interest study [1-5]. Their materials combined with carbon anode can make 4.0 V rechargeable lithium ion secondary battery. However, LiCoO_2 as a cathode material in high density lithium battery is based on portable electronic devices. In order to obtain low cost, environment friendly and thermally stable secondary batteries, lithium manganese spinel is noted as cathode material of large lithium ion battery for electric car. Ni-substitute lithium manganese oxide spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has exhibited charge/discharge behavior in the 5.0 V range [6]. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ materials have attracted significant attention as a high-voltage cathode material and high-energy density. The spray pyrolysis system to prepare cathode materials of lithium ion battery is an effective production technique for the rapid and much powders production [7-9]. Using ultrasonic spray pyrolysis system, we have prepared cathode materials for lithium batteries [10,11]. The amount of powders prepared by ultrasonic spray pyrolysis system has only a maximum at 1.0 g/h. We have developed internal combustion type spray pyrolysis apparatus using gas burner [12]. Using a gas burner as the heat source can increase the speed of powder synthesis for lithium ion secondary battery cathode materials. In this work, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ precursor was synthesized from different heating method by internal combustion type spray pyrolysis. We investigated characteristics of as-prepared and calcined $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles such as crystallinity, morphology and electrochemical properties.

2. EXPERIMENTAL

LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled water in the molar ratio of metal components (Li:Ni:Mn=1.0:0.5:1.5) to prepare aqueous solutions of 0.5 mol/dm³. A schematic diagram of large scale internal combustion type spray pyrolysis using gas burner is shown Fig.1. The use of two-fluid nozzle atomizer, combustion furnace with gas burner and powder collector system with bag filter have made possible speedy to synthesize powders. The mist with 4 dm³/h of aqueous nitrate solution was generated with two-fluid nozzle atomizer. The average of droplet size of the mist was about 10 μm . The temperature in internal combustion furnace kept 500 °C. The production capacity of powders was 1 kg/h in this system. As-prepared powders obtained by this apparatus were

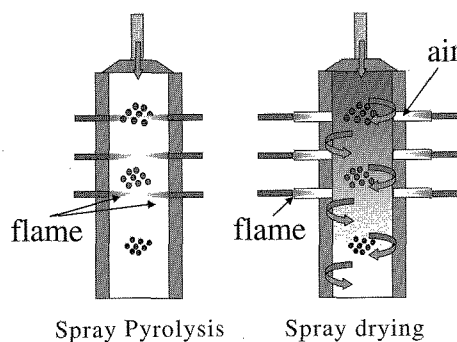


Fig.1 Schematic diagram of internal combustion type spray pyrolysis apparatus

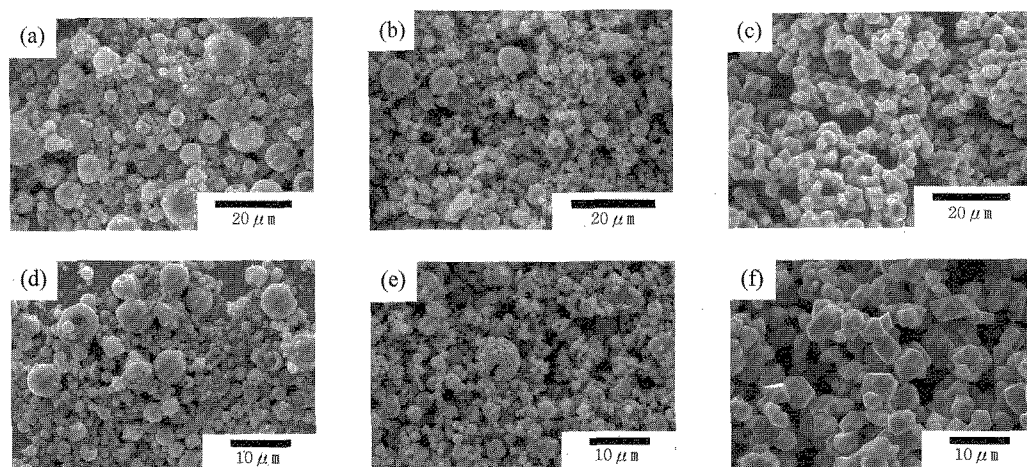


Fig.2 SEM photographs of as-prepared and calcined powders. (a)-(c): spray pyrolysis (d)-(e): spray drying (a),(d) as-prepared (b),(e) 800 °C (c),(e) 1000 °C

