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The Influence of Cycling, Temperature, and Electrode Gapping on the Safety of Prismatic Lithium-Ion Batteries

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Lithium-ion batteries are prevalent in every aspect of modern life (cell phones, laptops, electric vehicles, and energy storage systems for the electric grid). For all applications, the battery safety is an important consideration. Compared to numerous studies on the safety behavior of 18650-type cells, limited research has been conducted to characterize prismatic cells with their unique challenges including how electrode gapping, cycling history, electrolyte degradation, or lithium plating affect the safety. In this paper, a systematic study is reported on prismatic cells cycled at 0 °C, 23 °C, and 45 °C. The safety aspect of the cells with electrode gapping is evaluated using accelerating rate calorimetry (ARC). The evolution of gaps was monitored using X-ray computed tomography. Our study demonstrates that gaps are intrinsic even in fresh cells. The gaps can evolve during cycling and are closely related to the localized lithium plating and electrolyte degradation, which can be more severe for cells cycled at 45 °C. However, the safety behavior is not simply correlated to cell internal structure (e.g. gapping), or the amount of degradation products after cycling; the aging mechanism at different temperatures also plays an important role. Understanding the thermal stability of prismatic cells during their lifecycle is necessary for risk mitigation in numerous applications.

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Lithium-ion batteries have been adapted to fit a wide variety of form factors, enabling the use in applications ranging from head-phones and cell phones to electric vehicles and energy storage systems for the electric grid. While the overall structure (a positive and a negative electrode, separator and electrolyte) remains the same, lithium-ion cells can be produced in cylindrical, prismatic, and pouch form factors that can be customized to fit different applications.^{1,2} Different forms lead to different mechanical-electrical behaviors of lithium-ion batteries in real world applications, which has become a critical design consideration against mechanical abuse and/or daily wearing^{3–5} to avoid many catastrophic battery failures. Cylindrical cells, such as the widely used 18650-size and 21700-size cells,^{4,6} are mechanically robust due to their steel casings but offer little room for packing customization. Pouch cells are the least mechanically robust, being enclosed only in a metalized polymer pouch. However, they offer the most customization, with almost any length, width, and height combinations available upon request. Prismatic cells represent a middle ground, being encased in an aluminum can that is rigid but still customizable. Prismatic cells are often favored by devices that include a removable battery (e.g. laptops) because the mechanical protection of the cell can be achieved without requiring additional space for bulky plastic casings.⁷ It is worth noting that batteries not only suffer from the external impact and dynamic loadings, but also suffer from inevitable internal defects introduced during manufacturing and/or operating.⁵ In the case of prismatic cells, its manufacturing involves inserting a flat, flexible electrode winding into a hard cell can/enclosure and applying vacuum during electrolyte filling. These processes can result in winding deformation and the gapping between electrode layers even in the newly assembled prismatic cells, a feature that is rarely observed in fresh pouch cells or cylindrical cells in Exponent's experience of over ten years.

Such intrinsic electrode deformation and gapping may further develop during cell operation, since the charge and discharge of cells is accompanied by a volume change associated with lithiation and de-lithiation of the electrodes.^{8–10} The volume change has been measured to be up to 10% in the graphite anode with the thickness

change for a cell as a whole being 1%–6% depending on chemistry and packaging.^{8,11} This results in mechanical and structural changes that affect both the safety and performance of cells.⁹ In a rigid 18650-type cell, the volume fluctuation can lead to buckling of the innermost layers.^{12,13} In flat-format pouch cells, volume fluctuation can lead to the formation of gaps. In prismatic cells, volume fluctuation can create new gaps and enlarge the initial gaps already present between the electrodes. Further, the cycling induced chemical changes (e.g., degradation product builds up) around the gaps can lead to changes in the life, performance, and safety aspects of the cell. Once installed in a device, cells are exposed to a wide variety of conditions being charged and discharged in the field. The operating conditions such as currents and temperatures also have considerable influence on the cycling performance of the cells, and may be exacerbated by the gapping issue in prismatic cells.¹⁴ Understanding the performance and safety associated with the intrinsic gapping issue in prismatic lithium-ion cells during the lifecycle of a product is necessary for risk mitigation as product recalls due to cell issues can be incredibly expensive.¹⁵

Safety tests (e.g. UL 1642) are typically performed on lithium-ion cells before a product is released to the market. One of the limitations of today's lithium-ion cell certification process is that standards primarily test new cells. UN 38.3 (Transport of Dangerous Goods) evaluates cells that have been cycled up to 50 times, however, this number is well below the typical lifetime advertised by cell manufacturers (300–1000+ cycles). There is no regulation on battery performance and safety as the product reaches the end of its lifecycle. Even new cells that pass the same tests can show different safety properties as they age.¹⁶ Many studies tracking aging mechanisms and their effect on capacity and impedance have been conducted,^{15–17} but less attention has been focused on how the cell's safety and thermal characteristics change through cell's life. Accelerating rate calorimetry (ARC) can be used to probe the effect of different features in a cell by measuring the self-heating onset temperature and the self-heating rate of a cell. Research has focused on studying the 18650 form factor and how cell chemistry and state-of-charge affect the onset temperature of thermal runaway, as a way to drive innovation towards safer cell designs.^{17–20} However, less work has been done to characterize how electrode gapping, cycling history, electrolyte degradation, or lithium plating affect the thermal runaway characteristics of the prismatic cells.^{16,21}

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In this paper, we reported a systematic cycling study on commercial prismatic cells under three different temperature conditions. In addition to the tracking of cell capacity and impedance, we also monitored the evolution of gaps using the non-destructive X-ray computed tomography (CT). Destructive physical analysis (tear-down) was also performed on cells at 100% state-of-charge (SOC) before and after cycling to examine the gapping-related localized degradation issues. Additionally, the safety aspect of the cells with electrode gapping is also compared between the cycled cells and uncycled cells using ARC. Our study demonstrates that the intrinsic gaps widely exist even in fresh prismatic cells. The gaps can evolve during cycling and are closely related to the localized lithium plating and electrolyte degradation, which can be more severe for cells cycled at high temperatures. All cycled cells exhibited higher self-heating rates and lower onset temperatures than the uncycled cell, suggesting these cells became less thermally stable after cycling.

Experimental

The 2.1 Ah prismatic lithium-ion cell (model # ICP 515161HR) employed for this study is manufactured by Maxell Ltd with a specified voltage operation range of 2.75 V–4.35 V. The following techniques were used to examine cells with different cycle counts and cycle temperatures to evaluate the progression of cell aging and safety. Cell specifications were typical for a lithium-ion battery used in consumer electronics applications.

To visualize the internal structure of the cells, computed tomography scans were conducted on a subset of cells. Computed Tomography (CT) is a non-destructive technique that can be used to image the electrodes, without opening the cell. Denser materials, such as the nickel negative tab, will appear brighter than the less dense materials, such as the aluminum can and metal oxide cathode. Liquid electrolyte and degradation material (including lithium plating) absorb fewer X-rays, and thus appears dark. CT can thus be used to observe the progression of gaps and degradation through the cell's lifecycle. Cells were scanned prior to cycling, after 200 cycles, and after 500 cycles to evaluate their internal structure with respect to gapping and degradation. CT scans were conducted on a Nikon Metrology X-Tek MCT 225 computed tomography machine with a Perkin Elmer 1621 EHS Detector. Scan settings of 220 kV and 180 μ A with a 2 mm Cu filter and 1.4 s exposure ($\sim$ 1.25 h scan time) were used to generate 3D dataset of each cell. The voxel size of these scans was approximately 37.5 μ m.

Cells were then charge-discharge cycled at three temperatures: 0 $^{\circ}$ C (cold temperature), 23 $^{\circ}$ C (room temperature), and 45 $^{\circ}$ C (elevated temperature). Eight cells were cycled at each temperature condition. The cells were cycled using a typical constant-current-constant-voltage (CCCV) charge and a constant-current (CC) discharge with a 5 min rest between each charge and discharge. The current values and voltage limits used are summarized in Table I and are within the specifications provided by the cell manufacturer. Cycle testing was conducted on a Series 4000 MACCOR system. The channel voltage range was 0–5 V and current range was 0–5 A. Voltage and current accuracy was 0.02% of the full range.

