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Path dependence of lithium ion cells aging under storage conditions

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HIGHLIGHTS

- Aging tests are conducted under both static and non-static storage conditions.
- Capacity fade is path independent of both SOC and temperature.
- Resistance increase is path dependent on SOC, but independent of temperature.
- Rate-based aging model is developed for cell aging in static storage tests.
- The aging model is applicable to predict capacity fade in non-static storage tests.

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ABSTRACT

This work investigates path dependence of lithium ion cells that are stored under static and non-static conditions. In the static storage tests, the levels of temperature and state of charge (SOC) are kept constant. The results of 12 tests from a combination of three temperatures and four SOCs show that, as expected, the cell ages faster at higher temperature and higher SOC. However, the cell aging mode, while consistent for all the evaluated temperatures, is different at 95% SOC from that at lower SOCs. In the non-static storage tests, the levels of temperature and SOC vary with time during the test process. The effect of the sequence of stress levels on cell aging is studied statistically using the statistical method of analysis of variation (ANOVA). It is found that cell capacity fade is path independent of both SOC and temperature, while cell resistance increase is path dependent on SOC and path independent of temperature. Finally, rate-based empirical aging models are adopted to fit the cell aging in the static storage tests. The aging model for capacity fade is demonstrated to be applicable to the non-static tests with errors between −3% and +3% for all the tested conditions over 180 days.

1. Introduction

Lithium ion battery is a primary energy source for electric vehicles (EVs) due to excellent properties including light, safe, and compact with a high specific energy ranging between 100 Wh kg^{-1} and 150 Wh kg^{-1} [1]. To ensure a reliable, durable and safe use, a battery management system (BMS) is required with functions of state of charge (SOC) and state of health (SOH) estimation, thermal management, and fault diagnosis etc. [2,3]. It is well acknowledged that correct evaluation the aging of a cell is essential to fulfill those functions for BMS, and intensified effort has been put on the aging studies of cells in recent years [4–7].

Extensive experiments are needed to resolve the aging behavior of the cell, especially for developing empirical aging models [8–11]. Much of those studies are based on experimental conditions where the aging stresses are kept constant, such as storage under constant temperature or SOC. In real applications, however, cells are subject to dynamic stresses. Thus, aging path should be considered in real applications to provide more realistic and accurate life predictions for a cell. Two concepts, "path dependence" [12,13] and "memory

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effect" [14,15], have been proposed to study the effect of aging path on cell degradation.

Path dependence [12,13] concerns the effect of aging path on the current performance of a cell. For example, Gering et al. [12] compared cell capacity loss under various cycling conditions, in which cells output the same amount of cumulative discharge energy (the integral of power with respect to time) during a certain time period. The results of their study showed that cycling scenarios affect the C/1 capacity loss while have little effect on the C/25 capacity loss. And they concluded that the cell capacity fade at C/25 is path independent of the cycling conditions, and the cumulative discharge energy can be used as the input of models for cell aging. However, their conclusion should be further checked based on statistical methods to quantitatively prove its reliability. Furthermore, the utilization of cumulative discharge energy rather than cumulative capacity or other descriptors needs more discussion, and the appropriate descriptor for different types of cells should be further investigated.

Memory effect [14,15] concerns the influence of aging path to the future evolution of cell performance. Fig. 8 in Thomas's article [14] illustrates the succeeding degradation of three cells that reach a common SOH after being exposed to different degradation paths. Their study assumed that cell degradation is a "memoryless" process, which means cell aging does not depend on the history that produced the current SOH, but, instead, depends only on the current SOH and the future degradation paths. Based on such assumption, many aging models have been proposed. For instance, rate-based aging models [11,14–19] are widely used to study cell aging under dynamic conditions. However, the reliability of the memoryless assumption needs to be carefully checked so as to obtain high accuracy prediction for cell aging.

