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The 200 V 2 kWh energy storage multicell system with 25 Wh Li/LiV_3O_8 single cells

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Abstract

A 200 V 2 kWh Li/LiV_3O_8 multicell system was constructed by seventy-seven 25 Wh single component cells in series connection and was operated under connection with a commercial power line. The discharge power of 1.94 kWh and the energy efficiency of over 93% were demonstrated almost as designed. The rate capability of this multicell system was poor compared with that of a single cell. The internal resistance of the system resulted in the *iR* loss, and the safely set operating voltage limits for the system reduced the output energy of individual cells. The non-uniformity of the operating voltage and of the state-of-charge for all component cells were also analyzed in addition to the local temperature rise in the stack. © 1997 Elsevier Science S.A.

Keywords: Lithium secondary batteries; Multicell systems; Battery module

1. Introduction

Large-scale lithium secondary batteries having a high energy density and high energy efficiency are attractive for electric vehicles and electric power storage systems, since they can be operated at room temperature without any auxiliary equipment. The multicell technology of series and/or parallel connection of single cells, of course, should be established before a practical use.

From 1989 to 1994, CRIEPI and Yuasa Corporation carried out a joint work to develop relatively small-size energy storage systems (10 kWh class) for home use (named as 'load conditioners'). First LiV_3O_8 was selected as a positive pole active material from the viewpoint of a high specific capacity and moderate operating potentials [1–3]. Especially in the multicell system, at the same time, it seemed important to suppress the charging potential of a cathode in order to avoid the decomposition (oxidation) of the electrolyte. The effect of particle size on the positive pole performances of LiV_3O_8 was studied, and the interaction of its surface with some kinds of organic electrolytes was investigated [4]. Prototype 25 Wh Li/LiV_3O_8 cells were manufactured, which showed an energy density of 120 Wh/kg and a high energy efficiency of over 95%. Their cycle life, however, was not satisfactory: 100 cycles (at 100% depth-of-discharge (DOD)) and 400 cycles (at 50% DOD) [5]. A thinner cell design was then adopted in order to facilitate heat radiation.

In this work, 200 V 2 kWh multicells were designed, constructed and finally operated in series connection. This paper described the performance of these multicells as related to the available energy as a function of the discharge rate; some technological problems and their improvements are also discussed.

2. Experimental

The single cell consisted of LiV_3O_8, lithium metal and 1 mol/dm^3 $LiPF_6$ EC/DME (50/50 vol.%) electrolyte. Their size was 11 mm(W) × 100 mm(L) × 120 mm(H) (130 mm contained terminal). The setup of the ten-cell module is given in Fig. 1. Cooling fins were added between single cells and ten cells were stacked with two stainless-steel plates which were bound by four bolts to keep homogeneous pressure in the module.

Eight ten-cell modules were constructed and operated for five cycles individually to check the distribution of the initial capacity. Three cells obtained insufficient capacities and were

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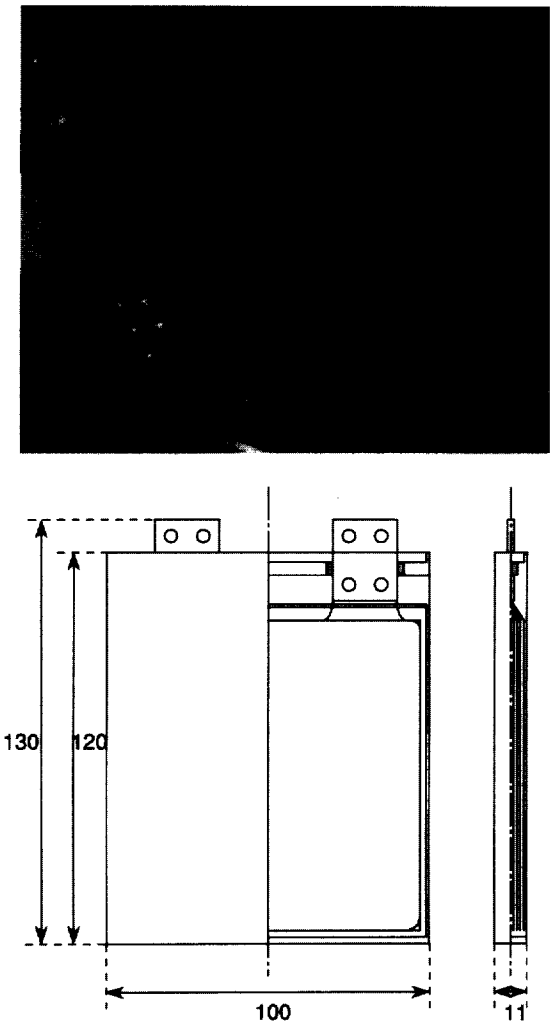

Fig. 1. Setup of a ten-cell module (top) and 25 Wh single cell (bottom).

removed when constructing the multicell. These eight modules were then connected in series in a battery box, Fig. 2. They were operated at room temperature.