The electrochemical impedance spectroscopy (EIS) of each cell prior to and after cycling was measured galvanostatically using a Gamry Interface 5000–04505 potentiostat. Cells were fully charged and subjected to an AC oscillation of 0.01 C (21 mA) amplitude over the frequencies from 100 kHz to 0.1 Hz.

Destructive physical inspection of cells was used to supplement CT analysis, allowing for observation of additional features that have similar X-ray absorbance, and thus cannot be distinguished in CT analysis. Cells selected for this analysis were fully-charged using the previously described protocol and transferred to an inert argon-filled glovebox. The cell cans were opened to visually examine and document the state of the positive electrode, negative electrode, and separators. Additional microscope and elemental analysis via scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) was performed to understand the nature of the degradation products.

Accelerating Rate Calorimetry (ARC) tests were performed with an ARC-EV + system manufactured by Thermal Hazard Technology (THT). ARC can measure the self-heating and gas evolution rate(s) of a chemical sample or material in an adiabatic environment (no heat loss to surroundings) as a function of temperature. For battery samples, an onset temperature is usually identified. Above this onset temperature, the sample's self-heating rate is sufficient to eventually drive the cell into thermal runaway. The self-heating rate can be tied to the kinetics of the exothermic reactions (e.g. decomposition) over a range of temperatures. The standard operating mode of the ARC uses a "heat-wait-see" (HWS) algorithm. In HWS, the ARC heats to the start temperature, waits for temperature equilibration, and then determines whether the exotherm has been found (seeks). This loop continues until a reaction is found (self-heat rate exceeds a sensitivity threshold), at which point the ARC switches to exotherm mode. Exotherm mode tracks heat evolved from the reaction and maintains an adiabatic environment, until the reaction is complete (e.g. battery thermal runaway occurs). A standard calibration test (<0.01 $^{\circ}$ C min $^{-1}$) and drift test using an aluminum metal plate were performed before each cell test. To conduct the tests, cells were charged at room temperature (regardless of their prior cycling temperature) to 4.35 V at 2.1 A with a taper of 0.105 A. Each cell was suspended in the ARC chamber without being in contact with the chamber wall. The ARC control thermocouple (N-type) was affixed to the center of one side of the cell with high-temperature adhesive tape. One additional auxiliary thermocouple (K-type) was affixed to the center of the other side of the cell and recorded through an external data-logger. Cell voltage was also recorded on the same data-logger with a sampling frequency of 1 Hz.

Results and Discussion

CT scan of uncycled cells.—CT was used to observe the progression of gaps and degradation through the cell's lifecycle. The purchased Maxell ICP 515161HR cells were first CT scanned prior to cycling to evaluate their internal structure and degrees of gapping. Consistent with Exponent's past observations on some prismatic cell types, CT scanning of the pristine cell population (total of 24 cells) revealed that almost all electrode windings exhibited gapping between adjacent electrodes. Figure 1 shows 2-dimensional planar and radial cross section views (from CT data) of two arbitrary uncycled cells. Electrode gapping was clearly observed in both cells (Fig. 1, yellow arrows). The extent of the uncycled cell gapping was similar across the cell population, but at different locations within the cell.

As illustrated in Fig. 2, electrode gapping is expected to result in a localized impedance increase between mating electrodes that prevents lithium-ions from flowing through the gapping region. While the cell experiences the same (external) charge rate, adjacent regions can experience localized high charge rates that exceed the rate capability of the negative active material, resulting in plating of metallic lithium at these locations. Plated lithium can react with the electrolyte, which can cause electrolyte dry out and further increase the impedance and lithium plating.²² Therefore, depending on the severity of the gaps, these gapping regions could either result in electrode surfaces prone to electrolyte degradation and/or lithium plating, electrochemically inaccessible regions (i.e. loss in capacity),

Table I. Cycling conditions used to simulate use of prismatic cells.

Capacity	2.1 Ah
Discharge Current	2.1 A
Voltage Min	2.75 V
Charge Current	2.1 A
Voltage Max	4.35 V
Current Taper Cut-off	0.105 A

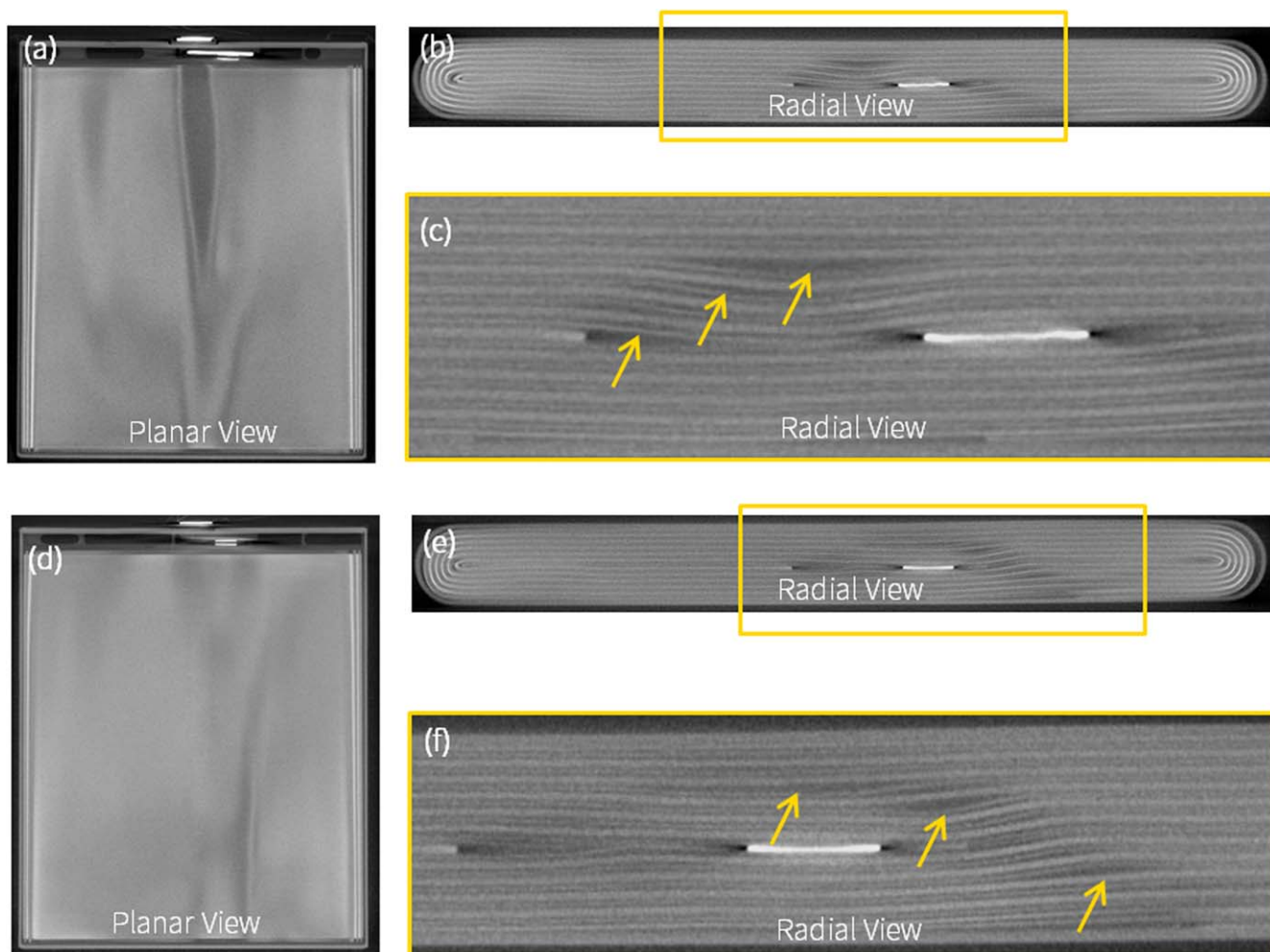


Figure 1. 2-dimensional cross section views, from CT data, of two representative uncycled cells: (a) planar view of Cell 1, (b) radial view of Cell 1, (c) zoomed-in radial view of Cell 1, (d) planar view of Cell 2, (e) radial view of Cell 2, and (f) zoomed-in radial view of Cell 2.

