Experimental Study to Investigate the Effects of Temperature Rise during Discharge on Li-ion Battery Degradation

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Abstract. Li-ion batteries with higher discharge C-rates show accelerated capacity fade rates. However, an inherent coupling exists between discharge C-rate and temperature as heat generation is inevitable during discharge. The effects of discharge C-rates on capacity fade under consideration of temperatures have not been investigated. This paper presents an experimental study that separates the temperature rise during discharge from the non-thermal effect of discharge C-rates. A design of experiment including two discharge C-rates (C/2 and 3C) and two controlled temperatures (controlled ambient temperature at 45 °C and controlled surface temperature at 45 °C) were used to provide cycling conditions. In controlled ambient temperature tests at 45 °C, battery surface temperature increased by 5.2 °C at the discharge rate of C/2 and 20.6 °C at 3C. In controlled surface temperature tests at 45 °C, battery surface temperatures were maintained at 45 ±1 °C. Experiment results show that the battery capacity degradation was the joint contribution of the temperature rise and non-thermal effects. Temperature rise during discharge contributes to the battery capacity degradation, while the non-thermal effect of discharge C-rate dominates the capacity loss.

Keywords. Li-ion battery; capacity degradation; discharge C-rate; temperature rise; non-thermal effect.

1. Introduction
Li-ion batteries have rapidly become the dominant energy storage components for consumer electronics because of their high energy density, long cycle life, and environmental friendliness [1]. However, irreversible capacity loss during cycling and storage is one of the key concerns associated with lithium-ion battery technology. Capacity degradation of Li-ion batteries is complex and can be affected by various stress factors, including temperature, discharge current, state of charge (SOC), and cycle numbers [2]. Understanding the aging behavior and capacity degradation mechanism under different stress factors is a prerequisite to design better batteries and ensure the performance reliability of lithium-ion batteries in the field.

Discharge C-rate is defined as the current through the battery divided by its nominal capacity. For example, a 2C rate is a 30-minute discharge, and the C/2 rate is a 2-hour discharge. Numerous studies have reported that higher discharge C-rate can accelerate capacity degradation over cycles [3]. Choi and Liam [4] performed degradation tests on 900 mAh LiCoO2/graphite-based prismatic cells and found that the cycle-life is reduced substantially as the rate increases from 1C to 1.4C. Ning et al. [5]
found the capacity fade of LiCoO2/C based 18650 batteries is proportional to the increase in discharge C-rates (1C, 2C, and 3C) and is mainly dominated by the loss of the secondary material (LiCoO2/C). At the discharge rate of 3C, the capacity loss of the whole cell was 16.9%, while the capacity loss due to the carbon electrode material alone was 10.6%.

Temperature is another stress factor for battery capacity degradation [6]. Commercial Li-ion batteries can operate over a temperature range from around −20 ºC ~ 60 ºC [7]. Pesaran et al. [8] studied the impact of temperature on large format Li-ion batteries and concluded that the optimal temperature range for Li-ion batteries is 15 ºC–35 ºC. Once the temperature is out of these comfortable regions, Li-ion batteries will face power limits at lower temperatures and faster degradation at higher temperatures. The charge-discharge performance [9], safety [10], and cycling lifetime [11] of Li-ion batteries can be affected when exposed to high temperatures due to accelerated electrochemical reactions.

Heat generation within Li-ion batteries is inevitable due to charge transfer and chemical reactions during charge and discharge [12]. The heat generated in an operating battery is generally from the reversible process [13] (entropy change) and the irreversible process [14] (active polarization process and ohmic heating process). Jeon et al. [15] studied the thermal behavior of cylindrical Li-ion batteries using transient and thermo-electric finite element analysis. The results showed that the surface temperature of the LiCoO2/C battery increased with the discharge rate. The entropy change was dominant in heat generation at a low discharge rate (C/2), and ohmic heating made a significant contribution at a high discharge rate (5C). Eddahech et al. [16] focused on the thermal behavior of 12 Ah high-power Li-ion cells during charge-discharge, and the experimental data indicated that higher discharge rates caused more heat generation. However, it is unclear whether the discharge C-rate affects the capacity degradation processes through rising battery temperatures or other non-thermal reasons.

The effect of temperature rise during discharge on the battery capacity degradation can be identified by comparing the capacity degradation with and without temperature rise of discharge C-rates. To remove the temperature rise caused by discharge C-rates, the battery surface temperature should be maintained constant during discharge. Troxler et al. [17] proposed a temperature control method using a proportional–integral–derivative (PID) controlled cooling system, which provides a solution to heat the battery at a higher temperature. In this study, the battery surface temperature was controlled at 45 ºC during cycling by applying a PID-controlled heating system. A controlled ambient temperature test at 45 ºC was conducted in a thermal chamber as a comparison. The rest of this paper is organized as follows. Section 2 describes the procedures of the experiment. Section 3 exhibits the details of the developed heating system. Section 4 shows the experiment results. Conclusions can be found in Section 5.

