Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 119–121 (2003) 893–896
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Manganese-based lithium batteries for hybrid electric vehicle applications

T. Horiba[a,*], K. Hironaka[a], T. Matsumura[a], T. Kai[a],
M. Koseki[a], Y. Muranaka[b]

[a] *Shin-Kobe Electric Machinery Co. Ltd., Okabe-machi Ohsato-gun, Saitama 369-0297, Japan*
[b] *Hitachi Research Laboratory, Hitachi Ltd., Ohmika-cho Hitachi, Ibaraki 319-1292, Japan*

Abstract

A manganese-based lithium ion battery was developed for hybrid electric vehicle (HEV) applications. The cell consists of an improved manganese spinel as the positive electrode and hard carbon for the negative electrode. The Mn-based Li ion cell for HEVs was developed by adding a high power density modification to a pure-EV (EV) cell of high energy density specification. It has a power density as high as 2000 W/kg at 50% depth of discharge (DOD) and 25 °C. Storage tests at various temperatures suggest a practical calendar life of more than 5 years. The 48-cell battery module was developed for use in an HEV. It also proved to have an excellent output power density of 1350 W/kg at 50% DOD. Based on the excellent characteristics of the lithium ion battery, it seems very promising to apply this battery not only to EV, HEV and other motor-assisting drive systems but also to other high power applications.

Keywords: Manganese-based lithium batteries; Hybrid electric vehicle; Lithium ion batteries

1. Introduction

In the mobile electronics market, lithium ion batteries are now very common and popular because of their high energy density [1]. The products trend to smaller, thinner and lighter weight packages such as the laminated sheet packaged gel polymer battery. The opposite intention is the new attempt to apply lithium battery technology to larger-sized products.

Besides the high energy density, the lithium ion batteries have other significant features for large-sized applications. The first is the high single cell voltage of about 4 V, which is three times that for Ni–MH batteries and two times that for lead–acid batteries. The higher the single cell voltage, the smaller the total cell number in the battery pack. This point is very important when trying to integrate a large system which consists of a large number of parts. The second feature is the high energy efficiency caused by the simple and straight-forward cell reaction mechanism. In other words, there is no side reaction in the lithium ion cell reaction. An energy efficiency of more than 95% is easily attained at a moderate charge–discharge rate [2]. The third feature is the good controllability of the thermal and electrical management, which comes from low heat generation in the charge–discharge reactions, excellent energy efficiency and easy state of charge (SOC) detection caused by the gradual voltage change upon discharge. All these features suggest the promising applicability of the lithium ion battery to large-sized applications such as electric vehicles (hybrid electric vehicle (HEV), pure electric vehicle (EV), etc.).

Most of the lithium batteries produced at present are Co-based ones which adopt lithium cobaltate as the positive electrode material. However, the small amount of Co resources could be a bottle-neck in large-sized battery applications such as the pure electric vehicle (EV) and the hybrid electric vehicle (HEV). We have concentrated on the development of the Mn-based lithium ion battery, expecting a steady supply of Mn in the future because of its large natural abundance. The thermal stability of the lithium–manganese spinel was another remarkable point for automotive applications, for thermal management and safety are very important in these applications [3].

Some concerns regarding the conventional regular lithium–manganese spinel were overcome by the introduction of a Li-substituted (or Li-rich) lithium manganate [4,5]. Also, some engineering technologies were added to make the cell performance practical [6].

---

[*] Corresponding author. Tel.: +81-48-546-1107; fax: +81-48-546-1138.
E-mail address: t.horiba@shinkobe-denki.co.jp (T. Horiba).

0378-7753/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0378-7753(03)00202-7

2. HEV cell

Our HEV battery technology is based on that for the EV battery because of our development history [6]. The materials used in the HEV battery include a Li-rich Mn spinel, as mentioned previously, for the positive electrode active material, hard carbon, which gives a gradually sloping voltage profile, for the negative electrode active material, and an organic electrolytic solution of lithium hexafluorophosphate dissolved in a mixture of organic carbonate solvents.

