Chapter 4
Lithium-Ion Battery Failures

The fact that batteries can fail on rare occasions in an uncontrolled manner has brought an increased public awareness for battery safety, in particular as a result of some very large product recalls of portable notebook computer and cell phone batteries.[1]

Both energetic and non-energetic failures of lithium-ion cells and batteries can occur for a number of reasons including: poor cell design (electrochemical or mechanical), cell manufacturing flaws, external abuse of cells (thermal, mechanical, or electrical), poor battery pack design or manufacture, poor protection electronics design or manufacture, and poor charger or system design or manufacture. Thus, lithium-ion battery reliability and safety is generally considered a function of the entirety of the cell, pack, system design, and manufacture (see footnote 8, 9 in Chap. 3).

Performance standards listed in Chap. 3: Summary of Applicable Codes and Standards are designed to test cell and battery pack designs. At the time of this

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[1] For example, see: US Consumer Products Safety Commission, Alert #10-752, "Asurion Recalls Counterfeit BlackBerry®-Branded Batteries Due to Burn and Fire Hazards," August 10, 2010.

US Consumer Products Safety Commission, Release #10-240, "HP Expands Recall of Notebook Computer Batteries Due to Fire Hazard," May 21, 2010.

US Consumer Products Safety Commission, Release #10-169, "Mobile Power Packs Recalled By Tumi Due to Fire Hazard," March 17, 2010.

US Consumer Products Safety Commission, Release #09-045, "Lithium-Ion Batteries Used with Bicycle Lights Recalled By DiNotte Lighting Due to Burn Hazard," November 18, 2008.

Darlin D, "Dell Recalls Batteries Because of Fire Threat," The New York Times, August 14, 2006.

Kelley R, "Apple recalls 1.8 million laptop batteries," CNNMoney.com, August 24, 2006: 4:38 PM EDT.

US Consumer Products Safety Commission, Release #06-231, "Dell Announces Recall of Notebook Computer Batteries Due to Fire Hazard," August 15, 2006.

US Consumer Products Safety Commission, Release #06-245, "Apple Announces Recall of Batteries Used in Previous iBook and PowerBook Computers Due to Fire Hazard," August 24, 2006.

writing, failures that occur in the field are seldom related to cell design, but are rather predominantly the result of manufacturing defects or subtle abuse scenarios that result in the development of latent cell internal faults. This can be considered one of the successes of the existing standards, and thus there is no strong link between failure modes actually observed in the field to the performance standards in Chap. 3: Summary of Applicable Codes and Standards. Ideally, an understanding of likely field failure mechanisms should provide direction for additional performance standards. However, at present there is no obvious performance standard that could be implemented readily to prevent field failures due to subtle manufacturing defects or abuse. The IEEE 1625 and 1725 Standards include requirements for the application of manufacturing best practices to attempt to reduce the rate of manufacturing defects. The Battery Association of Japan (BAJ) induced short circuit test[2] has been adopted by Japan but remains controversial and not applicable to large format cells because of the safety considerations associated with conducting the test (a fully charged cell is opened, a contaminant is placed within the cell electrodes, and the electrodes are then compressed to initiate a short circuit). UL is in the process of developing an Indentation Inducing Internal Short Circuit test for simulating internal faults. This test is being designed to indent a cell in such a way as to puncture separator within the cell (and induce an internal short) without puncturing the cell casing. This test method has been demonstrated on 18650 cells, but has not yet been demonstrated with prismatic or soft-pouch cells. Other organizations such as NASA and NREL have also been experimenting with internal short inducing test protocols.

In this chapter we discuss various known lithium-ion failure modes, and when during a cell or battery pack's life cycle they are most likely to occur (storage, transport prior to usage, early usage, after extended usage, during transport for disposal), as well as under what usage conditions they are most likely to occur (charging, discharging, storage, constant docking, SOC, and temperature).

Cell and Battery Failure Modes

Non-Energetic Failures

Lithium-ion batteries can fail in both non-energetic and energetic modes. Typical non-energetic failure modes (usually considered benign failures) include loss of capacity, internal impedance increase (loss of rate capability), activation of a permanent disabling mechanism such as a CID, shutdown separator, fuse, or battery pack permanent disable, electrolyte leakage with subsequent cell dry-out, and cell swelling.

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[2] This test is contained in JIS C 8714:2007, "Safety tests for portable lithium ion secondary cells and batteries for use in portable electronic applications."

Some of these non-energetic failure modes are commonly associated with cell-aging[3] mechanisms. The ideal lithium-ion battery failure mode is a slow capacity fade and internal impedance increase caused by normal aging of the cells within the battery. If a cell exhibits this failure mode, capacity will decrease and impedance will increase until the point the battery can no longer satisfy the power requirements of the device and must be replaced. The bulk of lithium-ion batteries in the field experience this type of failure.

Other non-energetic failure modes are related to root causes that can result in either energetic or non-energetic failures, depending upon the specific conditions under which failure occurs. Whether a specific root cause (initiating fault) will result in an energetic (i.e., cell venting, ignition of cell vent gases, or rapid disassembly of the cell) or non-energetic failure depends upon whether the initiating fault can cause sufficient heating of the cell to lead to a self-sustaining exothermic reaction within the cell. For certain failure root causes, rates of non-energetic failures will be linked to rates of energetic failures (e.g., a manufacturing defect may result in a high rate of benign warranty return failures, and occasionally, a thermal runaway failure event).

Electrolyte leakage can occur as the result of mechanical damage to cells or it can result due to internal corrosion of cells. Leakage from polymer cells is more common than leakage from hard case cells. Polymer cell seals are more delicate and failures of cell pouch protective coatings can result in pouch corrosion. In small cells, there is very little free electrolyte: it is primarily absorbed by active material. Puncture of a small cell is unlikely to result in escape of more than a few droplets of electrolyte. However, in some large format cell designs, there is an appreciable amount of free, liquid electrolyte within the cell case. For these cells, a puncture could cause a spill of hazardous material. The size of the spill would be governed by the volume of electrolyte contained in a cell, the size of the puncture, and the evaporation rate of the electrolyte solvent. Electrolyte leakage poses two potential safety hazards: human contact with electrolyte and electrolyte residue, and short-circuiting of adjacent electronic systems. An increase of internal pressure within prismatic or pouch cells will cause swelling. Swelling can be caused by a variety of non-ideal chemical reactions including: overcharge, elevated temperature aging, and moisture intrusion. Cell swelling can ameliorate some failure modes making it less likely that a cell enters thermal runaway, but it can also result in enhanced cell leakage rates. Swelling commonly results in damage to battery pack enclosures.

Cell and battery pack designs often include mechanisms to permanently disable cells or batteries if their performance degrades significantly; thus, forcing a graceful failure rather than a thermal runaway reaction. For example, a number of environmental and cell manufacturing factors can result in abnormal aging of cells that result in elevated internal impedance and early capacity fade (some of these

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[3] The chemical reactions that occur in lithium-ion cells are not all irreversible: nonreversible side reactions typically occur as slow rates resulting in cell aging.

will be discussed below). At the cell level, CIDs or thermal fuses may be activated by elevated temperatures or elevated pressures associated with increased internal impedance and permanently disable the cell. Abnormal aging of a prismatic or polymer cell may cause that cell to swell, separating the electrodes such that continued operation becomes impossible.

In multi-cell applications where cells are connected in series, individual series element voltages are measured, and charge and discharge is terminated based on the voltage of the weakest (lowest capacity, highest impedance) series element. Thus, a single abnormally aged series element (e.g., a block of cells that is exposed to higher temperatures than neighboring cells), will cause reduced capacity of the entire pack. Such battery pack behavior may force retirement of the battery pack. Alternatively, if the pack electronics design includes block imbalance detection,[4] large capacity imbalances can drive permanent disabling of the battery pack.

Energetic Failures: Thermal Runaway

Cell thermal runaway refers to rapid self-heating of a cell derived from the exothermic chemical reaction of the highly oxidizing positive electrode and the highly reducing negative electrode; it can occur with batteries of almost any chemistry. In a thermal runaway reaction, a cell rapidly releases its stored energy. The more energy a cell has stored, the more energetic a thermal runaway reaction will be. One of the reasons lithium-ion cell thermal runaway reactions can be very energetic is these cells have very high-energy densities compared to other cell chemistries. The other reason that lithium-ion cell thermal runaway reactions can be very energetic is because these cells contain flammable electrolyte, and thus, not only do they store electrical energy in the form of chemical potential energy, they store appreciable chemical energy (especially compared to cells with water-based electrolytes) in the form of combustible materials.

