LITHIUM ION BATTERIES
MORE DANGEROUS OR JUST MORE COMMON?
And a Simple Analysis
to Narrow the Possible Failure Modes

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Figure 1. Lithium-ion 18650 cell, and a failed cell that exploded in a victim's pocket.

ABSTRACT
Lithium-ion batteries have become a staple of modern life. Many of the devices we use daily depends on these batteries to make the portable and lightweight. Many people are not even aware that they carry one or more lithium-ion cells or batteries around with them daily, sometime even attached to their own bodies.

Lithium-ion batteries have the highest energy density for any commercially available on the market. Other benefits a maximum or minimum state of charge). It is this fact that makes them so popular. Uses have been found for lithium-ion batteries in automotive, marine, aerospace and military and communications applications to name but a few. No longer need someone lug around a heavy, awkward weighed in ounces and grams, not pounds and kilos. This fact also makes them potentially more dangerous, as more energy is packed into a tighter space with less means of containment.

All batteries will fail. It is simply a matter of chemistry, physics and time. This is true for any battery, whether alkaline, nickel-cadmium, or lithium-ion. Fortunately, the vast majority of batteries fail in a benign manner, causing little more than some aggravation and inconvenience to the user. Those batteries that fail in the other extreme the catastrophic failure is of concern to the fire investigator and others involved in public safety.

Since their introduction, there have been many fire and explosion incidents where LI cell or batteries were involved. Sometimes the batteries were the source of ignition and sometime even the source of the fuel. In some cases, however, the batteries were victims of the fire. Determining the order of events is not always easy. Proper understanding of battery fundamentals, and investigation methodology when dealing with lithium-ion technology, is crucial to making the correct determination.

BATTERY SCIENCE

Cells versus Batteries

While it is common practice
often misapplied.

The cell stores the energy in chemical form, and energy is released by the flow of electrons during a chemical reaction. Generally, a cell of a given chemistry will provide a fixed nominal voltage, although that voltage will decline as the charge is los non depleted alkaline cell will produce an approximate voltage of 1.8 Volts DC; a lead-acid cell 2.2 Volts DC; and a lithium-ion cell 4.2 Volts DC.

or more cells. The cells can be arranged in series, which will produce a higher (multiple) voltage than a single cell, while at the same current. The cells can also be arranged in parallel, which will produce a higher (multiple) current than a single cell at while the same voltage.

Primary versus Secondary

Primary cells and batteries are intended to be used only until the primary charge is exhausted. They are not intended to be recharged, or reused. Examples of primary cells are alkaline cells (AAA, AA, C or D cells), and lithium cells (LR44 or 2032 coin cells). The chemistry of these devices in non-reversible. Attempts to recharge primary cells or batteries can end catastrophically with a fire or explosion.

Secondary cells and batteries are intended to be recharged and reused. The chemistry is reversible (although some degradation of the chemistry occurs during each charge/discharge cycle). Examples of secondary cells and batteries are lead-acid automotive batteries, nickel-cadmium cells used in older cameras, and lithium-ion cells such as an 18650 cell.

Lithium versus Lithium-Ion

A distinction must be made between lithium and lithium-ion cells and batteries.

- Lithium cells are primary cells, are not rechargeable, and cannot be reused. Lithium cells use metallic lithium as an electrode.
- Lithium-ion cells are secondary cells, are rechargeable, and can be reused. Lithium-ion batteries use a lithium compound containing other elements as an electrode.

LITHIUM-ION CELLS

Basic Chemistry and Construction [1]

Lithium- Li-ion cells use an intercalated lithium compound as one of two electrode materials. (Intercalation is the reversible inclusion or insertion of a molecule (or ion) into compounds with a layered structure.) Lithium ions move from the positive electrode to the negative electrode during charging, and back during discharge.

Positive Electrodes (Cathodes)

Not all Li-ion cells are created equally. Performance, safety and chemistry are affected by the chemistry of the cell. Some of the lithium compounds used for the positive electrode include:

Rechargeable tools, medical devices, etc.

- Lithium iron phosphate ($LiFePO_4$)
- Lithium ion manganese oxide (LiMn2O4; Li2MnO3, or LMO)
- Lithium nickel manganese cobalt oxide (LiNiMnCoO2 or NMC)
- When compared to Lithium cobalt oxide:
    - Lower energy density
    - Longer lives
    - Inherently safer
- NMC cells have a promising future in transportation/automotive applications.