The transformation from EV batteries to HEV batteries caused novel demands on the battery specifications. The load for the HEV batteries is not a continuous charge or discharge but frequent pulses of narrow width. The energy to drive a car is stored in a fuel tank, therefore, the battery is not an energy battery of high energy density but a power battery of high power density. To meet the demand for high power density performance, reduction of the cell's internal resistance was the most effective approach. We applied some ideas to reduce the resistance. The first one was to make the electrode thinner than that for the EV battery. The thin electrode not only increases the electrode area to lessen the current density, but also makes the inter-electrode distance shorter, which also lowers the resistance. The second one was to adjust the active material mixture composition to reduce the electrode resistance and maintain the energy density. The third one was to improve the welding structure to reduce the electric resistance in the cell structure.

After the design innovation mentioned previously was implemented, single electrode tests consisting of a simple repetitive pulse pattern showed that the load put greater stress on the positive electrode than on the negative electrode. The electrode material for the positive electrode was modified to reduce the stress by increasing the surface area of the materials.

2.1. Results

An outline of the developed single cell for HEV applications is shown in Table 1 and a photograph of it is shown in Fig. 1. The cell is cylindrical and is 40 mm in diameter and 108 mm long. It weighs 300 g and has a capacity of 3.6 Ah in CC-CV charge up to 4.1 V. The power density of 2000 W/kg at 50% DOD and 25 °C was calculated by extrapolation of the 5 s constant current discharges at different current points. The charge–discharge characteristics for a single cell are shown in Fig. 2. Though the voltage difference between the start and end of the discharge is rather large, the smooth decreasing voltage curve profile enables us to monitor the state of charge (SOC) with good accuracy by just measuring the cell voltage. The voltage changes from 4.1 to 2.7 V and the difference is 1.4 V, while that for a Ni–MH cell is 0.4 V. Therefore, a Mn-based Li ion cell has a 3.5 times higher accuracy in SOC monitoring cell with the same voltage detection method of identical precision.

Table 1
Specifications of the HEV cell and the battery module

	Cell	Module
Dimensions (mm)	ϕ 40 × 108	541 × 260 × 160
Weight (kg)	0.3	20.2
Nominal voltage (V)	3.6	173
Capacity (Ah)	3.6	3.6
Output power density at 50% DOD (W/kg)	2000	1350
Cooling system	–	Compartment air suction

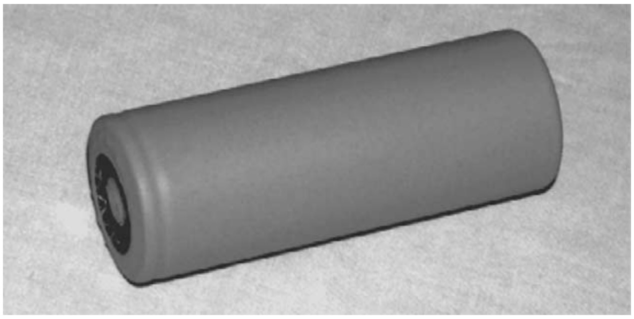

Fig. 1. Photograph of the HEV cell.

The high rate continuous discharge capability and temperature elevation during discharge are shown in Fig. 3. A continuous discharge up to 90 A is possible, though the discharge voltage is around 0.6 V lower than that of 5 A. At a 10 A discharge (=3C), the cell surface temperature increased by 2 °C from that of an isothermal box, and even at a 90 A discharge (=25C) the surface temperature elevation was merely 8 °C, though the cell discharge energy was reduced to 68% of the 10 A discharge energy. This result convinced us of the low heat generation in the charge–discharge process for our Mn-based Li ion cells, which is mainly caused by low enthalpy for the cell reaction and the small internal resistance as low as 4 mΩ/cell. These small resistance and voltage drop values must cause the low heat generation at frequent high power input–output operations in the HEV application.

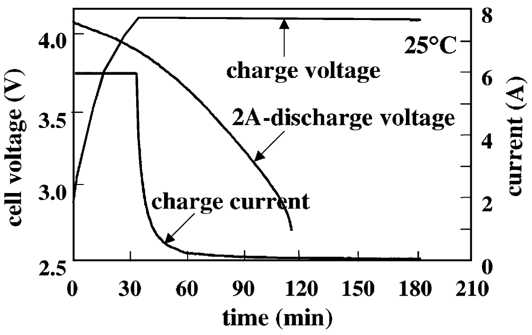

Fig. 2. Charge–discharge characteristics of the HEV cell (25 °C).