The likelihood of initiating cell thermal runaway is analogous to the likelihood of ignition of many typical combustion reactions: for initiation of cell thermal runaway (or ignition of fuel), the rate of heat generation must exceed the rate of heat loss. As discussed above, self-heating of lithium-ion graphitic anodes in the presence of electrolyte initiates at temperatures in the 70–90°C (158–194°F) range. Thus, if a cell is brought to this initiating temperature in an adiabatic environment, it will eventually self-heat to the point thermal runaway initiates. For a typical 100% SOC 18650 cell brought to its self-heating temperature, thermal runaway will occur after approximately two days if the cell is well-insulated. Should initial temperature be higher, time to thermal runaway will be shorter. For example, if a typical lithium-ion cell is placed into an oven at more than 150°C (300°F), such

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[4] For an example of battery pack protection electronics with imbalance detection, see http://focus.ti.com/docs/prod/folders/print/bq29330.html.

that separator melting occurs, additional heating due to shorting between electrodes will occur and cell thermal runaway will initiate within minutes. However, if heat is allowed to escape, time to thermal runaway may be longer, or the cell may never achieve thermal runaway. UN and UL consumer electronics standards (discussed in Chap. 3: Summary of Applicable Codes and Standards) effectively govern the minimum thermal stability of cells: they require that fully charged cells withstand extended storage at 70 or 75°C (158 or 167°F; 4 h or more), and short exposure (10 min) to 130°C (266°F) conditions. IEEE Standards require storage at 130°C for 1 h.

The severity of a cell thermal runaway event will depend upon a number of factors including the SOC of a cell (how much electrical energy is stored in the form of chemical potential energy), the ambient environmental temperature, the electrochemical design of the cell (cell chemistry), and the mechanical design of the cell (cell size, electrolyte volume, etc.). More details about the effects of these factors will be discussed below. For any given cell, the most severe thermal runaway reaction will be achieved when that cell is at 100% SOC, or is over-charged, because the cell will contain maximum electrical energy. If a typical fully charged (or overcharged), lithium-ion cell undergoes a thermal runaway reaction a number of things occur.

1. *Cell internal temperature increases*. Exponent and others have measured cell case temperatures during thermal runaway reactions. For fully charged cells, these temperatures can reach in excess of 600°C (1,110°F); case temperatures for lithium-iron phosphate cells are generally lower. The temperature rise is driven by reactions of the electrodes with electrolyte and release of stored energy. Some cathode materials will decompose and may change their crystalline structure. This structural change may result in the release of small quantities of oxygen that can participate in reactions internal to the cell (e.g., oxidation of the aluminum current collector). This fact has led to a misconception that lithium-ion cells burn vigorously because they "produce their own oxygen." This idea is incorrect. No significant amount of oxygen is found in cell vent gases.[5] Any internal production of oxygen will affect cell internal reactivity (see footnote 11 in Chap. 1), cell internal temperature, and cell case temperature, but plays no measurable role in the flammability of vent gases. Internal temperature increase results in separator melting and decomposition, and usually, melting of the aluminum current collector, which occurs at 660°C (1,220°F). Liquid aluminum may alloy with any exposed copper within the cell. Some copper and aluminum alloys have melting points as low as 548°C (1,018°F), so damage to the internal copper current collectors is likely to occur.

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[5] Analysis of cell headspace gases can reveal the presence of argon, nitrogen, and oxygen consistent with cell construction conditions. In one instance (testing of a prototype cell), trace quantities of oxygen and hydrogen were measured in cell vent gases, but spark ignition testing of those gases did not result in ignition. See Roth EP, Crafts CC, Doughty DH, McBreen J, "Thermal Abuse Performance of 18650 Li-Ion Cells," Sandia Report SAND2004-0584, March 2004.
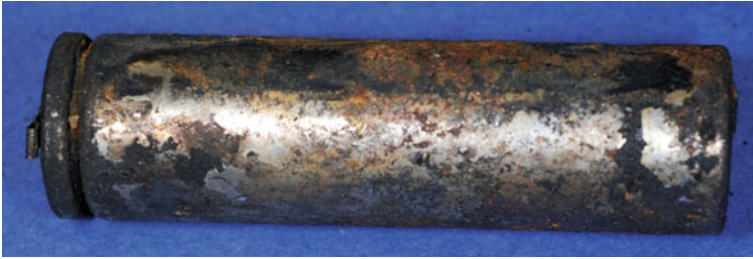
**Fig. 4.1** An 18650 cell that has undergone thermal runaway

**Fig. 4.2** An 18650 cell after thermal runaway— resolidified beads of melted aluminum are visible
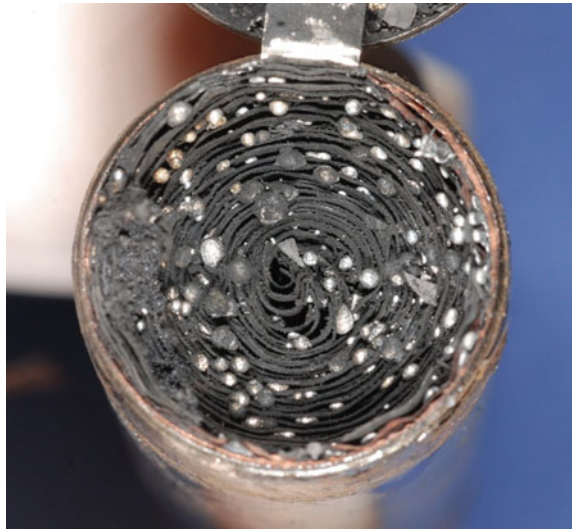
Temperatures produced by cell thermal runaway reactions are considered sufficient to cause hot surface ignition of flammable mixtures, but do not reach levels that will cause the melting of pure copper (1,080°C/1,976°F), nickel, or steel.[6] Figures 4.1, 4.2, 4.3, 4.4 show an 18650 cell that has undergone thermal runaway: aluminum within the cell melted, the cell separator consumed. What remains is the cell case (steel), the copper current collector from the anode, and a black friable material composed primarily of cathode material.

2. *Cell internal pressure increases*. This occurs because heated electrolyte will both vaporize and decompose, and some cathode materials can also decompose, releasing gas. In a pouch or prismatic cell, this will result in cell swelling. For a typical cylindrical design, appreciable swelling will not occur. However, if a

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[6] Sometimes evidence of very small points of pure copper, nickel, or steel melting are found within a cell. These points are the result of internal electric arcing/shorting and are not indicative of overall cell thermal runaway temperatures.
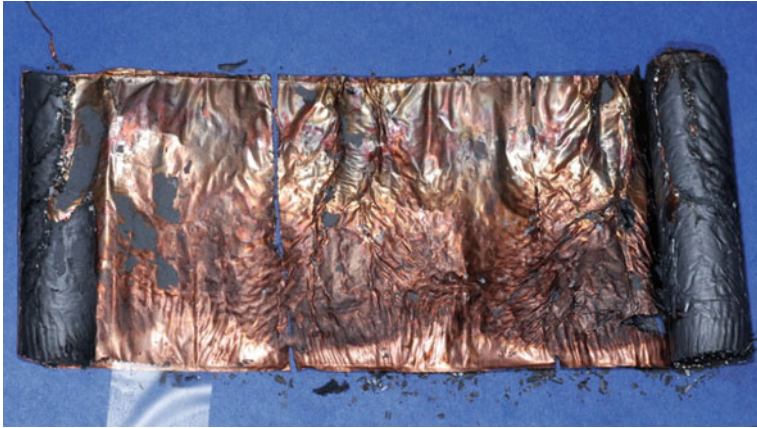
Fig. 4.3 Unrolling windings of an 18650 cell that underwent thermal runaway—note the copper current collector remains largely intact
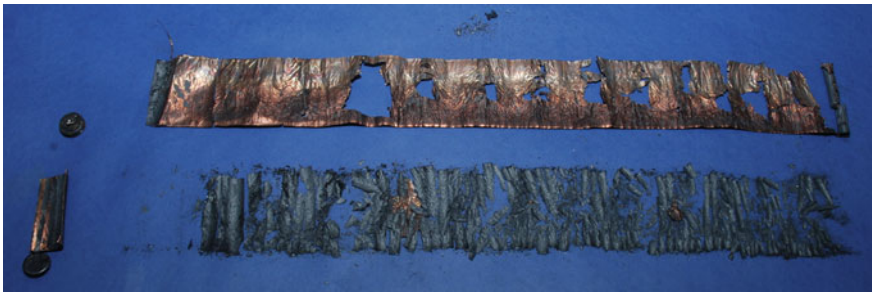
Fig. 4.4 Internal contents of an 18650 cell that underwent thermal runaway: copper current collector (*top*) and remains of active materials (*bottom*)

cylindrical cell has been sufficiently heated (usually from an external source), the case walls may soften sufficiently to allow bulging of the cell base.