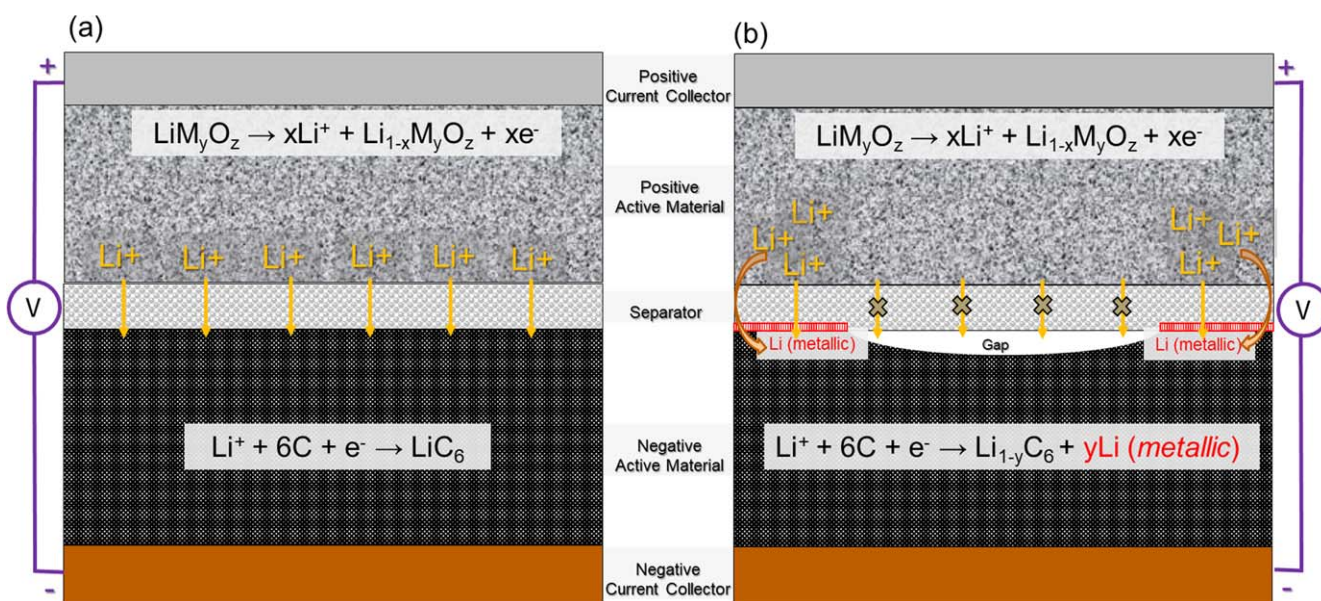


Figure 2. Schematic drawing of the lithium-ion flow between the positive and negative electrodes during charging in a battery (a) without gaps, and (b) with gaps; M represents metallic cations (e.g. Cobalt, Manganese, and Nickel).

or a combination of the two. Other secondary consequences, such as gas generation, can also occur at electrode gaps.

Cell cycling and EIS characterization.—The cycling protocol described in the previous section applied to cells at each of the temperatures of interest (i.e., 0 °C, 23 °C, and 45 °C). Cell capacity and Coulombic efficiency were measured for each cycle. It is well known that the performance and aging of lithium-ion batteries are dependent on temperature.²³ The diffusion of lithium ions into graphite slows down at low temperatures. On the other hand, elevated temperatures can increase side reactions. Figure 3 shows the average capacity of each group of cells cycled at the indicated temperatures. In cells cycled at 0 °C, an initial decrease in cell capacity is followed by an increase in capacity after a few cycles. The increase in capacity at 0 °C may indicate a continuation of cell formation and/or a more complete wetting of the electrodes by the electrolyte. No increase of capacity was observed for cells cycled at 23 °C or 45 °C, consistent with faster electrolyte wetting at higher temperatures. The rate of capacity fade was different for cells at each temperature group. As seen in Fig. 1, the capacity of cells at 0 °C and 23 °C drops faster than those at 45 °C during the first 400 cycles. However, beyond the 400 cycle count, capacity loss accelerated for cells cycled at 45 °C. The average observed capacity loss over the 500 cycles was 76%, 45%, and 35% for cells at 0 °C, 23 °C, and 45 °C correspondingly.

The impedance of the cells before and after cycling at different temperatures for 500 cycles was studied using EIS. The impedance was always measured at 100% SOC at room temperature. As shown in Fig. 4a, in a typical EIS of a prismatic lithium-ion cell, there is an arch at high frequency (usually composed of two or three partially overlapped semicircles) and a straight line at low frequency. The span of the arch section (R_i) represents the interfacial resistance, which includes the resistance of the solid-electrolyte interface (SEI) layer as well as the resistance of faradic charge transfer. R_b represents the bulk resistance of the cell, including the ohmic resistance of the electrolyte, separator, and electrodes, as well as the resistance of tab connections. Figure 4b shows that for cells cycled at 0 °C, the bulk resistance showed almost no change after 500 cycles, which was likely due to the slowed kinetics of electrolyte degradation at the low temperature.

Due to increased internal resistance at the low temperature, cells also yield a lower capacity, which results in lower cumulative charges being passed over the same 500 cycle procedure in the low-temperature cells compared to the room- and high-temperature cells. In comparison, for cells cycled at 23 °C and 45 °C for 500 cycles, the bulk resistance increased by 11.6% and 16.7%, respectively, which was likely due to the electrolyte dry out and/or electrode degradation, both of which raised the ohmic resistance. In addition, for the cells after 500 cycles at 0 °C and 23 °C, the interfacial resistance decreased by 17.3% and 28.6%, respectively. Such interfacial resistance drop is often observed during the early cycling of new cells and is usually due to the improvement of electrolyte wetting over the early cycles. On the contrary, the interfacial impedance of the cells cycled at 45 °C increased by 16.0%, implying the formation of a thicker SEI layer and/or the surface degradation of electrode materials. In general, cells cycled at 0 °C showed a reduction in total resistance, corresponding to the least degradation; the total resistance of cells cycled at 23 °C showed almost no change due to a slightly increased bulk resistance and a slight decreased interfacial resistance; while the cells cycled at 45 °C demonstrated the highest resistance increase, indicating the most severe degradation over cycles.

Reactions occur faster at higher temperatures due to thermodynamics. At 0 °C, the typical electrolyte degradation and SEI formation reactions occur at a slower rate, which may explain the negligible change in impedance. The cycling rate chosen was likely low enough so that other detrimental effects of cycling at the low temperature were not observed. For example, at low temperatures, the electrolyte and electrodes become less conductive for lithium

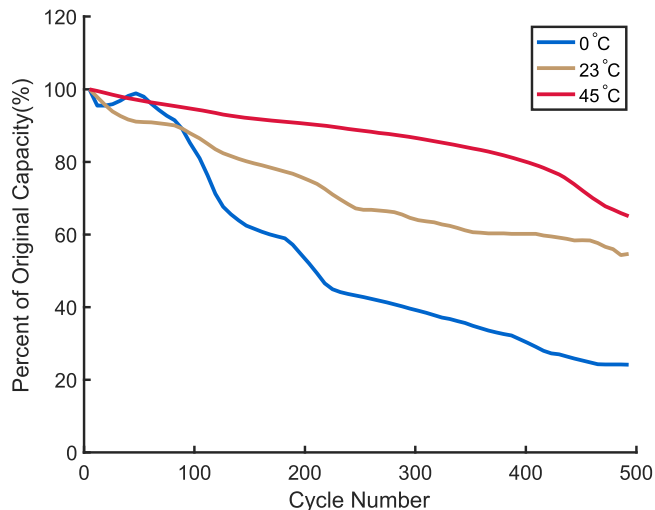


Figure 3. Percentage of original cell capacity as a function of cycle number for cells cycled at three different ambient temperatures (0 °C, 23 °C, and 45 °C).

