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Manganese type lithium ion battery for pure and hybrid electric vehicles

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Abstract

A manganese type lithium ion battery was developed for both PEV(pure EV) and HEV(hybrid EV) application by improving the weak points in conventional technology. A 90 Ah single cell was developed for PEV use, and it was applied to an integrated 8-cell module which has an energy density of 93 Wh/kg and 114 Wh/dm^3 and power density of 350 W/kg at depth of discharge (DOD) 85%. The Mn type Li ion cell for PEV use was modified to give it a high power density. The 48-cell module for HEV has the output power density of 1350 W/kg at DOD 50%. These batteries are already used in commercial vehicles and are proving to have excellent performance. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium Battery; Manganese; Electric Vehicles

1. Introduction

Lithium ion batteries have now very important and promising position in battery market, though most of the batteries are Co type lithium ion batteries which use lithium cobaltate as positive electrode material [1]. The Co type Li ion batteries surely show good and well-balanced characteristics, but the small amount of the natural resource for Co suggests the difficulty in large-sized battery use such as electric vehicles. On the other hand, Mn material has large natural abundance and an established status in battery industry, though the short life cycle and lower discharge capacity had remained in conventional technology. Thermal stability for Mn material (lithium manganate) was another remarkable point for large-sized applications, for thermal management and safety occupy much serious position in the applications [2]. Besides thermal stability, excess Li ion release capacity at overcharge conditions for lithium manganate which is smaller than that for lithium cobaltate or lithium nickelate guarantees better safety at overcharged states. Consequently, we selected lithium manganate as positive electrode active material for large-sized lithium ion batteries, and concentrated on the improvement of the weak points.

For the improvement of cycle life at room temperatures, we introduced Li-substituted (or Li-rich) lithium manganate [3]. The smaller size for lithium ions reduced the lattice constant and its change during charge/discharge cycles, strengthened the ionic bonds among the ions, and lightened the stress to crystal structure. The life cycle at higher temperatures was approached in another way. As it is already pointed out, the short life cycle at higher temperatures was caused not only by the positive electrode but also by the negative electrode [4]. So we improved the negative electrode applying physicochemical method for high temperature life cycle. Another demerit for manganese material was low discharge capacity. It was almost overcome by practical cell design and engineering. Of course, higher single cell voltage for manganese material supported to make the energy density higher.

Consequently, we developed a manganese type lithium ion battery which has almost the same level of performance in energy density and life cycle as that for the cobalt type lithium ion battery. Another important characteristic for electric vehicle use is power density. A better power capability for the manganese type lithium ion battery was already suggested in a small-sized cells [5]. We proved this fact in large-sized cells. In this way, we developed two types of Mn type Li ion batteries: one for PEV (pure-EV) use with a high energy density, and the other for HEV (Hybrid EV) use with a high power density.

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Table 1
Specifications for developed single cell for PEV use

Ratings	3.8 V–90 Ah
Dimensions	Ø 67 mm; $L = 410$ mm
Weight	3.2 kg
Energy density	107 Wh/kg; 237 Wh/dm^3

Table 2
Specifications for developed single cell for HEV use

Ratings	3.6 V–36 Ah
Dimensions	Ø 40; $L = 108$ mm
Weight	300 g
Output power density	2000 W/kg (DOD 50%)

2. PEV battery

The specifications for a PEV single cell is shown in Table 1. The single cell is cylindrical, 67 mm in diameter and 410 mm long with a nominal capacity of 90 Ah. The positive electrode active material is a modified lithium manganate [3] and the negative electrode active material is hard carbon. The combination of the electrode active materials predominantly determines the value of cell voltage and the gradual slope of the charge/discharge voltage curve. We adopted the constant current–constant voltage (CC–CV) charging mode. The cell voltage changes from 4.1 to 2.7 V during discharge, and the voltage difference is 1.4 V for 100 to 0% SOC. This value is sufficiently larger than that for the Ni-MH cell (0.3 V), and the good accuracy of SOC estimation by the cell voltage detection is supported by this fact. The cell surface temperature elevation after the continuous discharges were 1°C for 30 A, 3°C for 90 A, 10°C for 180 A, and 17°C for 300 A. The very small temperature elevation at low rate discharge, also at low rate charge, proves that the cell reaction heat or enthalpy is very small and the Joule heat is the main source for the heat generation during charge and discharge. As this single cell is designed for the use in a PEV, 3C rate discharge is the high rate limit and there was a large voltage decrease and a larger heat generation at the 300 A discharge. The energy densities for the single cell are 107 Wh/kg and 237 Wh/dm^3, and the power density is 470 W/kg at DOD 85% and 25°C. The energy density is almost the same as that for the Co type. The cycle life at DOD 40% and 25°C showed 1500 cycles.

