Development of Mn-type Lithium-Ion Batteries and Study for a Pure Electric Buses Applications

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From the viewpoint of reducing carbon dioxide emissions, the practical use of electric buses has been expected to be one of the effective solutions to global warming. Even though lithium-ion batteries using lithium manganese oxide have been studied for use in electric vehicles, it is still necessary to improve their characteristics such as energy density, maximum operating temperature and cycle performance. Manganese oxide lithium-ion batteries for an electric bus developed by internal-combustion spray pyrolysis methods and its performance in an actual road test have been studied. The performance of the electric bus was satisfactory; the bus could run for 74 km on a full charge.

Key Words : Lithium-Ion Batteries, Electric Bus, Spinel Type, Spray Pyrolysis, Energy Saving

1 Introduction

As a measure against global warming, the reduction in carbon dioxide emissions is required. Electric vehicles (EVs) are effective for achieving this aim. Electric buses are effective for reducing carbon dioxide emissions because public transport vehicles are used for mass transport. Therefore, a further reduction of carbon dioxide emissions is possible if diesel-engine buses are replaced with electric buses.

Conventionally, the power sources of electric buses have been lead-acid batteries.¹⁾ However, many batteries must be mounted because their energy density and power density are small. As a result, the vehicle body becomes heavy and riding capacity is reduced.

Spinel-type lithium manganese oxide batteries have been proposed owing to their lower cost, greater safety and greater quantity of natural resources than lithium cobalt oxide lithium batteries. Therefore, their applications in EVs, railcars²⁾ and electric energy storage devices have been encouraged. However, lithium manganese oxide batteries exhibit a marked deterioration in their cycle performance and maximum operating temperatures at high temperatures.^{3, 4)} Therefore, their improvement is an issue that must be resolved in order to apply them as a power supply of electric buses.

As a method of improving the properties of spinel-type lithium manganese oxide batteries, doping with different types of metals has been reported to be effective.^{5, 6)} On the other hand, at University of Fukui, internal-combustion spray pyrolysis, which enables the production of cathode materials with doped aluminum for lithium-ion batteries, has been developed.^{7, 8)} When this technique is used, cathode materials can be produced in large quanti-

ties at a low cost. Furthermore, the particles produced are small, leading to the improvement in the performance of lithium-ion batteries.

In this study, to improve battery cycle performance and maximum operating temperature, the cathode materials of lithium-ion batteries were produced by internal-combustion spray pyrolysis with doped aluminum and the electrochemical characteristics of the batteries were examined. Furthermore, the cathode materials produced by this method were used for the lithium-ion batteries. These batteries were mounted on the electric bus developed by the authors^{9, 10)} and the battery characteristics were examined in running tests.

2 Requirements for Batteries

The target specifications required for the practical use of electric buses and the battery performance required to achieve these targets were found by a numerical formulas.

2.1 Demand specifications of electric bus

The following specifications are required for the electric bus.

(a) Distance covered km: More than 50 km

Because 65.1% of community buses follow a course less than 20 km in length, the target distance covered km of the electric bus was more than 50 km.

(b) Battery life: More than three years

It is assumed that the battery price will in the future become one-twentieth of the current price; for the cost of an electric bus battery to become equal to that of a battery for a diesel bus, the battery life should be more than three years.

(c) Maximum power: 120 kW

The maximum power of a motor installed in an electric bus 120 kW.

(d) Possible use under summer temperature conditions

Lithium-ion batteries have maximum operating temperature problems.

2.2 Required specifications of lithium-ion batteries

Author calculates demand specifications of the battery for the electric bus as follow; it gives a detailed description.

2.2.1 Required specifications of the cathode of the cells

To remodel a diesel-engine bus into an electric bus, the weight of the batteries to be mounted was investigated. The engine, transmission and fuel tank were removed from the diesel-engine bus. Their gross weight was about 700 kg. The total weight of the motor and inverter installed in the electric bus was about 200 kg. Therefore, the weight of the batteries must be less than 500 kg.

The energy consumption rate (E_c) of the electric bus was assumed to be 2 km/kWh, as predicted from a simulation result. When the capacity deterioration (η_1) due to aging was estimated to be 30%, and the available capacity rate (η_2) of the batteries was assumed to be 90%, the required battery energy (C_b) for the electric bus to run 50 km (D) was calculated as follows.

$$C_b = D \cdot (1 - \eta_1) \cdot \eta_2 / E_c \quad (1)$$

Substituting into $D = 50$ km, $E_c = 2$ km/kWh, $\eta_1 = 0.3$ and $\eta_2 = 0.9$ Eq. (1), the required battery energy (C_b) was 40 kWh.

