

Development of Pure Electric Bus with Mn type Li-ion Battery

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Aluminum-doped lithium manganese powders were successfully produced by internal combustion-type spray pyrolysis using metal nitrate solution. As-prepared particles with an average diameter of about 4 μm had a porous microstructure and were nonagglomerated. Chemical analysis showed that the molar ratio of Li/Mn and the content of Aluminum were kept contact with the starting solution concentration. A lithium ion battery module for electric vehicle (EV) was also developed and its performance was examined. A 53 kWh lithium ion battery module was set on an electric microbus, and then its performance was examined.

Keywords: Lithium Ion Battery, Electric Vehicle, Electrode, Cathode, Powders, Manganese.

1. INTRODUCTION

Recently, as a measurer for energy-saving global warming measure, the use of new energy systems, such secondary batteries, fuel cells, and super-capacitors, has been expected to reduce carbon dioxide discharge. In particular, 24 % of total energy consumption and 20 of carbon dioxide discharge are attributed to the transportation section. So far, it is important to develop an energy-saving car. Thus, Pb and NiH batteries have been used for EV and HEV. From the viewpoint of battery performance characteristics, such as weight, energy and power density, a lithium ion battery is expected to be the candidate battery for EV and HEV. There are two types of typical lithium ion battery, i.e., LiCoO_2 [1] and LiMn_2O_4 [2]. LiCoO_2 is commercially applied in a portable telephone, a computer, a video, a digital camera as a high-energy-density power storage. However, the rare source of Co and its chemical activeness will obstruct mass use of LiCoO_2 .

As the solution, LiMn_2O_4 is proposed to be an alternative cathode material owing to its lower cost and higher output voltage than LiCoO_2 . LiMn_2O_4 is expected to be a cathode material of a large lithium ion battery for EV, such as cars, buses and railways. It should be used in EV to improve cycle time and heat resistance by doping a foreign element. As the foreign elements, Al, Mg and Cr have been used. In this work, a lithium ion battery in which aluminum-doped LiMn_2O_4 was used as a cathode was employed as a power source in a microbus. Currently 50,000 domestic microbuses are produced every year. About 10,000 of them are add to domestic every year. In addition, 140,000 microbuses are present in the whole country. Since most of these microbuses are run by a diesel engine, a much toxic substance, such as NO_x , CO_2 or Sox , is emitted by these microbuses.



Figure 1: Electric bus

This problem will be solved by using an electric microbus (Figure 1) in which a lithium ion battery is used as a power source. Battery characteristics, such as a long life cycle, heat-resistance and high power energy densities for electric microbuses. We have already succeeded in the production of LiMn_2O_4 [3]

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cathode materials in which the above-mentioned characteristics were satisfied. In this paper, a method of preparing lithium manganese powders by spray pyrolysis was reported. The electrochemical properties and battery performance of lithium manganese were presented. The performance of a pure electric bus by a large lithium ion battery was also described

2 Experimental Procedure

LiNO_3 , $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as starting materials. LiNO_3 and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were weighed to attain a molar ratio of metal components (Li:Mn) of 1:2 and dissolved in distilled water to prepare 1.0 mol/dm^3 starting aqueous solutions. The concentration of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ranged from 5 to 10 mol% for $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. A schematic diagram of a large internal combustion-type spray pyrolysis apparatus is shown elsewhere [4]. This apparatus consisted of a two-fluid nozzle atomizer, a combustion furnace with a gas burner, and a powder collector system with a bag filter. The mist of aqueous nitrate solution was generated with the two-fluid nozzle atomizer with $4 \text{ dm}^3/\text{hr}$ as the fuel. The average droplet size of the mist was about $10 \mu\text{m}$. LP-gas was used as a gas source. The central temperature of gas burner in combustion furnace was 500°C . The potential of powders production was 1kg/hr in this system. The particle morphology and microstructure of as-prepared powders were observed by scanning electron microscopy (SEM, Hitachi, S-2300). The average particle size was determined from the particle diameter measured by randomly sampling 200 particles from SEM photographs. The crystal form of as-prepared powders was determined by powder XRD. The chemical composition of as-prepared powders was measured by atomic absorption spectrometry (AAS, Shimadzu, AA-6800). Cathodes were prepared using 80 wt% lithium manganese powders, 10 wt% acetylene black and 10 wt% fluorine resin. Lithium manganese powders were mixed with acetylene black and fluorine resin to obtain slurry, and then coated on an aluminum sheet using a doctor blade. Metal lithium (The Honjo Chemical Corporation) or graphite (Osaka Gas) was used as an anode. The celgard (Heist Japan, Co., Ltd.) was used as a separator. $1 \text{ mol} \cdot \text{dm}^{-3} \text{ LiPF}_6$ in ethylene carbonate/1,2-dimethoxyethane (EC: DME = 1 : 1, Tomiyama Pure Chemical) was used as an electrolyte. A lithium ion battery was built up in a globe box under an argon atmosphere. The change in voltage during charge/discharge was measured with a potentiostat (Hosen, Battery cyler) between 3.5 and 4.3 V.