3. *Cell undergoes venting.* In a soft-pack polymer cell, the heat seals fail at fairly low temperatures, resulting in low-pressure venting. There may be an audible pop (sound) when the pouch is breached. Prismatic cell cases may have a vent port installed (large format cells) or may incorporate score marks in them to provide a weak point for case venting. In some cases, designers may have determined that the case weld points will break at appropriate cell internal pressures (e.g., small prismatic cells). Venting of small prismatic cells is usually accompanied by a loud pop. In small single cell applications (e.g., cell phones) venting usually causes the cell to eject from the device. A typical consumer description of cell thermal runaway from a cell phone is the user hears a loud sound, and upon investigation finds, the cell became detached from the device. This often creates a char mark on the surface below the cell.

Cylindrical cells have venting mechanisms installed in their cap assemblies that activate when internal pressures are high (commonly in excess of 200 psi). In most small commercial cells, CIDs connect to vent assemblies so venting is a two-stage process. First, the CID activates, creating a small hole for venting and a soft pop or click sound. Shortly thereafter, the full vent opens with a loud pop, followed by a rushing sound of venting gas. The vent gases usually appear as dark smoke. Sometimes bright sparks are observed in the vent gases.[7] Some observers have assumed these sparks are "burning lithium." However, this is highly unlikely as even under cell charging conditions, only very small quantities of lithium can plate onto electrodes. Rather, any observed bright sparks are most likely droplets of molten aluminum being ejected from the cell.

4. *Cell vent gases may ignite.* Depending upon the environment around the cell, the cell vent gases may ignite. The gases are not "self-igniting."(see footnote 27 in Chap. 1 and footnote 7 in this chapter) There must be sufficient oxygen in the surrounding environment to sustain combustion of hydrocarbons and there must be a competent ignition source to ignite the vent gases. A hot cell case could result in ignition of vent gases, as could hot metal sparks ejected with the vent gases. Lithium iron phosphate cells (cells with a $LiFePO_4$ cathode) are often described as "safer" than typical lithium cobalt oxide cells, because typical case temperatures of these cells during thermal runaway are unlikely to cause hot surface ignition of the vent gases. However, if other competent ignition sources are present, vent gases from iron phosphate cells will ignite.[8] Venting of isolated small cells (cell phone cells and smaller) seldom results in flame ignition. This is likely due to the limited volumes of vent gases released from these cells—that is, the gases become diluted before ignition can occur. In comparison, ignition of vent gases from 18650 and larger cells is fairly common: these cells contain more electrolyte (more fuel), and are usually used in multi-cell battery packs. If the flow of vent gases is "restricted" due to the configuration of a vent port (typical in hard case cells), flames emanating from the cell will be highly directional (e.g., flames from 18650 cells are often described as "torch-like").

5. *Cell contents may be ejected.* With hard case cells, internal pressure will develop prior to venting. Depending upon the mechanical design of the cell, release of pressure (due to a vent activating), may result in the ejection of the cell windings. This phenomenon is very common with cylindrical cells, particularly those without stiff center tubes (Figs. 4.5, 4.6, 4.7). Cylindrical cells have wound designs with an open center, similar to a roll of wrapping paper. When heating occurs, electrodes expand and collapse into the core of the roll; thus, creating an

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[7] Webster H, "Flammability Assessment of Bulk-Packed, Rechargeable Lithium-Ion Cells in Transport Category Aircraft," DOT/FAA/AR-06/38, September 2006, http://www.fire.tc.faa.gov/pdf/06-38.pdf.

[8] Roth EP, "Abuse Tolerance Improvement," DOE Vehicle Technologies Peer Review, Gaithersburg, MD, February 26, 2008.
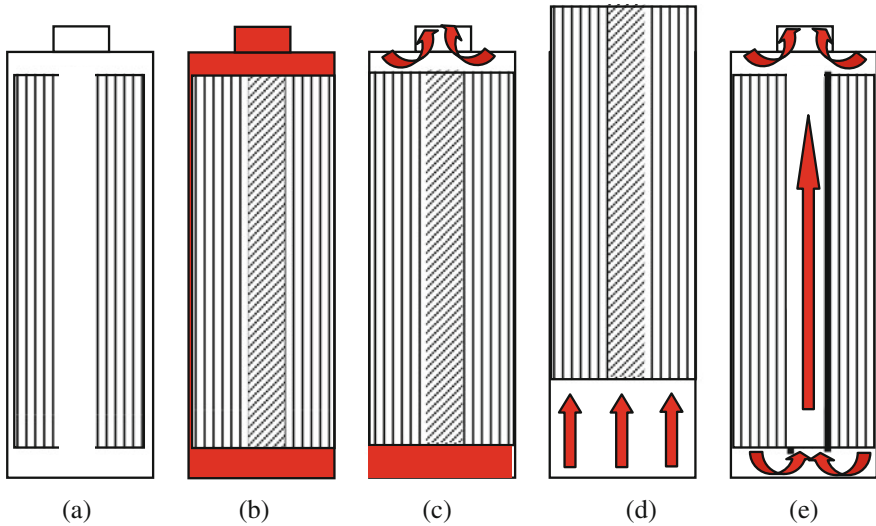
Fig. 4.5 Ejection of windings from a cylindrical cell subject to a thermal runaway reaction (*left* to *right*): **a** cross section of a cell without a stiff center tube; **b** during cell thermal runaway windings expand and collapse into the central core; **c** cell venting allows relief of pressure at cell cap but not at cell base; and **d** pressure at cell base acts like a piston, ejecting cell windings. In contrast, a stiff center tube **e** will maintain an open cell core and allow pressure equalization, preventing winding ejection
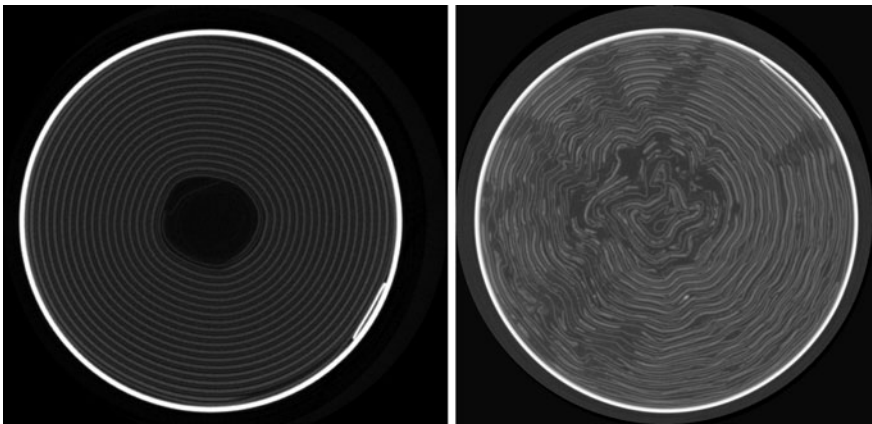
Fig. 4.6 CT scan of a normal 18650 cell showing an open center core (*left*), and a post thermal runaway 18650 cell exhibiting winding collapse into the core region (*right*)

internal obstruction to gas release at the base of the cell. When the cell vents at the cap, the pressure differential between the cell cap area and cell base can result in a piston-like effect that drives the electrodes out of the cell. Electrodes ejected in this manner (or even full cells if not well constrained by battery packs)

Fig. 4.7 CT scan cross
section of an 18650 cell that
underwent thermal runaway.
Although the electrodes were
not ejected, the base to cap
pressure differential caused
shifting of the electrodes
toward the cap

can travel significant distances (many meters), spreading heated material, and possibly flames, far from the original battery pack.

Circa 2004–2005, US notebook computer manufactures worked with cell manufacturers to reduce the likelihood of electrode ejection in the case of cell thermal runaway. Since that time the IEEE Standards (see footnote 8, 9 in Chap. 3) have been revised and they now require cell design elements to prevent ejection of cell electrodes if thermal runaway occurs. In response to these requirements cell manufacturers began to include a stiff center tube in cylindrical cells, usually a rolled metal pin to maintain an open cell core and allow equalization of pressures within the cell in the event of a cell thermal runaway. The use of center tubes has significantly reduced the likelihood of electrode ejection on thermal runaway with cylindrical cells. However, center tubes are not a required design element for cylindrical cells and are not present in all cell designs. In addition, center tubes will not always prevent electrode ejection.

6. *Cell thermal runaway may propagate to adjacent cells.* If one cell in a pack undergoes a thermal runaway reaction, it is likely to cause thermal runaway in adjacent cells by way of various heat transfer mechanisms: direct case-to-case contact, impingement of hot vent gases, or impingement of flaming vent gases. Recent FAA tests provide a demonstration of thermal runaway propagation through bulk-packaged 18650 cells.[9] Multi-cell pack design can affect the likelihood of thermal runaway propagation by adjusting cell spacing and orientation to minimize heat transfer between adjacent cells,[10] to direct vent gases away from adjacent cells, or to increase cell cooling.