calcined between 800 and 1200 °C in air for 10h. The crystalline structure of as-prepared powders and calcined powders was characterized by X-ray diffraction (XRD, Shimadzu, XRD-6100). The surface morphology, microstructure and average size of as-prepared powders and calcined powders were also observed with a scanning electron microscope (SEM, Hitachi, S-2300). Electrochemical measurements were carried out using two-electrode coin-type cell (CR2032) with lithium foil as an anode. The cathode was composed of active materials (78 wt.%), acetylene black powders (13 wt.%) and polyvinylidene fluoride (PVdF, 9 wt.%) in 1-methyl-2-pyrrolidinone (NMP). The slurry was coated on an aluminum sheet, followed by drying at 120 °C for 24 h in a vacuum oven. The electrolyte was 1 mol/dm³

LiPF₆ in ethylene carbonate / diethyl carbonate (EC : DEC = 1 : 1) (Tomiya Pure Chemical). Lithium battery was assembled in a glove box filled with argon gas. The galvanostatic charge/discharge tests were measured between 3.5 V and 5.0 V at different current density on a battery tester (BTS-2004, Nagano).

3. RESULT AND DISCUSSION

3.1 Powder characteristics

Figure 2 shows SEM photographs of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders synthesized from different method and then calcined at 800 °C and at 1000 °C for 10 hrs. The average particle size of as-prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles determined by SEM photograph was about 5 μm (spray pyrolysis : SP) and 2 μm (spray drying : SD). As-prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders had spherical morphology with non-aggregation and consisted of primary particles with about 10 - 100 nm. The calcined powders at 1000 °C have regular shapes with well crystal faces.

Figure 3 shows the XRD patterns of as-prepared, calcined $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders and as-prepared LiMn_2O_4 powders. As-prepared LiMn_2O_4 powders has impurity peak of Mn_2O_3 , but all the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders have the standard spinel structure with a space group of Fd3m. Thus, Ni replaced part of Mn and 16d octahedral site. The lattice parameter increased as the

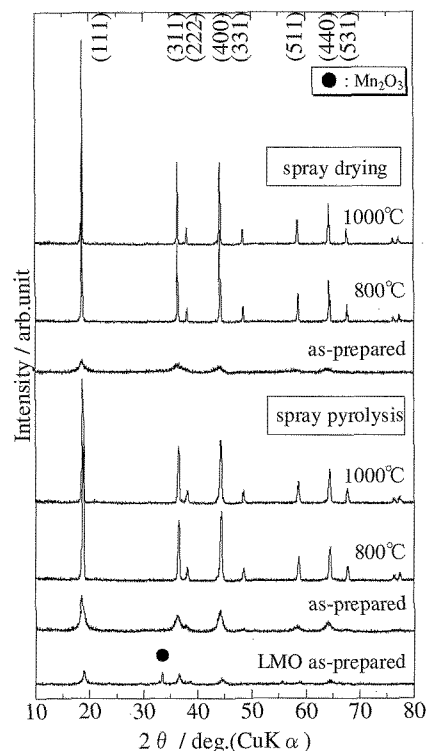
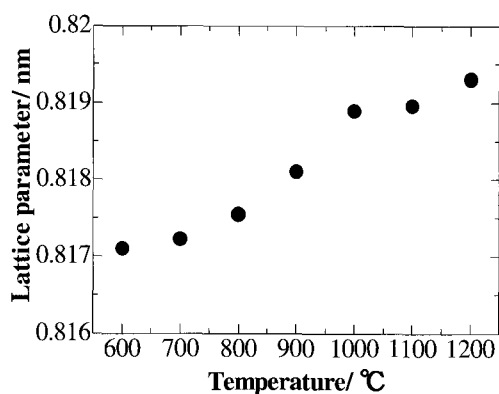


Fig. 3 XRD patterns of as-prepared and calcined $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders

calcination temperature increased (Fig.4). The oxygen deficiency in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ occurred at high temperature and the average valence of manganese ion would decrease owing to the charge balance compensation, implying some small fraction of Mn^{4+} (ion radius: 0.067 nm) is reduced to Mn^{3+} (ion radius: 0.079 nm) [13,14].

