Safety Test Methods Simulating Internal Short Circuit and the Mechanism for Safety Improvement of Li-ion Batteries by Heat Resistant Separators

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ABSTRACT

It is widely recognized that heat-resistant separators improve the safety of lithium-ion batteries. However, it is not clear how the separator contributes to battery safety, or how much heat resistance is required. The state of separators when a short circuit occurs in batteries was simulated and the following tests were conducted. As a first test, the edges of the separator were restrained, and hot air was applied only to a limited part of the specimen. For the second test, a model battery system was constructed and electrical heat generation during the early stage of a short circuit was observed. In these tests, several types of separators were compared with respect to the extent of damage and electrical heat generation. The separators that gave good results during nail penetration tests showed limited damage and electrical heat generation during the previously discussed tests. The heat resistance of a separator should be discussed with regard to whether it can maintain the separator function during electrical heat generation via short circuit.

1. Introduction

In recent years, safety has become a more critical issue as the capacity and energy density of lithium-ion batteries has increased. To solve this issue, the use of more heat-stable active materials,1-3 flame-retardant electrolyte additives,4 and separators with a thermal shutdown function5,6 have been proposed. Thermal shutdown is only an effective measure if the temperature remains within a certain range. Porous films made of polyolefins such as polyethylene (PE) and polypropylene (PP) are widely used as separators for lithium-ion batteries, and multilayer separators have a shutdown function. However, once the battery temperature exceeds the tolerable range, the separator may undergo meltdown, and loss of electrical insulation thereby causes thermal runaway. To extend the gap between the shutdown temperature and the meltdown temperature, some measures including the combination of heat-resistant materials such as polyimides and ceramic particles5-10 and the use of nonwoven substrates as more heat-resistant alternatives to heat shrinkable microporous films have been proposed.5,6,10,11 Nonwoven separators are reported to have higher output characteristics and longer life because they retain more electrolyte than microporous films.12-14 In addition to improvement of the thermal stability of the separator, the restraint of separators by adherence onto the electrode to prevent thermal shrinkage has also been proposed.5,13

It is widely recognized that heat-resistant separators improve battery safety; however, there is no established method for the evaluation of separator heat resistance. Dimensional stability at high temperature or differential scanning calorimetry (DSC) are used as heat resistance evaluation criteria.7,8,10,11,14 However, these techniques do not evaluate heat resistance with respect to what happens when an actual battery goes into thermal runaway.

The nail penetration test and internal short circuit test are standardized and widely adopted by the battery and related industries as methods to evaluate the likelihood of an internal short circuit that would result in thermal runaway.15-21 However, these methods require intensive work to assemble batteries, and give a limited indication of the intermediate phenomena because the battery is completely destroyed when thermal runaway occurs, and almost no trace of the intermediate phenomena remains. Furthermore, the results of tests such as thermal dimensional stability and DSC are nothing more than heat resistance and do not indicate how a separator improves battery safety. In addition, these tests do not simulate very localized temperature elevation, which is suspected in the early phase of thermal runaway; therefore, the relationship with battery safety is also unsure from this point of view. In this study, the behavior of the separator was observed while the separator was restrained inside of a battery with localized heat applied, as when a short circuit occurs. Furthermore, a model system that simulates the early phase of the battery thermal runaway was assembled, and the relationship between the heat resistance of various separators and the heat quantity generated by internal short circuit was investigated.

2. Experimental

Table 1 shows the separators used in this study: a ceramic uncoated PP-PE-PP trilayer film (Separator A), a ceramic-coated PE film (Separator B), and a ceramic-coated polyethylene terephthalate (PET) nonwoven (Separator X; Fig. S1). These separators have different safety improvement measures. Separator A has a thermal shutdown function, Separator B has a heat-resistant coating layer of aramid and ceramic particle, and Separator X consists of high heat-resistant PET nonwoven substrate and a ceramic coating layer. To observe the behavior of these separators in the state close to an actual short circuit inside a battery, hot air gun tests and simulated short circuit tests were performed. To investigate the relationship between the results and the actual safety of the battery, batteries were assembled with these separators and nail penetration tests were conducted. When the batteries were assembled, the coated layer of Separator B faced the positive electrode to prevent PE oxidation, while that of Separator X faced the negative electrode to suppress Li dendrite formation.
2.1 Hot air gun test
The following test was conducted using a hot air gun to simulate the state of a separator when a short circuit occurs in an actual battery. The left of Fig. 1 shows the setup of the hot air gun test. The separator was fixed to a metal frame, and a hole was made in the center with a pin with 0.69 mm diameter. The pinhole is intended to simulate the state of separator when an internal short circuit occurs. The hot air gun nozzle was set so that the tip of the hot air gun was at a designated distance from the separator, and the temperature was measured with a thermocouple placed at the same distance from the nozzle tip. To minimize the effect of wind pressure, the air volume was set to the minimum (6.1 L/min). After the measured hot air temperature became stable, the hot air gun was moved to apply hot air to the center of the sample separator. Thereby, heat is locally applied to a limited area of the separator while the surrounding area of the separator is restrained. This test is a better simulation of the actual state of the short circuit inside a battery than the conventional method of applying heat to the entire area. The temperature of the hot air was raised in steps of 10 °C. If expansion of the pinhole diameter was less than 2 mm, which can be judged to be almost the same as the original size, then the separator at that temperature was determined to have maintained the shape (passed). The maximum temperature at which the separator passed the test was determined as the heat-resistant temperature. The right of Fig. 1 shows the typical pass and fail results of this test.