The weight of the cells was 80% of the weight (W_{b1}) of the battery modules. The target gross weight (W_{b2}) of the cells and their target energy density (E) were calculated as follows.

$$W_{b2} = W_{b1} \cdot 0.8 \quad (2)$$

$$E = C_b / W_{b2} \quad (3)$$

Substituting $W_{b1} = 500$ kg into Eq. (2), the gross weight (W_{b2}) of the cells was 400 kg.

Substituting $C_b = 40$ kWh and $W_{b2} = 400$ kg into Eq. (3), the energy density (E) of the cells was 100 Wh/kg.

The average weight of the cathode materials to be used in the cells was 30% of the whole cell weight. Therefore, the target capacity (P_{ah}) of the cathode materials was calculated as below. In the calculation, the average voltage (V_c) of the cells was assumed to be 3.8 V.

$$P_{ah} = E / (V_c \cdot 0.3) \quad (4)$$

Substituting $E = 100$ Wh/kg and $V_c = 3.8$ V into Eq. (4), the discharge capacity (P_{ah}) was 90 mAh·g⁻¹.

2.2.2 Required specifications of the cells The structure of each cell was of the laminated layered type, which has better safety and heat radiation characteristics than the cylindrical type.

Because the gross weight (W_{b2}) of each cells was 400 kg and the weight (w_c) of each cell was almost 250 g, the

total number (N) of cells was calculated as follows.

$$N = W_{b2} / w_c \quad (5)$$

Substituting $W_{b2} = 400$ kg and $w_c = 250$ g into Eq. (5), the total number (N) of cells was 1,600.

The voltage range of the inverter for the main motor is 250 V – 425 V. On the other hand, the voltage range of the cell is 3.0 V – 4.2 V. Therefore, the battery modules consisted of 90 cells connected in series, and the voltage range of the battery modules was assumed to be 270 V – 378 V. Considering convenience in practical use, 15 series (45 V – 63 V) were chosen for one module. Therefore, the required specifications of the cell were calculated as follows.

(a) Energy density

The target energy density of the cells was 100 Wh/kg, as determined using Eq. (3).

(b) Number of cells connected in parallel (P_n)

$$P_n = W_{b2} / (S \cdot w_c) \quad (6)$$

Substituting $W_{b2} = 400$ kg, $S = 90$ series and $w_c = 250$ g into Eq. (6), the number of cells connected in parallel (P_n) was 18.

(c) Number of cycles

The target life is three years. Because a bus is used 300 days in a year, and then the battery cycle life is expected more than 1,000 cycles as a target.

(d) Power density

Because the maximum power (P_B) of the electric bus is 120 kW, the total number (N) of the cells is 1,620 and the weight of each cell is 250 g (w_c), the output density of the cells required (P_c) is calculated as follows.

$$P_c = P_B / (N \cdot w_c) \quad (7)$$

Substituting the above values into Eq. (7), the output density required (P_c) was 300 W/kg.

(e) Maximum operating temperature

With an outside temperature of 36 °C, the temperature inside the vehicle was 38 °C without an air conditioner. With an outside temperature of 40 °C, the temperature inside the vehicle was assumed to be 42 °C. To install the battery in the inside of the bus, the target maximum operating temperature of the cell was set to be 45 °C. The above-mentioned results are summarized in Table 1.

Table 1 Target characteristics.

Cathode	Target
Discharge capacity (mAh/g)	90
Cell	Target
Energy density (Wh/kg)	100
Number of cycles (times)	1,000
Power density (W/kg)	300
Maximum operating temperature (°C)	45

3 Experimental

3.1 Preparation of lithium-ion batteries mounted on electric bus

3.1.1 Preparation of cathode materials and test cells

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 prepared so that the molar ratio of Li to Mn was 1 : 2. The mixture was dissolved in distilled water to prepare a $1.0 \text{ mol} \cdot \text{dm}^{-3}$ starting aqueous solution. The concentration of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ranged from 5 to 10 mol% for $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. These were composed by internal-combustion spray pyrolysis and used as the cathode materials.

The $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ electrode of the test cells consisted of 80 wt% $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride as a binder. *N*-Methyl-2-pyrrolidinone (NMP) was added to the binders in the form of a slurry, which was coated on an aluminum sheet using a doctor blade. The sheet was dried in an oven at 120°C for 24 h under vacuum.⁷⁾

Lithium metal (Honjo Chemical Co., Ltd) was used as the anode of the test cells. A porous polypropylene sheet (Heist Japan, Co., Ltd) was used as a separator. The electrolyte was 1 M LiPF_6 dissolved in an ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1 by volume) solution. The concentration of LiPF_6 was adjusted to $1 \text{ mol} \cdot \text{dm}^{-3}$. The test cells were assembled in a glove box filled with argon gas.

