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PSOC cycle testing method for lithium-ion secondary batteries

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Abstract

A cycle testing procedure is proposed which carries out charge and discharge in a partial state of charge (PSOC) with some testing levels such as an averaged state of charge, temperature, etc. The PSOC cycle test with this procedure was carried out for a commercial lithium-ion cell for about 20,000 cycles, and the testing procedure and test results are discussed. The features of the degradation due to PSOC cycle test in the tested lithium-ion cell were clarified as follows. The degradation during the PSOC cycle test was greater at higher environmental temperature. The degradation was greatest at a high average SOC, and smallest at SOC = 50%. The degradation increased again at a low average SOC. In the test results for 2 years with 20,000 PSOC cycles, which converted to 2200 cycles of full-capacity charge and discharge, capacity degradation was 32% even at the greatest degradation at 318 K and 8% or less at 278 K. The proposed testing procedure is useful for evaluating a cell used on partial charge and discharge cycles.

Keywords: PSOC cycling test; Partial charge and discharge; Testing method; Lithium-ion battery

1. Introduction

The applications of the secondary battery are expanding in fields such as photovoltaic power generation and hybrid electric vehicles, in which the secondary battery is used generally by undergoing discharge and charge in a partial state of charge (PSOC). Therefore, some testing methods which simulate the discharge and charge pattern of a secondary battery utilized in such hybrid electric vehicles and photovoltaic power generation systems are examined to confirm the operation of secondary batteries in the respective applications [1,2]. For example, PSOC cycle testing procedure for lead-acid batteries for photovoltaic systems was established as a Japan Industrial Standard in 1997 in Japan [2].

Hybrid electric vehicles using the nickel–hydrogen battery have already been used practically. Large lithium-ion secondary batteries also are being developed for pure electric vehicles and hybrid electric vehicles. It is anticipated that the demand for a lithium-ion secondary battery undergoing discharge and charge in a partial state of charge under various environmental conditions will increase with the extension of utilization fields such as photovoltaic systems and hybrid electric vehicles in the near future. There is hardly any published data for the lithium-ion battery on a charge–discharge cycling test in a partial state of charge.

In this study, a cycle testing procedure is proposed which carries out charge and discharge in a partial state of charge with some testing levels such as an averaged state of charge, temperature, etc. The PSOC cycle test with this procedure was carried out for a commercial lithium-ion cell for about 20,000 cycles, and the testing procedure and test results are discussed.

2. PSOC cycle test method

2.1. PSOC cycle testing procedure

The testing method which confirms the operation of secondary batteries in the applications such as photovoltaic power generation systems and hybrid electric vehicles has many discharge and charge patterns due to the usage, but it cannot determine in which part of the discharge and charge pattern the battery tested deteriorated. This is not suitable for the new batteries such as the lithium-ion battery to examine the operating conditions utilizing their features in an application. The testing method proposed in this paper intends to

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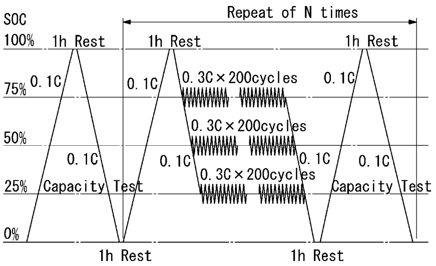

Fig. 1. PSOC charge/discharge cycle test sequence.

examine how a new secondary battery should be utilized in the application used under various partial discharge and charge conditions.

The PSOC cycle testing procedure proposed repeats a partial discharge and charge of an amount of capacity around some levels of the average state of charge as shown in Fig. 1, as an example for the test of a commercial lithium-ion cell. A capacity test for full charge and full discharge after certain cycles of partial charge and discharge is carried out. This PSOC charge–discharge cycle test is carried out at some temperature levels in order to also examine the effect of environmental temperature.

For the test of a commercial lithium-ion cell, ±5% of nominal capacity for the amount of partial discharge and charge, three PSOC levels of 75, 50 and 25%, three temperature levels of 278, 293 and 318 K, and capacity measurement every 200 PSOC cycles were adopted, as shown in Fig. 1. The discharge capacity test was carried out at the charge/discharge rate of 0.1 C, according to "Testing procedure of long discharge rate lead-acid batteries for photovoltaic systems" [2], and the PSOC charge–discharge at the rate of 0.3 C. The cell in the capacity test was fully charged at 0.1 C constant current charge, followed by 4.2 V constant voltage charge for a total period of 11 h, and the discharge was done at 0.1 C constant current to a termination voltage of 2.75 V.