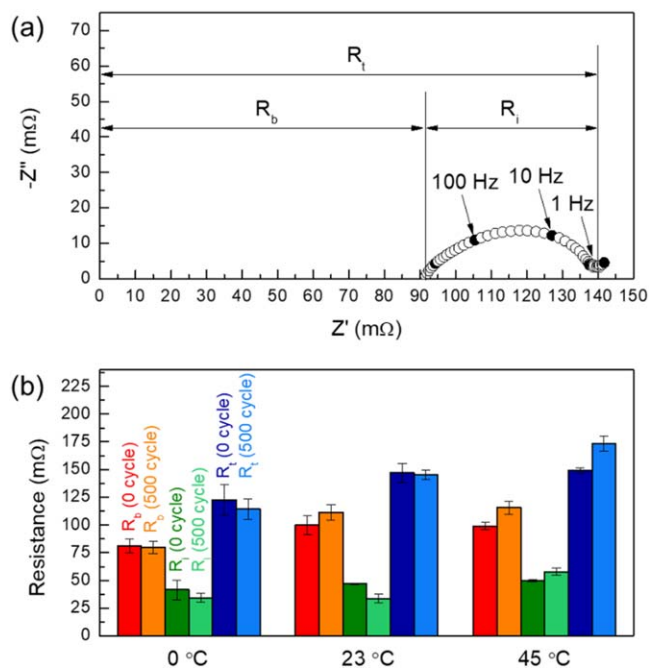


Figure 4. (a) Typical EIS of an example Li-ion prismatic cell before cycling. (b) The bulk (R_b), interface (R_i), and total resistance (R_t) of the cells before and after cycling at different temperatures. The error bars represent the standard deviation of at least three samples.

ions, thus the combination of fast cycling at low temperatures commonly produces lithium plating; however, this did not occur because the rate chosen/specified by the manufacturer was low enough not to enter this operating regime. Conversely, at the high temperature, degradation and SEI formation reactions occur more quickly, resulting in the largest impedance increase.

Effects of cycling on the internal cell structure by CT and teardown analysis.—CT scanning was used to monitor the evolution of gapping and material deposits on the electrodes throughout the cycling process. All cells were scanned after completion of 100, 200 and 500 cycles. Representative 2-dimensional cross section views along the radial plane of the cell are shown in Figs. 5a–5c for a cell from each cycling group, with the same cross section plane being

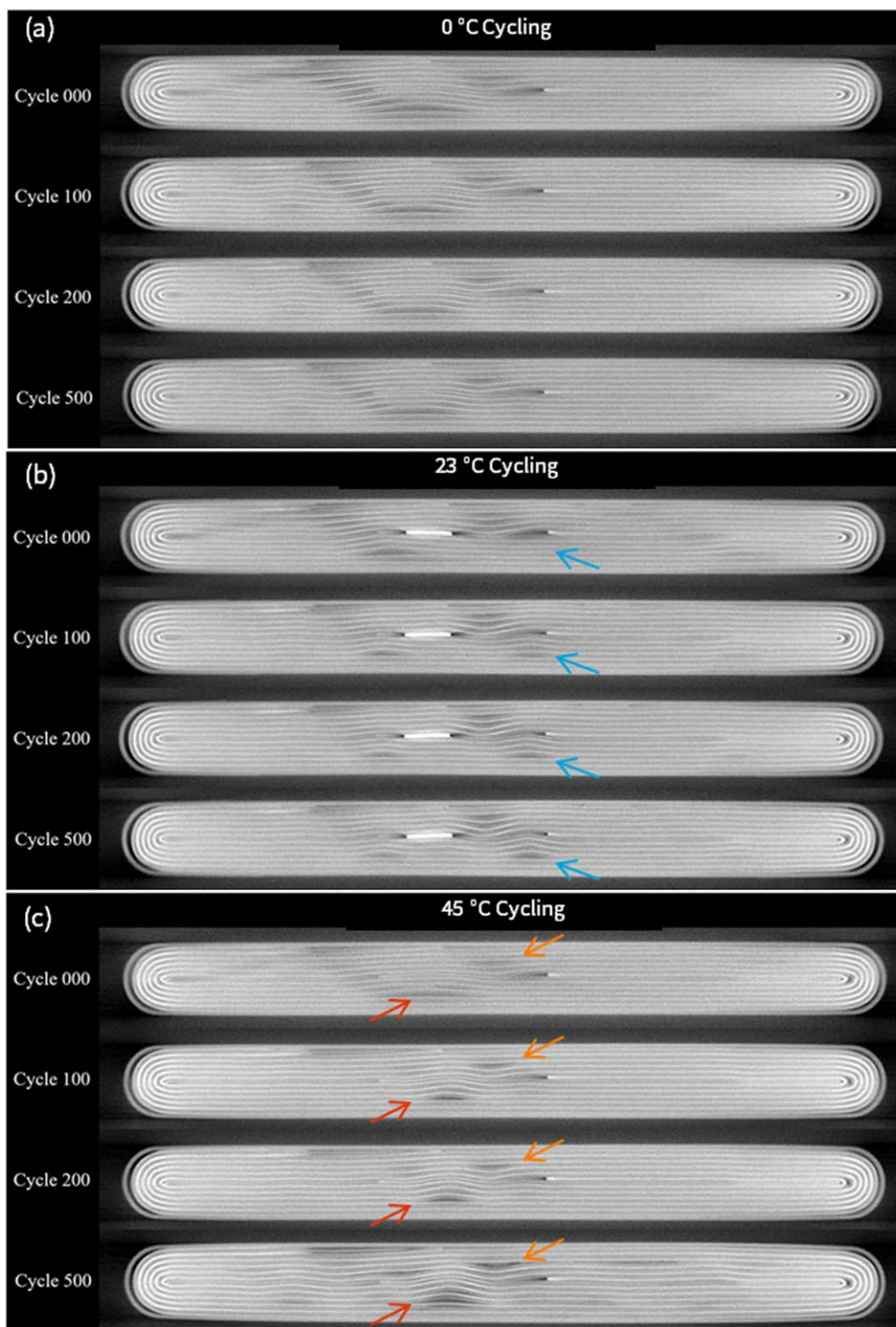


Figure 5. 2-dimensional radial cross section view of uncycled cell (Cycle 000) and cycled cells after 100, 200 and 500 cycles at (a) 0 °C, (b) 23 °C, and (c) 45 °C. The cross-section views were taken in the same plane.

shown at each cycling interval. The gaps in the as-assembled electrodes can be observed in the uncycled images (Cycle 000 set), and the progression of gapping with increased cycles can be observed in the cross-sections at 100–500 cycles. The cell cycled at 0 °C showed no apparent change in gapping over 500 cycles via CT scan analysis. The gaps present at the beginning were still in the same location and were the same size after 500 cycles, and no new gaps were observed. The cell cycled at 23 °C developed a new gap [Fig. 5b, blue arrow] that steadily grew over 500 cycles. Gap development was most severe in the cell cycled at 45 °C, with the

growth of two gaps being observed over 500 cycles [Fig. 5c, orange and red arrows].

It is well known that electrodes expand and contact with cycling,¹⁰ and all three cells were subjected to the same number of cycles. The difference in gap formation with temperature can be traced to the different amount of charge passed at each temperature. Similarly, while the voltage limits are the same for each set, cells at 45 °C yield a capacity of nearly twice of those at 0 °C, an effect that can be traced to the difference in internal resistance and lithium-ion kinetics with temperature. This means that although the cells all have

the same number of cycles, the cells at 45 °C see a much higher amount of total lithium-ion movement compared to the cells at 0 °C or even 23 °C. This results in more volume change, and thus, more gapping.

Two-dimensional planar cross section views across a gapped region of the electrodes at the cycling intervals are shown in Fig. 6 for cells cycled at (a) 0 °C, (b) 23 °C, and (c) 45 °C, respectively. The same cross section plane is shown for a particular cell at each cycling interval. The planar cross section views display material deposits (low-density features in CT) at the gapped regions for all three cells. The gapped region for the cell cycled at 45 °C shown in Fig. 6c significantly grew over 500 cycles. Further, electrolyte consumption or relocation can be qualitatively observed in the planar cross sections. At cycle 0, electrolyte can be observed as medium-density material at the top of each cell (Fig. 6, red arrows). Electrolyte is mostly absorbed in the porous electrodes and separator, but a small amount can be observed forming menisci between the top of the winding and the cell can. This excess electrolyte is no longer present in any Cycle 500 cell, regardless of temperature.

