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Cycle life estimation of lithium secondary battery by extrapolation method and accelerated aging test

K. Takei[*], K. Kumai, Y. Kobayashi, H. Miyashiro,
N. Terada, T. Iwahori, T. Tanaka

Central Research Institute of Electric Power Industry (CRIEPI), 2-11-1 Iwado-kita, Komae-shi, Tokyo 201-8511, Japan

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Abstract

The testing methods to estimate the life cycles of lithium ion batteries for a short period, have been developed using a commercialized cell with $LiCoO_2$/hard carbon cell system. The degradation reactions with increasing cycles were suggested to occur predominantly above 4 V from the results of operating voltage range divided tests. In the case of the extrapolation method using limited cycle data, the straight line approximation was useful as the cycle performance has the linearity, but the error is at most 40% in using the initial short cycle data. In the case of the accelerated aging tests using the following stress factors, the charge and/or discharge rate, large accelerated coefficients were obtained in the high charge rate and the high temperature thermal stress. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium ion batteries; Cycle life; Extrapolation method; Accelerated aging test

1. Introduction

Lithium secondary batteries for home-use load leveling systems are required to have the long life cycles of 3500 cycles [1,2]. These systems are assumed to be operated with midnight charge for 5–8 h and daytime discharge for the same duration. Consequently, time compression of testing duration is an indispensable means of evaluating life cycles of developed batteries for a given period.

In this study, firstly the influence of the cell's operating voltage ranging on cycle performance was investigated, based on the fact that the degradation reaction depends electrochemically on its potential. Moreover, two techniques were experimentally adopted in order to estimate the cycle lives. One was the extrapolation method in which limited experimental data obtained from the cycle operation under the standard conditions are used. The other was the accelerated aging test in which the following five stress factors, charge rate (CHG), discharge rate (DIS), charge and discharge rate (C/D), depth-of-discharge (DOD) and static thermal stress (TEMP), are used.

2. Experimental

A commercialized cylindrical lithium ion cell of 1.25 Ah capacity (type US18650) from SONY was used as a typical sample [3]. Considering the effective improvement of the load factors and cell performance, the standard operating conditions were determined to be the following four patterns:

1. c.c. + c.v. (constant voltage after constant current regulated by total charge period) charge at 8 h rate and 70% DOD discharge at 8 h rate;
2. c.c. + c.v. charge at 8 h rate and 80% DOD discharge at 5 h rate;
3. c.c. (constant current regulated by charge voltage) charge at 10 h rate and 70% DOD discharge at 8 h rate;
4. c.c. charge at 10 h rate and 80% DOD discharge at 5 h rate.

The limit of charge voltage was set at 4.2 V and the cell was discharged from the fully charged state limited at 2.5 V. The test parameters of the charge and/or discharge accelerated rate factors were changed from 0.2 to 1.0 C. The parameters of DOD were in the range from 70 to 100% (full discharge). All the operations, except for the TEMP test, were carried out at 25°C. The temperature of thermal stress was set between 10 and 55°C. Capacity tests consisting of a

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[*] Corresponding author.
E-mail address: takei@criepi.denken.or.jp (K. Takei).

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few cycles under c.c. + c.v. charge at 8 h rate and full discharge at 8 h rate were carried out every 50 cycles except under the 100% DOD condition and the TEMP test. Three cells were tested under the same conditions to grasp their performance dispersion. The cycle tests were started in 1995 under a total 22 sets of conditions including four sets of standard conditions. The cycle life was judged from the cycle in which the discharge capacity dropped to 70% of the initial capacity (0.875 Ah) under the capacity test conditions. However, the cycle tests were continued till 50% decrease of the capacity.