Root Causes of Energetic Cell and Battery Failures

There are a number of ways to exceed the thermal stability limits of a lithium-ion cell and cause an energetic failure. Energetic lithium-ion battery failures may be induced by external forces such as exposure to fire or severe mechanical damage, or they may be the result of problems involving charge, discharge, and/or battery protection circuitry design and implementation, or they may be caused by internal cell faults that result from rare and/or subtle manufacturing problems. Generally, the root causes of energetic cell and battery failures can be classified into:

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[9] Webster H, "Fire Protection for the Shipment of Lithium Batteries in Aircraft Cargo Compartments," DOT/FAA/AR-10/31, November 2010, http://www.fire.tc.faa.gov/pdf/10-31.pdf.

[10] See for example, Spotnitz RM, Weaver J, Yeduvaka G, Doughty DH, Roth EP, "Simulation of abuse tolerance of lithium-ion battery packs," Journal of Power Sources, 163 (2007), pp. 1080–1086.

- Thermal abuse;
- Mechanical abuse;
- Electrical abuse;
- Poor cell electrochemical design; and
- Internal cell faults associated with cell manufacturing defects.

Thermal Abuse

The most direct way to exceed the thermal stability limits of a lithium-ion cell is to subject it to external heating. The external heat could be applied to the bulk of the cell, often simulated by "hot box" testing, or it could be localized to one portion of the cell, causing local reactions that propagate to the entire cell. At Exponent, we commonly use small heaters applied to the exterior of cells to initiate thermal runaway reactions and rely on bulk heat transfer to cause propagation of thermal runaway to adjacent cells in a battery pack.[11]

In Exponent's experience, very few[12] energetic field failures of consumer electronic devices have been attributed to long-term storage of cells at temperatures just above the self-heating point of 70–90°C (158–194°F). Such failures require not only elevated temperature, but an adiabatic (highly insulated) environment, and extended times to reach a self-sustaining thermal runaway condition. Although possible, these sorts of conditions are seldom achieved with consumer electronic devices in the field. They may become more likely for very dense packed large format batteries, where the high density of cells may prevent heat removal from cells at the center of the battery pack and allow long-term self-heating. Failure via this mode may also occur under certain extreme storage scenarios. Some examples might include lithium-ion batteries stored on high racks in non-climate controlled warehouses during summer months, or lithium-ion batteries stored adjacent to heaters.

Acute exposure of a cell to high temperatures (e.g., due to flame attack, exposure to hot combustion gases from a proximate fire, or contact with adjacent cells undergoing thermal runaway reactions) will readily induce thermal runaway in that cell. Typically, if an internal cell fault is sufficient to cause thermal runaway in a single cell of a multi-cell battery pack, heat transfer from the faulting cell will cause thermal runaway in neighboring cells of the battery pack. Thus, the thermal

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[11] Harmon J, Gopalakrishnan P, Mikolajczak C, "US FAA-style flammability assessment of lithium-ion batteries packed with and contained in equipment (UN3481)," US Government Docket ID: PHMSA-2009-00095-0117, PHMSA-2009-00095-0119.1, PHMSA-2009-00095-0119.2, and PHMSA-2009-00095-0120.1, March 2010.

[12] The authors have investigated hundreds of thermal runaway failures from the field and can only ascribe one or two of the investigated failures to this failure mode.

runaway reaction will propagate through a battery pack. For example, an internal cell fault in one cell of a notebook computer battery pack will first result in thermal runaway of the faulting cell, and can subsequently cause thermal runaway reactions to propagate through all the rest of the cells in the pack. Occasionally, if heat transfer is limited between cells (e.g., the cells are well separated) thermal runaway does not propagate.

Propagation of cell thermal runaway has significant implications for fire suppression and fire protection. A fire suppressant or low oxygen environment may extinguish flames from a battery pack, but the thermal runaway reaction will propagate if heat is not sufficiently removed from the adjacent cells. Responders to fires involving lithium-ion battery packs have often described a series of re-ignition events. Typically, responders report they used a fire extinguisher on a battery pack fire, thought they had extinguished the fire, and then observed the fire re-ignite as an additional cell vented.

From a fire protection standpoint, particularly in bulk storage areas, isolation (thermal separation) of lithium-ion batteries from each other, from hot combustion products, and from oxidizers is important in mitigating and preventing fire spread following an initiating incident such a single cell undergoing thermal runaway.

Mechanical Abuse

Mechanical abuse of cells can cause shorting between cell electrodes, leading to localized cell heating that propagates to the entire cell and initiates thermal runaway. The mechanical abuse can be severe and result in immediate failure, or it can be subtle, and create a flaw in the cell that results in an internal cell fault much later (i.e., after the cell has undergone numerous cycles). UN and UL consumer electronics standards govern the minimum tolerance of cells to some forms of severe mechanical abuse: they require fully charged cells (100% SOC) withstand flat plate crushes and more concentrated point crushes perpendicular to their electrode surfaces. Some cell manufacturers will also conduct nail penetration tests and UL is considering adding a blunt nail test to UL 1642. Like crush tests, nail tests are conducted to perpendicularly penetrate electrode surfaces. The UN and UL Standards only address a few mechanical damage modes. For example, they do not address mechanical damage to electrode edges, mechanical damage to internal tab regions, or continued usage of a cell after mechanical damage has occurred.

Mechanical damage (crush or penetration) that occurs at electrode edges is significantly more likely to cause cell thermal runaway than damage perpendicular to electrode surfaces (Fig. 4.8). Exponent demonstrated this susceptibility by conducting crush tests on cells in differing orientations. When crush damage is perpendicular to electrode surfaces, it may deform the electrodes and separator layers, but it may not cause penetration of the separator, and thus, minimal or no internal shorting occurs (certainly, if the separator is penetrated, shorting and thermal runaway can occur). If the cell case is penetrated (e.g., during a nail test),

Fig. 4.8 Crush or
penetration perpendicular to
electrode edges (*red arrows*)
is more likely to cause cell
thermal runaway than crush
or penetration perpendicular
to electrode surfaces (*green
arrows*)
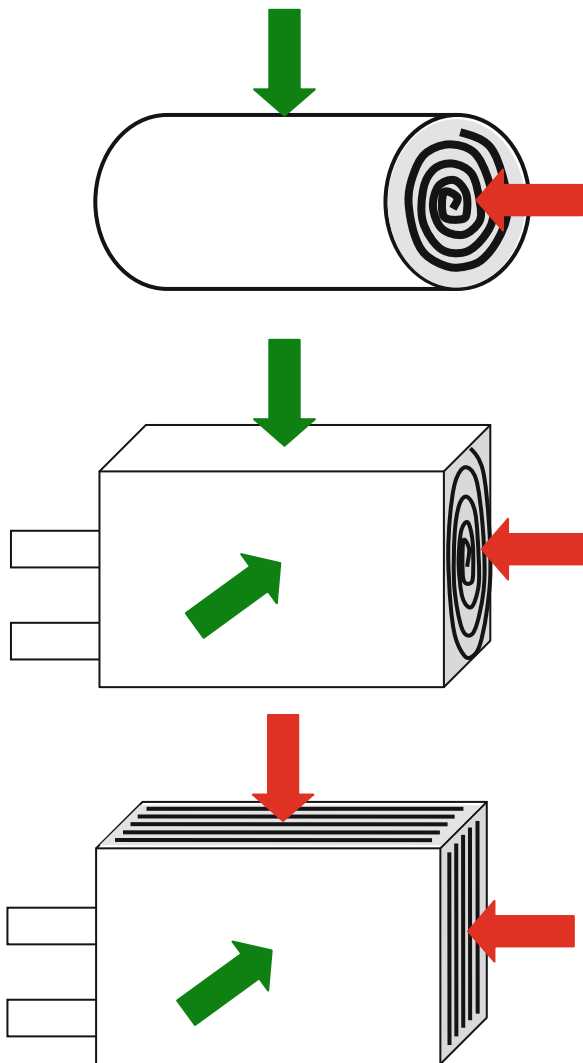
it is likely that low impedance shorting will occur between current collectors
bridged by the penetrating nail, and cell heating may be too low to result in cell
thermal runaway. However, if crush or penetration occurs perpendicular to elec-
trode edges, that deformation is likely to result in high impedance shorting
between electrode layers and initiate cell thermal runaway. Maleki and Howard[13]
have also studied the effect of nail penetration and crush location on inducing

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[13] Maleki H, Howard JN, "Internal short circuit in Li-ion cells," Journal of Power Sources, 191
(2009), pp. 568–574.

immediate cell thermal runaway. They found "pinch" damage at the edge of electrodes in a prismatic cell was more likely to induce immediate thermal runaway than crush damage on the flat face of a cell.