3.2 Electrochemical characteristics

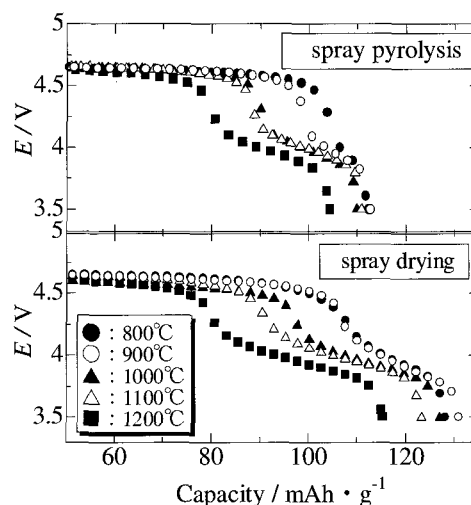
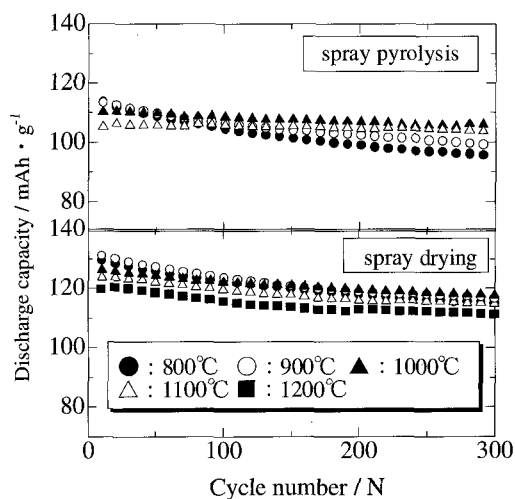
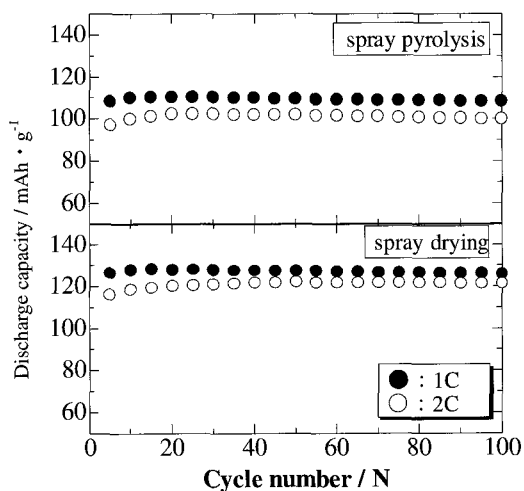
Figure 5 shows the first discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined various temperatures from 3.5

Fig.4 Lattice parameter of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

V and 5 V at rate of 1C, respectively. The discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (SP) calcined at 800 °C was 112 mAh/g. The two plateaus with a voltage jump were observed at 4.1 V and 4.6 V in the discharge curve and the discharge capacity decreased to 112 mAh/g with increasing calcined temperature. The 4.6 V plateau is caused by the redox reactions of $\text{Ni}^{2+}/\text{Ni}^{4+}$, while the 4.1 V plateau is caused by the redox reactions of $\text{Mn}^{3+}/\text{Mn}^{4+}$ [6]. And it corresponds with the consideration of the result of lattice parameter (Fig.4). The discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (SD) calcined at 800 °C and 1000 °C was about 130mAh/g. The discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined at 1200 °C decreased to 115 mAh/g. Figure 6 (SP) shows the cycle performance of calcined $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at various temperatures. The discharge curve of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined 800 °C has smallest plateau in all samples, but the discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined 800 °C was very poor cycle performance. More than 95 % of the initial discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined at 1000 °C was retained after 300 cycles. On the other hand, the discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders obtained from SD gradually decreased as increasing cycle number. More than 93 % of initial discharge capacity of calcined at 1000 °C was retained after 300 cycles. Figure 7 shows the cycle performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined 1000 °C at various discharge rates. All samples exhibited very stable cycle performance at the various discharge rates.

4. CONCLUSION

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were synthesized by internal combustion type spray pyrolysis apparatus using gas burner with production capacity of 1 kg/h. As-prepared powders had a homogeneous spherical form with a diameter of about 5 μm (spray pyrolysis) and 2 μm (spray drying) with narrow size distribution. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders calcined at all temperatures were crystallized to a spinel structure with Fd3m space group. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders calcined at 1000 °C shows good cycle performance with initial discharge capacity of 112 mAh/g and 95 % retention after 300 cycles (spray pyrolysis). On the other hand, the discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders obtained from spray drying was 130 mAh/g and 93 % retention

Fig.5 Discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 1CFig.6 Cycle performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 1CFig.7 Cycle performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined 1000 °C at various discharge rates

after 300 cycles. The most of electrochemical properties of LiNi_{0.5}Mn_{1.5}O₄ powders that spray drying method offered superior performance to spray pyrolysis method.

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