3. Results and discussion

3.1. Operating voltage range divided test

We determined the operating voltage range required to divide cell capacity equally into four (RNG2, 4, 6, and 8), as shown in Fig. 1. Regulated charge and discharge voltages were determined, from the charge and the discharge curves, respectively, to be between 4.2 and 2.5 V considering the polarization. Hence, these operating voltage ranges partially overlapped. Moreover, RNG1, 3, 5, 7 and 9 were obtained from the division shifted half of the above capacities. RNG1 included the overcharge voltage range to 4.27 V, and RNG9 included the overdischarge voltage range to 0.5 V, but in this range the capacity did not have enough as the same capacity.

Experimental results of cycle performance in each range are shown in Fig. 2 normalized with one unit on the discharge capacity of the tenth cycle. Numerical curves were added under the assumption that the capacity decreased tendency was exponentially ($\eta = 0.999 - 0.99995$), where η represents the ratio of the preserved discharge capacity per one cycle. Smaller η was obtained with higher operating voltage ranges. Discharge capacities slightly decreased in the operations with 1000 cycles under 3.92 V. As a result, the degradation reactions with increasing cycles were suggested to occur predominantly above 4 V.

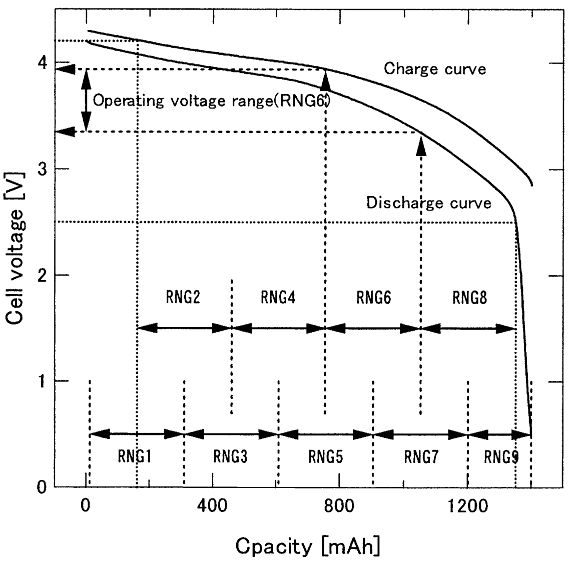

Fig. 1. Operating voltage range required to divide cell capacity equally into four.

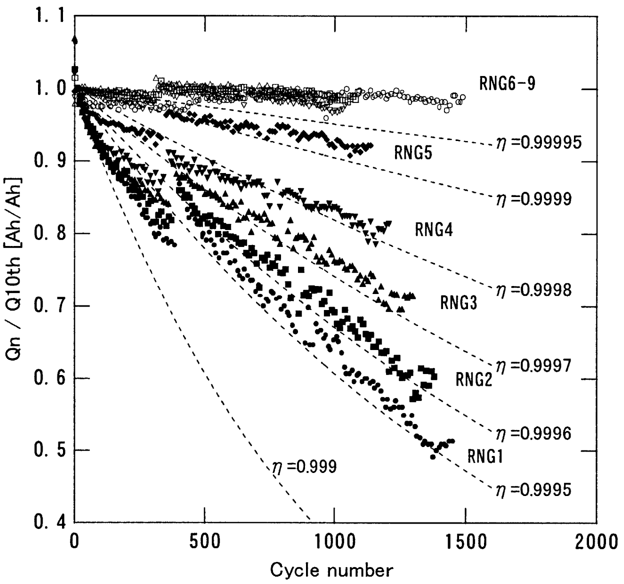

Fig. 2. Normalized experimental cycle performance of cell capacity divided test and numerically fitted curve (dashed lime).

3.2. Extrapolation method

Discharge capacities under the capacity test conditions decreased almost linearly. The cycle lives under the four standard conditions were about 2000 cycles on average. They were affected by the charge methods and were independent of both charge and discharge rates and DOD within the limit of the standard conditions. Under c.c. + c.v. charge conditions (1) and (2), 1700 cycles were obtained, and 2240 cycles was obtained under c.c. charge conditions (3) and (4). These results were considered to cause the difference in the period experienced high operating voltage over 4 V, as described in results of divided operating voltage range tests.

