

Synthesis of Lithium Manganate Powders by Spray Pyrolysis and its Application to Lithium Ion Batteries for Trams

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Spinel type lithium manganate nanopowders were prepared by spray pyrolysis using metal nitrate solution. Chemical analysis and X-ray diffraction showed that homogeneous and high purity lithium manganate powders were obtained. The charge/discharge capacity of lithium manganate was 110mAh/g at 1C. A lithium ion battery module was also developed for the tram and its performance examined. The energy and power density of lithium ion cells were 110Wh/kg and 1920W/kg, respectively. The performance of a tram using a 20kWh type lithium ion battery module was examined. The tram ran for 20km on one charge.

Keywords: Lithium Ion Battery, Tram, Vehicles, Battery Pack, Powders

1. INTRODUCTION

Lithium ion batteries have been extensively used as energy storage devices for portable electronics, including notebook PCs, mobile phones and digital cameras. Lithium cobalt oxide (LiCoO_2) [1] is generally used as the cathode material of commercial lithium ion batteries due to its high energy density and excellent cyclic life. However, a more widespread application of LiCoO_2 is restricted by the rare resource of cobalt and its toxicity. Lithium manganate (LiMn_2O_4) [2] is regarded as a promising candidate for the replacement of LiCoO_2 because of its high output voltage, high safety, low toxicity and low cost. Recently, lithium manganate was utilised as cathode material in a large lithium ion battery suitable for vehicles such as cars, buses and trams. Lithium manganate powders have been usually prepared by solid state reaction between lithium salt and manganese oxide. Many preparation techniques have been proposed to improve the electrochemical performance of lithium manganate since the power density and discharge capacity of lithium manganate powders derived from solid state reaction is low.

Spray pyrolysis for powder processing has been used to prepare cathode materials of lithium ion batteries and potentially offers the following advantages [3-5]: (1) the particles are spheres of submicrometre size with a narrow size distribution and have large surface areas, (2) the chemical homogeneity is enhanced as compared with that of powder prepared by solid state reaction, and (3) oxide or metal powders can be prepared directly,

in much shorter time than that required for solid state reaction. Lithium transition metal double oxide [6-8] has been already successfully prepared by spray pyrolysis. Cathode materials prepared by spray pyrolysis exhibited higher charge/discharge capacity and long life cycle compared with those obtained from solid state reaction. We previously developed an internal combustion type of large spray pyrolysis system [9] in which a two-fluid nozzle was used as an atomiser and a gas burner was used as a heat source of the furnace.

In this paper, the electrochemical properties and battery performance of lithium manganate powders obtained by spray pyrolysis were investigated. The running performance of one tram run on a large lithium ion battery is also described.

2. EXPERIMENTAL

LiNO_3 and $\text{Mn}(\text{NO}_3)_2$ were used as starting materials. LiNO_3 and $\text{Mn}(\text{NO}_3)_2$ were weighted out to provide the

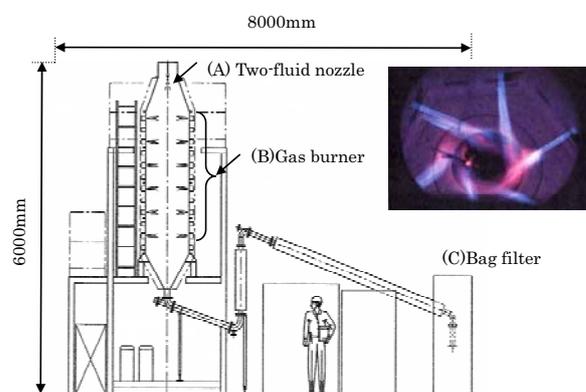


Fig 1 Schematic diagram of spray pyrolysis apparatus

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molar ratio of metal components (Li:Mn) of 1.08:2 and were dissolved in double distilled water to prepare aqueous solutions of 1.0 mol/dm^3 . A schematic diagram of the internal combustion type spray pyrolysis apparatus is shown in Fig.1. This apparatus consisted of a two-fluid nozzle (A) atomiser, a combustion furnace with six gas burners (B), and a powder collector system with bag filter (C). The mist of aqueous nitrate solution was generated with the two-fluid nozzle atomiser at $4 \text{ dm}^3/\text{hr}$. The average droplet size of mist was about $10 \mu\text{m}$.

LP-gas was used as the gas source. The flame temperature of the gas burner in the combustion furnace was 500°C . The potential of powder production was 1 kg/hr using this system. The average particle size, morphology and microstructure of the as-prepared powders were observed with a scanning electron microscope (SEM).

The crystal phase of the as-prepared powders was identified by powder X-ray diffraction (XRD). Chemical composition of as-prepared powders was analysed by atomic absorption spectrometry (AAS).