2.2. Test sample and test conditions

The test samples were US18650 cells which were removed by disassembling battery packs of NP-F730 sold by Sony Co. The initial measurements such as capacity test, impedance measurement and weight measurement were done on 48 cells for 12 battery packs. The initial capacity test was carried out at 298 K under the following conditions: 0.1 C constant current charge, followed by 4.2 V constant voltage charge for a total period of 11 h, and 0.1 C constant current discharge to a termination voltage of 2.75 V after a 1 h rest period. The rest period after the discharge is taken within 12 h from the start of discharge. The averaged value of discharge capacity in the three cycles of initial charge and discharge was defined as the initial capacity. Initial cell impedance from 0.1 Hz to 10 kHz was measured at 298 K in the fully charged condition.

The initial weight of 48 cells was in the range of 38.7118 ± 0.1770 g where each positive electrode cap was drilled to form a hole of 2 mm in diameter in order to hold the cell. From the initial capacity test results, 48 cells were classified into two groups, a small capacity group of 1295.9 ± 5.3 mAh, and a large capacity group of 1345.6 ± 8.0 mAh. The cells of the large capacity group have greater impedance than the cells of the small capacity group. Two cells in each group were tested of a total of four cells at each test level. A total of nine test levels consisted of three levels of an average state of charge and three levels of temperature. The levels of temperature were 278, 298 and 318 K. The levels of the average state of charge were 75, 50 and 25%. The total number of tested cells was 36, and each cell was given a number from 201 to 236 in the order of test levels.

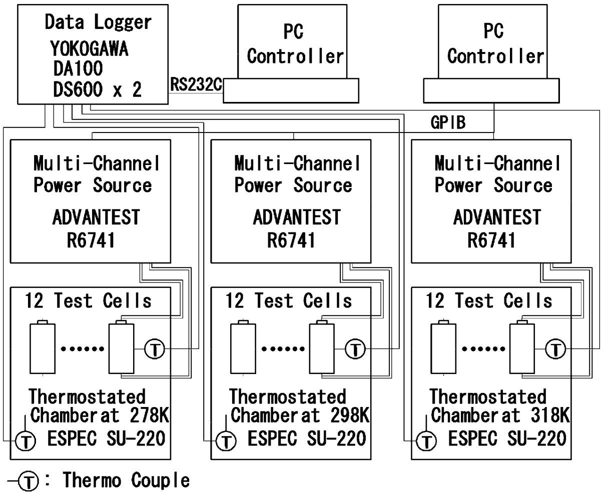

Fig. 2. A system for PSOC charge/discharge cycle testing.

2.3. Testing system

The configuration of the testing system used in the PSOC charge–discharge cycle test is shown in Fig. 2. Three 12-channel programmable DC voltage/current sources (ADVANTEST R6741) were used for charge and discharge. A 12-channel source undertook a temperature level consisting of three averaged SOC levels, four samples for each level and a total of twelve samples. Three thermostated chambers (ESPEC SU-220) were used to set the sample temperature at three levels. The temperature of each cell was continuously monitored by the thermocouple adhered on the cell surface accompanying the thermostated chamber temperature. All cell temperatures were within ±1 K of the setting temperature, respectively.

The impedance measurement was carried out under the each setting condition at about every 400 through 2000 cycles (as marked in Fig. 4) to evaluate the cell degradation based on the cell impedance. Using the Solartron1286/1255 system, the impedance was measured for a frequency range from 0.1 Hz to 10 kHz in a galvanostat mode with zero direct current and 50 mA alternating current. At 2700, 7694, 8690, 16,735, and 19,800 cycles, the cells were returned to room temperature by power cuts, etc. and the following measurements were carried out: cell weight, discharge capacity at 298 K, and impedance in the fully charged condition at 298 K.

3. Results and discussion

3.1. Change in discharge capacity with cycle

Discharge capacity for the each test level of all samples versus cycle number in about 20,000 cycles is shown in Fig. 3. The cycle number of the transversal axis in the figure is the simple sum of the cycle number in the PSOC charge–discharge cycle and the cycle number in the full-charge/full-discharge cycle for the capacity measurement. The cycle number converted into full-capacity discharge and charge cycles is about 2200 cycles. The test duration in a calendar year is about 2 years including the idle period for the power cut, various measurements and adjustments, etc.

