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Short communication

Life prediction and reliability assessment of lithium secondary batteries

Seung-Wook Eom[a,c,*], Min-Kyu Kim[b], Ick-Jun Kim[a],
Seong-In Moon[a], Yang-Kook Sun[c], Hyun-Soo Kim[a]

[a] Battery Research Group, Korea Electrotechnology Research Institute (KERI), P.O. Box 20, Changwon 641-600, South Korea
[b] Reliability Assessment Center, Korea Electrotechnology Research Institute (KERI), P.O. Box 20, Changwon 641-600, South Korea
[c] Department of Chemical Engineering, Hanyang University, Seoul 133-791, South Korea

Abstract

Reliability assessment of lithium secondary batteries was mainly considered. Shape parameter (β) and scale parameter (η) were calculated from experimental data based on cycle life test. We also examined safety characteristics of lithium secondary batteries. As proposed by IEC 62133 (2002), we had performed all of the safety/abuse tests such as 'mechanical abuse tests', 'environmental abuse tests', 'electrical abuse tests'.

This paper describes the cycle life of lithium secondary batteries, FMEA (failure modes and effects analysis) and the safety/abuse tests we had performed.

Keywords: Lithium secondary batteries; Cycle life; Reliability; Safety; Assesment

1. Introduction

Lithium secondary batteries are widely used for portable applications because of their high energy density of over 200 Wh kg^{-1}. In recent years, lithium secondary batteries have found new applications in a rapidly expanding market, such as cellular phones, notebook PCs, camcorders, CD players and MP3 players. For this reason, the reliability of lithium secondary batteries is of increasing importance. Reliability-assessment of lithium secondary batteries can be divided into three groups; initial performance tests, lifetime endurance, and safety/abuse tests. Of these three, safety/abuse tests and life cycle tests are the most important.

In the case of lithium secondary batteries, the safety of the batteries is no less important than the lifetime. If the battery is out of order, it could not only malfunction, but potentially injure consumers as well.

1.1. Life distribution

The Weibull distribution is an empirical, flexible distribution that expresses various modes of failure. It is widely used in reliability analysis [1–6]. Two parameters, shape parameter (β) and scale parameter (η), define the type of Weibull distribution. Shape parameter explains the types of failure, and scale parameter explains the characteristic life cycle of devices. The scale parameter is the lifetime for which 63.2% of the devices have failed. It is analogous to the mean of the normal distribution. The mean time to failure (MTTF) of lithium secondary batteries can be described as the number of charge/discharge cycles until failure.

The failure rate (λ), reliability function (R), cumulative distribution function (F), and probability density function (f) can be expressed as follows:

$$\lambda(t)=\frac{\beta}{\eta}\left(\frac{t}{\eta}\right)^{\beta-1},\qquad R(t)=1-F(t)=\mathrm{e}^{-(t/\eta)\beta},$$

$$F(t)=1-\mathrm{e}^{-(t/\eta)\beta},\qquad f(t)=\frac{\beta}{\eta}\left(\frac{t}{\eta}\right)^{\beta-1}\mathrm{e}^{-(t/\eta)\beta}$$

where, η and β are positive.

1.2. Types of failure according to shape parameter

The failure mode of devices can be determined by the shape parameter. For example, a shape parameter of 0.5 describes that the devices will have defect in the initial step. This can be caused by poor assembly or quality. A shape parameter of

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[*] Corresponding author. Tel.: +82 55 280 1664; fax: +82 55 280 1590.
E-mail address: sweom@keri.re.kr (S.-W. Eom).

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1.0 represents a random failure step, such that device failure will occur independent of time. Reasons for this type of failure tend to be complicated, but could include poor maintenance. Failures of electronic devices belong to this case.

Devices which have a shape parameter of 3.0 have been affected by initial abrasion phenomena. And if the shape parameter of a device is 6.0, then the failure mode of that device will be abrasion caused by aging. Bearings and other components and other component which can be corroded easily belong to this case.

2. Experimental

Lithium ion batteries were tested to verify the life distribution of lithium secondary batteries. They have 3.7 V of nominal voltage and 1000 mAh. Prior to testing, all external safety devices outside of the battery, for example PCM (Protect Circuit Module), were eliminated as shown in Fig. 1.

The batteries were electrically connected to the charge/discharger so that their current and voltage during charge and discharge periods could be controlled and monitored. The time durations of the charge and discharge periods were controlled using a MACCOR charge-discharger (series 2000, USA) and its software. To analyze life distribution and to calculate each life distribution parameter, we used MINITAB statistical software (release 13.1).