Typical cycle performance under the standard conditions (1) is shown in Fig. 3. The straight line extrapolated from the data of initial 500 cycles was added. In this case, the cycle life was estimated to be 2200 cycles from this line; this value includes about 20% error compared to the experimental result. Errors were larger in extrapolation with the exponential curves, as shown in Fig. 2. Therefore, the errors in the case of each standard condition pattern were estimated by the extrapolation method using the straight line approximation. The changes in the errors with the experimental number of cycles are shown in Fig. 4. The linearity of cycle performance was different for each cell but it was almost independent of operating conditions. It was doubtful that the

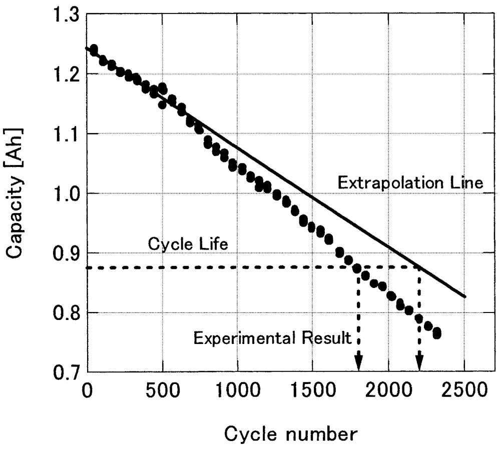

Fig. 3. Typical cycle performance under standard conditions. Solid line is the extrapolation from the initial 500 cycles.

error would be at most 40% in the case of the estimation from the initial short experimental cycle data.

3.3. Accelerated aging test

Time compressible coefficients (α) and degradation accelerative coefficients (β) are shown in Fig. 5 against each parameter of CHG [A], DIS [B] and C/D [C] as accelerated factors. The compressible ratio (α) of the charge and discharge period of each accelerated test to that of standard condition (1) per one cycle. It can be calculated easily from the test conditions, but was obtained from the real operational duration time including the rest time and the capacity test. The inverse ratio (β) of the cycle life of each accelerated test to 1690 cycles under the standard condition (1). In the case of the CHG or DIS accelerated factor, β became slightly larger as the rate got higher. On the other hand, in the case of the C/D accelerated factor, the cycle life extended over 4000 cycles under 0.5 C rate condition.

Acceleration coefficients (γ) against the parameters of each accelerated factor are shown in Fig. 6. Where γ represents the compressible ratio of total testing duration time up to the cycle life under the accelerated test conditions to that under standard condition (1). It corresponds to the multiplication of α and β. Collectively, γ tends to increase monotonically with parameters. The high temperature of the TEMP factor showed the most remarkable acceleration of all factors and the high rate (1.0 C) of the CHG factor was the second. These two operating conditions forced cell degradation with increasing number of cycles. In this graph, the dispersion in cells at 55°C was large but the cycle lives were actually in the range of 200 and 300 cycles. The high-temperature accelerated test is favorable because of the short test duration. However, degradation reaction different from those of the standard operation cycle life test conditions may occur considering that the potential and the activation energy are functions of temperature. In this experiment, showed an exponential relation to absolute temperature, but it is necessary to examine the change of the cell component materials as a parameter of temperature, by postanalysis.

Except for the above two conditions and some of the C/D condition, no significant differences in the cycle lives under all sets of the conditions were obtained. In the case of Li/MoS_2 cell system, the cycle life is reported to depend on both DOD and the charge rate by Kumai et al. [4]. In this SONY's cell system, DOD accelerated factor were found not