Cell susceptibility to severe mechanical damage is a factor in cell shipping and handling. Damage during handling can occur readily in a number of ways. Packages of cells, battery packs, or equipment containing packs can be subjected to severe shocks (i.e., they can be dropped), crushes, and punctures[14] causing mechanical damage to cells. This susceptibility drives the transport packaging requirements for sturdy containers. It drives the "Lithium and Lithium Ion Battery Industries' Voluntary Air Transportation Communications Program," administered by the Rechargeable Battery Association (PRBA).[15] Under this program, battery shippers mark packages containing lithium-ion cells and battery packs with warnings to quarantine packages that might be "… crushed, punctured or torn open to reveal contents." Similarly, it motivates the IEC 62281 requirement to quarantine damaged packages until contents can be inspected and repackaged (see footnote 7 in Chap. 3).

If mechanical damage does not cause cell thermal runaway immediately or within hours of occurrence, it can still cause cell thermal runaway if the cell continues to be cycled and used. A point of mild mechanical damage can become a point of electrode or separator degradation over multiple cell cycles. Ultimately, severe lithium plating (another root cause that may have the potential to result in cell thermal runaway) occurs at the point of degradation, or a significant hole in the cell separator develops, so that during or after cell charging, the cell undergoes a thermal runaway reaction. Failure by this mode, like most cell internal shorting failures, is most likely to occur during cell charging, or immediately after charging (mechanism discussed below).

Failures due to latent mechanical damage have prompted certain precautions taken by electric model aircraft (i.e., radio-controlled aircraft) enthusiasts. Lithium-ion pouch cells have long been favored by this community due to their light weight. However, because these cells are not enclosed by sturdy cases, they are very susceptible to mild mechanical damage, and routinely exposed to potential sources of mechanical damage. Fires during charging of these cells are very common even with cells that do not appear significantly damaged.[16,17] Thus, enthusiasts have learned to expect that fires will occur periodically and recommend charging cells in fire-safe areas or containers such as fire safes, fire places, and sand pits.

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[14] In particular, forklift operations can result in puncture of packages with forklift tines. A 1999 incident at LAX involving lithium primary (lithium metal) batteries was the result of a pallet tipping over during transport via forklift and subsequent puncture of packages with the forklift tines in an attempt by the forklift operator to right the pallet.

[15] http://www.prba.org/prba/programs/lithium_ion_program/Default.ashx

[16] Schleicher R, *How to Build and Fly Electric Model Aircraft*, MBI Publishing Company, St. Paul, MN, 2005.

[17] McPherson J, Complete Guide to Lithium Polymer Batteries and LiPo Failure Reports, http://www.rcgroups.com/forums/showthread.php?t=209187.

Because of the risk associated with latent mechanical damage, battery pack assemblers, particularly those that are experienced with soft-pouch lithium-ion batteries, typically have policies in place to scrap any cell that may have become mechanically damaged, even if damage is not apparent (e.g., a cell is dropped on the floor during assembly).

Exponent has observed numerous field failures caused by latent mechanical damage, particularly of soft-pouch cells where mild mechanical damage did not cause immediate failure, but rather failed during subsequent cycling. Exponent has conducted testing to attempt to determine whether specific levels of mechanical damage will ultimately result in cell thermal runaway reactions. We have found no nondestructive way to definitely rule out a future cell failure. For example, we have X-rayed mechanically damaged cells to determine if any gross electrode deformation has occurred. However, this technique is typically not sufficient to show small cracks or delamination in electrode materials or mild amounts of electrode over-compression that can lead to lithium plating and cell thermal runaway. We have applied some destructive methods to assess whether specific levels of damage may lead to lithium-plating and cell thermal runaway. These techniques provide results specific to cell design and degree of mechanical deformation, and thus are not applicable to every lithium-ion cell.

To prevent fires from occurring due to cell mechanical damage, it is important to quarantine and monitor cells or packs that have suffered mechanical damage. Mechanically damaged cells and battery packs should then be disposed of, rather than placed back into service, unless extensive studies have been carried out specific to the cell chemistry in use and the degree of mechanical damage experienced, to show that the damage did not induce a defect likely to cause cell thermal runaway. Should mechanical damage exposure be suspected but not confirmed, the suspect batteries should be quarantined, during and after, all subsequent charging processes. Packs should be monitored for excessive self-discharge rates and charging processes should be monitored carefully for evidence of cell internal shorting (noisy voltage signals, extended charging times).[18] Any evidence of poor behavior should trigger proper disposal of the battery pack.

Electrical Abuse

There are a number of ways in which lithium-ion cells can be abused electrically, leading to cell thermal runaway reactions. Some of these mechanisms are described below.

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[18] Mikolajczak C, Harmon J, White K, Horn Q, Wu M, Shah K, "Detecting lithium-ion cell internal fault development in real time," Power Electronics Technology; March 2010.

Overcharge

Overcharge of a lithium-ion cell can cause significant degradation of both anode and cathode. On the anode, overcharge can cause plating rather than intercalation of lithium. Plated lithium forms dendrites that can grow over time and then cause internal shorting. Plated lithium also interacts exothermically with electrolyte. On the cathode, overcharge can cause excess removal of lithium from cathode material structures, such that their crystalline structure becomes unstable, resulting in an exothermic reaction. Reactions at both the anode and cathode, as well as lithium dendrite shorting can push a cell out of its thermal stability limits and result in a thermal runaway reaction.[19] The more severe the degree of overcharge, the more likely the cell is to experience thermal runaway.

There are a few ways in which overcharge can occur. The most obvious overcharge mode is charging a cell to too high of a voltage (over voltage overcharge). For example, charging a 4.2 V rated cell above 5 V will likely cause an immediate, energetic failure. Charging at excessive currents, but not excessive voltages, can also cause an overcharge failure; in this case, localized regions of high current density within a cell will become overcharged, while other regions within the cell will remain within appropriate voltage limits.

Severe overcharge failures are not common with mature consumer electronics devices since these usually contain redundant overcharge protection mechanisms within the pack protection electronics. Occasionally, a design or manufacturing defect can cause bypassing of protection mechanisms and result in severe overcharge failures. These types of failures also occur as a result of human error with systems that either lack hardwired protection (e.g., prototype systems that are being tested) or in charging schemes with manual voltage and current settings (e.g., radio-control aircraft batteries).

Although severe overcharge will lead to immediate cell thermal runaway, repeated slight overcharge of a cell may not cause a failure for an extended timeframe, but can eventually result in thermal runaway. Until circa 2008, it was common to set secondary over voltage protection limits in multi-series battery packs to voltages that represented a slight overcharge level. As the cells in these packs aged, the capacity of series elements diverged. Then, weak cells were allowed to repeatedly reach the secondary protection limit (when a weak cell hit this voltage limit charging would terminate). This could cause repeated, slight overcharging of the weakest cells in the pack, but not the other cells. In some instances, this led to thermal runaway reactions. Industry awareness of this problem prompted requirements in IEEE 1725 and IEEE 1625 for cell manufacturers to communicate specific high voltage limits appropriate for secondary protection settings specific to each cell design to pack and device designers who

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[19] For a detailed discussion of reactions that can occur during overcharge, see: Belov D, Yang MH, "Failure mechanism of Li-ion battery at overcharge conditions," Journal of Solid State Electrochemistry, **12** (2008), pp. 885–894.

purchase their cells. IEEE 1625 adopted the concept of a safe charging current and charging voltage envelope relative to temperature from the Battery Association of Japan (BAJ) "Guidance for Safe Usage of Portable Lithium-Ion Rechargeable Battery Pack."[20]

External Short Circuit

High rate discharging (or charging) can cause resistive heating within cells at points of high impedance. Such internal heating could cause cells to exceed thermal stability limits. Points of high impedance could include weld points within a cell (internal tab attachment) or electrode surfaces. As cell size and capacity increases, the likelihood of internal impedance heating leading to thermal runaway also increases. Larger cells exhibit slower heat transfer to their exteriors, and they usually have higher capacities. Thus, they have the potential to convert more electrical energy to internal heat. UN and UL testing requirements provide a minimum requirement for cell external short circuit resistance: discharge through a resistance of less than 0.1 ohm in a 55°C (131°F) environment. International and domestic shipping regulations (as found in the US CFR, as well as IATA and ICAO publications) require that cells or batteries be protected from short-circuiting. Investigation of a number of thermal runaway failures that have occurred during transport has revealed that improper packaging, particularly a failure to prevent short circuits is a common cause of these incidents.

Over-Discharge

Simply over-discharging a lithium-ion cell to 0 V will not cause a thermal runaway reaction. However, such over-discharge can cause internal damage to electrodes and current collectors (i.e., dissolution of copper) (Fig. 4.9), can lead to lithium plating if the cell is recharged (particularly, if the cell is repeatedly over-discharged), and can ultimately lead to thermal runaway. Most consumer electronics devices set specific discharge voltage limits for their lithium-ion battery packs, at which point an electrical switch will disconnect the electrical load from the battery pack to prevent over-discharge. This switch is reset upon charging. However, such a mechanism cannot completely prevent over-discharge. For example, a battery pack may be discharged to the low voltage cutoff and then stored for an extended period of time during which self-discharge of the cell ultimately results in over-discharge. Most pack protection electronics will allow

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[20] "Guidance for Safe Usage of Portable Lithium-Ion Rechargeable Battery Pack," 1st Edition, March 2003, Battery Association of Japan.