The multicell was connected with a commercial power line through a 1 kV A power conversion system (a.c.–d.c.–a.c.) and the charging condition was, in principle, a constant current at 1 A. After reaching the terminal voltage of 240 V (about 3.1 V per single cell), charging was continued at a constant voltage until the current decreased to 0.5 A. The discharge rate varied from 1 to 4 A until 170 V (about 2.2 V per single cell). The terminal voltage of all single cells and some typical surface temperature were monitored; the multicell operation was stopped for safety reasons when the voltage of a certain single cell exceeded 3.5 V — or lowered at 2.0 V — or when the temperature of a certain cell exceeded 50 °C. The stacking pressure of the modules was measured with a strain gauge (Kyowa Dengyo) plugged in the bolts. At the same time, the total voltage and a.c./d.c. current were measured with a digital power meter (Yokogawa Electric, Model 2533). All data were monitored using a remote scanner (Yokogawa Electric, Model 3882E) and logged into a PC.

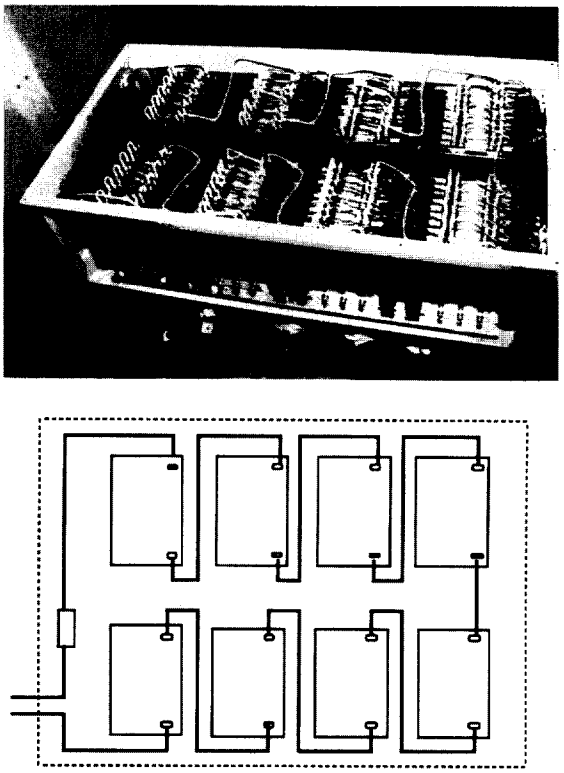

Fig. 2. Series connection of eight ten-cell modules in a multicell box.

3. Results and discussion

3.1. Performances of multicell operation at a 10 h rate

The rest potential curve of LiV_3O_8 versus x in $Li_{1+x}V_3O_8$ is obtained by the pulse current–relaxation method, Fig. 3, where the superimposed voltage ranges (a) and (b) correspond to the controlled operating limits of the multicell and the single cell, respectively. LiV_3O_8 has a wide reversible lithiation range of $\Delta x = 3$ (280 Ah/kg capacity) and shows

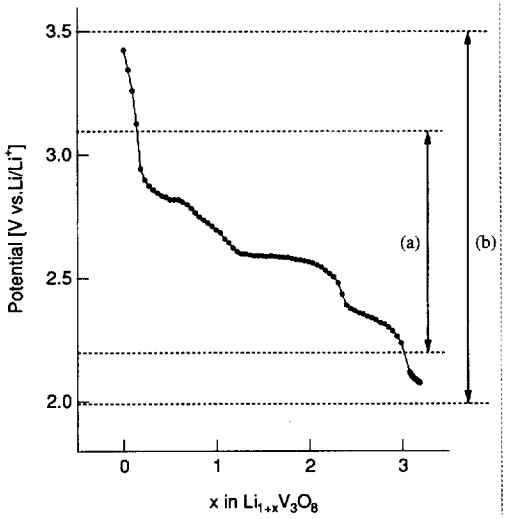

Fig. 3. The open-circuit voltage of a single cell versus x in $Li_{1+x}V_3O_8$ obtained by pulse discharge method (1 h discharge at 0.2 mA/cm^2, 4 h rest). (a) 77 single cells: the voltage range allowed for multicell system operation. (b) Voltage range allowed for individual cell operation.

