Operando Analysis of Thermal Runaway in Lithium Ion Battery during Nail-Penetration Test Using an X-ray Inspection System

Tokihiko Yokoshima, Daikichi Mukoyama, Fujio Maeda, Tsuyoshi Osaka, and Shun Egusa

1 Research Organization for Nano & Life Innovation, Waseda University, Tokyo 162-0041, Japan
2 Toshiba Infrastructure Systems & Solutions Corporation, Kanagawa 212-8585, Japan

The safety of energy storage devices, especially lithium ion batteries (LIBs), is a critical issue, because LIBs are characterized by high operation voltage, high energy density, and use flammable organic electrolytes and hence can potentially catch fire.1–3 Thus, LIBs designed for commercial use must pass safety standards and safety tests, such as electrical tests, environmental tests, and mechanical tests, to ensure that they conform to certain standards.4–7 The nail-penetration test is widely used for evaluating internal short circuiting in an LIB, which is one of the major causes of battery fires, because of its simplicity.8–19 The main results of this test are smoke generation, fire, explosion, or the absence of all of the above. This type of safety test is only used to verify whether an LIB is safe. Therefore, the direct real-time observation of the internal state of the electrodes, electrolyte, and separator during the test is not easy. Only the voltage, temperature, and external conditions of the LIB are observed in real time, if needed.20–23 Visualization or observation of the internal state of a battery cell can be considered the most important safety measure, which is not made in current approaches. To the best of our knowledge, operando analysis of the internal behavior of commercial LIBs during thermal runaway has only been reported using synchrotron radiation.24

To meet this need, we have developed a LIB internal short-circuit observation system with an X-ray scanner, hereafter abbreviated as the LiSC scanner, for detailed analysis of the electrode behavior and the associated changes in real time.25 This system allowed us to capture fluoroscopic moving images of the anode and cathode in the layered LIB structure, as we added a viewing window for X-ray fluoroscopy.26 We were able to observe, for the first time, the internal state of the LIB when processes such as pouch ballooning or gas generation was observed outside the cell, owing to the internal short circuiting during the nail-penetration test. In this study, details of the behavior of the inner LIB during the nail-penetration test under optimized conditions were observed using the newly developed LiSC scanner. Then, using the results of the LiSC scanner and X-ray computed tomography, X-ray CT, the short circuiting and thermal runaway of LIB during the nail-penetration was analyzed.

Experimental

Preparation of LIB samples for X-ray fluoroscopy.—CELLSEED C-5H (lithium cobalt oxide, LiCoO₂, Nippon Chemical Industrial Co., Ltd.) and graphite CGB-10 (Nippon Graphite Industries, Co., Ltd.) were used as the active materials for the cathode and anode, respectively. The cathode was prepared on both sides of an aluminum foil using LiCoO₂, acetylene black (DENKA BLACK, DENKA Company Ltd.), Ketjen black (Lion Specialty Chemicals Co., Ltd.), and polyvinylidene difluoride (PVDF; KF Polymer, Kureha Corp.) at the ratio of 87:6:2:5 by weight. The thickness of the aluminum foil was 20 μm. The anode was prepared on both sides of a copper foil using graphite, acetylene black, and PVDF at the ratio of 90:5:5 by weight. The thickness of the copper foil was 20 μm. The areal discharge capacities of the cathode and anode were 1.0 and 1.1 mAh cm⁻², respectively. The electrolyte used was 1 M lithium hexafluorophosphate (LiPF₆) in a 1:1 (v:v) mixed solvent of ethylene carbonate and diethylene carbonate (Kishida Chemical Co., Ltd.). UPORE UP3085 (Ube Industries Ltd.) was used as the separator. Details of the preparation technique can be found in another report.25,26