Although it is hard to overstate how powerful CT scanning can be when studying batteries, there are limitations to the technique that require the use of complementary techniques to fully understand

observations made via CT. For example, the low-density CT features previously described in Fig. 6 could correspond to a variety of low-density materials present in the cell, from electrolyte degradation/dry-out products to lithium plating. In order to understand the nature of those deposits, three cells that cycled at different temperatures were charged to 100% SOC and opened inside an argon-filled glovebox. Figure 7 shows photos of representative negative electrodes from the teardowns of four cells corresponding to (a) an uncycled cell and cells cycled at (b) 0 °C, (c) 23 °C and (d) 45 °C, respectively. Compared to the uncycled cell, the cell cycled at 23 °C exhibited small silver/gray deposits (black arrows) visually consistent in color and texture with lithium plating; no electrolyte degradation was observed. The cell cycled at 0 °C [Fig. 7c] exhibited more silver/gray deposits visually consistent with lithium plating than the cell cycled at 23 °C. The cell cycled at 45 °C [Fig. 7d] exhibits large amounts degradation products and non-uniform lithiation, along with electrolyte degradation (green ovals).

Figure 8 shows SEM and EDS analysis of a discolored negative electrode panel [Fig. 8a] from the cell cycled 500 times at 45 °C. A zoomed-in photo [red box, Fig. 8b] exhibited three distinct regions: golden colored region (free of deposits), red- and dark-colored region, and silver/gray colored region with deposits. The sample was transferred using an airless transfer sample holder to a SEM

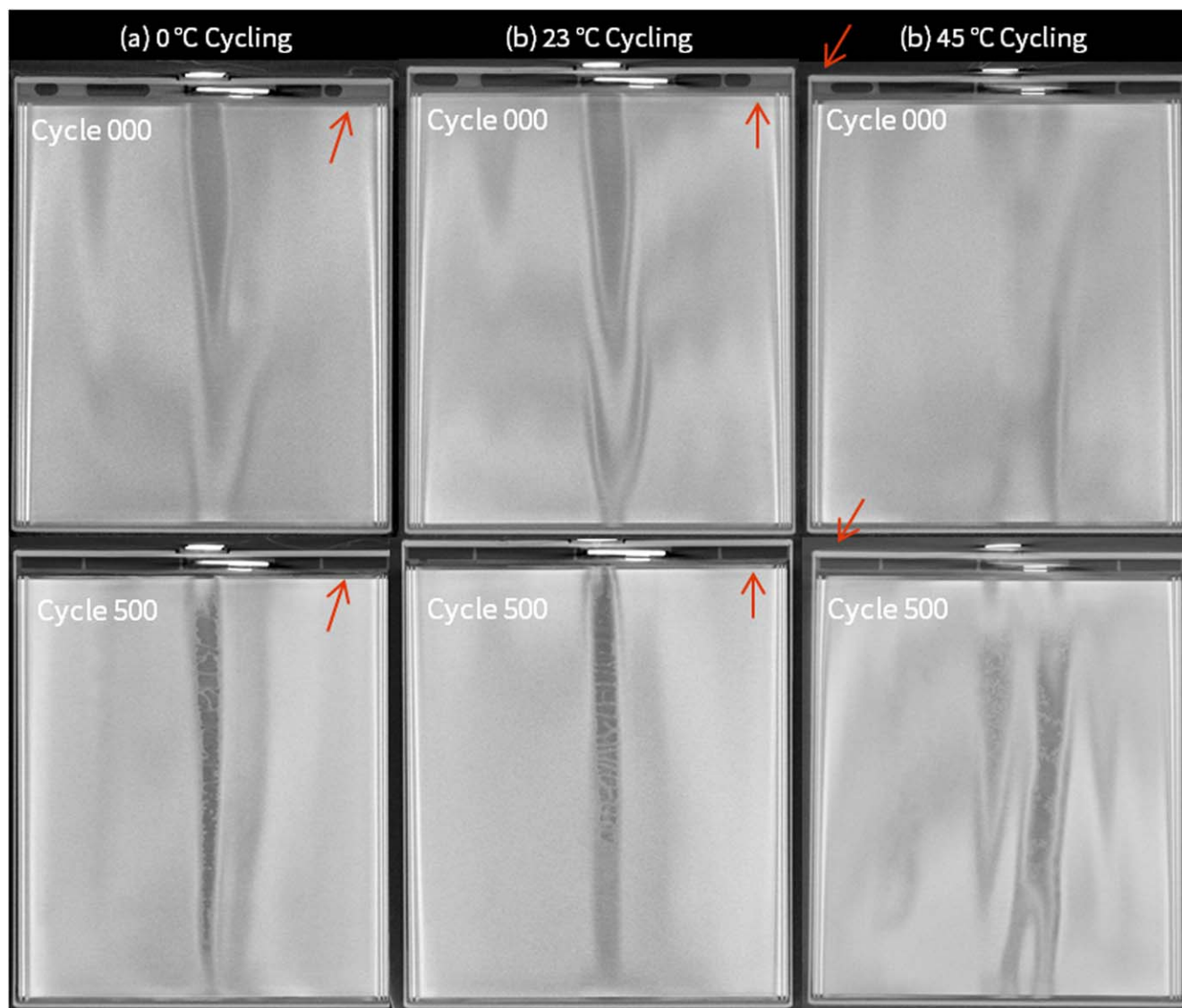


Figure 6. 2-dimensional planar cross section view of uncycled cell (Cycle 000) and cycled cells after 100, 200 and 500 cycles (a) 0 °C, (b) 23 °C, and (c) 45 °C. The cross-section views were taken in the same plane.

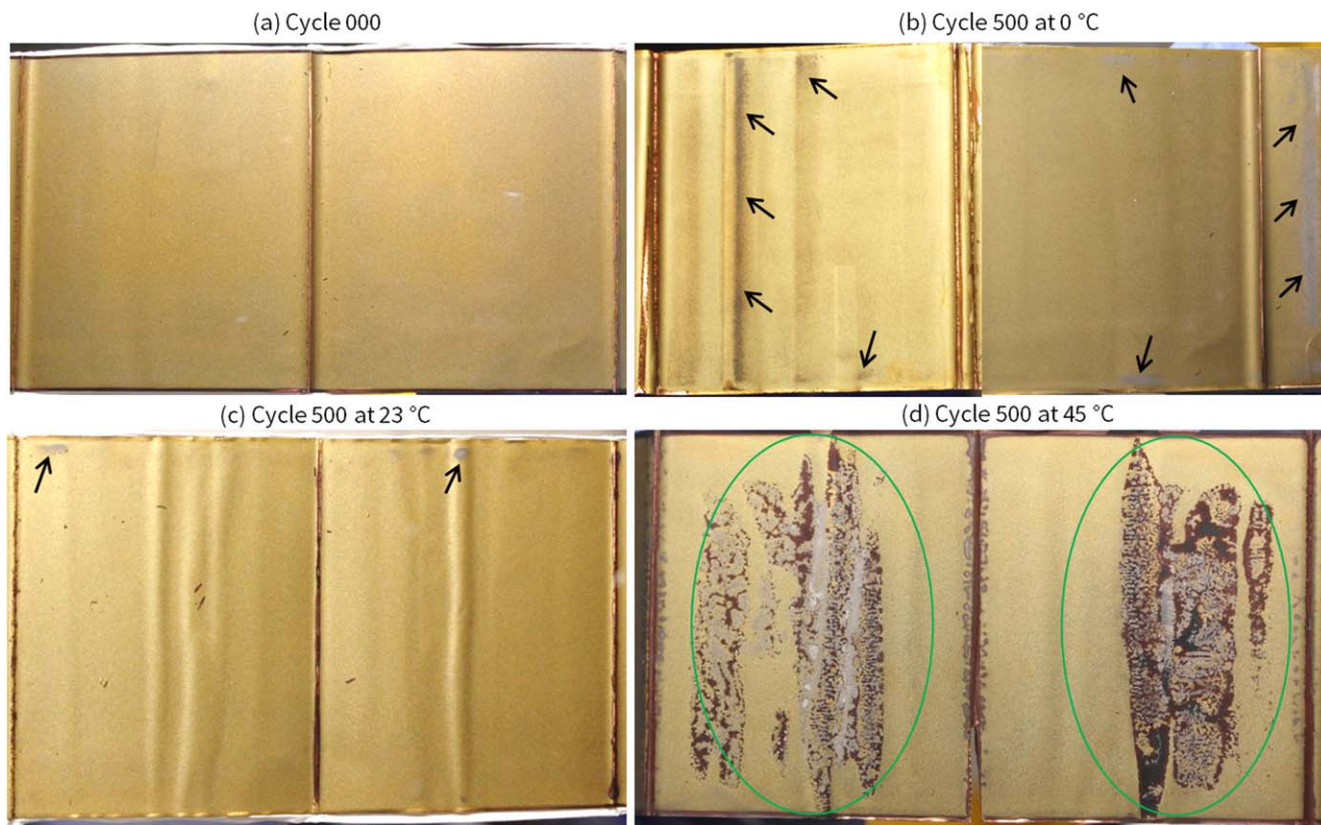


Figure 7. Representative teardown photos the anodes of different cells for (a) Uncycled cell, (b) Cycle 500 at 0 °C, (c) Cycle 500 at 23 °C, and (d) Cycle 500 at 45 °C.

chamber, where it was imaged in backscatter electron mode. A low magnification (30 $\times$) SEM image shows the material deposits on the negative electrode surface [Fig. 8c].