Handheld electronic devices (i.e. cell phones, laptop computers, etc.).

- Lithium cobalt oxide ($LiCoO_2$).

(Note: Because it has the highest energy density, it also has highest safety concerns, especially when damaged).

Niche and specialty applications.

- Lithium nickel cobalt aluminum oxide ($LiNiCoAlO_2$ or NCA)

Chemistries still in development.

- Lithium sulfur batteries
    - May provide energy density higher than Lithium Cobalt Oxide

Negative Electrodes (Anodes)

As with the positive electrode, various chemistries are in use and in development for the negative electrode as well. Some of the materials used include:

- Graphite (Graphene)
    - Currently the most common in use
- Lithium titanate ($Li_4Ti_5O_{12}$ or LTO)
- Hard carbon
- Tin/cobalt alloy
- Silicon/carbon alloy

Electrolytes [2, 3]

An electrolyte is a chemical or chemical solution placed between the positive and negative electrodes of a cell and serves as a pathway for electrons to flow from one electrode to the other. This is true for both charging and discharging of the cell. In traditional primary and secondary cells, such as alkaline or lead-acid cells, water or a water acid solution was used as the electrolyte. In a Li-ion battery, however, water cannot be used. Metallic lithium reacts strongly to water, and even lithium compound will produce a weaker reaction. The resulting chemical reactions would destroy the cell.

Common electrolyte solutions contain a mixture of an organic carbonate (oxygenated hydrocarbon) and a lithium salt. Typical organic carbonates include:

- Ethylene carbonate $(CH_2O)_2CO$
- Diethyl carbonate. $OC(OCH_2CH_3)_2$

(Note: Both of these compounds are ignitible liquids.)

Typical salts include:

- Lithium hexafluorophosphate ($LiPF_6$)
- Lithium hexafluoroarsenate monohydrate ($LiAsF_6$)
- Lithium perchlorate ($LiClO_4$)
- Lithium tetrafluoroborate ($LiBF_4$)
- Lithium triflate ($LiCF_3SO_3$).

Separators [4]

A layer of porous polyethylene or polypropylene (or combination) separates the anode and cathode, allowing the electrolyte to exchange ions between the two.

Construction
Li-ion cells are available in a number of shapes and sizes, their construction generally falls into four categories. These are small and large cylindrical cells, and prismatic and pouch cells.

All Li-ion cells share some common elements in their construction. These are the positive electrode (cathode), negative electrode (anode), electrolyte, separators, casing and terminals.

Typical Assembly of the cell core.
The materials are generally arranged in the following manner.
- A permeable separator sheet is laid down. The layer contains an electrolyte.
- The anode (negative electrode) material is spread over the sheet as a paste.
- A terminal (pin, metal strip or wire) is placed into the anode paste.
- A permeable separator sheet is laid over the anode layer. The layer contains an electrolyte.
- The cathode (positive electrode) material is spread over the sheet as a paste.
- A terminal (pin, metal strip or wire) is placed into the cathode paste.
- Depending on the final configuration of the cell, a third separator layer may be applied.

Cylindrical Cells
As their name implies, cylindrical cells are shaped like a cylinder. The outside is typically a pressed steel can. Next an insulator disk is placed into the can. For this type of construction the cell core assembly is

resemblance to the pastry. In a small cylindrical cell, a second insulator disk is place over the jelly roll. A steel cover is placed over the insulator disk and the edge of the can in rolled or crimped for a permanent assembly. The terminal pins in the jelly roll penetrate the insulator disks and touch the can (anode or negative) or cover (cathode or positive).