The cell design, especially the electrode sizes, was optimized to obtain fluoroscopic images. In this investigation, a micro focus X-ray source was used in the LiSC scanner. Micro focus X-ray source is a point source and X-ray from a point source is not completely transmitted though a layered structure of the electrodes in large-capacity cells such as 800 mAh cells because X-ray spreads radially from the point source. For the LiSC scanner developed in this study, the limitation of the electrode width to obtain fluoroscopic images is not more than 10 mm. Therefore, the dimensions of the cathode and anode in a standard cell used for the observation were set to 64 mm × 6 mm and 74 mm × 10 mm, respectively. The cell consisted of 7 electrode layers (cathode: 4 layers, anode: 3 layers). Each battery cell consisted of 6 unit cells (6 pairs of anodes and cathodes), since three double-sided anodes and four double-sided cathodes were used. All unit cells consisting of one anode–cathode pair were connected in parallel. The unit cell of electrodes was held by two polypropylene (pp) plates with a though-hole for nail penetration to suppress the distortion of the cell during the test. The capacity of the standard cell was 20 mAh. The dimensions of the cathode and anode of an 800 mAh cell were 70 mm × 70 mm and 74 mm × 74 mm, respectively. The cell consisted of 17 electrode layers (cathode: 8 layers, anode: 7 layers). No pp plate was used for the 800 mAh cell. To form an 820 mAh LIB cell, a 20 mAh cell and an 800 mAh cell were connected in parallel. Schematic illustrations and photographs of the prepared LIB cells are shown in Fig. 1. The 820 mAh stacked well and 20 mAh cell were as the typical gas-generating and non-gas-generating cell for the test, respectively. The corresponding characteristics of these two cells were observed with high reproducibility. X-ray fluoroscopy was carried out during the nail-penetration for both the 20 mAh in stacked 820 mAh cell and...
The nail-delivery speed was 10 mm s⁻¹. During the nail penetration test, gas generation was observed. Therefore, an inner case was used for preventing the diffusion of the generated gas into the X-ray system.

X-ray CT images were obtained before and after the nail-penetration test with an industrial micro-CT scanner (TOSCANER-32300qFD-Z, Toshiba IT & Control Systems Corporation).

Results and Discussion

Changes in 820 mAh LIB during nail-penetration test.—Figure 2 shows changes in the temperature and voltage of the 820 mAh stacked cell during the nail-penetration test. The nail delivery and nail-penetration results are also shown in the figure. Both the results of external observation and those of high-speed X-ray fluoroscopic moving image (movie 1, see Supplemental Material) are also shown. The fluoroscopic image was selected from the moving image (movie 1, see Supplemental Material) shown in Fig. 3.

As shown in Fig. 2a, the voltage of the cell dropped quickly from 4.2 V to 2.0 V because of short circuiting. The temperature of the cell and the inside of the chamber increased from 3 s onwards. Externally, thermal runaway, which comprised gas generation from the cell, was observed upon performing the nail-penetration test. Anode tabs connecting the 20 mAh cell and 800 mAh cell, which were made of nickel, were red-hot after 1 s. After 2 s, gas generation at the outside of the pouch began. The red-hot state of the tab ceased at 23 s. In contrast, the color of cathode tabs, which were made of aluminum, did not change. This difference is due to the difference in the resistance of the tabs; the resistance of the anode Ni tab is six times higher than that of the cathode Al tab. After 5 s, the voltage of the cell decreased slightly, and the voltage decrease stopped at 25 s. These results indicate that the internal short circuit and external short circuit occurred within 20 s with large current. If the cell was discharged from 100% to 10% within 20 s, it can be seen that ~150 A was runaway in the short circuit during 20 s. However, the gas generation continued over 50 s, indicating that the cell was hot enough to boil the electrolyte even after stopping the large current.

Figure 2b shows the initial temperature and voltage of the cell during the nail-penetration test. Initially, the temperature of the cell surface and inner case did not change. Figure 3 shows the X-ray fluoroscopic images of the electrodes in the LIB during the nail motion (movie 1, see Supplemental Material). Using a high speed moving image captured at 500 frame s⁻¹, the nail position in the layers and the layer-by-layer nail penetration were observed. The voltage decreased quickly at the second, fourth, and sixth layer; these layers were anodes. In particular, upon reaching the fourth layer, a large decrease in voltage could be observed. In general, the voltage decreased with increasing penetration layers because of the decrease in the electric resistance of the circuit due to short circuit.