3 Results and Discussion

3.1 Powder characteristics and electrochemical properties of lithium manganese powders

A SEM photograph of aluminum-doped lithium

manganese powders obtained by spray pyrolysis is shown in Figure 2. The SEM photograph showed that as-prepared lithium manganese particles are spherical and have an average size of $4.0 \mu\text{m}$. As-prepared powders had also a porous microstructure. The specific surface area determined by the Brunauer-Emmett-Teller (BET) method was about $4 \text{ m}^2/\text{g}$. AAS revealed that the chemical composition of as-prepared powders is in good agreement with the starting solution component. It was also confirmed by XRD that aluminum ions are homogeneously doped in lithium manganese. The lattice parameter of the lithium manganese crystal decreased with increasing aluminum ion content.

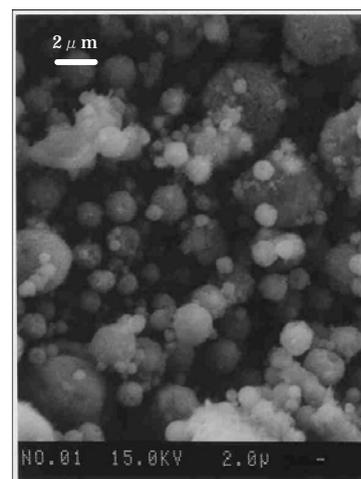


Figure 2: SEM of aluminum doped lithium manganese powders.

Figure 3 shows the electrochemical characteristics of lithium manganese and aluminum (5mol%)-doped lithium manganese between 3.5 and 4.3V. The discharge capacity of lithium manganese was 130 mAh/g at 0.5C. The voltage jump was cured at 4.1 V. The discharge capacity decreased to 120 mAh/g with the addition of

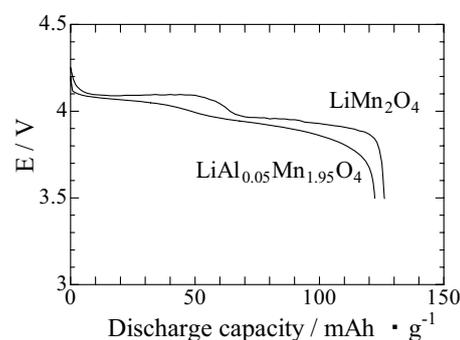


Figure 3: Discharge curves of lithium manganese and aluminum doped lithium manganese.

aluminum ions. However, an S-shaped discharge curve

was obtained and a clear voltage jump disappeared at 4.1 V with the addition of aluminum ions to lithium manganese. This finding suggests that the electrochemical reaction of lithium manganese during lithium insertion and desertion is a homogeneous phase reaction. This leads to the improvement of cycle performance.

Figure 4 shows the change in discharge capacity as a function of cycle number. The discharge capacity of lithium manganese gradually decreased with increasing

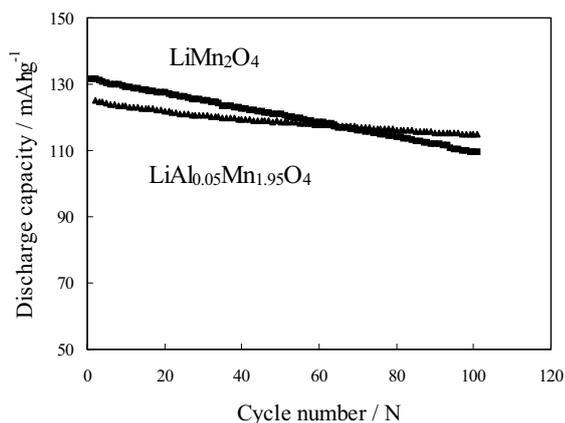


Figure 4: Cycle performance characteristics of lithium manganese and aluminum-doped lithium manganese.

cycle number, while the decrease in discharge capacity was mitigated in aluminum-doped lithium manganese.