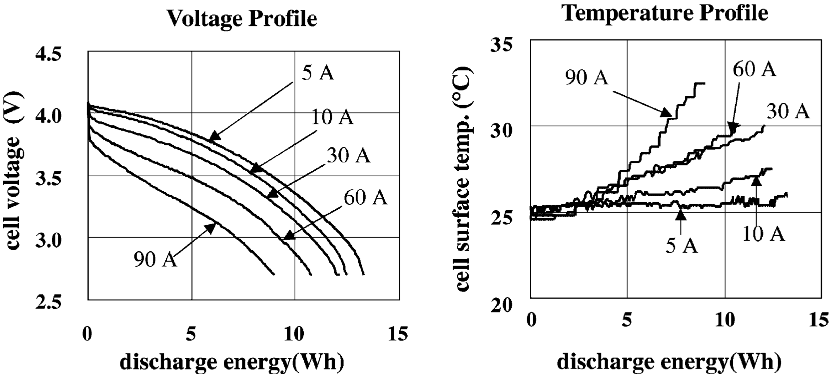

Fig. 3. Discharge rate characteristics of the HEV cell (25 °C).

2.2. Discussion

If we define the "P/E ratio" as the quotient of the power density (W/kg) divided by the energy density (Wh/kg), the P/E for our HEV cell is 37, and that for our EV cell is 7. The power densities used in these calculations are the values at 50% SOC. This remarkable difference between the two types of cells is caused by the reduction of the internal resistance mentioned previously. The reduction is well explained by the relationship between the capacity and internal resistance: the EV cell has a capacity of 90 Ah and internal resistance of 1 mΩ, while the HEV cell has a capacity of 4.3 Ah and internal resistance of 4 mΩ based on the same measurement criteria. If we reduce the capacity of the cell from 90 to 4.3 Ah by simple reduction of electrode area, the internal resistance would increase from 1 to 21 mΩ according to the inverse proportion relation of capacity and internal resistance. But the result was one-fifth of the expected value, therefore, our effort to decrease the internal resistance resulted in the factor of 1/5.

The co-existence of the high power density of 2000 W/kg and high energy density of 54 Wh/kg may suggest that Li ion batteries have a quite superior potential to super capacitors as a power and energy storage system for HEV applications.

Storage life is a very important characteristic for an HEV cell, since the battery for this application will be stored for most of the total life time. Also, another feature for this application is that the SOC is kept around 50% on average to cope with the random charge or discharge demand from the vehicle. Therefore, the storage life at 50% SOC is the most important criterion. The capacity change by storage at 50% SOC and different temperatures showed a tendency that the higher the temperature, the faster the capacity changes [7]. However, the capacity change showed the tendency of saturation at every temperature. The capacity change in storage at 50% SOC at 25 °C for 3 years showed the capacity change <10% of the initial value and it is estimated that it will remain enough higher than 80% of the initial capacity even after 5 years. As the role for an HEV battery is to supply and to accept power, the change in the internal resistance of the cell is also important as a good index for the power capability [7]. The result of the internal resistances measured simultaneously showed a similar trend of temperature-dependency as the capacity. At 50% SOC at 25 °C, the direct current internal resistance (DCR) showed tendency of saturation in 3 year storage, and this result supports lower change than doubling within 5 years. From these results and the estimated temperature distribution in a battery module during practical HEV use [7], and the evaluation of pulsative input–output power load stress to the battery in driving, we evaluated the practical life time of the HEV battery as more than 5 years.

3. HEV battery module

3.1. Results

We developed a 48-cell battery module to adapt our HEV single cells to an HEV application (Fig. 4). The module consists of 48 cells connected in series, six cell controllers, a fuse and a module case which contains all the parts. The cell controller is a printed circuit including a microcomputer to detect individual cell voltages and temperatures in the module box and to communicate the data to the upper level computer in the vehicle that controls the cell SOC in a balanced state. The specifications for the module is already

Fig. 4. Photograph of the HEV battery module.

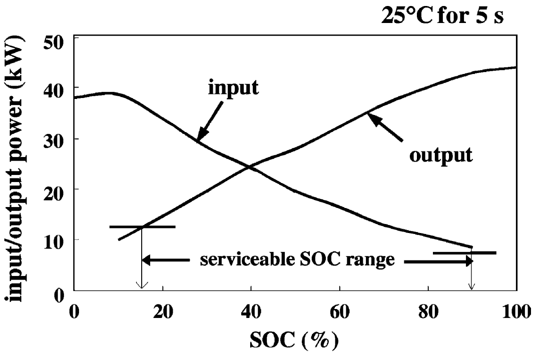

Fig. 5. Input–output power for the HEV module.