The initial capacity is dependent on the temperature levels, and it is lower at lower temperature, but it does not differ among the test levels of an average SOC. There are some discontinuous changes in the capacity at cycle numbers of 241, 2823, 7694, 8696, and 16,735 in some cycle curves, especially at the low temperature level of 278 K (Fig. 3(a)–(c)). This discontinuous change may be caused by returning the cells to room temperature, because each discontinuous point corresponded to the point at which the cells were returned to room temperature. Though the mechanism is not proven, it is shown in the experimental result that the effect of temperature change increases at lower temperature. Except for cells #213 and #221, four cells of the each group at each test level showed almost the same capacity change versus cycle number. Cells #213 and #221 showed greater degradation after about 7000 cycles in comparison with the others. Although the cause of this could not be determined, there was a trend for the degradation rate to increase also in #225, #229, #233, etc., when the degradation reached a certain extent. #213 and #221 seemed to be a special case, which this trend appeared remarkably.

3.2. Degradation rate

The averaged capacity of four samples for each test level is shown versus cycle number in Fig. 4. The capacity degradation from the initial capacity was greater at higher temperature levels. As for the test levels of the average SOC

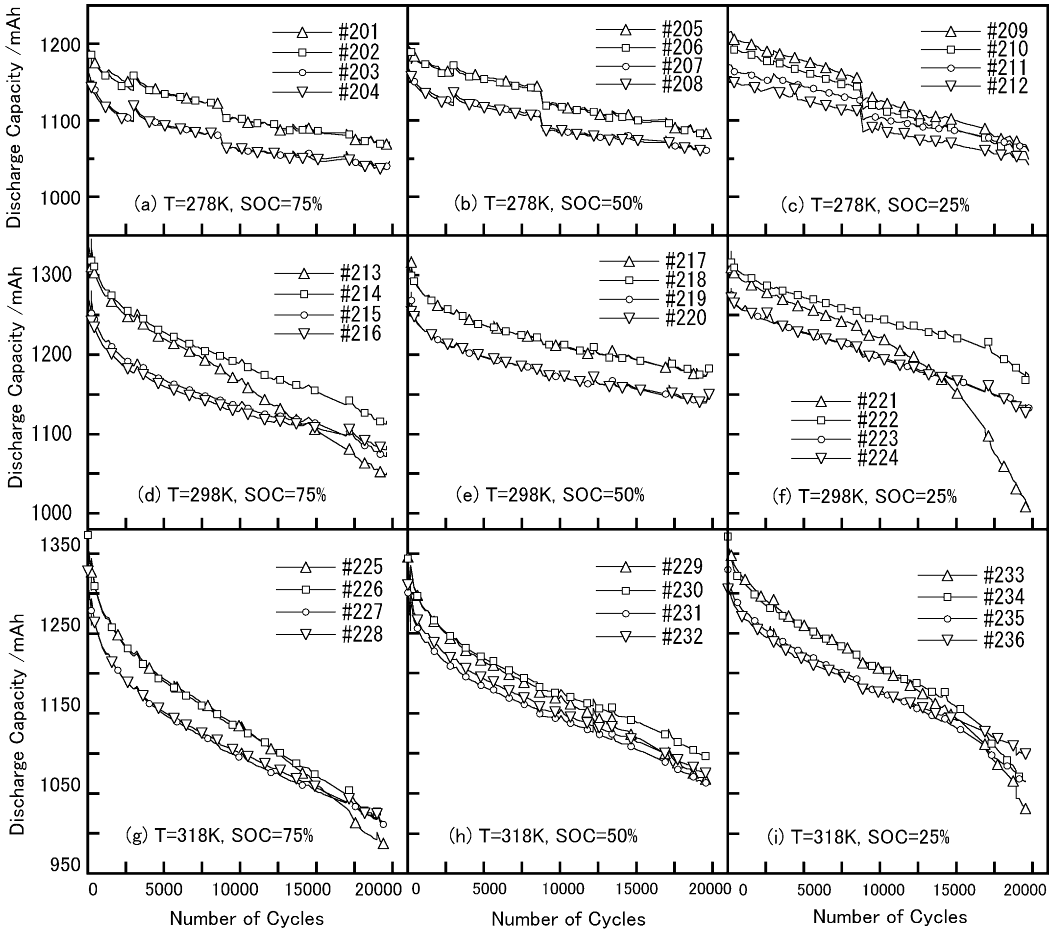

Fig. 3. Results of PSOC charge/discharge cycle test for 36 commercial lithium-ion cells at three levels of an average SOC at three levels of temperature.