Cathode was prepared using 80 wt% lithium manganate powders, 10 wt% acetyleneblack and 10 wt% fluorine resin. Lithium manganate powders were mixed with acetylene black and fluorine resin to obtain slurry, then coated on aluminum sheet using doctor blade.

Hard carbon and graphite was used as an anode. Micro porous polypropylene sheet was used as a separator. $1 \text{ mol/dm}^3 \text{ LiPF}_6$ in ethylene carbonate / 1,2-dimethoxyethane (EC : DME = 1 : 1) was used as the electrolyte. Lithium ion battery was assembled in a globe box under an argon atmosphere. Change of voltage during charge/discharge was measured with a battery tester (BTS2004, Nagano Co., Ltd) at between 3.0 V and 4.3 V.

3. RESULTS AND DISCUSSION

A representative SEM photograph of the as-prepared lithium manganate powders is shown in Fig.2. The as-prepared lithium manganate particles can be seen to have spherical morphology with non-aggregation. The particle size was seen to range from 10 nm to $5 \mu\text{m}$ from

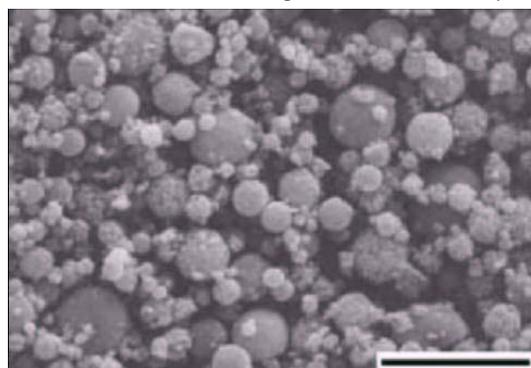


Fig. 2 SEM photograph of as-prepared powders

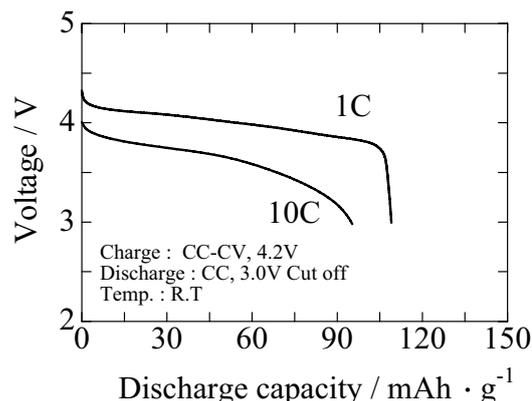


Fig.3 Discharge curves of the cell with lithium manganate at 1C and 10C (Anode: graphite, 2032 type coin cell)

the SEM photograph. The average particle size was determined from measurement of particle diameter by randomly sampling 100 particles from SEM photographs. The average particle size of the as-prepared lithium manganate particles was about $2 \mu\text{m}$. Specific surface area measured by the BET method was $2 \text{ m}^2/\text{g}$. XRD patterns showed the as-prepared lithium manganate powders were well crystallised to spinel structure with a space group (Fd3m). Diffraction lines except for the spinel phase were not observed. AAS analysis showed that the molar ratio of Li/Mn was kept at the starting solution composition.

The electrochemical properties of lithium manganate cathode were investigated using 2032 type coin cells. Figure 3 shows the first discharge curves of the cells with lithium manganate cathode at 1C and 10C. The discharge capacity for the cell with lithium manganate cathode was 110 mAh/g at 1C. The discharge capacity of lithium manganate cathode decreased to 96 mAh/g at 10C. Figure 4 shows the relation between charge/discharge capacity and cycle number up to 2000 cycles. The charge and discharge rate was 1C. The charge and discharge capacity were maintained at about

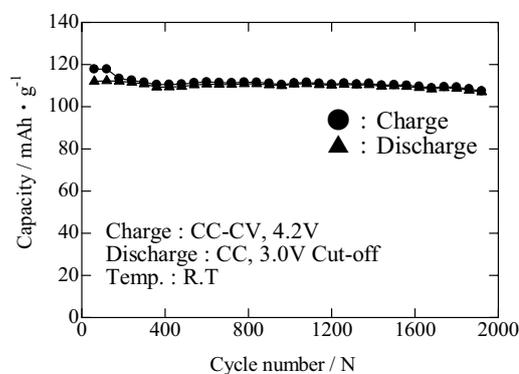


Fig. 4 Relation between cycle number and discharge capacity at 1C (Anode: graphite, 2032 type coin cell)