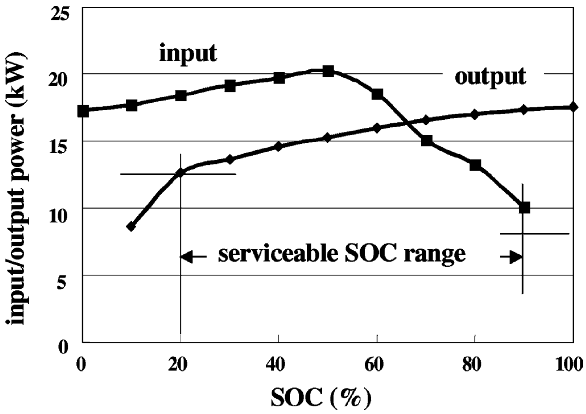

Fig. 6. Input–output power for the HEV module (limited to 100 A).

summarized and shown in Table 1 and its photograph is shown in Fig. 4. As mentioned previously, the heat generation for our battery is small, therefore, the battery module can be cooled by air in spite of the frequent input–output during HEV operation. There are cooling air inlet and outlets on the top of the module case.

The input–output power at 25 °C for a module calculated by extrapolation of *I–V* curves for a 5 s constant current charge–discharge is shown in Fig. 5. As the rated output–input power for the module is 12.5 and 8 kW, we can use the module between 15 and 90% SOC.

3.2. Discussion

This wide serviceable DOD (SOC) range means the ability to supply or receive power at almost anytime, and allows the battery to have a large capacity for power assist and regeneration. Thus, it is expected that the high fuel efficiency during HEV application and reduction of fuel consumption would contribute to the global environmental issue, which is the main purpose of developing the HEV system for automobiles.

As the data shown in Fig. 5 is based on the extrapolation for the *I–V* characteristic measurement, we added some regulation to keep the module heat balance under good control and to apply the data to a practical vehicle application. Fig. 6 is the result in which we applied the current limit of 100 A for the charge and discharge to the data of Fig. 5. Though both the input and output power in Fig. 6 became smaller than that in Fig. 5, it shows the practical power characteristics and sufficient high power to drive a hybrid vehicle. The rated power of a 12.5 kW output and 8 kW input for a module can be supplied between the SOC of 20 and 90%.

The developed Mn-based lithium ion batteries of high power density for HEV applications were derived from EV batteries. The batteries are being used in the Nissan Tino Hybrid already released into the market [8,9]. If the technology can be further refined and production increases, the cost will be expected to drop, as the small-sized lithium batteries for consumer products proved, because of the lower price of the raw materials for the Mn-based lithium battery. It will then be promising to apply these batteries not only to EVs, HEVs and other motor-assisting drive systems but also to other power sources judging from the superior and flexible characteristics mentioned in this paper.

Acknowledgements

A part of this study depended on the results from the Development of Dispersed Type Battery Energy Storage Technology sponsored by METI and NEDO.

References

[1] K. Tamura, T. Horiba, T. Iwahori, J. Power Sources 81–82 (1999) 156.
[2] T. Horiba, M. Kosei, K. Takahashi, et al., in: Proceedings of the Forty-first Battery Symposium, Japan, vol. 3C13, 2000, p. 354.
[3] S. Hossain, S. Megahed, in: Proceedings of the Thirteenth International Electric Vehicle Symposium, vol. I-45, 1996.
[4] T. Takada, H. Enoki, E. Akiba et al., Mat. Res. Symp. Proc. 496 (1998) 257.
[5] Japan Patent P3120984.
[6] T. Horiba, K. Hironaka, M. Matsumura et al., J. Power Sources 97–98 (2001) 719.
[7] F. Saito, N. Hirata, S. Ogata, et al., in: Proceedings of the Eighteenth International Electric Vehicle Symposium, vol. 1C-3, 2001.
[8] T. Miyamoto, E. Oogami, M. Origuchi, et al., in: Proceedings of the SAE 2000 World Congress, vol. 00PC-166, 2000.
[9] M. Origuchi, N. Hirata, K. Suzuki, et al., in: Proceedings of the Seventeenth International Electric Vehicle Symposium, vol. 3B-4, 2000.