Fig. 4.9 The anode of a repeatedly over-discharged cell coated with copper

the recharge of over-discharged cells, despite the potential for the negative electrode to become damaged. Therefore, over-discharge does periodically cause thermal runaway of lithium-ion cells.

Forcing a cell into "reversal" (charging to a negative voltage, "forced over-discharge") may cause thermal runaway. UL and UN tests provide a minimum requirement for resistance to forced over-discharge for cells used in multi-cell packs. These tests are designed to simulate the most likely mechanism of forced discharge, which occurs when a cell with lower capacity than its neighboring series elements is present in a multi-series battery pack that is externally short-circuited. A lower capacity cell of this type can occur due to aging of the battery pack. In this scenario, current flow from the higher capacity series elements in the pack will drive the discharged series element into reversal. The UN and UL testing does not include repeated forced discharge. Thus, if a system does not include protection electronics that will detect and disable charging of a damaged cell, it is possible a cell could be repeatedly force over-discharged and ultimately undergo a thermal runaway reaction.

Poor Cell Electrochemical Design

Commercial cell testing will generally ensure cells perform adequately when new. However, on occasion, cell aging will result in unexpected degradation of a cell component such as one of the electrodes, the separator, or the electrolyte that can

result in thermal runaway failures.[21] Usually, in these instances, field usage conditions were not well understood when the cell was designed and selected. Thus, conditions used for initial safety and reliability testing were not wholly appropriate to the application.

Internal Cell Fault Related to Manufacturing Defects

Exponent has worked on understanding cell faults for over a decade. In our experience, most commercial electronics cells and battery packs are robustly designed and do not have obvious design problems. The cell designs pass transportation and commercial testing standards and a wide range of cell and pack manufacturer internal reliability tests. Commercially available notebook battery packs have redundant protection devices in place in order to prevent cell overcharging and other potentially damaging or unsafe conditions (charging at high temperatures, charging at high rate when cell voltage is low, etc.). The battery packs are designed to sufficiently prevent expected mechanical and thermal abuse; nonetheless, thermal runaway failures still occur. In Exponent's experience, for commercial lithium-ion battery packs with mature protection electronics packages, the majority of thermal runaway failures in the field are caused by internal cell faults related to cell manufacturing defects.

There are numerous flaws that can occur during cell manufacturing that can ultimately result in cell thermal runaway reactions. Fundamentally, problems at any step of the cell manufacturing process can result in an internal cell fault. For example, there can be defects in cell raw materials, defects in electrode coatings, contaminants introduced during assembly processes, and misplaced, misapplied, or damaged components. Exponent has observed cell thermal runaway failures resulting from cell contamination (either by materials foreign to the battery or loose pieces of battery material itself), manufacturing-induced electrode damage (scratches, punctures, tears, active material displacement), burrs on electrode tabs, weld spatter from cell tab attachment points, wrinkles or kinks in windings or tabs, and electrode misalignment (Fig. 4.10).

There are many ways to classify manufacturing faults. Fouchard and Lechner[22] classified internal shorts by impedance: hard shorts were characterized by low

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[21] See for example: Horn QC, "Application of microscopic characterization techniques for failure analysis of battery systems," Invited presentation, San Francisco Section of the Electrochemical Society, March 27, 2008.

  Horn QC, White KC, "Novel imaging techniques for understanding degradation mechanisms in lithium-ion batteries," Advanced Automotive Battery Conference, Tampa, FL, May 13, 2008.

  Horn Q, White KC, "Understanding lithium-ion degradation and failure mechanisms by cross-section analysis," 211th Electrochemical Society Meeting, Chicago, IL, Spring 2007.

[22] Fouchard D, Lechner L, "Analysis of Safety and Reliability in Secondary Lithium Batteries," Electrochimica Acta, **38**(9), pp. 1193–1198, 1993.
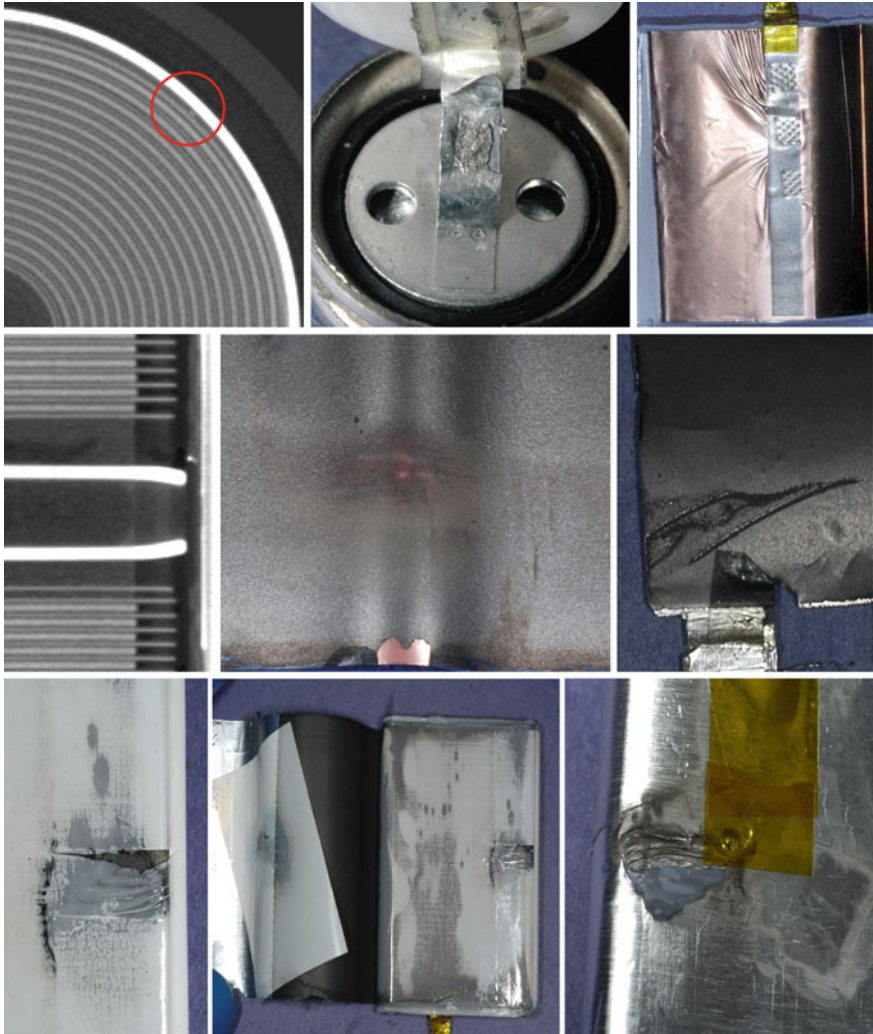
Fig. 4.10 Examples of manufacturing flaws that can lead to cell internal shorts including contamination, poor welds, weld spatter, flaws in electrode coatings, and tears in electrodes and separators

impedance resulting in quick discharge of a cell, while soft shorts were characterized by high impedance resulting in relatively slow discharge of a cell that might appear as a high self-discharge rate. They noted external protective devices could not protect against sudden hard shorts, while imbalance detection might detect soft shorts, and potentially disable battery packs preventing soft shorts from evolving into hard shorts. Exponent attempted classification by component

or manufacturing process,[23] which proved applicable to cell manufacturing auditing.[24] The IEEE 1625 and 1725 Standards take this approach and include component-by-component best manufacturing practice guidance. During revisions of the IEEE 1625 Standard, efforts were made to determine critical locations within a cell where shorting is most likely to lead to heat generation.[25] This analysis led to improvements in cell design to eliminate particularly susceptible locations from commercial cell designs. Efforts have been made to characterize the "size" of a given internal short that will lead to thermal runaway ("size" can refer to the physical size of a contaminant particle, or to the amount of energy that must be transferred)[26] in order to identify mechanisms to detect incipient cell faults (see footnote 18).[27]

It is beyond the scope of this document to describe the possible cell manufacturing flaws.[28] However, a discussion of how internal faults related to

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[23] Mikolajczak CJ, "Causes of Li-Ion Internal Cell Faults," IEEE 1625 Meeting, San Jose, CA, November 15, 2006.

Mikolajczak CJ, "Causes of Li-ion internal cell faults," Portable Rechargeable Battery Association Membership Meeting, Dallas, TX, October 12, 2006.