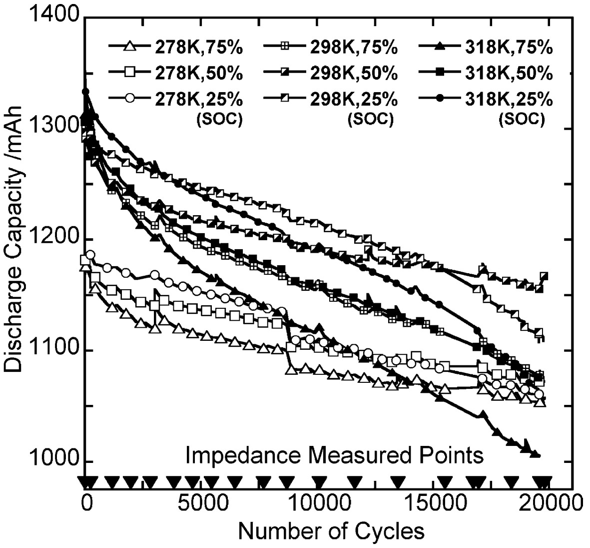

Fig. 4. Averaged discharge capacity for each test level vs. cycle number.

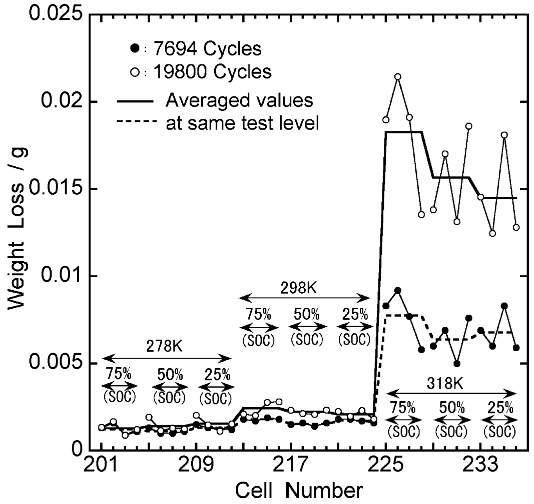

Fig. 6. Weight loss of cells after the PSOC charge/discharge cycle test from the initial for each test sample.

in a PSOC charge–discharge cycle, the degradation is the greatest at 75% SOC. In the comparison between 25 and 50% SOC, the capacity degradation was smaller at 25% than at 50% by the cycle 10,000 and several, while it became greater at 25% near 20,000 cycles. The degradation rate in the discharge capacity at 298 K at 8696 and 19,800 cycles relative to the initial is shown in Fig. 5. The degradation rate is also greater at higher temperature levels and also greater for the higher average SOC levels by 8690 cycles, but the degradation at 19,800 cycles was the smallest at 50% average SOC.

The test results for 2 years for 20,000 PSOC cycles, converted to 2200 full-capacity charge–discharge cycles, are summarized as follows: capacity degradation of the tested cells was 32% even at the greatest at 318 K, and it was 8% or less at 278 K.

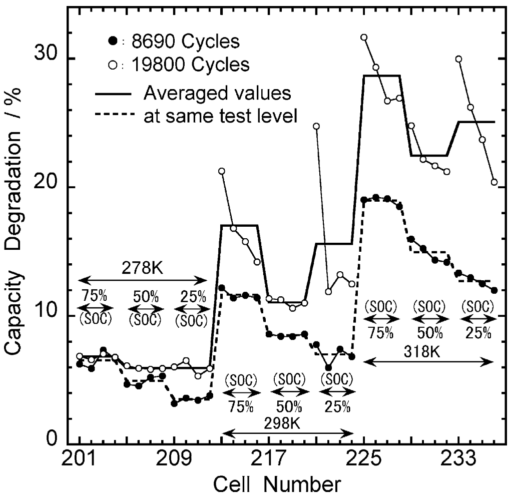

Fig. 5. Capacity degradation after the PSOC charge/discharge cycle test for each test sample.

3.3. Weight loss of cell

Cell weight measured at 7694 and 19,800 cycles is shown as weight loss from the initial in Fig. 6. The weight loss of the cell was greater at the higher temperature in which the capacity degradation was greater, and it was higher at higher average SOC. It is considered that weight loss means a decrease in the electrolytic solution. This maximum was about 20 mg and under 1% of the total weight of the electrolytic solution. It is considered that such a decrease in the electrolytic solution did not affect the cell performance. Weight loss was not caused by the electrolytic solution leaking directly from the cell. Because it is dependent on temperature and average SOC levels, it is assumed that the gas generated irreversibly by charge and discharge, resulting in higher internal pressure in the cell, caused the gas leakage.