3.1.2 Preparation of cells We used $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ for the laminated layered type cells in the battery modules of the electric bus. The anode of the cells was made of graphite and hard carbon (Osaka Gas Co., Ltd). The average particle diameter was $10 \mu\text{m}$. The cells had a layered laminated sheet structure ($170 \text{ mm} \times 160 \text{ mm} \times 5.3 \text{ mm}$). The average weight of the cells was 233 g.

3.1.3 Structure of the battery modules The batteries used in the electric bus consisted of 1,620 lithium ion cells. Six modules were connected in series; in each module, 15 units, each consisting of 18 cells connected in parallel, were arranged in series. Battery management systems (BMS) were installed in each series of cells. They consist of a 4-ohm bypass resistor with a switch, voltage sensors and a thermal sensing device.

When the voltage of the parallel cells reaches 4.2 V during charging, an electric current passes through the 4-ohm resistor when the switch is closed, and the voltage of the cells is lowered. In addition, when the voltage of the parallel cells reaches 4.3 V, an overcharging signal is transmitted to the battery charger.

On the other hand, when the voltage of the parallel cells decreased to 3.0 V during running, an overdischarge signal is transmitted to the control unit of the electric bus. In addition, when the battery temperature during charging and running reaches 60°C , an overheating signal is transmitted to the control unit of the electric bus.

Figure 1 shows the structure of the batteries mounted on the electric bus. The voltage range of these battery

Fig. 1 Whole constitution of batteries mounted on electric bus.

modules was 270 – 378 V. The rated energy capacity of the modules was 53 kWh and the total weight of the modules was 480 kg.

3.2 Examination of battery characteristics using electric bus

The test run of the electric bus was performed on a public road along a course of 1.4 km. In the test run, the voltage and current of the batteries were recorded with a data logger.

4 Results and Discussion

4.1 Characteristics of lithium manganese cathode

The chemical composition of the manganese cathode was measured by atomic absorption spectrometry (AAS, Shimadzu, AA-6800). The molar ratios of metal components (Li:Mn) were 1.06 – 1.13:1.95. Furthermore, 5% aluminum doping was confirmed by inductive coupled plasma (ICP) analysis.

Figure 2 shows the discharge curves of $\text{Li}/\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$. The rate of discharge was 1 C. The data for the case without aluminum doping are added for comparison.

Fig. 2 Discharge curves of Li/LiAl_xMn_{2-x}O₄ and Li/LiMn₂O₄ for X = 0.00, 0.05 and 0.10. The data were measured at 25 °C with a rate of 1 C.

Fig. 3 Plots of discharge capacity vs numbers of cycle of Li/LiAl_{0.05}Mn_{1.95}O₄ and Li/LiMn₂O₄ at 25 °C with a rate of 1 C.

A typical voltage jump that is characteristic of the lithium manganese cathode was observed in the vicinity of 4.0 V in the discharge curves of Li/LiMn₂O₄. However, the jump in the curve became unclear in the case of 5% aluminum doping. It was observed that the voltage had instability around 3.9 V in the case of 10% aluminum doping. The discharge capacity decreased to 112.4 mA·g⁻¹ as an effect of 5% aluminum doping, whereas Li/LiMn₂O₄ exhibited a discharge capacity of 120 mA·g⁻¹. Furthermore, the discharge capacity decreased to 100.7 mA·g⁻¹ in the case of 10% aluminum doping.

Figure 3 shows plots of discharge capacity vs number of cycles at 25 °C. The discharge capacity after 100 cycles of Li/LiMn₂O₄ decreased to 90.0% of the initial discharge capacity. It was considered to be influenced by the Jahn-Teller distortion. On the other hand, the cycle performance was improved by aluminum doping because the discharge capacity after 100 cycles was 92.2% for Li/LiAl_{0.05}Mn_{1.95}O₄. The cycle performance of the aluminum-doped manganese by internal-combustion spray pyrolysis was very stable.

Figure 4 shows plots of discharge capacity vs number of cycles at 60 °C. The data were measured at 25 °C at a

Fig. 4 Plots of discharge capacity vs number of cycles of Li/LiAl_{0.05}Mn_{1.95}O₄ and Li/LiMn₂O₄ at 60 °C with a rate of 1 C.

rate of 1 C. The discharge capacity after 100 cycles for Li/LiMn₂O₄ decreased to 62.8% of the initial discharge capacity. On the other hand, the discharge capacity after 100 cycles remained at 86.9% for Li/LiAl_{0.05}Mn_{1.95}O₄. From these results, discharge capacity was found to improve at high temperatures with aluminum doping. It is thought that the dissolution of manganese at high temperatures was restrained because the average valence of manganese ions increased to more than 3.5 as a result of aluminum doping.^{5, 6)} Therefore, cathode materials doped with 5% aluminum were adopted in the cells for the electric bus.