As proposed by and RS C 0017 [7] and IEC 61960 [8], batteries were charged at a constant current of $0.5I_tA$ until the voltage of the batteries was increased to 4.2 V, and charged at a constant voltage of 4.2 V until the charging current fell to $0.1I_tA$. After the charging step, batteries were discharged at a constant current of $0.5I_tA$ until the voltage of the batteries fell to 2.7 V. These charge/discharge steps were repeated in an ambient temperature of 23 °C until the capacity fell to 80% of initial capacity. For experimental purposes, we defined failure as occurring at 80% of initial capacity.

And we conducted safety/abuse test according to standard of IEC 62133 [9].

3. Cycle life analysis

3.1. Cycle test and life distribution analysis

Results of discharge capacity were obtained according to the cycle number and failure time of each sample as shown in Fig. 2 and Table 1, respectively. The life cycle of the tested cells was 637–1520 cycles, and the MTTF was 1024 cycles.

Fig. 1. Test sample.

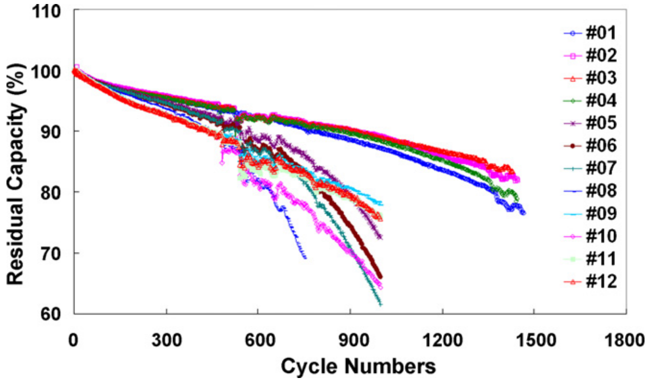

Fig. 2. Results of the life cycle tests.

From these data, we considered four kinds of life distribution; Weibull distribution, exponential distribution, Normal distribution, and logistic distribution as shown in Fig. 3.

Using the Anderson–Darling adjustments, results indicated that the life cycles of lithium secondary batteries were adequately represented by a Weibull distribution. Anderson–Darling adjustment values provide information about goodness-of-fit, such that the lower values indicates better correspondence with the distribution mode.

We achieved Weibull shape scale parameters of $\beta = 3.55$ and $\eta = 1138$, respectively. Fig. 4 shows the probability plot for the life cycles of lithium secondary batteries, which is adequately represented by a Weibull distribution. The corresponding two-sided approximate 95% confidence limits plot as curves.

3.2. *B_{10} life and zero failure tests*

If the failure rate of certain devices is 100_q%, then the life of the device at that point of time can be defined as B_{100q} life. B_{10} or B_5 life is generally defined by the reliability engineer. B_{100q} life of batteries can be represented by the following equation [3]:

$$B_{100q} = \eta\{-\ln(1-q)\}^{1/\beta} \qquad (1)$$

Table 1
Failure time (cycles) of tested samples

Specimen number	Failure time
01	1373
02	1470
03	1520
04	1427
05	892
06	814
07	777
08	637
09	927
10	688
11	857
12	886