2. Design of experiment
In this study, commercial Li-ion pouch cells with a nominal capacity of 3.3 Ah and operating voltages of 4.2 V–3.0 V were selected to conduct tests. A maximum current of 2C and operating temperatures of -20 ~ 45 ºC during discharge are recommended by the manufacturer. The temperature distribution inside of the battery can be assumed uniform since the thickness of the battery is 5.2 mm. During testing, the battery surface temperature was measured and considered as the battery temperature.

A design of experiment including characterization tests and cycling tests was conducted on eight cells to investigate the effect of temperature rise on capacity degradation. Characterization tests were conducted to describe the battery capacity degradation behavior during cycling. Hence, characterization tests were conducted at the beginning of cycling tests to set up a baseline, and repeated every 50 cycles. Cycling tests were conducted to expose cells to different levels of temperatures and discharge C-rates.
In the characterization test, the battery was charged at 1C constant current (CC) up to 4.2V, and then the constant voltage (CV) was held until the charging current dropped below C/20. After a 10-min rest, the battery was discharged at C/2 constant current to 3.0V. Characterization tests were conducted at 25 °C ambient temperature for two cycles, and the average discharge capacity of two cycles was used as the real capacity measurement.

In the cycling test, the battery was charged using the 1C CC-CV charge profile of the characterization test. After a 10-min rest, the battery was discharged at C/2 or 3C constant current to 3.0V. Cycling tests were conducted under controlled surface temperature at 45 °C or controlled ambient temperature at 45 °C for 1100 cycles. Every 50 cycles, batteries will be taken out from cycling conditions to conduct characterization tests.

The test matrix for cycling tests was summarized in Table 1. In test #1 and test #3, batteries were charged-discharged in a thermal chamber with a constant ambient at 45 °C. In test #2 and test #4, batteries were charged-discharged by an Arbin tester while heated by a developed heating system. The battery surface temperature was maintained at 45 °C during charge-discharge by adjusting the heating rates. The battery heating system is described in the following section.

| Temperatures                              | Discharge C-rates |
|-------------------------------------------|-------------------|
| Controlled ambient temperature at 45 °C    | Test #1           |
| Controlled surface temperature at 45 °C   | Test #2           |

### 3. Experiment Set-up

To conduct the above charge-discharge cycling tests, different equipment and facilities were used to control the temperatures and discharge C-rates. In test #1 and test #3, batteries were charged and discharged by an Arbin tester, and a DVS 402 thermal chamber was utilized to provide 45 °C constant ambient temperature for batteries. To make sure the ambient temperature constant at 45 °C during testing, a K-type thermocouple was used to monitor the internal temperature of the chamber.

In test #2 and test #4, batteries were charged and discharged using an Arbin tester while heated using a PID-controlled heating system. The heating system was developed to keep the battery surface temperature constant at 45 °C during testing. Figure 1 shows the schematic diagram of the heating system. During the cycling test, the battery surface temperatures of two different locations were measured by two K-types thermocouples and collected by the Agilent 34970 data logger. The average temperature of two thermocouples was used to compare with 45 °C, and the difference was fed back to the proprietary LabView script. If the battery surface temperature is higher than 45 °C, the PID controller will control the DC power supply to decrease the output voltage, and then the heating wire will stop heating the battery until the battery cools down to 45 °C. On the contrary, the heating wire will continue heating the battery until the surface temperature reaches 45 °C. The maximum output voltage of the DC power supply was set as 10 V to meet the heating requirements.

**Figure 1.** Schematic diagram of the developed heating system
To make sure the battery temperature distribution is uniform, two Al plates with a thickness of 0.635mm were placed at each side of the battery and heated by heating wires, as shown in Figure 2(a). The Al plates were covered by heat-resistant tapes to avoid short-circuits. Two K-type thermocouples were attached to the top and bottom of the battery to monitor the temperature differences, as shown in Figure 2(b). Figure 2(c) shows the collected surface temperatures of two different locations during one charge and two discharge processes. It can be seen that the battery surface temperature can be maintained at 45 ± 1 °C.