4. 2 Characteristics of the cells

The average weight per laminated layered type cell of the lithium-ion battery with the cathode material of LiAl_{0.05}Mn_{1.95}O₄ was 233 g. Figure 5 shows the discharge curve of a cell. The discharge energy was 23.9 Wh and the energy density was 103 Wh/kg. The curve was smooth without a voltage jump. In addition, the energy density was more than 100 Wh/kg, which was a responsible value.

Figure 6 shows plots of capacity rate vs numbers of cycles of the cells. The capacity of the cell not doped with aluminum decreased to 70% of the initial discharge capacity after 450 cycles and was considered to be influenced by the Jahn-Teller distortion. On the other hand, the cell doped with aluminum deteriorated to 70% of the initial discharge capacity after 850 cycles. Although the target of 1,000 cycles was not attained, the battery characteristics were improved by aluminum doping.

Figure 7 shows plots of the discharge capacity vs number of cycles of the cell doped with aluminum at 25 °C and 45 °C. The data were measured at 1 C. The discharge capacity was maintained high and it was stable with increasing number of cycles at both temperatures. It is thought that the dissolution of manganese at a high temperature was inhibited by part of the manganese being substituted by aluminum.^{5, 6)}

Figure 8 shows the measured power densities of the cells at different states of charge (SOC). The measure-

Fig. 5 Discharge curve of cell mounted on electric bus.

Fig. 6 Plots of capacity rate vs number of the cycles of aluminum-doped cell and the nondoped cell at 25°C with a rate of 1C.

Fig. 7 Comparison of plots of discharge capacity vs number of cycles of aluminum-doped cell at 25°C and 45°C with a rate of 1C.

ment of the power density was performed by impressing a pulse current on the cell. SOC of the cells were 10, 20, 35, 50, 65, 80 and 90%. At each SOC, the rates of discharge current were 1, 3, 5, and 10 C for ten seconds. Ten seconds later, the voltage of the cell was measured.

Fig. 8 Power density of cell at 25°C.

Table 2 Target characteristics and obtained values.

Cathode material	Target value	Obtained value
Discharge capacity (mAh/g)	90	112
Cell	Target value	Obtained value
Energy density (Wh/kg)	100	100
Number of cycles (times)	1000	850
Power density (W/kg)	300	349
Maximum operating temperature (°C)	45	45

Fig. 9 Electric bus during running test.

The current at the discharge cutoff voltage was obtained from the voltage by the least-squares method. Then output density was obtained.

The range of use of the batteries was from 10 to 100% of SOC. Power density was 349 W/kg at an SOC of 10%, and 2,920 W/kg at an SOC of 100%. The cells exceeded the target value of 300 W/kg.

The target and actual values for the cells developed in this study are shown in Table 2. The performances of the battery modules were satisfactory for use in electric buses.

Figure 9 shows the electric bus, whose weight without passengers was 4,120 kg. The original diesel-engine bus weight was 4,100 kg. The increase in weight was only 20

Fig. 10 Characteristics of the electric bus around a public course of 1.4 km.

kg. The capacity of the original diesel-engine bus was 29 passengers. The electric bus has a capacity of 28 passengers because the battery modules took the space of one seat.

Figure 10 shows the characteristics of the electric bus that ran around a public course of 1.4 km after a full charge. The total running distance was 74 km, which exceeded the target value of 50 km. The electric consumption required for the run was 36 kWh. The energy consumption rate was 2.1 km/kWh, which was very near the target value of 2.0 km/kWh. In addition, the maximum power was 63.0 kW and the power density of the cells was 131 W/kg.

5 Conclusions

The maximum operating temperature of batteries to be mounted on the electric bus have been a problem that has prevented the practical use of such batteries. In particular, their deterioration at high temperature was the main problem. Also, the spinel-type lithium manganese oxide used as the cathode materials in the batteries required improvement. As a result of aluminum doping, the use of the cathode materials produced by internal-combustion spray pyrolysis resulted in improved maximum operating temperatures and cycle performance compared with those of non-doped aluminum.

The weight reduction of the batteries was another problem preventing their practical use in EVs. In particular, as the power supply of the buses increases, maintaining the capacity and extending the discharge covered km by improving the energy density become neces-

sary.

Compared with that of conventional lead-acid batteries, the energy density of the lithium-ion batteries developed in this study was greatly improved. As a result, compared with the original diesel-engine bus, the weight of the developed electric bus without passengers was only 20 kg heavier. Furthermore, the capacity of 28 was only one less than that of the original diesel-engine bus.

In addition, the electric bus was able to run for 74 km on a full charge, which exceeded the target value of 50 km.

These results indicate that the electric bus is applicable for short-distance use, for example, as a community bus or a pickup bus.

The lithium-ion batteries developed in this study generally satisfied the characteristics required for use in an electric bus such as the energy density, power density, maximum operating temperatures and number of cycles.

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