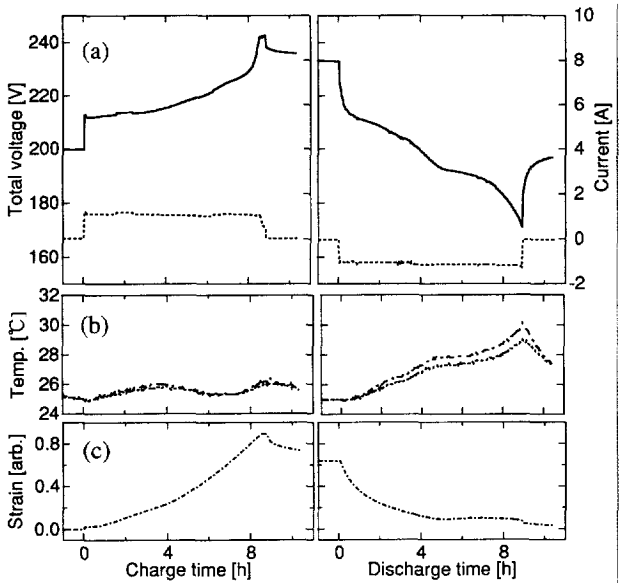

Fig. 4. Charge/discharge performances of the multicell system. (a) (———) Voltage and (- - -) current. (b) Surface temperature of certain two cells. (c) Stacking pressure of a certain ten-cell module.

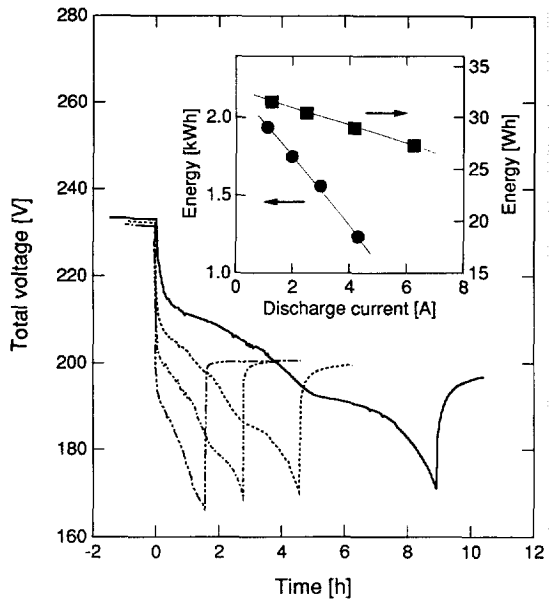

Fig. 5. Typical discharge curves of the multicell system at several rates. Inset: output energy of the system compared with that of a single cell. (———) 1 A; (- - -) 2 A; (– · –) 3 A, and (–· · ·) 4 A.

200 Ah/kg at 10 h rate charge/discharge. The voltage ranges of 3.5–3.1 V and 2.2–2.0 V are allowed only for individual single cells taking into account the deviated cell performance.

Typical charge/discharge performance of the multicell system is shown in Fig. 4. Total voltage curves in (a) are similar to those of a single cell except from a large *iR* loss. Currents have the ± 10% range of fluctuation during charging/discharging. The multicell system behaves as one at constant power mode operation. This response may be dependent on the performance of the power conditioner, but the multicell could follow up sufficiently against its motion.

The discharge energy of 1.94 kWh and the energy efficiency of 93.3% are demonstrated for this 2 kWh system. The energy density reaches 90 Wh/kg and 185 Wh/l based on the weight and volume of 77 single cells, respectively. The cell temperature increases at the end of discharge especially at the center-located cell. The stacking pressure increases monotonically on charge and decreases again on subsequent discharge. This phenomenon may be related with the deposition and dissolution of lithium metal as pointed out by Wainwright and Shimizu [6]. The average stacking pressure becomes gradually higher with repeating cycles.

3.2. *Rate capability of multicell*

The discharge curves of the system at various rates are shown in Fig. 5, where the calculated output energy of the system is compared with that of a single cell at the same time. In case of single cells, operating voltage limits are 3.1 and 2.0 V. The following three reasons may be considered why the multicell system shows a lower rate capability than the single cell.

First, the multicell should have a high total resistance due to many electrical contact points and lead conductors. The total resistance estimated from *iR* loss in Fig. 4(a) amounts to about 5 Ω, which is approximately twice higher than 77 times the single cell resistance (determined by a.c. method at 1 kHz).

