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Series-connected multi-cell operation of lithium-ion cells by floating method

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Abstract

The resistance to damage during overcharge and overdischarge of a single cell and the possibility of series-connected multi-cell operation have been investigated using a commercialized lithium-ion cell. The single cell showed sufficient cycleability in overcharge up to 4.5 V and small reversible capacity in overdischarge under 2.5 V. An overdischarged cell below 0 V did not generate subsequent electromotive force and behaved like a resistor of an electron conductor. Multi-cell operations including imbalanced cells both in a preshifted state-of-charge between +30 and −5% and in various ambient temperatures were performed for over 1000 cycles of charge/discharge by the floating method. © 1997 Published by Elsevier Science S.A.

Keywords. Lithium secondary cells; Multi-cells, Overcharge, Overdischarge

1. Introduction

Lithium secondary batteries are expected to be used as a large-scale energy storage system for electric vehicles, as well as for the electric power load leveling [1]. The series-connected high-voltage multi-cell technology of the 100–400 V class cells has become important, in addition to the scaling up and improvement of component cells. In the multi-cell system, a certain cell generally can be overcharged or overdischarged, since no two cells have identical properties. In other words, individual component cells in a multi-cell system have different initial capacities and state-of-charge (SOC), and hence the operating temperature is not uniform over all cells. In the case of lithium cells, the multi-cell performances should be considered to be relatively poor because of lack of durability against overcharge and/or overdischarge.

In this work, the overcharge and overdischarge phenomena of Li/$LiCoO_2$ cells were investigated. In addition, the cycleability and the allowable distribution ranges of each cell in the series-connected multi-cell operation were investigated by the floating method [2]. The series-connected multi-cell system containing an imbalanced component cell was satisfactorily simulated by this method which was originally applied for only several cells.

2. Experimental

2.1. Specifications of the test cell

1 Ah class cylindrical lithium-ion cells (type 18 650) for used in video equipment and 2 Ah class sister cells (type 26 650) were obtained from SONY. According to the manufacture's instructions, the nominal operation voltage was between 4.2 and 2.5 V and the operating temperature was between 0 and 40 °C. $LiCoO_2$ and carbon were described as the active materials in the positive and negative electrodes, respectively [3].

2.2. Operating conditions of a single cell and disassembled analyses

In galvanostatic overcharge cycle experiments, the upper voltage limit was typically shifted up to 4.5 V. In galvanostatic overdischarge cycle experiments, on the other hand, 110% of charged electricity was obliged to discharge without voltage limitation. After the occurrence of the final failure mode, cells were disassembled. The electrolyte and gas com-

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ponents were analyzed by gas chromatograph mass spectroscopy (GC/MS), and the positive electrodes were investigated by X-ray diffraction (XRD). Positive and negative electrodes were observed by scanning electron microscopy (SEM), as was the separator.

2.3. *Multi-cell operation by floating method*

The electrical circuit for the floating method is compared with that for normal series connection, as shown in Fig. 1. In the floating method, the imbalanced cells ((1)–(5) in this figure) cannot be voltage-controlled and only their charge and discharge duration can be controlled. The imbalanced cells were connected in series with four other cells ((6)–(9)) under voltage control.

Two kinds of imbalanced cells were prepared taking into consideration the series-connected real multi-cell. The SOC was intentionally changed by +30 to −5% from the normal value, where type 18 650 cells were used, and the multi-cell system was operated under various conditions. In another case, the imbalanced cells were operated at various temperatures between 40 and 10 °C, under forced cooling with a fan at 25 °C and under covered with heat-insulating material at 25 °C, where type 26 650 cells were employed and the multi-cell was operated at a high 1 h rate.

3. Results and discussion

3.1. *Overcharge and overdischarge behaviors of the single cell*

The additional discharge capacity of about 0.4 Ah is obtained during the initial cycles between 4.5 and 4.2 V, which ensures sufficient cycleability. When charged to over 4.8 V, the cell does not rupture, but shows high impedance probably because the internal vent opens due to increased internal pressure resulting from gas evolution [4]. The main electrolyte components of a fresh cell are analyzed to be propylene carbonate (PC), dimethyl carbonate (DMC) and methylethyl carbonate (MEC). After overcharge to above 4.4 V, the amount of DMC decreases and diethyl carbonate (DEC) forms, in addition to some derivatives of PC. Moreover, much CO_2, which may be formed by the decomposition of lithium carbonate contained in a positive electrode, as reported by Ozawa and Yokokawa [3], is detected from the pressurized gas phase.

Typical overdischarge data in Fig. 2 show clearly that there is a small reversible capacity below 2.5 V. The operating voltage drops to below 0 V at the end of the third discharge, and the voltage does not recover to 1.0 V at the succeeding rest. In both cases A and B, shown in this figure, the electromotive forces of these cells are not generated and the cells behave like a resistor of an electron conductor after five cycles.