In this study, storage conditions are selected as the first step towards understanding cell aging under real conditions. Both static and non-static storage tests are conducted. In the static tests, three temperatures and four SOCs are designed. In the non-static tests, the variation in the levels of both temperature and SOC are considered. The cell capacity and resistance are periodically monitored by non-destructive electrochemical characterizations, and the experiment results are reported in section 3. Then, in section 4, cell aging is discussed in terms of three aspects: (i) the relationship between the capacity and the corresponding resistance during the aging process is studied for all the tested conditions, (ii) a statistical method, analysis of variation (ANOVA), is utilized to investigate path dependence of temperature and SOC for cell aging, and (iii) rate-based aging models are used to fit the capacity fade and resistance increase in the static storage tests. Finally, the applicability of the capacity fade model to non-static storage conditions is demonstrated.

2. Experiment

All the tests were conducted using a MACCOR Series 4000, three high-temperature cabinets ESPEC STH-120, and an environment chamber GDJW-225 (Yashilin, China). The accuracy is ±0.3 °C and ±0.5 °C for the ESPEC STH-120 and the GDJW-225, respectively. The tested samples were commercial Samsung INR18650-29E, and 36 of them were used in this study. Table 1 shows nominal specifications of the cell. Before the aging study, those cells were cycled three times at 0.5 C to get stable performance. Then, the initial characteristics of those cells were measured using reference performance tests (RPT), as detailed in section 2.3. The tested results showed that the capacity and resistance of cells followed the normal distribution with more than 95% confidence intervals, and no outlier existed among the 36 tested cells, as discussed in section 3.1. Therefore, those cells were used for the further static and non-static storage tests.

2.1. Static storage tests

In the static storage tests, twelve conditions were designed, which included three temperatures (45 °C, 53 °C, and 60 °C) and four SOCs (40%, 60%, 80%, and 95%). The highest temperature was chosen according to cell specifications shown in Table 1, while the lowest temperature was chosen based on the ability of the high-temperature cabinets, which could stably control the temperature that was 15 °C higher than the room temperature. Two cells were put under each condition to verify the reliability of the tests, and all the cells were taken out monthly to characterize the SOH using the RPT.

2.2. Non-static storage tests

In the non-static storage tests, the variation of the levels for both the temperature and the SOC were concerned. Two types of non-static storage tests were designed: non-static temperature tests and non-static SOC tests. In the non-static temperature storage tests, the SOC was kept at 95% during all the test process, while the temperature varied among 45 °C, 53 °C and 60 °C, as shown in Fig. 1 (a). In the non-static SOC storage tests, the temperature was kept at 60 °C, while the SOC varied among 40%, 60% and 95%, as shown in Fig. 1 (b). Three cases were designed for each non-static storage test, and two cells were put in each case. All of the cells were taken out monthly to characterize the SOH using the RPT. Furthermore, an additional 0.1 C cycling test was conducted at 25 °C every three months for diagnostics. The cycling protocol was typical CCCV-CC protocol, which was constant current followed by constant voltage charging and constant current discharging. The cut-off current in the CV stage was 0.02 C.

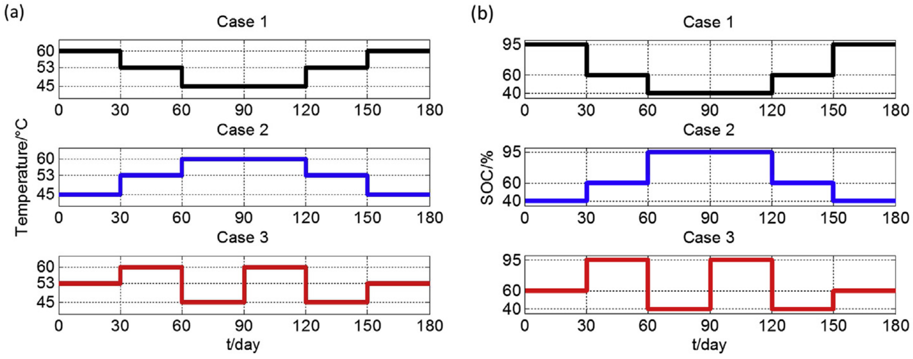

Fig. 1. (a) Non-static temperature storage tests and (b) non-static SOC storage tests.