2.2 Simulated short circuit test
To simulate the electrical heat generated when a short circuit occurs, a model battery system based on the equivalent circuit shown in Fig. 2 was investigated. Only the external cell voltage ($V'$) and the short circuit current ($I$), $VI$, is the heat quantity generated at the short circuit point, while the product of the difference between the open circuit voltage $E$ and the cell voltage $V'$ and the short circuit current, $(E-V')I$, results in temperature elevation of the entire cell. This heat generation represents only electrical heat generation and does not include chemical heat generation caused by various successive reactions.

Figure 3 shows a schematic diagram of the simulated internal short circuit test. The model battery consists of a positive electrode, a negative electrode, and a separator, and does not contain electrolyte; therefore, it does not have an electromotive force. Although any electrodes can be used in the simulated battery, an aluminum (Al) current collector foil was used as the positive electrode and a copper (Cu) current collector foil was used as the negative electrode in this test. A small piece of Ni (according to JIS C 8714) was placed between the positive electrode and the separator of the model battery, and a mechanical load was applied to cause a short circuit. At this time, a short circuit current is supplied by the lithium-ion battery connected as a power source. By having the short circuit point outside of the power supply battery, both the cell voltage and the short circuit current can be measured with this experimental system. Thereby, it is possible to calculate the heat quantity generated at the short circuit as the product of the cell voltage $V'$ and the short circuit current $I$. A 10 Ah lithium-ion battery was used as the power supply battery. A resistor ($R_l$) can be inserted into the circuit to simulate batteries with various internal resistances. The short circuit current was measured by connecting a 5 mΩ shunt resistor. In the model battery, a short circuit that triggers thermal runaway is observed; however, no actual thermal runaway occurs. Therefore, the trace of the short circuit remains and can be observed after the experiment. Other details to be noted in the test are described in Supporting Information.

Table 1. Separator properties.

| ID | Separator A | Separator B | Separator X |
|----|-------------|-------------|-------------|
| Composition | PP-PE-PP film | PE film + aramid + alumina | PET nonwoven + boehmite |
| Grammage (g/m²) | | | |
| Total/Substrate | 10 | 10/3 | 22/10 |
| Thickness (µm) | | | |
| Total/Substrate | 18 | 17/13 | 25/15 |
| Gurley permeability (sec/100 cc) | 300 | 300 | 10 |

Figure 1. Setup of the hot air gun test and examples of separator state after the test.
2.3 Safety tests with actual batteries

Pouch cells with a capacity of 3 Ah were assembled, which consisted of a LiMn$_1$/3Ni$_1$/3Co$_1$/3O$_2$ positive electrode, a graphite negative electrode, and the separator. At the fully charged state of 4.3 V, a 4.5 mm diameter nail was pushed into the cell at a penetration speed of 20 mm/s, and the cell voltage and visual status of the battery were observed. The cell voltage was measured at a sampling rate of 1 kHz.

3. Results and Discussion

3.1 Hot air gun test results

When the pinholes were punctured in the separators, the heat-resistant temperature at which no expansion of the hole was observed was 180 °C for Separator A, 140 °C for Separator B, and 260 °C for Separator X. When the pinhole was not punctured in the separators, Separator B retained its shape even at 500 °C (Fig. 4). However, when an internal short circuit occurs in an actual battery, the separator must incur some damage due to the conductive material passing through. Thus, the test with a pinhole more appropriately represents actual short circuit conditions. The heat-resistant temperature was the lowest for Separator B. However, when tested with hot air at 500 °C, expansion of the hole was the largest for Separator A and smallest for Separator X.

3.2 Simulated internal short circuit test results

Table 2 shows the results of a simulated internal short circuit test for each separator, the heat quantity in 1 s or 5 s, and the degree of the damage to the separator after the test for 5 s. The short circuit current patterns are shown in Fig. S2, and the model battery state diagrams at the time are shown in Fig. S3. In the case of Separator X, the short circuit current ceased within 1 s (Fig. S2a). On the other hand, for Separators A and B, the short circuit current did not stop (Figs. S2b, S2c or S2d), and the separators were more severely damaged than Separator X.