Thus, the relationship between the behavior of the electric short circuit and nail motion was clearly observed. Gas generation out of the pouch cell was observed after 2 s; this observation indicates that gas generation did not occur at the same time as the short circuit. In general, gas generation is caused by Joule heating due to the current passing through the nail and current collector. The circuit materials began to heat the neighboring materials such as the electrolyte and active materials almost immediately after the short circuit. After some time, gas generation on the outside of pouch began with enough heat being generated for continuous boiling of the electrolyte.

Changes in 20 mAh LIB during nail-penetration test.—Figure 4 shows the changes in the temperature and voltage of the cell during the nail-penetration test. Both the nail delivery and nail-penetration results are shown in this figure. The results of external observation and those of high-speed X-ray fluoroscopic moving image (movie 2, see Supplemental Material) are also shown. The fluoroscopic image was selected from the moving image (movie 2, see Supplemental Material) in Fig. 4d.

As shown in Fig. 4a, the voltage of the cell dropped quickly from 4.2 V to 0.6 V because of short circuiting. The voltage changed to 1 V at 7 s, subsequently decreased slightly, and then the voltage change...
stopped at 25 s. However, the temperature of the cell and the inside of the chamber did not change. No change was observed externally. In other words, gas generation from the cell was not observed during the nail-penetration test, and no thermal runaway occurred. This result indicates that the cell temperature was not high enough to boil the electrolyte. The results of the change in voltage indicate that the internal short circuit and external short circuit occurred within 20 s with large current. The discharging of the charged cell from 100% to 10% within 20 s indicates that \(\sim 4\, \text{A}\) was runaway in the short circuit by 20 s. It is thought that the initial few second incurred higher current because of the lower voltage of the cell. However, Joule heating by the short circuit current was not enough to cause gas generation out of the pouched cell.

Figure 4b shows the initial state of the temperature and voltage of the cell during the nail-penetration test. Figure 5 shows the X-ray fluoroscopy images of the electrodes in the LIB during the nail motion (movie 2, see Supplemental Material). Using high-speed moving images captured at 1000 frame s\(^{-1}\), the nail position in the layers and the layer-by-layer nail penetration were observed. The voltage dropped rapidly upon reaching the 2nd layer, resulting in a short circuit. The voltage decreased with increasing penetration layer, which implies that the voltage decrease was caused by the increasing number of short circuits. Thus, the relationship between the behavior of the electric short circuit and nail motion was clearly observed.

**CT images before/after the nail penetration test.**—Figures 6 and 7 show the CT images of the 820 mAh stacked cell and 20 mAh cell after the nail penetration test, respectively. Whereas the cathodes of the 820 mAh cell were broken, indicating the active materials peeling off, all the electrodes of the 20 mAh cell remained unchanged. This result suggests that the damage to the 820 mAh cell was not caused by the physical disruption of the electrodes caused by the nail because the 20 mAh cell suffered no damage. As the electrode damage was only observed near the nail, the damage was caused by Joule heating because of the current flowing through the high resistance materials of the nail and contact between the nail and electrode. The rapid volume expansion due to the boiling of the electrolytic solution in the electrodes and deterioration of the active materials are considered to be the causes of the damage to the cathodes. Table I shows the diameter of the hole in the electrode penetrated by the nail. The hole in the second layer is the largest. These results indicate that non-uniform damage occurred during/after nail motion. Unfortunately, the changes occurring in the anode could not be observed, because carbon materials cannot be imaged by X-ray fluoroscopy.