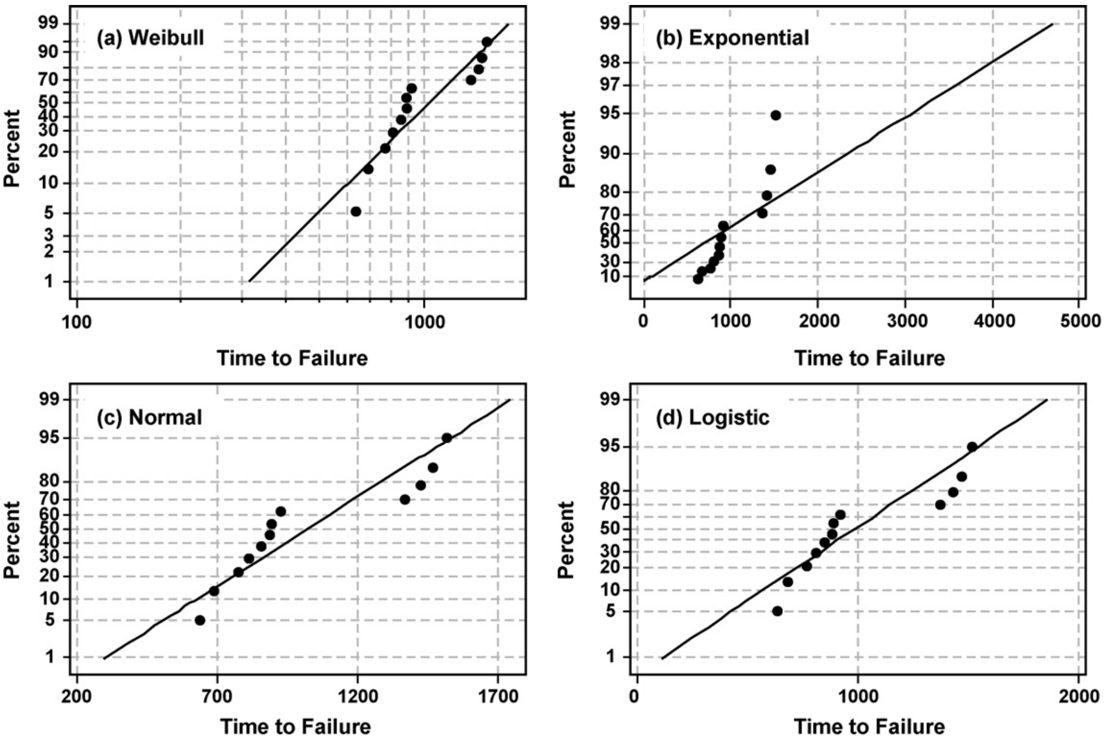

Fig. 3. Four kinds of probability plot for the life cycles of lithium secondary batteries: (a) Weibull distribution (Anderson–Darling adjustment: 1.682), (b) exponential distribution (Anderson–Darling adjustment: 3.521), (c) normal distribution (Anderson–Darling adjustment: 1.767), and (d) logistic distribution (Anderson–Darling adjustment: 1.804).

For example, when $\beta = 3.5$ and $\eta = 1140$ (cycles), B_{10} life can be expressed as below

$$B_{10} = 1140 \times \{-\ln(1-0.1)\}^{1/3.5} = 599.3\,(\text{cycles})$$

That is, 10% of the cumulative hazard probability is found when performed up to 600 cycles.

When the shape parameter is known in the Weibull distribution, the estimation of scale parameter (η) with a lower confidence limit of $100(1-\alpha)\%$ can be represented as follows:

$$\eta = [2nt_c^{\beta}/\chi^2_{\alpha}(2r+2)]^{1/\beta} \tag{2}$$

where t_c is test time, $\chi^2_{\alpha}(2r+2)$ is the Chi-square distribution with $(2r+2)$ degrees of freedom at the confidence limit of $100(1-\alpha)\%$, and γ is the number of failed samples in the life cycle test.

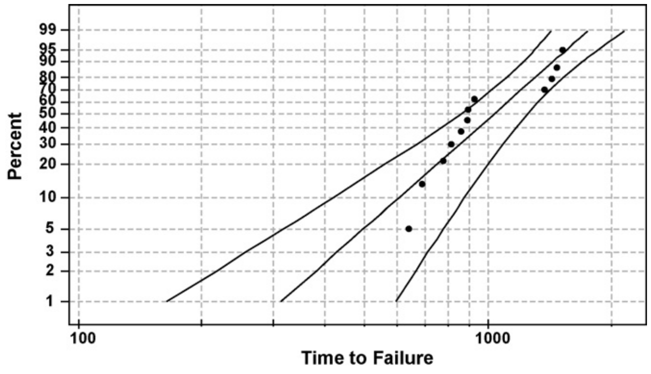

Fig. 4. Plot of the Weibull fit with the failure-time data for cyclic life tests of lithium secondary batteries. The curved lines represent the corresponding two-sided approximate 95% confidence limits for the function.

In the reliability demonstration test, a test plan with a minimal sample size (N) for the Weibull distribution of a shape parameter can be performed successfully when no failures have occurred during the test time t_c of N samples. The sample size depends on the confidence limit of $100(1-\alpha)\%$, 100_qth Weibull percentile, test time t_c and the shape parameter. Thus, the sample size to guarantee the expected life of the device should be decided as a constant number larger than the result of the following relations [10]:

$$N \geq \left(\frac{t_0}{t_c}\right)^{\beta} \frac{\ln \alpha}{\ln(1-q)} \tag{3}$$

where t_0 is the expected lifetime. If the number of failure samples is zero, a statistical quantity of $\chi^2_{\alpha}(2\gamma+2)/2$ in the Chi-square distribution can be calculated as $\chi^2_{\alpha}(2)/2 \approx -\ln(\alpha)$.