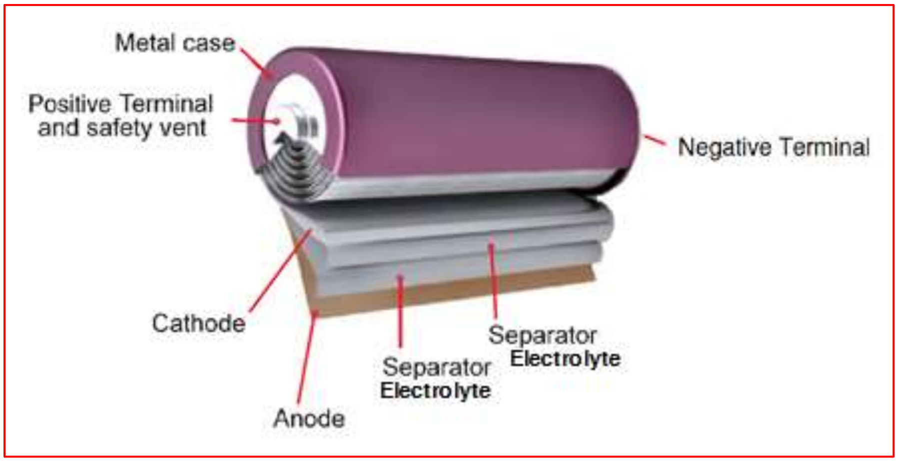

Figure 2. Core layer in a cylindrical cell.

Common small cylindrical cell nomenclature is based on the size of the cylinder. The most common size currently in production is the 18650 cell. This cell is 18 mm [0.71 inch] in diameter by 65.0 mm [2.56 inch] long. Common uses for small cylindrical cells are flashlights, cameras, electronic cigarettes and laptop computer batteries.

Large cylindrical cells usually have threaded terminals, and the manufacturing method will vary accordingly. Common uses for large cylindrical cells industrial applications and backup power systems.

Prismatic and Pouch Cells

Prismatic cells are rectangular shaped cells with a hard case. Pouch are rectangular shaped cells with a soft case, and are also known is Lithium-

cells chemistry, but instead to its casing material.

Both prismatic and pouch cells can be easily configured to fit almost any shape and thickness, making them the popular choice for small handheld devices.

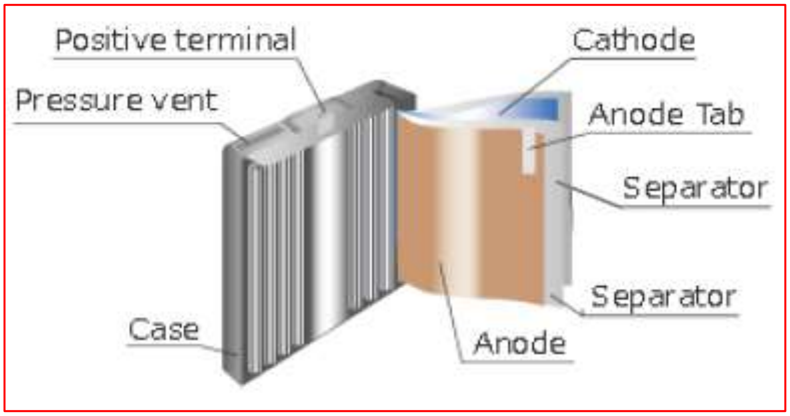

Figure 3. Construction of a prismatic cell.

Assembly of a flat cell differs somewhat from the cylindrical cell. The electrode core assembly can be used in a single layer, rolled, or folded into multiple layers, depending on the thickness of the finished cell. This is then placed into the outer casing. The terminals are threaded through the casing or connected to metal tabs. The casing is then sealed, typically by thermal or sonic welding, or with an adhesive.

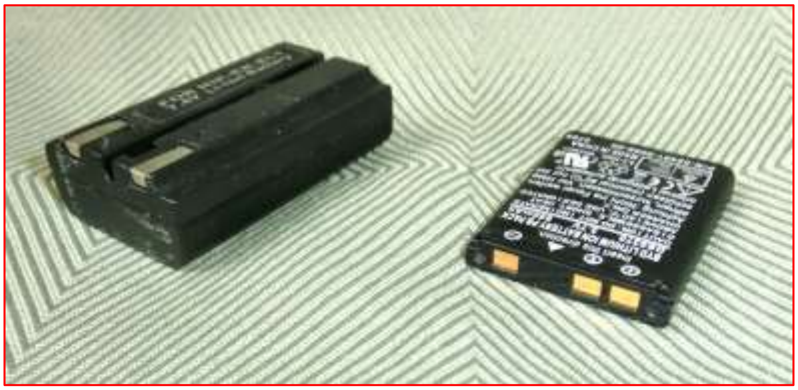

Figure 4. Prismatic cell (left) and Pouch cell (right).

Prismatic and pouch cells do not have a standard nomenclature. Common uses for cell phones, cameras and tablets.