Figure 8 shows the schematic of the circuit where each electrode layer is regarded as a closed loop circuit with the charged unit cell, resistance, and a switch triggering the electrical local short circuit. The number of short circuits is defined by the number of layers penetrated by the nail. \(R_n\) is the contact resistance between the nail surface and...
one pair of electrodes that formed the unit cell, $R_{\text{in}}$ is the internal resistance, $R_{\text{iw}}$ is the resistance of inner wiring, $R_{\text{ew}}$ is the resistance of external wiring, $I_{\text{ls}}$ is the current from the local internal short circuit, $I_{\text{is}}$ is the current from the internal short circuit, and $I_{\text{es}}$ is the current from the external short circuit. When a short circuit was formed by the nail, it led to the formation of another unit cell, and $I_{\text{ls}}$ flowed through the inner short circuit, which consisted of the two electrodes and the nail. $I_{\text{es}}$ flowed through the short circuit in the unit cell whose circuit shorted. Moreover, $I_{\text{is}}$ also flowed through the short circuit from the unit cell whose circuit was not shorted. Moreover, in the case of using a stacked cell, large $I_{\text{es}}$ was supplied to the 20 mAh cell from the 800 mAh cell.

Figure 9 shows a schematic of the short circuit of the cell during the nail-penetration test. The formation of the first short circuit is shown in Fig. 8a. $I_{\text{ls}}$ and $I_{\text{is}}$ (and $I_{\text{es}}$ in the case of 820 mAh stacked cell) flowed at the top of the nail tip, between the 1st layer and 2nd layer. The top of the nail tip is very fine, with a diameter of tens of micrometers. The short circuit current was concentrated at one point, the top of the nail. The formation of two short circuits is shown in Fig. 8b. The short circuit between the 2nd layer and 3rd layer was similar to the first.

### Table I. The diameter of the hole in the electrode penetrated by the nail.

| Layer No.     | 820 mAh stacked cell (mm) | 20 mAh cell (mm) |
|---------------|----------------------------|------------------|
| 1st layer (cathode) | 1.3                       | 1.1              |
| 2nd layer (anode)   | 2.0                       | 1.6-2.0          |
| 3rd layer (cathode) | 1.3                       | 1.1              |
| 4th layer (anode)   | 1.6                       | 1.1              |
| 5th layer (cathode) | 1.3                       | 1.1              |
| 6th layer (anode)   | 1.6                       | 1.1              |
| 7th layer (cathode) | cannot measured            | cannot measured  |
short circuit formed between the 1st layer and 2nd layer in Fig. 8a. The nail tip is a circular cone, and the surface contact between the nail surface and edge surface of the electrode(s) increased with an increase in nail penetration. Thus, it is thought that the resistance between the nail and edge of electrode decreased. Therefore, that the resistance of short circuit between the 1st layer and 2nd layer is thought to be lower than that between the 2nd and 3rd layer. The short circuit current $I_s$ (and $I_{es}$ (in the case of 820 mAh stacked cell)) was divided between the two short circuits. In general, the divided current is inversely proportional to the resistance of the circuit. Therefore, the current in the short circuit between the 2nd and 3rd layer is considered to be lower than that between the 1st and 2nd layer. In other words, the current in the newly formed short circuit is speculated to be lower than that of the already developed short circuit. In particular, the formation of the 1st short circuit is quite different from that of others. The details of the first short circuit were therefore investigated. As shown in Table I, the hole in the 2nd layer is larger than other holes. In our previous study, the stainless steel nails were observed to melt during the formation of the first short circuit, indicating that the temperatures rose up to 1000°C or higher at the top of the nail tip. Therefore, it is possible that the tip of the nail heated significantly and the copper foil melted, leading to a larger hole in the 2nd layer compared with the holes formed in the other layers.

A larger hole in the 2nd layer compared with those of other layers was also observed in the case of the 20 mAh cell, and the hole was not circular. Moreover, Cu particles were found on the pouch sheet around the hole. These results suggest that the tip of the nail possibly heated and the copper foil melted and stuck partly to the nail. It is also possible that the welded copper foil was broken and a part of it stuck to the film when the nail was drawn out. That is, the large hole in the 2nd layer is due to these reasons. From the above results, it can be considered that in case of 820 mAh cell, the electrode melted with the contact of the nail with the second layer; subsequently, the hole became larger and there was no stable contact between the nail wall and electrode, and when the nail reached the fourth layer, it touched completely. Thus, there was a thermal runaway with the maintenance of the short circuit with a large current. In contrast, for the 20 mAh cell, the nail is considered to make complete contact with the second layer. Because the current is small compared with that of the 820 mAh cell, loss of contact owing to an increase in the hole diameter due to electrode melting was not observed. However, there was no thermal runaway despite the maintenance of the short circuit because the current flowing in the 20 mAh cell was insufficient.