SEM and EDS analysis of the golden colored region (orange box) exhibited a typical graphite (carbon) negative electrode morphology with a strong carbon peak [Figs. 8d and 8g]. The red- and dark-colored region (yellow box, [Figs. 8e and 8i]) did not show notable chemical or morphological differences from the golden colored region. This indicates that the red- and dark-color is from incomplete lithiation of the graphite⁸ and correspond to the gaps that result in poor contact between the electrodes. High resolution SEM imaging [Fig. 8f] of the silver/gray deposits exhibited a mossy morphology that is characteristic of lithium plating, with some areas appearing to contain dendrites. EDS spectrum showed a dominant oxygen peak after exposed the sample in air [Fig. 8h], which is also consistent with localized lithium plating. Lithium cannot be readily detected by EDS, but metallic lithium reacts with moisture (water) in air and forms LiOH, which would show strong oxygen signals in EDS spectrum. Elevated levels of fluorine and phosphorous indicate that the electrolyte degradation is co-located with lithium plating. Overall, gaps result in electrochemical dead-spots surrounded by regions of non-uniform current density, leading to a combination of non-uniform lithiation and lithium plating. This effect is more evident at 45 °C because of increased electrolyte degradation, which is also evident from the impedance results.

In all three cells, close correlation between the CT data and physical features was observed. For example, the deposits observed in the CT data for the cell cycled at 45 °C, Fig. 6c, were confirmed during teardown (Fig. 9). The matching features observed in CT are likely from electrolyte degradation built up in or around the lithium plating at the gapping regions. This emphasizes the synergy between CT scanning and cell teardown: while the CT scan is able to detect and monitor the electrode gap, teardown can provide unique insights into understanding the nature of the features. Furthermore, the

differences observed between the three cycled cells through teardown suggest that different degradation mechanisms can take place around the electrode gaps at different temperatures, which can impose different degrees of reliability and/or safety risk(s).

Effects of cell cycling on the thermal stability by Accelerating Rate Calorimetry (ARC).—As introduced in the Experimental section, Fig. 10 shows the cell temperature and voltage as a function of time during a typical ARC test. During HWS mode (left inset of Fig. 10), the ARC heats to the start temperature of 50 °C, waits for 25 min to reach temperature equilibration, then seeks the exotherm (self-heating of >0.02 °C min⁻¹) for 10 min. If no self-heating is detected, the ARC increases the temperature to the next threshold, and repeats. Once the self-heating rate exceeds 0.02 °C min⁻¹, the ARC switches to exotherm mode and the ARC tracks the temperature of the sample and maintains an adiabatic environment until battery thermal runaway occurs (self-heating of >15 °C min⁻¹, right inset of Fig. 10). Before the onset of thermal runaway, a sudden voltage drop and cell venting (right inset of Fig. 10) occur almost simultaneously. It is noted that prior to thermal runaway failure of the cell (at ~ 1100 min), there is an initial voltage drop that recovers to >4.0 V before continuing to fall then entering thermal runaway. This behavior is consistent with the cell initially shorting due to separator failure then either (a) the electrodes / short being separated by sudden gas generation from the locally heated electrolyte or (b) local heating of the separator leading to melting/closing of the shorting location. State of the art polymeric separator materials in lithium-ion cells employ “shut-down” layers that close when subjected to heat while other layers maintain mechanical integrity due to higher melting points. Either possibility is considered plausible from Exponent’s experience with ARC testing of lithium-ion cells and could not be confirmed after the test due to the extent of damage sustained in thermal runaway.

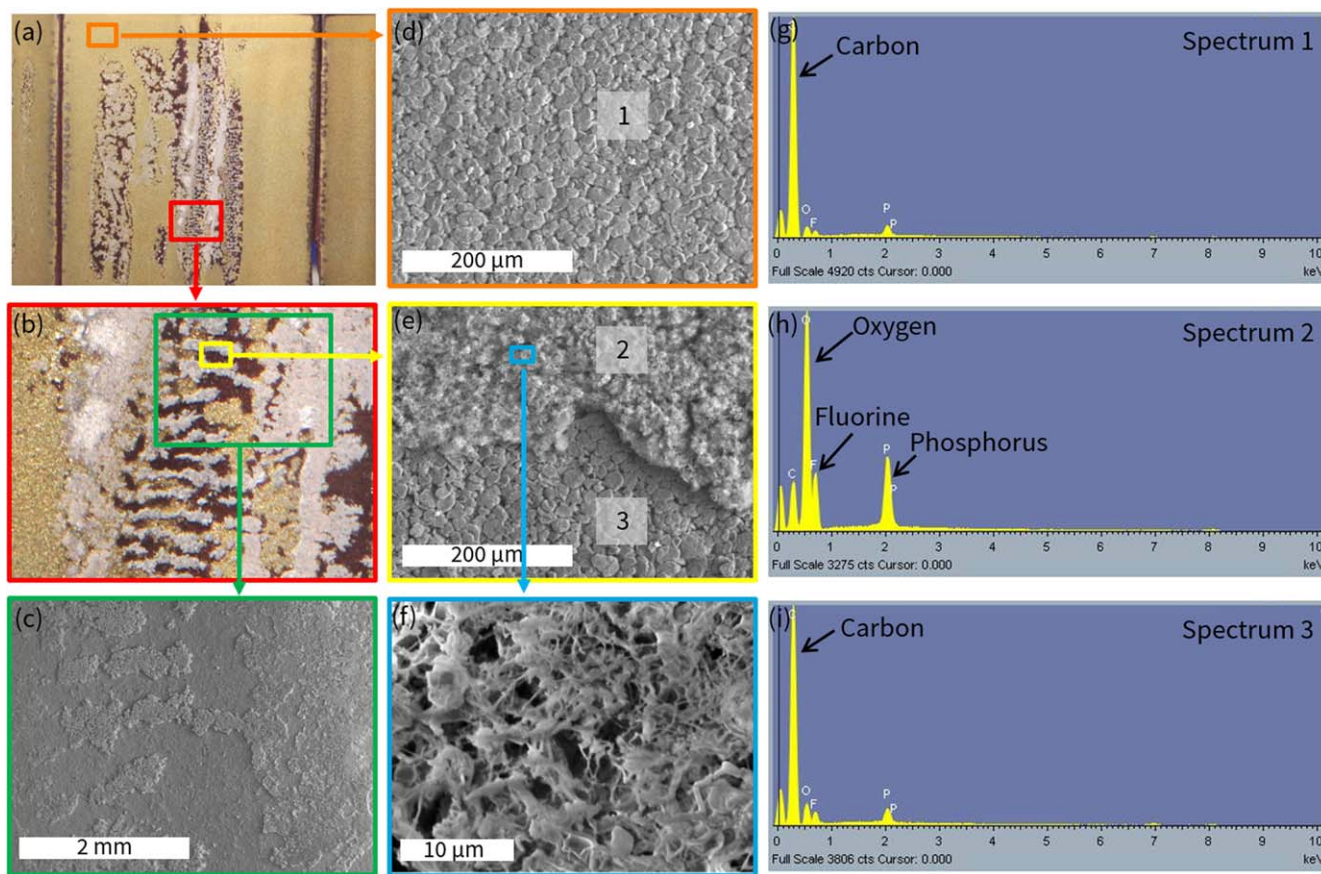


Figure 8. SEM and EDS analysis of the discolored negative electrode from the cell cycled 500 times at 45 °C: (a) teardown photo of one discolored electrode panel, (b) zoomed-in photo (red box region), (c) SEM image of the green box region, (d) SEM image of the clean golden region (orange box region), (e) SEM image of the red- and dark-colored region with silver/gray deposits (yellow box region), (f) high resolution SEM image of the silver/gray deposits (blue box region), (g) EDS spectrum of the golden region, (h) EDS spectrum of the silver/gray region after air exposure, and (i) EDS spectrum of the red- and dark-colored region.