LITHIUM-ION BATTERIES

History

Theoretical and development work on lithium- working experimental rechargeable cells appearing about 1979.

The first commercial Li-ion cells were produce by Sony Electronics and Asahi Kasei and released in 1991. They were used in laptop computer batteries.[5]

Since their introduction a quarter of a century ago, Li-ion cells and batteries have found their way into almost every corner of consumer and industrial use, including but certainly not limited to the following:

- Cell phones
- Tablets
- Computers
- Video Games
- E-readers
- Cameras
- Power tools
- Toys
- Electric toothbrushes
- Electric razors
- Flashlights
- E-cigarettes
- Vehicle starting batteries
- Vehicle primary power
- Industrial machinery
- Telecommunications
- Aerospace
- Military
- Emergency power supplies
- Pacemakers

Abundance
How many Li-ion cells and batteries are there? The numbers are staggering.

In the United States, it is estimated that the number of cell phones in use is about 327,558,000, or 1.03 per person. If that sounds like a high number to you, try Brazil, at 1.41 per person, the United Arab Emirates at 2.04 per person, or Hong Kong at 2.40 per person.[6]

It is estimated that there are 160 million laptop computers in use in the U.S.[7, 8] At an average of 6 cells per laptop battery, that is 960 million cells.

A Tesla Model S electric car alone currently uses over 7,000 type 18650 cells. The company has a goal of having 40,000 cars on the road in the next few years.[9]

And that does not include the batteries for all the other uses previously mentioned applications.
As of 2012, worldwide annual production of cylindrical Li-ion cells was 660 million. Prismatic and pouch cells were a close runner up, with demand expected to hit over 700 million by 2013. The United States,

there are literally billions of Li-ion cells and batteries currently in use in the use in the U.S.

LITHIUM-ION CELL FAILURE
As previously stated in this paper, every electrical cell and battery will eventually fail. It is simply a matter of physics, chemistry and time. Most batteries will fail in the most benign way. They will simply not supply power when demanded due to interior and/or exterior chemical deterioration which has rendered the device useless. While the end result can vary from annoying to life threatening depending on the situation, the cell or battery itself does no harm.

On the other hand, in far rarer occurrences, the failure of the can be catastrophic. The end result can be a fire or explosion resulting in property damage, injury or even death.

Notable Lithium-Ion Failures
Since their introduction to the market place in 1991, there have been a number of notable failure of Li-ion

Products Safety Commission has issued a number of recalls for products containing Li-ion cells batteries for creating fire hazards.[10]

- Sony Electronics the original seller of Li-ion battery powered computers has had four recalls of their laptop computers in 2006, 2008, 2010 and 2014.

- Hewlett Packard/Compaq laptop computers were recalled in 2005 and 2008. Additionally, Hewlett Packard was fined in 2014 for failing to notify the CPSC when they knew of problems prior to the 2008 recall.

- Boeing had to ground the entire fleet of its new 787 Dreamliner in 2014 when problems developed with overheating of Li-ion batteries aboard the planes as part of their electrical system.[11]

- Hoverboards, the hottest and most sought after present of the 2015 Christmas season, became one of the quickly recalled products ever in 2016 when numerous fires were reported and recorded around the U.S.

Figure 5. Dell laptop exploding at computer conference.

- Dell Computer had a recall of their laptop computers in 2006. They also suffered the embarrassment of have a laptop fail at a computer technology conference and be seen by numerous attendees, and caught in photos and videos.

Figure 6. Recalled Pelican light, and recalled fire truck.

- Pelican Products had to recall a rechargeable flashlight in 2016. Ironically, these flashlights were installed as standard equipment aboard a line of firefighting equipment, forcing a recall of the firetrucks as well.

Catastrophic Failure of Lithium-Ion Cells and Batteries

A catastrophic failure is a sudden and total failure from which recovery is impossible. Catastrophic failures often lead to cascading systems failure. [12] In the context of Li-ion cells and batteries, a catastrophic failure is one that is likely to lead to thermal event which in turn can result in the ignition of a fire or cause an explosion.

This leads to the first question, how often do Li-ion cells fail catastrophically? As not all failures lead to subsequent fires, explosions, damage, injuries or death, it should be obviously that not all incidents are reported, nor is there a central data base to record incidents that are reported. We must therefore rely on estimates instead of hard data. The author has heard estimates ranging from one in one million, to one in ten million.