Figure 5 shows the relationship between discharge capacity and cycle number at 60°C. The charge and discharge capacities were maintained at about 80mAh/g after the 30th cycle. It was found that the lithium ion battery functions at 60°C.

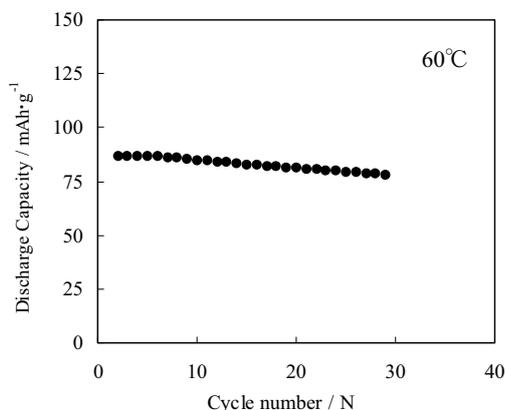


Figure 5: Cycle performance characteristics of Aluminum-doped lithium manganese at 60°C.

3.2 Development of lithium ion battery module

Figure 6 shows a photograph of a layered type laminate sheet cell. To obtain a large lithium ion battery module, the layered type laminate sheet cell



Figure 6: Layered type laminate sheet cell.

(160×170×5.3mm) was produced using a mixture of graphite and hard carbon as anode materials.

Figure 7 shows the discharge curves of the laminate sheet cell, and shows the cell can be used at 40 to -20°C. A total of 1600 sheet cells were used to build up a lithium ion battery module with an electrical capacity of about 53kWh. The weight of such a module was about 480kg.

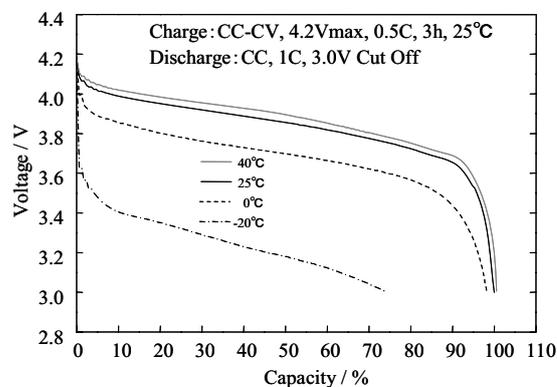


Figure 7: Discharge curves of laminate sheet cell from 40 to -20°C.

Figure 8 shows the discharge curves of the laminate sheet cell. The energy density was 130 Wh/kg at a state of charge (SOC) of 100%. The power density at a SOC of 100% estimated from that measured at a SOC of 30% was 2250W/kg.

Figure 9 shows DC impedance as affected cycle number. The inner resistance was about 7 mΩ from DC impedance. The inner resistance was very low and remained constant during charge and discharge. This suggests that the laminate sheet cell has a high reliability in the electrochemical reaction. The lithium

ion battery module was put on the electric microbus based on Mitsubishi Rosa. The results of a running test were examined at a test course in National Institute of Advanced Industrial Science and Technology. The running performance characteristics of the microbus, such as maximum speed, running distance and accelerating power, were investigated.

Aluminum-doped lithium manganese powders were successfully produced by internal combustion-type spray pyrolysis. Spherical, homogeneous lithium manganese particles were obtained.

The addition of aluminum ions to lithium manganese led to the improvements in the heat-resistance and cycle time of a lithium ion battery. The charge and discharge of the lithium ion battery could be done from 40 to -20°C . DC impedance was stable during 300 cycles. The discharge capacity of lithium manganese was 120 mAh/g at 0.5C. The energy and power densities of laminate sheet cell were 130 Wh/kg and 2250 W/kg, respectively. A large lithium ion battery module was made from the laminate sheet cell. The electric capacity of the module was 53kWh.

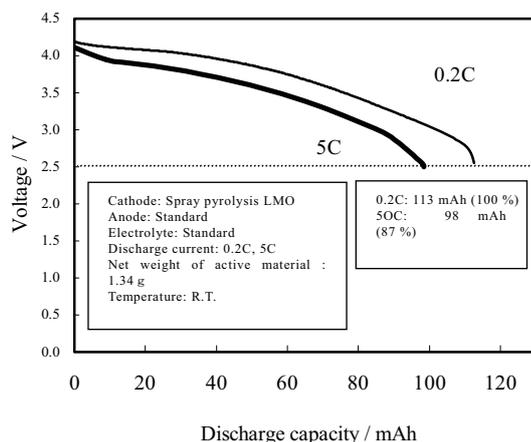


Figure 8: Discharge curves of laminate cell.

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