Second, the operating voltage ranges are different for the multicell system and the single cell. Although the discharge capacity from 3.1 to 2.2 V is only slightly smaller than that from 3.5 to 2.0 V, see Fig. 3, the polarization at the final discharge stage becomes larger at the higher discharge rate. Moreover, the current increasing at the end of discharge depends on the performance of the power conditioner, and may emphasize the polarization. As a result, the capacity corresponding to the 2.4 V plateau in Fig. 3 could not be used at high discharge rate.

Third, the deviations of the operating temperature, initial capacity and the state-of-charge (SOC) in individual cells from those mean levels should be clarified. The temperature rise curves at the cell bottom are shown in Fig. 6. At the 4 A discharge end, the surface temperature of the center cell is higher by about 5 °C than that of edge cells in the module. Furthermore, the correlation between the initial cell capacity and SOC for all single cells is checked, see Fig. 7. SOC can be determined from the open-circuit voltage after charge referring to the potential curve in Fig. 3. At a high rate, the multicell operation is terminated not because the total voltage becomes 170 V but because a certain cell (No. 25), having the second smallest capacity and the lowest SOC among all, shows a limit voltage of 2.0 V. Both the small initial capacity and the low SOC of any single cell should result in a poor rate capability of the multicell system.

4. Conclusions

The 200 V 2 kWh class energy storage system was constructed with seventy seven 25 Wh Li/LiV_3O_8 single cells in

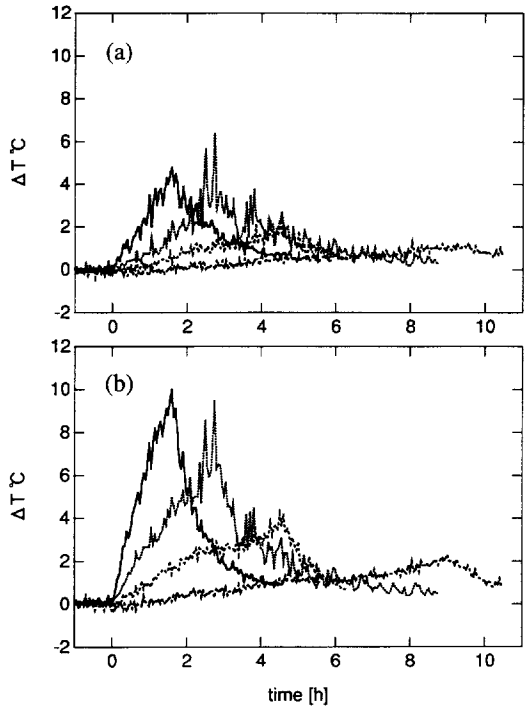

Fig. 6. Changes in the surface temperature of a cell during discharge at various rates. (a) Cell located at the edge of a module. (b) Cell located in the center of a module. (– · –) 1 A; (– – –) 2 A; (· · ·) 3 A, and (———) 4 A.

series connection. The performance of this multicell system was as following:

1. The output energy of 1.94 kWh and the energy efficiency of over 93% could be achieved at about 10 h rate almost as designed as 2 kWh system.

2. The rate capability of the multicell system was poor compared with that of a component single cell. The internal resistance of the system, the safe setting of operational voltage limits, and the non-uniform characteristics of the assembled single cells were considered to lower the rate characteristics of the multicell system.

The following improvements to obtain better rate capability are: (i) control of component cell quality, and (ii) temperature rise, especially at discharge, should be minimized

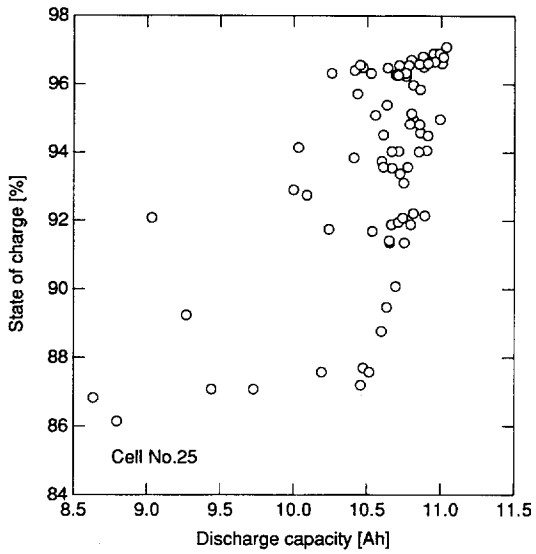

Fig. 7. Initial cell capacity vs. state-of-charge for all component cells involved in the multicell system.

and the development of temperature insensitive single cells may be expected at the same time.

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