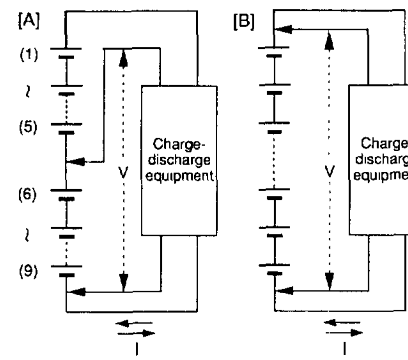

Fig. 1. Electrical circuits of the floating method (A) and the normal series connection (B): ((1)–(5)) floating cells free from voltage control, and ((6)–(9)) controlled cells.

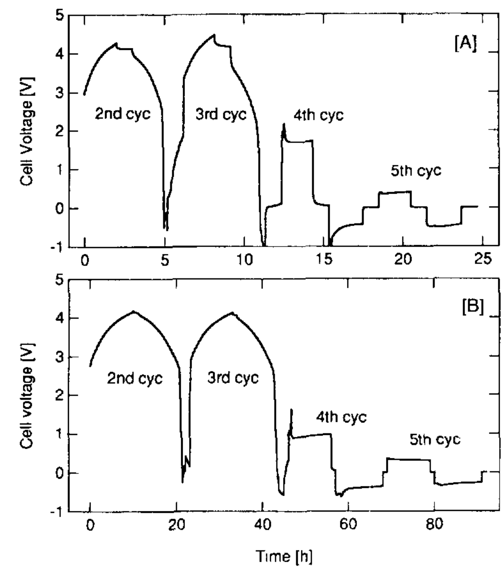

Fig. 2. Typical charge/discharge curves of cycle numbers 2–5 under forced overdischarge condition: (A) 0.5 A×2 h/0.5 A×2.16 h, and (B) 0.1 A×10 h/0.1 A×11 h.

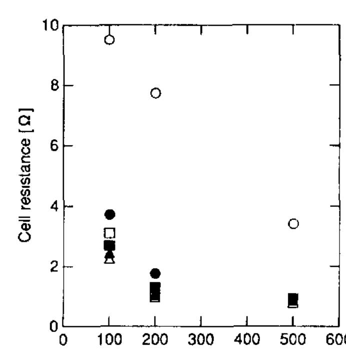

Fig. 3. Changes in cell resistance with charge/discharge currents under forced overdischarge (○) 4th cycle; (□) 5th cycle, and (△) 6th cycle (black: at discharge).

The apparent cell resistance estimated from the cell voltage/current ratios is shown in Fig. 3, where the resistance decreases markedly at a large current. Both the positive and negative electrodes in an overdischarged cell are found to be covered with copper, as seen in Fig. 4. This indicates that the

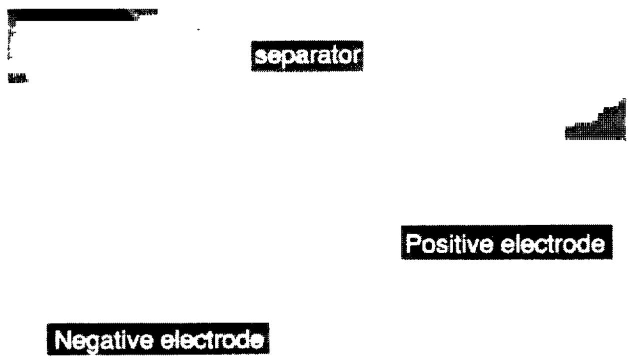

Fig. 4. Disassembly of overdischarged lithium-ion cell after loss of electromotive force.