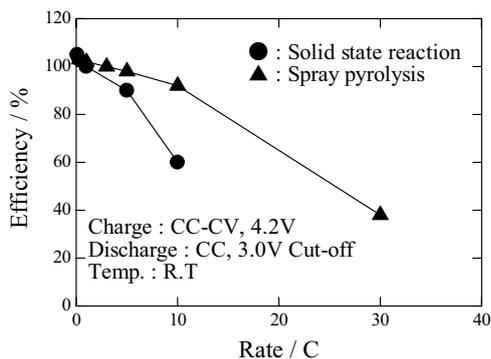


Fig. 5 Relation between discharge rate and discharge efficiency (Anode: graphite, 2032 type coin cell)

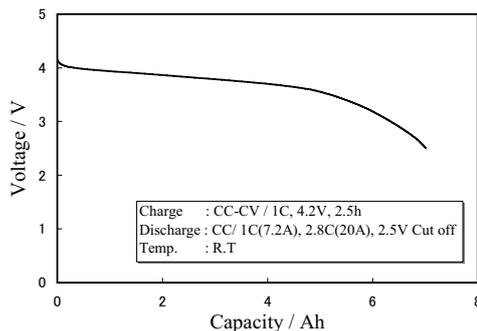


Fig. 7 Relation between voltage and capacity (Anode: mixture of hard carbon and graphite)

110mAh/g at 1C after the 2000th cycle. The charge and discharge capacity for the cell with lithium manganate was constant until 2000 cycles and stable cycle performance was exhibited.

Figure 5 shows the relation between the discharge rate and discharge efficiency. To compare the power of battery, lithium manganate cathode fabricated by commercial lithium manganate powders which were prepared by solid state reaction was used. The discharge efficiency of lithium manganate cathode fabricated by lithium manganate powders derived from spray pyrolysis was 90% at 10C. That with lithium manganate cathode fabricated by commercial powders was 60%. The discharge efficiency of the cell with lithium manganate cathode fabricated by lithium manganate powders prepared by spray pyrolysis decreased to 30% at 30C.

On the other hand, lithium manganate cathode fabricated by commercial powders was not discharged at 30C. This suggests that the electrochemical properties of lithium manganate powders derived from spray pyrolysis are superior to commercial lithium

manganate powders. To obtain a large lithium ion battery module, a layered type laminate cell sheet (Fig.6) was produced by using a mixture of graphite and hard carbon as anode materials.

Figure 7 shows the discharge curve of the laminate sheet type lithium ion cell. The energy and power density of lithium ion cell determined by the discharge curve were 110Wh/kg and 1920W/kg, respectively. A lithium ion battery module for trams was also developed and its performance was examined. One

Table 1 Specification of 20 kWh module

Item	Type
Average output voltage	636V
Operation voltage range	430 - 680V
Capacity	30Ah
Maximum discharge current	150A
Weight	192kg
Size	D700 x W500 x H450mm



Fig. 6 Laminate sheet type lithium ion cell (Weight: 190g, D170mm x W160mm x H5mm)



Fig. 8 20kWh type lithium ion battery module



Fig. 9 Nagoya railroad moha 682 type tram (DC600V, Weight: 13.2t)

lithium ion battery submodule consisted of 108 lithium ion cells that were connected in series.

Figure 8 shows the photograph of the 20 kWh module with a weight of 192kg which consisted of six lithium ion battery submodules. Table 1 shows the specification of the module. The rating of one lithium ion battery module was 636V and 30Ah.

Figure 9 shows the photograph of a tram (Nagoya Railroad, moha 682 type) in which the lithium ion battery module was set up. The weight of the tram was 13.2t. The running test was carried out at Nishitakefuyard at Fukui railway.

Figure 10 shows the relation between running time and voltage, current and integrating watt. The tram was run when the module was discharged between 620V and 540V. The electric power of 20kWh was consumed for 3700s. It was confirmed that a current of 150A flowed to the module when the tram was accelerated up to 50km/hr. Afterward, the current decreased to 20A and the current of 150A flowed again in the module after the tram had accelerated. The tram ran while repeating this behavior.

Figure 11 shows the relation between running time and temperature of the module. Temperature gradually