Mikolajczak CJ, Hayes T, Megerle MV, Wu M, "Li-Ion internal cell faults," Extended Battery Life Working Group Meeting, San Jose, CA, October 4, 2006.

[24] Hayes T, Mikolajczak C, Horn Q, "Key manufacturing practices and techniques to achieve high quality Li-ion cells," Proceedings, 27th International Battery Seminar & Exhibit for Primary & Secondary Batteries, Small Fuel Cells, and Other Technologies, Ft. Lauderdale, FL, March 15–18, 2010.

[25] Zhang Z, "Li-ion in EDV and Safety Perspectives," Proceedings, 28th International Battery Seminar & Exhibit, March 14–17, 2011, Ft. Lauderdale, FL.

[26] See for example: Mikolajczak C, Harmon J, Hayes T, Megerle M, White K, Horn Q, Wu M, "Lithium-ion battery cell failure analysis: The significance of surviving features on copper current collectors in cells that have experienced thermal runaway," Proceedings, 25th International Battery Seminar & Exhibit for Primary & Secondary Batteries, Small Fuel Cells, and Other Technologies, Ft. Lauderdale, FL, March 17–20, 2008.Barnett B, Sriramulu S, "New Safety Technologies for Lithium-Ion Batteries," Proceedings, 28th International Battery Seminar & Exhibit, March 14–17, 2011, Ft. Lauderdale, FL.

[27] Mikolajczak C, Harmon J, Stewart S, Arora A, Horn Q, White K, Wu M, "Mechanisms of latent internal cell fault formation: Screening and real time detection approaches," Proceedings, Space Power Workshop, Manhattan Beach, CA, April 20–23, 2009.

[28] Exponent has produced numerous publications on the topic of cell internal faults, including: Godithi R, Mikolajczak C, Harmon J, Wu M, "Lithium-ion cell screening: Nondestructive and destructive physical examination," NASA Aerospace Workshop, Huntsville, AL, November 2009.

Mikolajczak C, Harmon J, Wu M, "Lithium plating in commercial lithium-ion cells: Observations and analysis of causes," Proceedings, Batteries 2009 the International Power Supply Conference and Exhibition, French Riviera, September 30–October 2, 2009.

Hayes T, Mikolajczak C, Megerle M, Wu M, Gupta S, Halleck P, "Use of CT scanning for defect detection in lithium-ion batteries," Proceedings, 26th International Battery Seminar & Exhibit for Primary & Secondary Batteries, Small Fuel Cells, and Other Technologies, Ft. Lauderdale, FL, March 16–19, 2009.

Horn QC, "Battery involvement in fires: cause or effect?" Invited seminar, International Association of Arson Investigators—Massachusetts Chapter, Auburn, MA, March 19, 2009.

manufacturing defects manifest themselves can be useful from a fire protection standpoint.

An internal cell fault results in a short circuit inside a cell. If the point of shorting is minor (a micro-short), separator shutdown (i.e., physical blockage of lithium ion transport at a localized region within the cell) may isolate the flaw and allow the cell to continue functioning normally. If the point of shorting releases sufficient energy, it can heat the cell past its thermal stability limits and cause cell thermal runaway.

Internal faults related to gross manufacturing defects usually occur very early in the life of a cell. These types of failures can occur on manufacturer assembly lines where cells are being charged, or in the hands of consumers: a user purchases a device, plugs it into charge, and during that first charge, the cells undergo thermal runaway. These failures inevitably occur during, or immediately after, charging. There are some potential reasons for this phenomenon:

- Often early cell cycling causes dimensional changes in cell components (e.g., volume expansion) and increased pressures within a cell case. If a sharp contaminant or burr is present within a cell, dimensional changes or pressure increases may cause it to puncture separator layers and cause direct shorting.
- Charging provides electrical energy to the cell raising its state of charge, and susceptibility to thermal runaway.
- Charging provides energy to any shorting point within a cell. If a shorting point was present in a cell prior to charging, it may have caused the cell to self-discharge before sufficient heat was generated to induce thermal runaway. However, when attached to a charger, a short may draw energy continuously until thermal runaway is initiated.

There are a number of manufacturing quality control techniques that are commonly employed to detect gross defects. However, very subtle defects can escape notice during manufacturing and allow years of seemingly normal cell cycling


(Footnote 28 continued)

Horn QC, White KC, "Characterizing performance and determining reliability for batteries in medical device applications," ASM Materials and Processes for Medical Devices, Minneapolis, MN, August 13, 2009.

Horn QC, White KC, "Advances in characterization techniques for understanding degradation and failure modes in lithium-ion cells: Imaging of internal microshorts," Invited presentation, International Meeting on Lithium Batteries 14, Tianjin, China, June 27, 2008.

Hayes T, Horn QC, "Methodologies of identifying root cause of failures in lithium-ion battery packs," Invited presentation, 24th International Battery Seminar and Exhibit, Ft. Lauderdale, FL, March 2007.

Loud JD, Hu X, "Failure analysis methodology for Lithium-ion incidents," Proceedings, 33rd International Symposium for Testing and Failure Analysis, pp. 242–251, San Jose, CA, November 6–7, 2007.

Mikolajczak CJ, Hayes T, Megerle MV, Wu M, "A scientific methodology for investigation of a lithium-ion battery failure," IEEE Portable 2007 International Conference on Portable Information Devices, IEEE No. 1-4244-1039-8/07, Orlando, FL, March 2007.
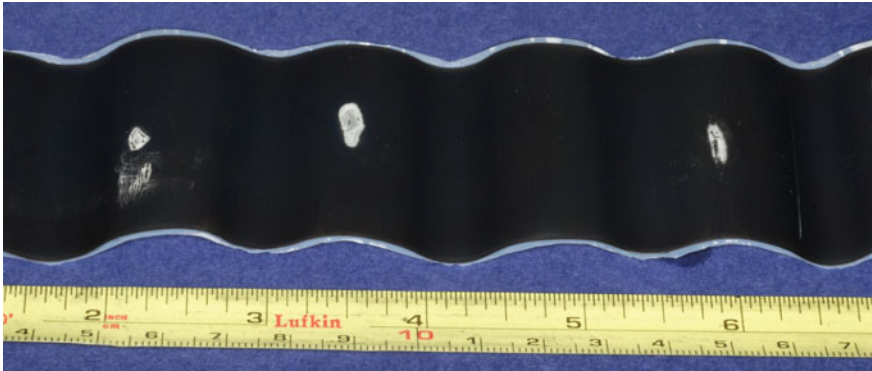
Fig. 4.11 Regions where lithium has plated on an anode are visible as white spots: upon exposure to moisture, very small, and thin deposits react to form lithium-hydroxide (a *white crystal*)

before a thermal runaway reaction occurs. Exponent has postulated[29] that any number of minor defects on a cell anode can cause very localized lithium plating. A few examples include a scratch in the anode, a point of anode delamination, a point of anode over-compression, a thin spot in the anode, or a point where a metallic contaminant has plated. Such lithium plating results in the formation of lithium dendrites and a mat of "dead lithium" composed of detached lithium dendrites. Individual dendrite shorting is usually not significant, as resistive heating quickly breaks the dendrite. However, if such shorting and heating occurs in the midst of a mat of dead lithium, it may be possible to ignite sufficient material to initiate an internal short of sufficient size to cause cell thermal runaway. Note that the amount of plated lithium postulated is in the microgram regime, and will have negligible effect on the behavior of the cell once thermal runaway is initiated (Fig. 4.11).

One important aspect of this lithium plating failure mechanism is that lithium dendrite growth only occurs during cell charging, since charging is accomplished by moving lithium ions (Li^+) and electrons from the cathode to the anode. Normally, the lithium ions intercalate into the anode safely. However, lithium ions can form lithium metal on the anode surface during charging if they are unable to

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[29] Mikolajczak C, Harmon J, Gopalakrishnan P, Godithi R, Hayes T, Wu M, "From lithium plating to cell thermal runaway: A combustion perspective," Proceedings, 27th International Battery Seminar & Exhibit for Primary & Secondary Batteries, Small Fuel Cells, and Other Technologies, Ft. Lauderdale, FL, March 15–18, 2010.

Mikolajczak C, Harmon J, Gopalakrishnan P, Godithi R, Wu M, "From lithium plating to lithium-ion cell thermal runaway," NASA Aerospace Workshop, Huntsville, AL, November 2009.

Mikolajczak C, Stewart S, Harmon J, Horn Q, White K, Wu M, "Mechanisms of latent internal cell fault formation," Proceedings, 9th BATTERIES Exhibition and Conference, Nice, France, October 8–10, 2008.