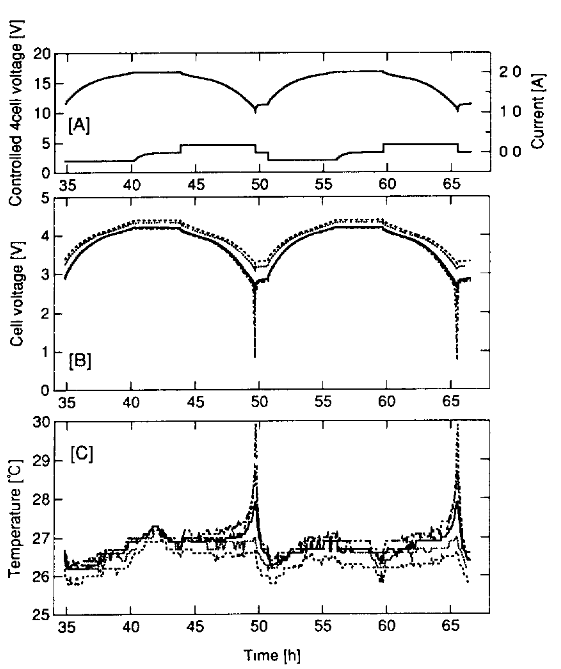

Fig. 5. Typical charge/discharge performances of series-connected multi-cell by floating method: 16.8 V/10 V, 0.2 A/0.2 A (A) Total voltage and current of 4 cells under voltage control, (B) each cell's voltage-preshifted overcharge and overdischarge, and (C) cell surface temperature. (———) controlled standard cell; (- - -) +30% preshifted cell, (· · ·) +20% preshifted cell; (– · –) −2% preshifted cell, and (– · –) −5% preshifted cell

dissolution of copper occurs from the negative pole current collector and that copper is deposited on both electrodes during cycling. Although changes of the electrolyte phase after overdischarge below 0.05 V are almost analogous to those after overcharge, some derivatives of EMC and DMC can be detected with an negligible amount of CO_2. The lattice structures of $LiCoO_2$ remain substantially unchanged even after overcharge or overdischarge. However, the main XRD peak shifts slightly to a higher angle in both cases, and the removal of lithium from $LiCoO_2$ [5] is suggested. Neither change of the electrode particles nor of the separator is detectable by SEM observation after various cell operations.

3.2. Multi-cell operation by floating method

3.2.1. Effects of intentionally combined preshifted cells

Typical initial performances at 5 h rate are shown in Fig. 5, where floating imbalanced cells preshifted to overcharge and overdischarge states show higher and lower operation voltages than the standard cell, respectively. In particular, the −5% preshifted cell exhibits a rapid voltage drop at the discharge end, and its surface temperature increases by about 4 °C. The influences of the discharge voltage on cell heat generation become considerable at below 3.0 V.

The changes of the discharge capacity, charge end voltage and discharge end voltage for each imbalanced cell with increasing number of cycles are shown in Fig. 6. The negatively preshifted cells (−2 and −5%) lose electromotive force within several hundred cycles just as a single cell under overdischarge cycle conditions. Nevertheless, there is no serious problem for current flow in the multi-cell system. The positively preshifted cells (+20 and +30%), on the other hand, show higher charge end voltages gradually with increasing number of cycles. Although the discharge capacity at 1200 cycles is reduced to half, these two cells can operate satisfactorily. The cycle life of these multi-cell systems stays at 900–1500 cycles, depending on the charge/discharge conditions, which is shorter than that of a single cell. The reasons why one of the four controlled cells shifted to overdischarge

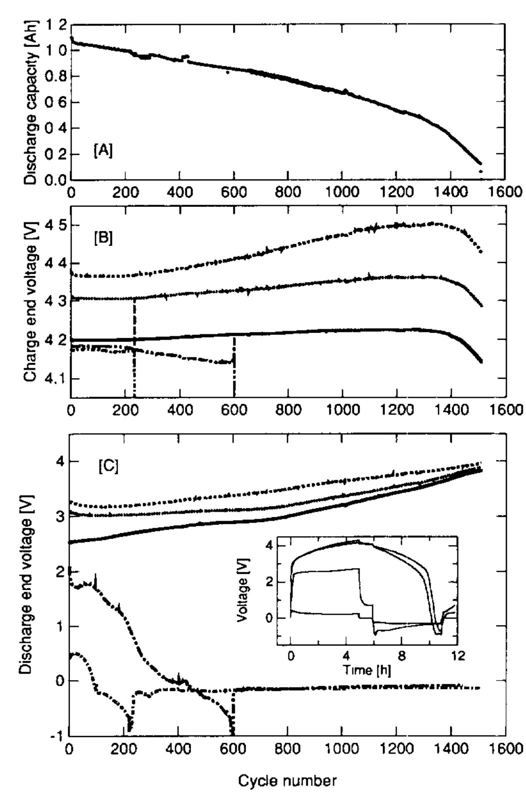

Fig. 6. Typical cycle performances of series-connected multi-cell by floating method: 16.8 V/10 V, 0.2 A/0.2 A (A) Discharge capacity; (B) charge end voltage, and (C) discharge end voltage. Inset· 232nd–235th charge/discharge curves of −5%-shifted overdischarge cell. (———) standard, (- - -) +30%; (· · ·) +20%;, (– · –) −2%, (– · –) −5%.

and the other cells were forced to operate under the condition of narrow voltage range should be considered.