The acceptance criterion of the zero failure condition in the reliability demonstration test can be changed by using the Eq. (3). Finally, B_{100_q} life with a lower confidence limit of $100(1-\alpha)\%$ in service has the following relationship

$$B_{100_q} = \left[\left\{\frac{2Nt_c}{\chi^2_{\alpha}(2\gamma+2)}\right\} \times \ln(1-q)^{-1}\right]^{1/\beta} \tag{4}$$

When we calculate the number of test samples according to Eq. (3), we obtain 22 test samples at a confidence level of 90% and 29 test samples at confidence level of 95%.

4. Safety/abuse tests

4.1. Overcharge test

Overcharge test is to evaluate the ability of a cell to withstand a charger malfunction where the upper voltage if only limited by the charger. If battery is overcharged, internal pressure and temperature of battery will be increased by reason of abnormal chemical reactions (exothermic reactions); reduction of electrolyte by the anode, thermal decomposition of the electrolyte, oxidation of the electrolyte by the cathode, thermal decomposition of the anode, thermal decomposition of binder in the electrode and thermal decomposition of the cathode material structure. Consequently, it is possible that battery is exploded or catches on fire during the overcharge state.

A full-discharged battery used in this test. Constant charge current of 0.5$I_t$$A$ applied to the battery until charge capacity reaches to 250% of rated capacity.

Fig. 5 shows the result of overcharge test. Charge current is closely related to increasing of cell temperature. The higher charging current applied to the test cell, the more accelerated increasing of cell temperature. During the charge, cell voltage and cell temperature was not increased abruptly. Tested cells have a good balance between the heat generation and dissipation. As a result, any indication to identify smoke, explosion or fire was not found.

4.2. Short circuit test

External short circuit of batteries may occur when are connected with each other to make ‘battery pack system’, or they may be misused by users. If battery is in short circuit, temperature of the battery will be increased due to internal ‘joule heating’. So phenomenon of short circuit may lead to explosion or firing of battery.

The fully charged cell was subjected to a short circuit condition with a total external resistance of less than 50 mΩ. Test was conducted at room temperature, and continued until the cell case temperature has returned to a value within 10 °C of the original ambient temperature. Test was continued for 1 h.

Fig. 6 is the results of short circuit test during the initial 0.2 h. Voltage of battery was falling down as soon as battery was short circuited. And ‘short circuit current’ was increased to about 65 A abruptly. However, in spite of flow of high current, temperature of battery was increased no more than 90 °C. Based on these results, we found satisfaction in design of battery.

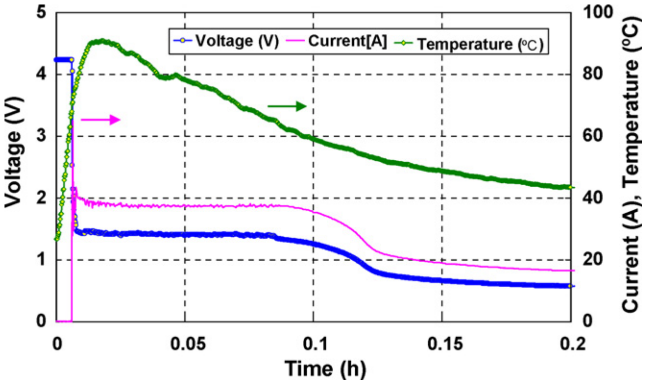

Fig. 6. The results of short circuit test.

4.3. Forced discharge test

This test is to evaluate the ability of a cell to withstand a forced deep discharge that could occur, during the discharge of a multi-cell, series configuration battery pack if one cell has a lower capacity or is at a greater depth-of-discharge than the other cells. The fully charged battery was discharged for 12.5 h with a constant of 0.1$I_t$$A$ in an ambient temperature of 23 °C Fig. 7 shows the results of this test.

After normal discharge copper current collector of anode starts dissolve electrochemically, and deposited on the cathode. So open-circuit-voltage of batteries becomes 0 V. But any dangerous incident was not occurred.

4.4. Nail penetration test

During penetration test, battery is penetrated with a steel nail, and then consequently internal electrical short circuit happens inside the battery.