The above heating system and heating structure describe the principle of controlling battery surface temperature for a single battery during testing. However, the surface temperatures of multiple batteries need to be controlled in this study. Because of the inevitable manufacturing error, any two different batteries cannot be synchronous in one charge-discharge cycle even though they share the same testing profile and are started at the same time. The temperature rise of different batteries then will vary. Thus, it is not feasible to control the surface temperature of multiple batteries at the same time using two Al plates with larger dimensions. To address the problem, an improved heating system was proposed to control the surface temperature of different batteries separately. Figure 3 shows the schematic diagram of the improved heating system for multiple batteries. It can be seen that each battery was equipped with a set of DC power supply, heating wires, and two thermocouples. Multiple repeating units share the same PID controller, Arbin tester, Agilent 34970 data logger, and the LabView program.
(c) Battery surface temperature at different locations during charge and discharge. 

Figure 2. The heating structure for each tested battery.

Figure 3. Schematic diagram of the improved heating system for multiple batteries

As mentioned in Section 1, elevated temperatures can accelerate battery capacity degradation. However, according to the manufacturer’s specifications, the maximum operational temperature during discharge was 45 °C. Thus, the baseline temperature for the above four cycling tests was 45 °C instead of other temperatures. Two different levels of discharge C-rates (C/2 and 3C) were selected to make sure the significant difference in temperature rise during discharge.

4. Experiment Results

Figure 4 shows the different temperature control results. In the controlled ambient temperature tests, the baseline temperature was 45 °C, and the surface temperatures of batteries showed a steady increase during discharge. The maximum surface temperature increased by 5.2 °C at the discharge rate of C/2 and 20.6 °C at 3C. This result is consistent with previous studies that more heat is generated at increasing discharge C-rates [16]. In the controlled surface temperature tests, the surface temperatures of batteries were well maintained at 45 ± 1 °C in test #2 and test #4. The heating system stops heating the battery when the battery surface temperature exceeds 45 °C. At the ambient temperature of 25 °C, the natural convection can cool down the battery. Cells in test #2 need a shorter time to cool down the surface temperature rise, showing a smaller temperature variation during discharge than cells in test #4. Normally, the temperature difference of 10 °C can be considered as different stress levels in various studies [18]. The temperature variations for cells in test #2 and test #4 are acceptable; thus, the experimental set-up was proved to meet the requirement as designed for controlling surface temperatures of multiple batteries.
After 1100 cycles, cycling tests were ended since all batteries have degraded to 80% of their nominal capacity. Figure 5 displayed the degradation curves of all batteries. In controlled ambient temperature tests at 45 °C, the capacity degradation curves at 3C show a faster drop than the curves at C/2, indicating the increased discharge C-rates can accelerate the battery capacity degradation. Similar capacity degradation can be found between test #2 and test #4, where the temperature rise caused by discharge C-rates were removed during testing. Therefore, the non-thermal effect of discharge can accelerate the battery capacity degradation over cycles.

At the C/2 discharge C-rate, batteries in test #1 and test #2 show similar degradation curves. That’s because the average temperature rise during discharge at C/2 is only 2.53 °C which is not significant enough to cause different capacity degradation curves. However, when the discharge C-rate increases to 3C, the average temperature rise during discharge is 11.9 °C, which can be considered as different levels. Thus, batteries in test #3 show a faster degradation rate than batteries in test #4. After 1100 cycles, the normalized capacity difference between test #3 and test #4 was 5.53%.

5. Conclusions
To separate the temperature rise and non-thermal effects of discharge C-rates, this study conducted a design of experiment including two discharge C-rates (C/2 and 3C) and two controlled temperature conditions (controlled ambient temperature at 45 °C and controlled surface temperature at 45 °C).

A heating system with PID control was developed to control the battery surface temperature at 45 °C during testing. The tested battery was covered and heated by two Al plates to keep the temperature distribution uniform. The heating system was then improved to control the surface temperatures of multiple batteries separately. In controlled ambient temperature tests at 45 °C, the average temperature increased by 2.53 °C at C/2 discharge rate and 11.9 °C at 3C discharge rate. In controlled surface temperature tests, temperatures of multiple batteries were maintained at 45 ±1°C.

After 1100 cycles, in controlled surface temperature tests, batteries cycled at 3C show a faster capacity degradation rate than batteries cycled at C/2, indicating the non-thermal effect of discharge C-rate is one of the reasons for battery capacity loss. At 3C, batteries from controlled ambient temperature tests degrade faster than batteries from controlled surface temperature tests, suggesting the temperature rise caused by discharge C-rate contributes to the battery capacity loss. Therefore, the temperature rise during discharge and non-thermal effects of discharge C-rate were experimentally decoupled in this study. The battery capacity degradation was proved the joint contribution of the temperature rise and non-thermal effects of discharge C-rates.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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