Mikolajczak C, Harmon J, Wu M, "Lithium plating in commercial lithium-ion cells: observations and analysis of causes," Proceedings, Batteries 2009 The International Power Supply Conference and Exhibition, French Riviera, Sept 30–Oct 2, 2009.

intercalate (e.g., due to the presence of defects mentioned above). The structure of the lithium metal formation manifests itself as dendrites due to the physical nature of the process, and thus, thermal runaway failures associated with this mechanism will only occur during or immediately after charging. In Exponent's experience during investigating field failures, the majority of thermal runaway failures that occur in the field after extended "normal" use of a lithium-ion battery pack occur during, or directly after charging. The reasons for this phenomenon are:

- Lithium dendrite formation occurs during charging; thus, shorting of dendrites (which will provided highly localized heating that could potentially trigger other exothermic reactions) is most likely to occur during charging.
- Charging provides electrical energy to the cell raising its SOC, and susceptibility to thermal runaway.
- Charging provides energy to any shorting point within a cell. If a shorting point was present in a cell prior to charging, it may have caused the cell to self-discharge before sufficient heat was generated to induce thermal runaway. However, when attached to a charger, a short may draw energy continuously until thermal runaway is initiated.

Because failures due to both gross manufacturing defects and more subtle manufacturing defects generally occur during cell charging, we believe that charging cells or battery packs in bulk transport or storage should be avoided if at all possible.

Factors that Influence the Effect of Failure

The severity of a lithium-ion cell failure will be strongly affected by the total energy stored in that cell: a combination of chemical energy and electrical energy. Thus, the severity of a potential thermal runaway event can be mitigated by reducing stored chemical energy (i.e., by reducing the volume of electrolyte within a cell), or by changing the electrolyte to a noncombustible material (an area of active research but not yet commercialized). As an example, a short within a cell that has lost its electrolyte due to leakage is unlikely to result in an energetic failure. Reducing electrical energy can be done by using low capacity electrodes, or by reducing cell SOC. Finally, changing the heat transfer environment of a cell and thus affecting the removal of energy can also influence the severity of thermal runaway.

Cell Chemistry

Lithium-ion cell chemistry can affect the severity of a cell failure. Certain cathode materials allow higher energy densities than others, and cells produced from these higher energy density materials will be subject to more severe thermal runaway

reactions. Cathode material reactivites are often examined and used to compare relative cathode "safety." This may be a factor in determining whether a localized fault within the cell can cause the sufficient heating to bring the entire cell to thermal runaway. However, once a cell achieves thermal runaway, the ultimate severity of the reaction is dominated by whether the cell itself will reach sufficient temperature to ignite flammable vent gases. Hot surface ignition usually requires temperatures well above gas auto-ignition temperatures—for hydrocarbons, usually in the range of 600–1,200°C (2,200°F) depending on the composition and various geometric factors of the heated surfaces.[30] Thus, unless a cathode material has sufficiently low energy density to ensure a cell remains below 600°C (1,110°F) during thermal runaway, the severity of the thermal runaway reaction will not be significantly affected by cathode chemistry.

The application of flame retardant additives to cell electrolytes and the development of non-flammable electrolytes continue to be active areas of study.[31] Although researchers have reported effective retardants or non-flammable electrolytes, these have not become commercialized due to several potential concerns such as poor cell lifetime, poor performance, and/or elevated toxicity hazards.

State of Charge

It has been observed that the vast majority of thermal runaway reactions that occur in the field occur during or shortly after cell charging. From an energy perspective, cell thermal runaway is unlikely to occur in a cell at a low SOC. Exponent's own testing showed that for many lithium-ion cells, even severe crushing of cells that are below approximately 50% SOC will not lead to a severe reaction.[32] Testing of a variety of 18650 cells at ambient temperatures has demonstrated that below 50% SOC, cell shorting will cause heating to cell case temperatures up to approximately 130°C (266°F) followed by cell cooling.

ARC testing by Exponent (see footnote 22 in chap. 1) of commercial 18650 cells of a variety of chemistries at a variety of SOC has shown that self-heating onset temperature and self-heating rate is a function of the stored electrical energy stored as chemical potential energy within the cell rather than cell chemistry

[30] Babrausksas V, *Ignition Handbook*, Fire Science Publishers, 2003, pp. 83–89.

[31] See for example: Dalavi S, et al., "Nonflammable Electrolytes for Lithium-Ion Batteries Containing Dimethyl Methylphosphonate," Journal of the Electrochemical Society, **157**(10), A1113-A1120, 2010. Sazhin SV, Harrup MK, Gering KL, "Characterization of low-flammability electrolytes for lithium-ion batteries," Journal of Power Sources, **196**(2011), 3433–3438. Feng JK, Ai XP, Cao YL, Yang HX, "Possible use of non-flammable phosphonate ethers as pure electrolyte solvent for lithium batteries," Journal of Power Sources, **177** (2008), 194–198.

[32] General approach described in IEEE 17th Annual Battery Conference on Applications and Advances paper, Loud J, Nilsson S, Du Y, "On the Testing Method of Simulating a Cell Internal Short Circuit for Lithium Ion Batteries," Long Beach, CA, 2002.

(stored electrical energy was held constant across cells of equivalent volume but varying chemistry). ARC testing by researchers at Sandia[33] showed that self-heating onset temperature can be strongly impacted by SOC. In testing one commercial cobalt-oxide cell model, the researchers found self-heating onset occurred at 80°C (176°F) for cells at 100% SOC, and at 130°C (266°F) for cells at 0% SOC. In testing of multiple cell models, Sandia researchers found that thermal runaway onset temperature is reduced for cells at increased SOC.[34] Similarly, direct electrode shorting tests (see footnote 25) have shown that reducing SOC significantly reduces the maximum temperature achieved at the point of shorting. Fire calorimetry[35] measurements (per ASTM E2058) by Ineris have shown that decreased SOC corresponds with lower peak heat-release rates for pouch cells.

Heat Transfer Environment

Finally, the heat transfer environment of a cell undergoing a thermal runaway reaction can play a large role in the severity of the reaction. High ambient temperatures or adiabatic insulation will increase the likelihood that any given internal fault can drive a cell to thermal runaway, and increase the energy available to heat the cell. Conversely, if a cell is surrounded by thermally conducting media (e.g., surrounded by densely packed cells or coolant), heat loss may prevent or mitigate a thermal runaway reaction.

If cells are assembled in close proximity, and not sufficiently heat sunk, thermal runaway in one cell can propagate to nearby cells. Exponent used this technique to initiate thermal runaway reactions (see footnote 11) in tests examining thermal runaway propagation and the effect of SOC on propagation. One cell in a battery pack at low SOC was disconnected from the other cells, charged to 100% SOC and replaced into the pack. A small heater was attached to the 100% SOC cell, and then heated locally above the melting point of its separator (approximately 150°C/300°F). At 100% SOC, ignition of cell vent gases after thermal runaway of a single cell is common, as cell case temperatures will exceed vent gas auto-ignition temperatures. Vent gas ignition in combination with the thermal runaway reaction results in measured cell surface temperatures of approximately 650°C (1,200°F). This initiating cell will then propagate thermal runaway to other cells in the battery pack, and the effect of other factors such as local heat transfer conditions can be observed.

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[33] Roth EP, "Thermal Stability of Electrodes in Lithium-Ion Cells," Sandia Report: SAND2000-0345 J. Roth EP, Crafts CC, Doughty DH, "Thermal Abuse Studies on Lithium Ion Rechargeable Batteries," Sandia Report: SAND2000-2711C.

[34] Roth EP, "Final Report to NASA JSC: Thermal Abuse Performance of MOLI, Panasonic, and Sanyo 18650 Li-Ion Cells," Sandia Report: SAND2004-6721, March 2005.

[35] Ribiere P, Laruelle S, Morcrette M, Grugeon S, Tarascon JM, Marlair G, Bertrand JP, Paillart A, "Li-ion battery: safety tests," Poster, Advanced Automotive Battery Conference (AABC).

A number of researchers have experimented with embedding cells in materials that can enhance heat transfer away from cells. Kizilel et al.[36] report thermal modeling results that suggest a phase change material produced by All Cell Technologies[37] can absorb sufficient heat from embedded cells to prevent thermal runaway propagation. NASA conducted abuse testing on battery packs incorporating a heat absorbing material placed around cells (see footnote 37 in Chap. 1). The Tesla Roadster batteries are designed with a liquid cooling system to maintain cells at uniform temperatures during normal operation and to "guarantee safety."[38]

Note that heat transfer internal to cells themselves may be slow due to the thermally insulating properties of many cell components. Thus, localized heating within large cells can be problematic, particularly during high rate discharge processes. Many manufacturers limit cell dimensions to ensure that an external short circuit will not cause sufficient internal heating to drive a cell into thermal runaway.

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[36] Kizilel R, Sabbah R, Selman R, Al-Hallaj S, "An alternative cooling system to enhance the saftety of Li-ion battery packs," Journal of Power Sources, **194** (2009), pp. 1105–1112.

[37] http://www.allcelltech.com

[38] http://www.teslamotors.com/roadster/technology/battery