After the test with Separator X, Al was observed around the Ni piece on the copper based negative electrode (Fig. 5), which indicates that the Al current collector was fused by the heat generated from the short circuit current. The melting point of Al is 660 °C; therefore, the local temperature around the Ni piece exceeded 660 °C. The fusion of the Al current collector destroyed the short circuit conductive path (Fig. S3a), and it caused the short circuit current to stop within 1 s in Separator X. Fusion of the Al current collector was also observed with the model battery using Separator B; however, the short circuit current did not stop. In this case, the short circuit conductive path was not completely destroyed (Figs. S2b and S3b), or expansion of the hole was caused by heat shrinkage or meltdown of the separator, and direct contact between the electrodes formed a new (Figs. S2c and S3c), more critical short circuit conditions.

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**Figure 2.** Equivalent circuit for the early stage of a short circuit.

**Figure 3.** Schematic diagram of the simulated internal short circuit test.

**Figure 4.** Hot air gun test with or without pinhole.
circuit current path (Figs. S2d and S3d). This caused the short circuit current to continue to flow and the heat quantity to increase.\textsuperscript{21} When the current collector is fused without expansion of the hole, shrinkage in the separator, or creating other new short circuit current path, the heat quantity caused by the short circuit is very limited.

3.3 Nail penetration test results

In the nail penetration tests, batteries with Separators A and B underwent thermal runaway, while those with Separator X did not. The EUCAR hazard levels for the Separator A, B, and X batteries were 5, 4, and 2, respectively (Movie S1 of the Supporting Information). Figure 6 shows the cell voltage behavior at the very early stage of nail penetration. There is a rapid voltage drop and voltage recovery in this very short time period of 0 – 1 s after the test initiation. The extent of this voltage drop is a dominant factor in the outcome of the safety test, as calculations indicate that the voltage drop has a direct relation to the amount of heat generated by the short circuit. It would also be closely related to the heat quantity by the short circuit current, as shown in Table 2.

On the other hand, if the separator maintains its shape, the short circuit current conductive path is fused by the heat generated from the short circuit current, so that the short circuit current stops and the battery goes into a safe state. The voltage recovery in Fig. 6 can be explained as follows. The Al or Cu current collector around the nail, which acts as the short circuit conductive path, was fused by the heat generated from the short circuit current, as observed with the model battery test discussed with Fig. 5. The destruction of the current path increases the short circuit resistance and the voltage is recovered, even though the nail remains in the cell.

The voltage sampling rate at nail penetration and with internal short circuit test is generally 1 Hz; however, in this test, the sampling rate was set to 1 kHz. This value was chosen since with a sampling rate of 1 Hz, the voltage behavior that occurs during 1 s cannot be observed. When analyzing the battery behavior during a short circuit, it is important to observe the voltage change at a much higher sampling rate from the initial instance of nail penetration.

3.4 Highly safe battery design

From these results, the heat resistance of the separator was determined to affect the behavior in the very early stage of the short circuit, and causes a significant difference in the heat generation quantity in this phase. Figure 7 shows the conceptual relationship between the cell temperature after triggering a short circuit and the heat generation quantity. Regardless of how high the heat resistance of the separator is, it is not safe if the cell reaches the thermal runaway temperature due to the heat generated by the short circuit (Fig. 7a, red dotted line). However, when the temperature remains below the threshold temperature, the battery gradually goes into a safer state as the state of charge (SOC) of the cell decreases, and the thermal stability of the other materials increases (Fig. 7a, red solid line). An additive that suppresses heat generation would help to avoid thermal runaway (Fig. 7b, red solid line). Therefore, not only should a heat-resistant separator be used, but also, the threshold temperature of the battery system should be increased to improve the safety of batteries.

Table 2. Heat quantity in the simulated internal short-circuit tests and separators after the tests (scale bar: 10 mm).

| Separator | Separator A | Separator B | Separator X |
|-----------|-------------|-------------|-------------|
| Heat Quantity in 1 s (J) | 238 | 153 | 15 |
| Heat Quantity in 5 s (J) | 983 | 914 | 15 |

Figure 5. SEM-EDS image of a Ni piece after the simulated internal short circuit test. Blue: Ni, Red: Al.

Figure 6. Voltage behavior in the early stage of the nail penetration tests.

Figure 7. Semi-conceptual relationship between the cell temperature after triggering a short circuit and the heat generation quantity.
4. Conclusion

The hot air gun test and simulated internal short circuit test, which are closer reproductions of what happens with the separator at an internal short circuit, showed a better correlation with the actual nail penetration test results. The separator that had the highest safety in an actual battery had the least increase in the short circuit area in these tests. These tests are useful to study phenomena that occur in the early phase of thermal runaway.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00100.

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