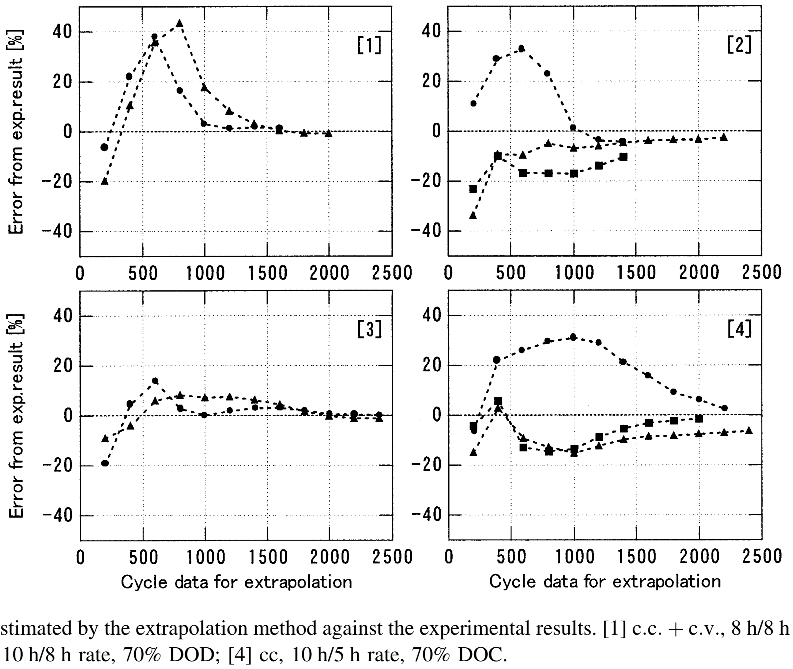

Fig. 4. Errors is the life cycles estimated by the extrapolation method against the experimental results. [1] c.c. + c.v., 8 h/8 h rate, 70% DOD; [2] c.c. + c.v., 8 h/5 h rate, 80% DOD; [3] cc, 10 h/8 h rate, 70% DOD; [4] cc, 10 h/5 h rate, 70% DOC.

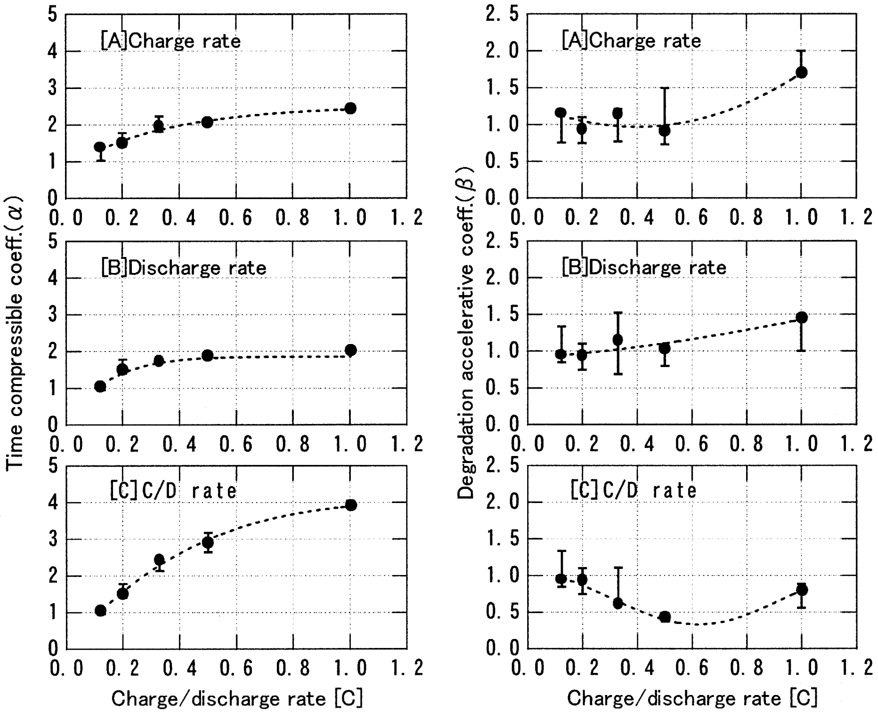

Fig. 5. Time compressible coefficients (α) and degradation accelerative coefficients (β) of charge rate [A]; discharge rate [B]; charge and discharge rate [C]. Error bars represent the dispersion of three cells.