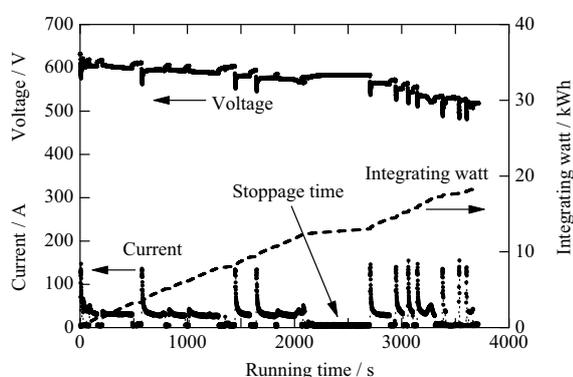


Fig.10 Relation between running time and voltage, current and integrating watt

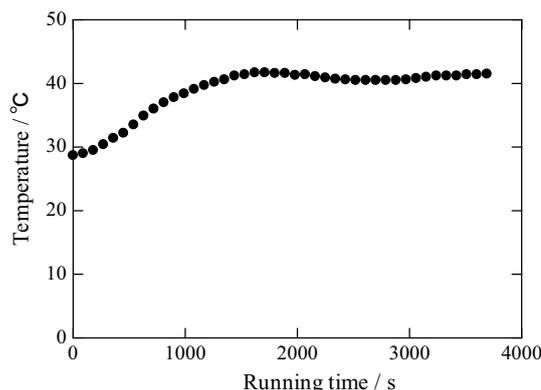


Fig.11 Relation between running time and temperature of module

increased with increasing running time. After 3700s, the temperature of the module reached up to 43°C. On one charge, the tram could run for about 20km. It was found from the running test that the mileage was 1km/kWh and the maximum speed of the tram was 50km/hr.

It was confirmed that lithium manganate powders prepared by the above-mentioned method were suitable as the cathode materials of lithium ion battery. As compared with the lithium manganate powders prepared by solid state reaction and spray drying, the particle size distribution is narrow and the dispersibility of particles is good. Therefore, it is thought that high packing density of cathode is achieved and then shows excellent electrochemical properties such as high power and energy density. In future, the capacity of lithium ion battery module will be increased up to 60kWh and the running test of a tram with the weight of 40t (Nagoya Railroad, moha 600 type) will be conducted and its practical application evaluated. Furthermore, it is also expected that lithium ion battery with lithium manganate will be utilised as a battery for the pure electric bus and truck.

4. CONCLUSION

Spherical and homogeneous lithium manganate powders were synthesised by spray pyrolysis. The as-prepared powders were well crystallised to the spinel structure with Fd3m space group. The discharge capacity of lithium manganate was 110mAh/g at 1C and offered stable cycle performance. The energy and power density of the lithium ion battery module were 110Wh/kg and 1920W/kg, respectively. The lithium ion battery module of 20kWh was utilised in a tram and ran for about 20km on one charge. The mileage was 1km/kWh. The maximum speed attained was 50km/hr.

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REFERENCES

- [1] K.Mizushima, P.C.Jones, P.J.Wiseman and J.B. Goodenough: "Li_xCoO₂ (0<X<1): A New Cathode Material for Batteries of High Energy Density", Mater.Res.Bull., Vol. 15, pp.783-789, 1980.
- [2] D.Guyomard and J.M.Trascon: "The Carbon / Li_{1+x}Mn₂O₄ System", Solid State Ionics, Vol. 69, pp. 222-237, 1994.
- [3] G.L.Messing, S.C.Zhang and G.V.Javanthi: "Ceramic Powder Synthesis by Spray Pyrolysis", J.Am.Ceram. Soc., Vol. 76, pp.2707-2726, 1993.
- [4] H.Ishizawa, O.Sakurai, N.Mizutani and M.Kato: "Homogeneous Y₂O₃ Stabilized ZrO₂ Powders by Spray Pyrolysis Method", Am.Ceram.Soc.Bull., Vol. 65, pp.1399-1402, 1986.
- [5] B.Dubois, D.Ruffier and P.Odier: "Preparation of Fine, Spherical Ytria-Stabilized Zirconia by the Spray – Pyrolysis Method", J.Am.Ceram.Soc., Vol. 72, pp.713-715 1989.
- [6] T.Ogihara, N.Ogata, S.Yonezawa, M.Takashima and N.Mizutani: "Synthesis of Porous LiNiO₂ Powders by Ultrasonic Spray Pyrolysis and Their Cathode Property", Denki Kagaku, Vol. 66, pp.1202-1205, 1998.
- [7] I.Taniguchi and Z.Bakenov: "Spray Pyrolysis Synthesis of Nanostructured LiFe_xMn_{2-x}O₄ Cathode Materials for Lithium-Ion Batteries", Powder Technol., Vol. 159, pp. 55-62, 2005.
- [8] S.H.Park and Y.K.Sun: "Synthesis and Electrochemical Properties of 5V spinel LiNi_{0.5}Mn_{1.5}O₄ Cathode Materials Prepared by Ultrasonic Spray Pyrolysis Method", Electrochimica Acta, Vol. 50, pp.431-434, 2004.
- [9] K.Myojin, T.Ogihara, N.Ogata, N.Aoyagi, H.Aikiyo, T.Ookawa, S.Omura, M.Yanagimoto, M.Uede and T.Oohara: "Synthesis of Nonstoichiometric Lithium Manganate Fine Powders by Internal Combustion Type Spray Pyrolysis Using Gas Burner", Advanced Powder Technol., Vol. 15, pp.397-403, 2004.



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