3.4. Change in cell impedance

Cyclical change in the Cole–Cole plots of cell impedance measured at a test level condition every about 400–2000 cycles is shown typically in Fig. 7. The Cole–Cole plot of each cell for 0.1 Hz to 10 kHz consisted of three parts: a positive imaginary component by an inductance between several kHz and 10 kHz, a small semicircle for the higher frequency range, and a larger semicircle for the lower frequency range. Except for the test levels of 278 K, the diameter of the large semicircle for the lower frequency range increased with cycle number. At the test levels at 278 K, the semicircle in the lower frequency range was reduced at the average SOC test levels of 25 and 50% up to 2823 cycles, and it increased with increasing cycle number as same as the others afterwards. The change in the semicircle in the higher frequency range was not clear, while the series resistance component, which is the real

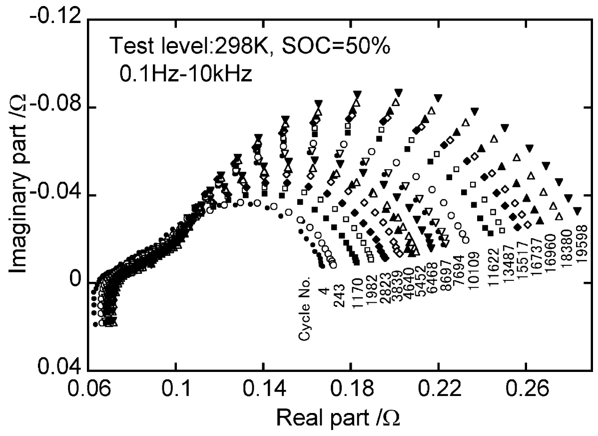

Fig. 7. Typical change in the Cole–Cole plot of cell impedance for 0.1 Hz to 10 kHz with the PSOC charge/discharge cycle.

number at the high frequency edge, increased slightly with increasing cycle number.

In order to clearly show impedance change before and after the PSOC cycling test, parameter fitting was done by an equivalent circuit shown in Fig. 8(a) to cell impedance measured under 298 K in the fully charged condition for 0.1 Hz to 10 kHz. As a result, each resistance component in the equivalent circuit for the initial cycle and after 19,800 cycles is shown in Fig. 8(b). The time constant of each RC parallel circuit in the equivalent circuit increases with the order of the subscript number. As shown in Fig. 8(b), each resistance from R_0 to R_4 without R_3 increased with the PSOC cycling test, and especially the increase in R_4 is remarkable. The increase in resistances is remarkable under the testing condition of an average SOC of 75% at higher temperature, and it well corresponds with the capacity degradation. That is, the sample with the larger degradation in capacity also had a greater increase in cell impedance.

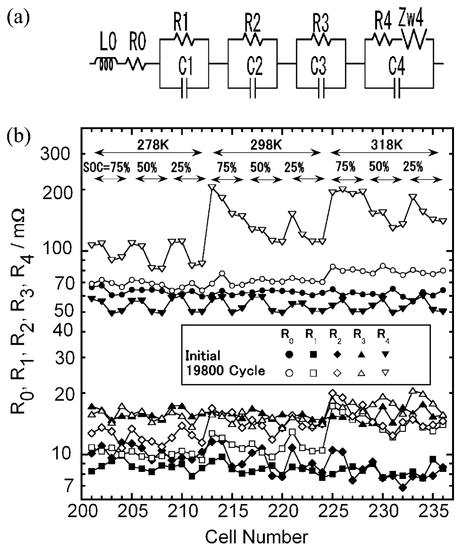

Fig. 8. Impedance change in each cell by PSOC charge/discharge cycling: (a) an equivalent circuit for the cell; (b) resistive components in the equivalent circuit before and after the test.

The equivalent circuit of Fig. 8(a) assumed double layer capacities, reaction resistances, and possible solid electrolyte interfaces at the negative and positive electrodes, etc. Each element of the equivalent circuit did not completely correspond with the cell components. However, according to a separate experiment which could separate cell impedance into the positive electrode part and the negative electrode part in a beaker cell [3], it was clear at least that the semicircle of lower frequency (R_4C_4 parallel circuit) originated mainly from the positive electrode. Based on this fact, it can be said that the impedance increase with PSOC cycling was mainly caused by the impedance increase in the positive electrode.