The eight-cell module integrates eight cells connected in series, a module case designed for cooling air flow from bottom to top, a fuse to prevent excess current flow, and a cell controlling circuit put on the module case. The module has the rating of 30 V– 90 Ah, energy density of 93 Wh/kg and 114 Wh/dm^3, and power density of 350 W/kg at DOD 85% and 25°C. The power density was calculated from 10 s constant current discharge. Though, the DOD dependence of the power density is rather large because of the cell voltage dependence on DOD, the power density itself is much larger than that for the Ni-MH battery in all the DOD range essential for practical PEV use.

3. HEV battery

Using the same cell chemistry as that for the PEV cell, a reduced size high power cell for HEV use was developed by decreasing the internal resistance. The specifications for the single cell is shown in Table 2. The cell has the dimensions of a 40 mm diameter and 108 mm length, the weight of 300 g and the capacity of 3.6 Ah in CC–CV charge by 4.1 V. The power density calculated from the 5 s constant current discharge was 2000 W/kg at DOD 50% and 25°C as shown in Table 2. The high rate continuous discharge capability and temperature elevation during discharge are shown in Fig. 1. At a 10 A discharge (≈3 C), the cell surface temperature increased by 2°C, while for a 60 A discharge (≈17 C), the cell discharge capacity reduced to 86% of the 10 A discharge but the surface temperature increase was only 10°C. This result reconfirms the low heat generation in the discharge process for our Mn type Li ion cells again in HEV cells. These good high rate discharge performances are supported by the low internal resistance as low as 4 mΩ/cell in DCR at 25°C.

The module battery for HEV use integrates 48 cells connected in series, cell controllers, a fuse and a module case which contains all the parts. The module weighs 20 kg with the dimensions of 260 mm × 540 mm × 160 mm, and has a power density of 1350 W/kg at DOD 50%. A gradual voltage change for the module as discharge proceeds is utilized as a good scale to calibrate the SOC. The high rate continuous discharge is capable up to 90 A (=25 C) for the module at 25°C. The continuous discharge at 90 A corresponds to a 16–12 kW discharge. The input/output power density for the module was calculated from a 5 s constant current charge/discharge measurement. If we assume the maximum input power of 8 kW and maximum output power of 12.5 kW for a module, we can use this module between 15 and DOD 85%. The wide serviceable DOD range guarantees a large capacity for the power assist and the regeneration and high fuel efficiency during HEV use.

The batteries described in this paper are already used in some commercial vehicles and are proving their practical

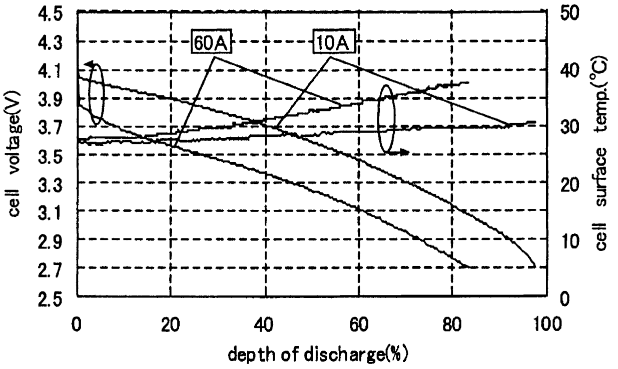

Fig. 1. Discharge characteristics for an HEV single cell.

applicability [6]. It is promising to apply these batteries to PEV, HEV and other motor-assisting drive systems based on the flexible characteristics mentioned above and the high reliability proved in practical tests.

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References

[1] K. Tamure, T. Horiba, T. Iwahori, J. Power Sources 81-82 (1999) 156.

[2] S. Hossain, S. Megahed, in: Proceedings of the Symposium EVS-13, Osaka, Japan, I-45, 1996.

[3] M. Kasai, Y. Kumashiro, K. Nishimura, et al., J. Power Sources, submitted for publication.

[4] M. Gee, J. Reimer, Y. Wang, in: Proceedings of the 9th International Meeting on Lithium Batteries, IMLB-9, Poster II Thur 83, 1998.

[5] A.M. Wilson, J.N. Reimers, J. Power Sources 81/82 (1999) 642.

[6] T. Miyamoto, E. Oogami, M. Origuchi, et al., in: Proceedings of the SAE 2000 World Congress, 00PC-166, Detroit, MI, USA 2000.