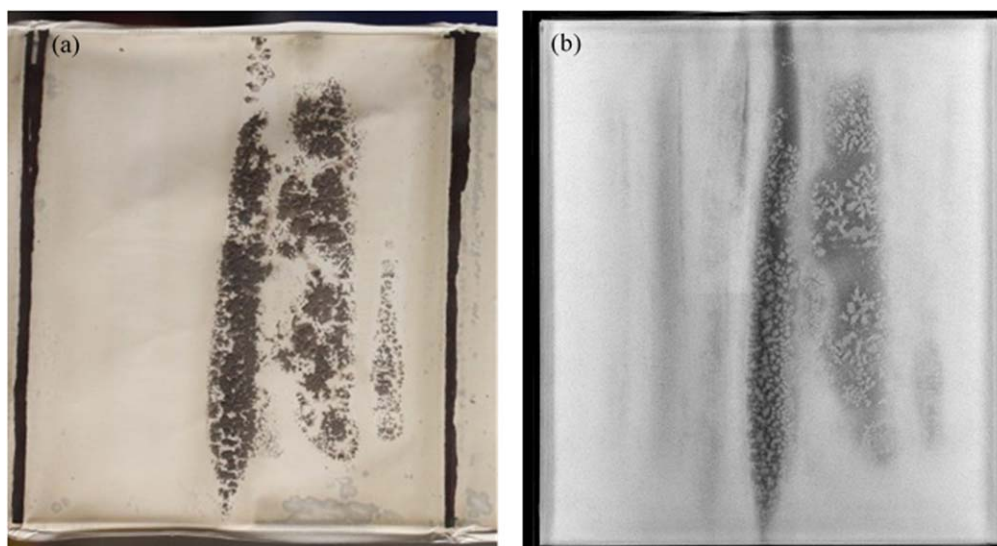


Figure 9. (a) A photograph of a separator facing the negative electrode from a cell cycled at 45 °C. (b) Corresponding view/region in CT data.

Figure 11 shows the self-heating rate as a function of temperature for an uncycled cell and the three Cycle 500 cells from different temperatures. Self-heating increased exponentially with the temperature above the onset ($>0.02\text{ }^{\circ}\text{C min}^{-1}$) for all cells. All cells also exhibited sudden drop (gray oval) of self-heating at 129 °C–144 °C; this is attributed to the actuation of the cell vent and electrolyte

evaporation. The three cycled cells exhibited higher self-heating rates and lower onset temperatures (refer to Table II) than the uncycled cell, indicating they are less thermally stable. The thermal stability of the cells typically decreases with cycling because the temperature at which the cell could self-heat and sustain thermal runaway becomes lower. The cells cycled 500 times at 0 °C and 23 °

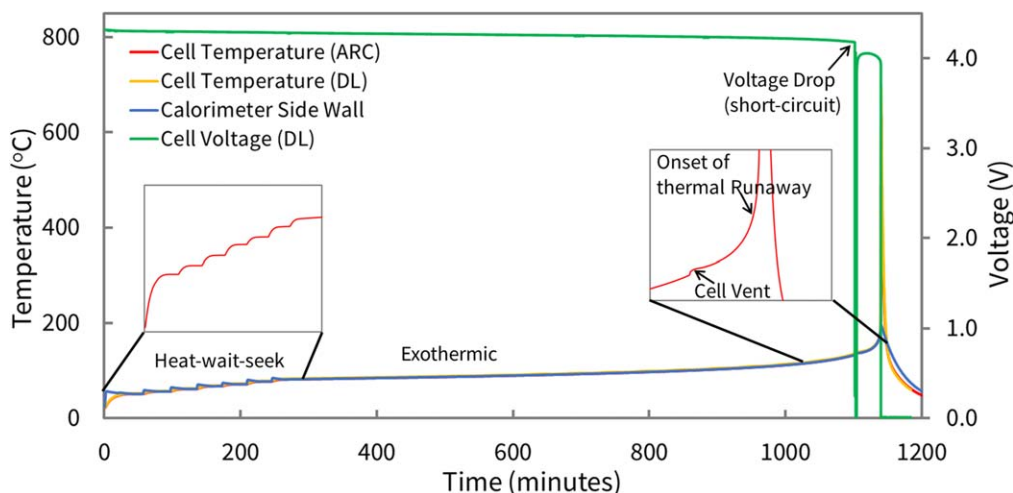


Figure 10. Cell temperature and voltage as a function of time during a typical ARC testing: after heat-wait-seek mode, the ARC enters exotherm mode (self-heating of $>0.02\text{ }^{\circ}\text{C min}^{-1}$) until thermal runaway occurs.

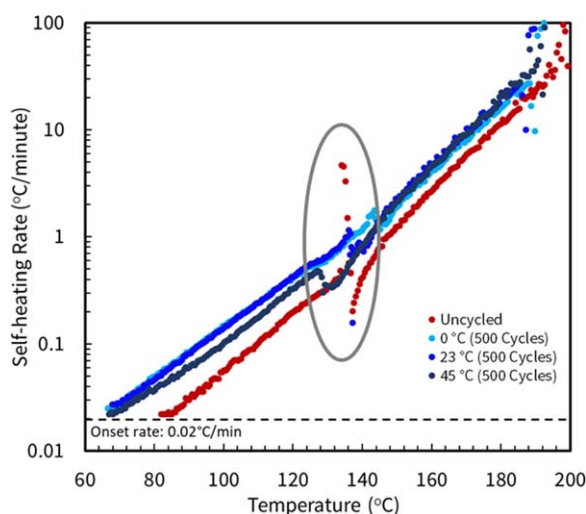


Figure 11. Cell self-heating rate as a function of temperature for the uncycled cell and the three cells cycled 500 times under different temperatures.

C showed similar self-heating rates, while the cell cycled at $45\text{ }^{\circ}\text{C}$ showed lower self-heating rates at lower temperatures (e.g. $<140\text{ }^{\circ}\text{C}$). Although teardown of the Cycle 500 cell at $45\text{ }^{\circ}\text{C}$ exhibited large amounts of electrolyte degradation and/or lithium plating, this did not appear to pose lower thermal stability compared to cells cycled at lower temperatures (e.g. $0\text{ }^{\circ}\text{C}$ and $23\text{ }^{\circ}\text{C}$). A possible reason is that the cell cycled at $45\text{ }^{\circ}\text{C}$ presented more loss of cyclable lithium from electrolyte dry-out and SEI growth on the anode surface.¹⁶ In addition, the $45\text{ }^{\circ}\text{C}$ cell presented regions of lower lithiation (lower SOC), which is known to increase the onset temperature,²⁰ thus acting against lithium plating, which has been shown to decrease the onset temperature. This result is consistent with some studies on 18650 cells. For 18650 cells cycled at $45\text{ }^{\circ}\text{C}$, Börner et al. reported the onset temperature was shifted to higher temperatures,²⁴ while Waldmann et al. reported no significant changes of the onset temperature comparing to the uncycled cells.¹⁶ In both cases, the thermal stability properties are not compromised by the involved aging mechanism (e.g. electrolyte dry-out and SEI growth) at $45\text{ }^{\circ}\text{C}$.

Figure 12 shows the self-heating rate as a function of temperature for cells with different cycles at (a) $0\text{ }^{\circ}\text{C}$, (b) $20\text{ }^{\circ}\text{C}$, and (c) $45\text{ }^{\circ}\text{C}$. Again, all cells exhibited sudden drop (gray ovals) in self-heating at $127\text{ }^{\circ}\text{C}$ – $144\text{ }^{\circ}\text{C}$ due to actuation of the cell vent and electrolyte

evaporation. For cells cycled at $0\text{ }^{\circ}\text{C}$ [Fig. 12a], onset temperature decreased and self-heating rates increased with cycle count, suggesting the thermal stability become worse with cycling at low temperatures. Waldmann et al. reported the main aging mechanism of lithium plating on graphite anodes after cycling at $0\text{ }^{\circ}\text{C}$ leads to significantly lower onset temperatures ($<40\text{ }^{\circ}\text{C}$) compared to the uncycled cell ($>80\text{ }^{\circ}\text{C}$).¹⁶ However, the lithium plating observed in Waldmann et al.'s work was far more severe than our observation [Fig. 7b]. Therefore, the onset temperatures for cycled cells at $0\text{ }^{\circ}\text{C}$ in our work were $67\text{ }^{\circ}\text{C}$ – $72\text{ }^{\circ}\text{C}$, only $10\text{ }^{\circ}\text{C}$ – $15\text{ }^{\circ}\text{C}$ lower for the cycled cells compared to the uncycled cell (i.e. $82\text{ }^{\circ}\text{C}$) and within the cell specifications.