For this nail penetration test, a nail with the velocity of less than 1 cm s^{-1} and the diameter of 5 mm penetrated into the center of electrode of the fully charged test cell. The orientation of the

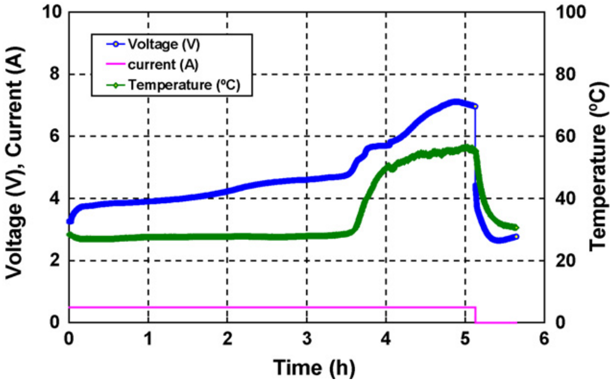

Fig. 5. The results of overcharge test.

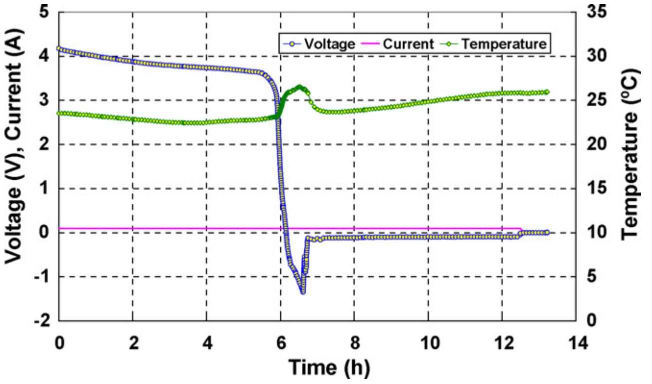

Fig. 7. The results of forced discharge test.

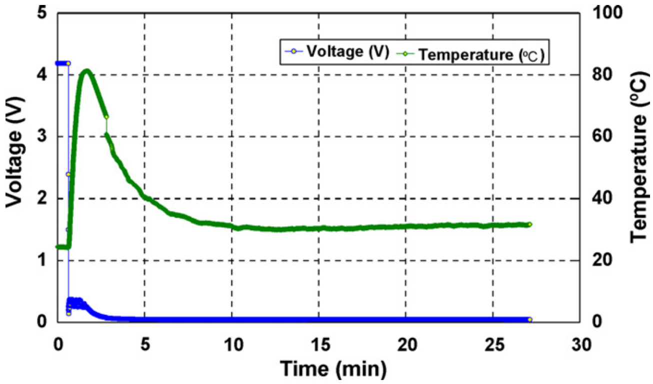

Fig. 8. The results of nail penetration test.

Fig. 9. Specimen after thermal exposure test.

penetration was perpendicular to the electrode plates, and the test cell was penetrated thoroughly by nail.

Soon after the test, cell is pierced by the nail, temperature of test cell increased to 82 °C caused by internal short of battery as shown in Fig. 8. However although rapid increasing of temperature, the battery did not have smoke.

4.5. Thermal exposure test

A thermal exposure test is the most fundamental environmental safety/abuse test. The failure mode is an explosion by an internal short circuit. When batteries are subjected to higher temperature than melting temperature of separator, direct contact between cathode and anode will be occurred. The melting temperature of separators is 125 and 155 °C for polyethylene and polypropylene, respectively. The used separator adapted to test batteries was polyethylene. So this test carried out in ambient temperature of 130 °C for 30 min.

Fig. 9 shows the photograph of specimen after thermal exposure test. The batteries were swelled but their cases were not opened.

5. Conclusion

In this study, the MTTF of the failure time data of tested samples was calculated as 1024 cycles. A Weibull plot based on these lifetime data showed a good linear regression with a lower Anderson–Darling value against the time to failure in the charge/discharge cycle test. Consequently, a shape parameter of 3.5 and a scale parameter of 1140 were obtained by the maximum likelihood estimates (MLE) with MINITAB statistical software. By using the parameters representing the Weibull distribution, a reliability demonstration test method including the criterion on the failure, test condition such as sample size and test time to assess the reliability of lithium secondary batteries was determined. Specifically, in order to assess the reliability of the lithium secondary battery by the B_{10} life of 600 cycles indicating the 10% Weibull percentile at the confidence limit of 90% and 95%, the minimum sample size of batteries shall be larger than 22 and 29, respectively in the case of zero failure conditions during a test time of 600 cycles.

And the safety/abuse evaluation and the failure analysis of lithium secondary batteries were performed. All of the results were enough to satisfy the IEC 62133 (2002) conditions.

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