3.5. Change in discharge curve

Discharge curves and their derivatives at the initial, 8696 and 19,800 cycles are shown for a typical degraded cell in Fig. 9. It can be recognized that the degradation with the cycling was appeared as a large decrease in the voltage for the greater depth of discharge over about 50% of capacity,

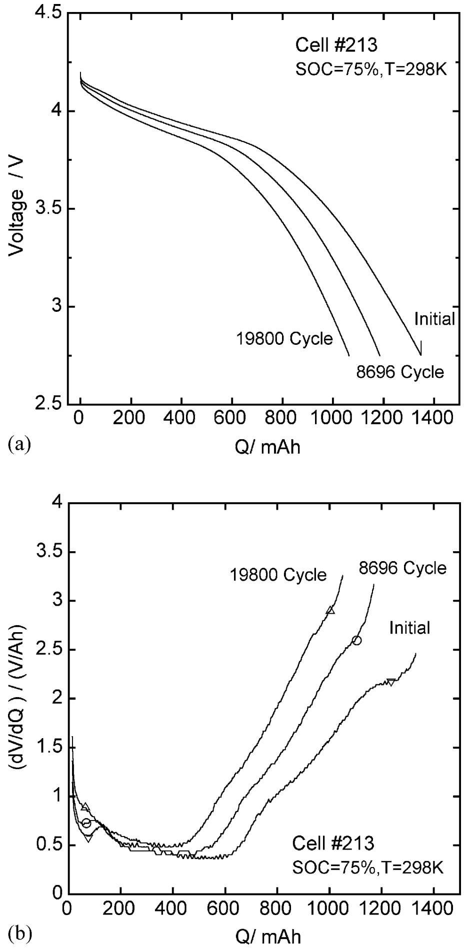

Fig. 9. Typical change in discharge curve (a) and differential discharge voltage curve (b) with the PSOC charge/discharge cycle.

resulting in a decrease in discharge capacity. Though that is not clear in the discharge curve, there are two characteristic features of the degradation in the differential curves of discharge voltage as shown in Fig. 9(b). The one concerns a peak near 150 mAh in the differential curve for the initial discharge. This peak was caused by a phase transition in the cathode active material ($LiCoO_2$) [4]. The peak moved with the degradation on the left and might disappear in certain cases. This fact indicated that the positive electrode could not be sufficiently charged due to the degradation. However, this effect of decreasing capacity is comparatively small. Another concern is the bend near 600 mAh and a knee near 1200 mAh in the initial differential curve. These were characteristic features of the hard carbon in the negative electrode [5]. The bend in the differential curve moved approximately similarly with the decrease in capacity, except for the knee near 1200 mAh which became indistinct with the degradation. This fact indicates at least that the active material quantity effectively working in the negative electrode decreased. However it was not clear whether the active material quantity effectively working in the positive electrode decreased.

3.6. Results of post-test observation

Optical and SEM observations were carried out on some representative samples disassembled after the PSOC cycling test. Two samples, #209 and #212, with small degradation, and three samples, #221, #222 and #225, with large degradation, etc., were disassembled and observed. The largest difference between the large degradation samples and the small degradation samples is as follows: both sheet electrodes of the negative and positive in the low degradation cells could be taken out by disassembling them in good condition with almost uniform appearance, while in the large degradation cells, the cathode active material adhered to the separator, and it peeled off from the aluminum collector in many places during the disassembly. There was also a clear discoloration different from other part in the negative electrode surface in some places. In the SEM observation, no remarkable features related to the degradation could be found.

4. Conclusions

A PSOC charge–discharge cycle testing procedure which was carried out by partial charge and discharge with ±5% of capacity at three levels for an average SOC at three levels of environmental temperature was proposed in order to evaluate the condition under which a cell used on partial charge and discharge cycles deteriorated. The proposed testing procedure was applied to a commercial lithium-ion cell, and a PSOC cycle test with about 20,000 cycles was carried out. The following items are clarified as features of the degradation due to the PSOC cycle test for the tested lithium-ion cell.

The degradation due to the PSOC cycle test was greater at higher environmental temperature.

The degradation was greatest at an average SOC of 75% and smallest at $\mathrm{SOC} = 50\%$. The degradation increased again at an average $\mathrm{SOC} = 25\%$.

In the test results for 2 years with 20,000 PSOC cycles, which converted to 2200 cycles of full-capacity charge and discharge, the capacity degradation was 32% even in the largest degradation at 318 K and 8% or less at 278 K.

Based on these results, it is clarified that the proposed testing procedure is useful for evaluating a cell used in partial charge and discharge cycles.

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