From these results, detailed behavior of the short circuit during the nail-penetration test could be analyzed with the X-ray fluoroscopy images obtained using the LiSC scanner and X-ray CT. Formation of

**Figure 4.** Changes in the temperature and voltage of the 20 mAh stacked cell during the nail-penetration test: (a) wide time range, (b) initial time range. Both the results of external observation and those of high-speed X-ray fluoroscopic moving images are also shown. Triangles and diamonds in (a) represent the temperature of the cell surface and inner case, respectively. The nail delivery is also shown in (b), and diamonds indicate the layer number reached by the pointed tip of tip across the cross section. The fluoroscopic image was selected from the moving image, and the labels in rectangular boxes in (a) and (b) correspond to the image labels in Fig. 5.
Figure 5. High-speed X-ray fluoroscopic images of the 20 mAh battery cell during the nail-penetration test. The images were selected from a moving image (movie 2, see Supplemental Material).

Figure 6. X-ray CT images of the 820 mAh stacked cell before and after the nail-penetration test: (a) before the test, (b)–(f) after the test ((b) center, (c) 0.66 mm from the center, (d) 0.99 mm from the center, (e) 2.02 mm from the center, and (f) 3.06 mm from the center).

Figure 7. X-ray CT images of the 20 mAh cell after the nail-penetration test: (a) center, (b) 0.56 mm from the center, and (c) 1.32 mm from the center.

the short circuit and thermal runaway, which caused gas generation, were successfully separated from this investigation. It was realized that the gas generation and the damage of electrodes in 820 mAh cell were caused due to Joule heating by the current flowing though the high resistance materials of the nail and contact between the nail and electrode. Moreover, these results indicate that the shape of the nail tip and nail motion have an effect on the results of an internal short circuit test.
defined by the number of layers penetrated by the nail. The number of short circuits is separately. Thus, this system was able to analyze the details of the internal short circuit during the nail-penetration test. The internal layer-penetration test was observed using a LiSC scanner. The internal layer-penetration test: (a) 820 mAh stacked cell, (b) 20 mAh cell.

Figure 9. Schematic of the short circuit of the 820 mAh stacked cell during the nail-penetration test: (a) Formation of the first short circuit, (b) formation of two short circuits.

Thermal runaway of lithium ion batteries during the nail-penetration test was observed using a LiSC scanner. The internal layer-by-layer short circuit caused by the nail was clearly observed during the nail penetration. Gas generation, which is well-known to occur during the internal short circuit of the cell, and the electrical behavior of the short circuit during the nail-penetration test were observed separately. Thus, this system was able to analyze the details of the internal short circuit of the cell. In particular, the first short circuit formation, that is, the contact of the 1st layer and 2nd layer by the nail, is different from other short circuit formations, and a very large short circuit current flowed at one focused point of the nail tip. These results indicated that the shape of the nail tip and nail motion have an effect on the results of an internal short circuit test. In the case of LIB studied here, the gas generation and the damage of electrodes were found to be caused by Joule heating due to the current flowing through the high resistance materials of the nail and contact between the nail and electrode. These results of analysis of the thermal runaway phenomenon represent an important step toward the prevention of battery fires. The study also constitutes an important step toward the visualization of safety tests and analysis of the thermal runaway phenomenon. The developed system is expected to lead to significant developments in the safety of LIBs.

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ORCID

Tokihiro Yokoshima https://orcid.org/0000-0003-0645-070X
Tetsuya Osaka https://orcid.org/0000-0001-8307-132X

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