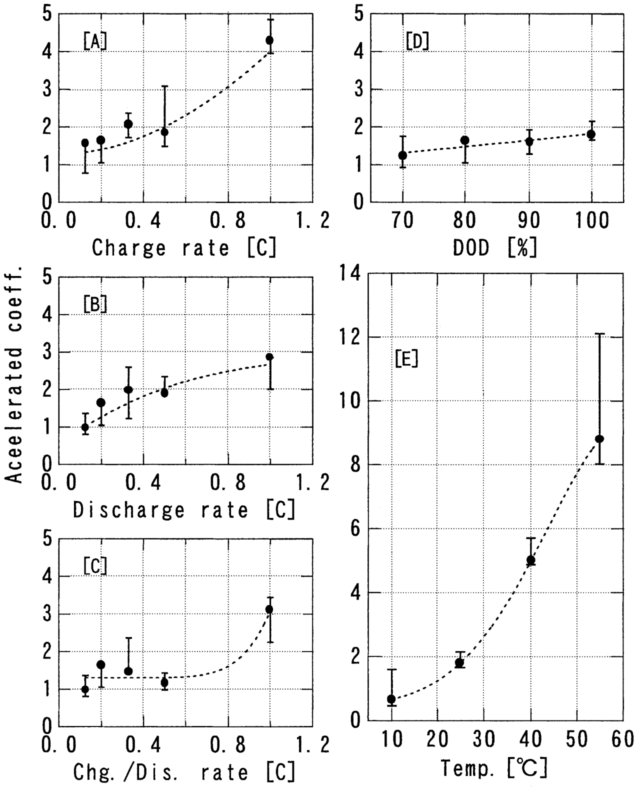

Fig. 6. Accelerated coefficients of charge rate [A]; discharge rate [B]; charge and discharge rate [C]; DOD [D]; the TEMP [E]. Error bars represent the dispersion of three cells.

to have much influence on the cycle lives, at least when discharge from fully charged state.

The accelerated test conditions with larger α and the same β as in the standard conditions would be useful because a similar rate of the degradation reaction may occur with increasing number of cycles.

These series tests were the operations under the constant current charge and discharge conditions. So, the above techniques cannot be used to apply the fluctuating load such as DST and SFUDS [5] for the more practical use like electric vehicles.

4. Conclusion

Two techniques were experimentally investigated in order to estimate the cycle life of lithium ion cells within a limited period. Cycle lives could be estimated by the extrapolation method via linear approximation, but the error is at most 40% when using the initial short cycle data. The stress factors of both the high charge rate and the high-temperature thermal stress are promising candidates in SONY's $LiCoO_2$/hard carbon cell system. The operating conditions of both factors above forced cell degradation with increasing number of cycles. However, in an unknown cell system, the accelerated test conditions with larger α and the same β as in the standard condition would be useful because a similar rate of the degradation reaction may occur with increasing number of cycles.

In evaluating the cycle life within limited periods, the accelerated conditions suitable for the cell system must be selected. Then both the extrapolation method and the accelerated aging test should be conducted in parallel.

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References

[1] T. Iwahori, Y. Ozaki, A. Funahashi, H. Momose, S. Shiraga, S. Yoshitake, H. Awata, J. Power Sources 81/82 (1998) 872–876.
[2] S. Yoda, K. Ishihara, J. Power Sources 81/82 (1998) 162–169.
[3] K. Ozawa, M. Yokokawa, in: Proceedings of the Tenth International Seminar on Primary and Secondary Battery Technology and Application, Deerfield Beech, FL, 1–4 March 1994.
[4] K. Kumai, T. Ikeya, K. Ishihara, T. Iwahori, N. Imanishi, Y. Takeda, O. Yamamoto, J. Power Sources 70 (1998) 235–239.
[5] D.D. Brandt, J. Power Sources 40 (1992) 73–79.