For the cells cycled at $23\text{ }^{\circ}\text{C}$ [Fig. 12b], although the onset temperature decreased and self-heating rates increased after 200 cycles compared to the uncycled cell, no notable changes were observed in self-heating rates between 200 cycles and 500 cycles. For the cells cycled at $45\text{ }^{\circ}\text{C}$ [Fig. 12c], the Cycle 200 cell showed decreased onset temperature and increased self-heating rates compared to the uncycled cell. At temperature of $<100\text{ }^{\circ}\text{C}$, onset temperature decreased and self-heating rates increased with cycling counts for the cells cycled at $45\text{ }^{\circ}\text{C}$, but no notable changes were observed in self-heating rates at temperature of $>100\text{ }^{\circ}\text{C}$ between 200 cycles and 500 cycles.

From the summarized ARC test results (Table II), the Cycle 200 cells exhibited onset temperature of $72\text{ }^{\circ}\text{C}$ – $78\text{ }^{\circ}\text{C}$ and the Cycle 500 cells exhibited onset temperature of $67\text{ }^{\circ}\text{C}$ – $68\text{ }^{\circ}\text{C}$. The onset temperature consistently decreased with cycle count, indicating that the temperature required for the cell to potentially sustain a thermal runaway is lower. Similarly, slightly lower runaway temperatures were observed for cycled cells compared to the uncycled cell. The maximum recorded surface temperatures for the Cycle 500 cells was significantly lower than the uncycled and Cycle 200 cells, which could be due to the lower cell capacity (loss of cyclable lithium) after cycling. This is especially evident in the $45\text{ }^{\circ}\text{C}$ /Cycle 500 cell, which had the lowest peak temperature and was the only cell to present lower-lithiation regions (lower capacity). Waldmann et al. also reported that the T_{max} is correlated to the charged capacity and not to the aging mechanism for 18650 cells.¹⁶

The time from $82\text{ }^{\circ}\text{C}$ (the highest onset temperature) to thermal run-away was much less for the cycled cells than for the uncycled cell. This indicates the cycled cells are less thermally stable compared to the uncycled cell. This is consistent with the self-heating rate being higher for cycled cells at all temperatures (Fig. 11).

Table II. Summary of ARC Test Results.

Cell ID	Onset Temp (°C)	Suspected Can Breach/ Venting (°C)	Heating Rate >1 °C min ⁻¹	Voltage Drop Temp (°C)	Runaway Temp (°C)	Max. Surface Temp Recorded (°C)	Time from 82 °C ^{a)} to run- away (min)
Uncycled	82	135	147	134	185	732	859
200 Cycle 0 °C	72	141	147	138	181	706	477
200 Cycle 23 °C	73	136	132	133	178	740	369
200 Cycle 45 °C	78	127	124	124	175	740	516
500 Cycle 0 °C	67	144	138	142	179	605	340
500 Cycle 23 °C	68	137	136	136	177	666	347
500 Cycle 45 °C	67	129	142	176	178	589	466

a) The highest onset temperature among all ARC tests.

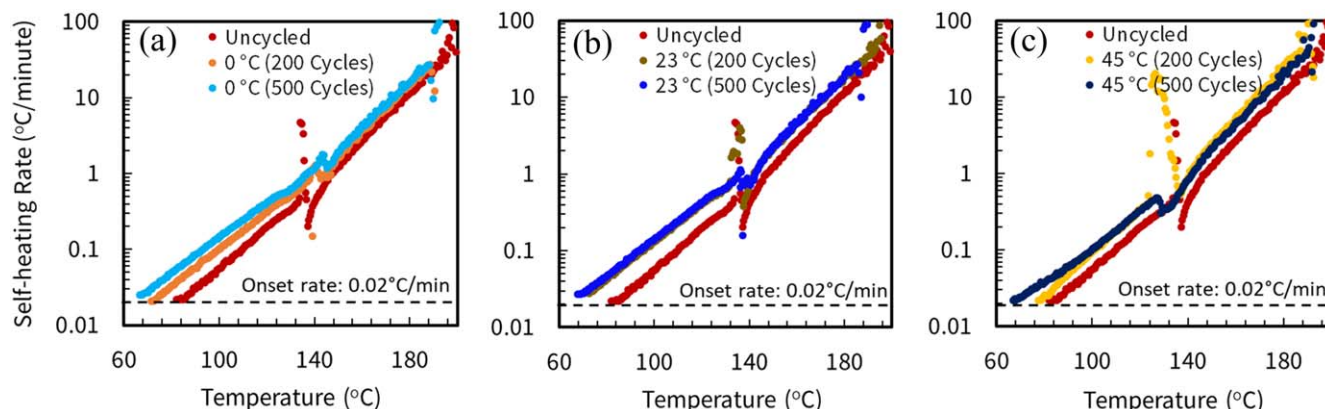


Figure 12. The self-heating rate as a function of temperature for cells with different cycle counts at (a) 0 °C, (b) 23 °C, and (c) 45 °C.

Conclusions

In this work, a systematic investigation into the effects of cycling on the internal cell structure (gapping), cell capacity, impedance, and the thermal properties of prismatic lithium-ion cells was conducted. The effects of electrode gapping and cell cycling (including cycle count and temperature) were characterized via electrochemical, non-destructive CT analysis, destructive teardown, and ARC.

Cycling prismatic cells up to 500 cycles at three different temperatures (i.e. 0 °C, 23 °C, and 45 °C) exhibited different gap evolution and degradation mechanisms in each cell group. Cells cycled at 0 °C showed small silver/gray deposits visually consistent with lithium plating at the gapping regions, though the gaps were not significantly enlarged by cycling. By comparison, cells cycled at 45 °C did show gaps enlarging as a function of cycling and exhibited large amounts of degradation products visually consistent with electrolyte degradation and/or lithium plating surrounding the gapping regions. EIS characterization suggests the degradation product at 45 °C is due to electrolyte dry-out and SEI growth. The cell cycled at 23 °C exhibited minor gap evolution and the least amount of electrolyte degradation or lithium plating after cycling.

All cycled cells exhibited higher self-heating rates and lower onset temperatures than the uncycled cell, suggesting these cells became less thermally stable after cycling. Although Cycle 500 cell at 45 °C exhibited large amounts of degradation product build up at the vicinity of the gapping region, this did not appear to pose higher safety risk compared to cells cycled at lower temperatures (e.g. 0 °C and 23 °C). These results indicate that the safety properties are not compromised by the involved aging mechanism (e.g. electrolyte dry-out and SEI growth) at 45 °C and may be offset by the incomplete charging due to increased gapping in this cell. The cell cycled at 0 °C exhibited onset temperature decreased and self-heating rate increased with cycling counts, suggesting the thermal stability becomes worse when lithium plating is the main degradation mechanism for low temperature cycling. The decreased safety properties regarding lithium plating in this paper are most likely due to the exothermic reactions of lithium metal with electrolyte and are not related to the localized shorting induced by lithium dendrite formation, since no evidence of cell shorting and accelerated voltage decay was observed from cell cycling.

The comprehensive analysis of prismatic cells presented in this work shows that safety behavior is not simply correlated to cell internal structure (e.g. gapping), or the amount of degradation products after cycling; the aging mechanism at different temperatures also plays an important role. Understanding the thermal stability performance of prismatic lithium-ion cells during their lifecycle is necessary for risk mitigation in numerous applications. The results discussed in this work apply primarily to lithium-ion prismatic cells, a cell format chosen for its use in both consumer electronics and electric vehicles and may not apply to other cell formats with no intrinsic gapping. Further work will focus on the

enthalpy released during the runaway process to evaluate the probability of the thermal runaway propagation to adjacent batteries in real-world applications.

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