3.2.2. *Operation in various atmospheres as imbalanced cells*

Charge/discharge profiles of each imbalanced cell are shown in Fig. 7 at the tenth cycle. The capacity under this condition was obtained to be about 2 Ah which corresponds to 80% depth-of-discharge (DOD) operation. Cell performances depend on operating temperature, and they are better at higher temperatures within the present test conditions. Consequently, the voltage in discharge decreases both at 10 °C and under 25 °C forced cooling. This behavior is attributed to the difference in operational temperature. Under covered with heat-insulating material at 25 °C, the cell surface temperature rises to over 30 °C at the end of discharge, but it cools down to almost the initial temperature during the subsequent rest time of 30 min and charging. The amount of heat generated was negligible accumulated at over a 1000-cycle operation.

Cycle performances of each imbalanced cell are shown in Fig. 8 as the charge and discharge end voltages and energy efficiencies. The voltage range of a cell operated at 10 °C spread with shift to overcharge because of low cell performances. On the other hand, the cell operated at 40 °C suddenly shifted to overdischarge at about the 900th cycle, resulting in loss of electromotive force at about the 1100th cycle. The degradation with increasing number of cycles might be accelerated by operation at higher temperatures. Neither cells under forced cooling nor those covered with heat-insulating material show large change of their operational voltage range with increasing number of cycles. However, the energy efficiency of the former cell is about 7% lower than that of the latter and the difference increases with cycles.

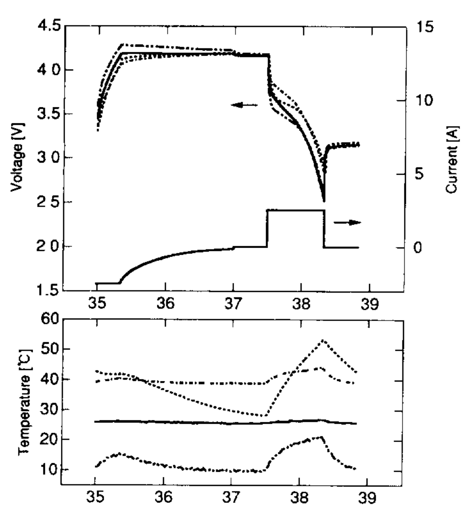

Fig. 7. Typical charge/discharge performances of series-connected multi-cell by floating method at the tenth cycle at various temperatures. 16.8 V (2 h constant voltage)/10 V, 2 A/2 A (– · –) under 10 °C natural heat radiation; (– –) under 40 °C natural heat radiation, (———) under 25 °C forced cooling with fan, and (·) under 10 °C covered with heat-insulating material

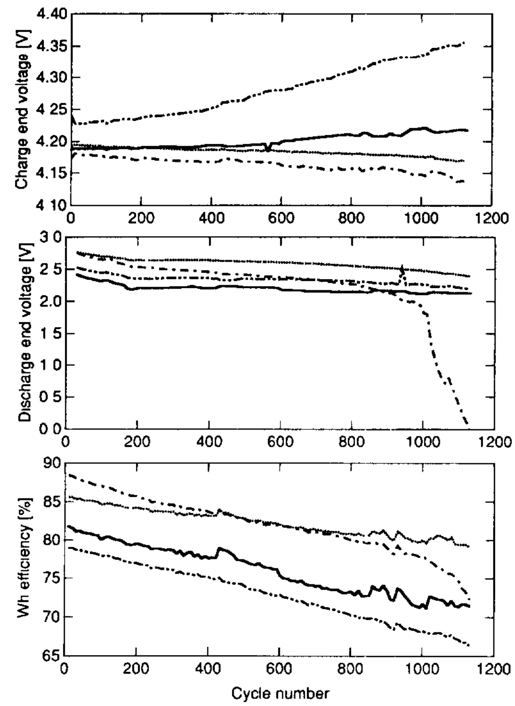

Fig. 8. Typical cycle performances of series-connected multi-cell by floating method, 16.8 V (2 h constant voltage)/10 V, 2A/2 A. (– –) under 10 °C natural heat radiation; (– · –) under 40 °C natural heat radiation; (———) under 25 °C forced cooling with fan and (- - -) under 25 °C covered with heat-insulating material

4. Conclusions

Bearing in mind application to electric power storage, the durability of a single cell and allowable distribution ranges of series-connected multi-cells have been investigated using commercial lithium-ion cells. Overcharged cells preshifted up to +30% are operable for over 1000 cycles because of sufficient additional reversible capacity between 4.2 and 4.5 V. On the other hand, for overdischarged cells, even small capacity preshift led to loss of electromotive forces within hundreds of cycles but no serious problems occurred for current flow in the multi-cell system because of the small resistance of 1–3 Ω.

In terms of the thermal problem in assembling the pack of multi-cells, this cell system is operable for over 1000 cycles even at a high 1 h rate under typical heat insulating and forced cooling condition. Further investigations should be necessary in scaling up of a cell, because the amount of the heat generation increases and heat transferring path gets longer.

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