For the sake of argument, let us assume that there are 2.5 billion Li-ion cells currently in use in the U.S. That is about 8 Li-ion cells for every person (the amount in the average laptop battery, plus a cell phone and one other device). Let us further assume that the each cell is replaced every 5 years. That would mean 500 million new batteries on the U.S. market each year. At a failure rate of 1 in 10 million, that would mean 50 catastrophic failures per year. At a failure rate of 1 in 1 million, that would mean 500 catastrophic failures per year. Given the number of reported incidents, and recalls for Li-ion powered products by the CPSC, the author is more inclined to believe the 1 in 1 million estimate is closer to the truth.

Let us now make the further assumption that approximately half of the catastrophic failures of Li-ion cells do not result in a subsequent event resulting in damage, injury or death.

If the author is correct in his assumptions, then there are approximately 250 catastrophic Li-ion battery failures a year that result in damage, injury and/or death. This is, of course, only an estimate based on some known data and some logical assumptions. The number may in fact be higher. The damage that results from a fully involved fire often obscures or obliterates the evidence of the ignition source or fire cause. Many Li-ion cell and battery fires are likely

How Lithium-Ion Cells Fail [13, 14, 15]

Under normal use, a rechargeable cell, Li-ion included, goes through a chemical reaction each time the cell discharges. When the cell is recharged, the chemical reaction is reversed, although not entirely. A small amount of degradation occurs to the cell each time the cycle repeats. Eventually, the cell becomes too degraded to hold a usable charge. A rechargeable cell can also degrade if left for a long period in an uncharged state

chemistry. These are examples of benign failure.

When charging and discharging, the chemical reaction taking place within the cell generates heat. Under normal circumstances, this heat generation is minimal. If, however, the charging or discharging takes place at a higher rate than normal, the heat generated can be excessive. Excessive heat can cause the separator layer between the anode and cathode layers to fail leading to an internal short, and catastrophic failure.

Flaws in the cell can make it more susceptible to the effects of excess heating. One of the more common defects observed in Li-ion cells is contamination. The separator between the cathode and anode layers is made of a polymer, typically mylar or a similar material. Any conductive or semi-conductive contaminant in the separator can potentially create a short circuit between the anode and the cathode layers. If the contaminated layer is in a cell subjected to even normal heating, the layers is more likely to fail wherever contamination exists.

excess tension when the roll is being made, and often the result of a misadjusted machine during automated assembly. The result is wrinkles in the jelly roll, particularly the separator. This can lead to failure of the separator and a short circuit between the anode and cathode layers. Again, this can be aggravated when the battery is subjected to heating during charging and discharging.

Li-ion cells can also be induced to fail catastrophically. A cell can fail if subjected to physical abuse. Dropping the cell, hitting it, or puncturing can have result varying from broken terminal leads to internal short circuits. In the case of a Li-ion cell, a short circuit can lead to a catastrophic failure and the sudden release of energy in the form of heat.

External heating of a Li-ion cell can also cause it to fail catastrophically. Whether heated from within or without, the cell will eventually rupture, vent and/or explode. After the fact, it can be difficult if not impossible to determine how the cell was heated.

The Danger of Catastrophic Failure in Lithium-Ion Cells and Batteries
While the possibility of fire or explosion during a catastrophic failure has been mentioned, a bit more detail is in order.

When a catastrophic failure occurs in Li-ion cell, it is a thermal event and produces extremely high temperatures and pressures. It is occurs when the cell is heated, whether absorbed or internally generated, is in excess of what can be dissipated through conduction, convection or radiation. This condition is known as a thermal runaway. The cell temperature increases until a critical internal temperature is reached (~300^{o}C). At that point, the separator layers begin to break down and a massive internal short circuit begins. The internal temperature then rises exponentially until the casing ruptures.

One possible result is venting, in which the electrolyte can be expelled under high pressure at high velocity and temperatures (1,000^{o}C or more). The electrolyte contains ignitible liquids that will often ignite as soon as they are exposed to oxygen.

The other possible result is an explosion of the cell itself. If the cell fails to vent, sufficient pressure can build causing a massive rupture of the casing. The jelly role (electrode core) can be ejected outward, at high velocity and high temperatures. As with venting, the electrolyte is also likely to ignite as soon as it is exposed to oxygen. This is most like to occur in a cylindrical cell with a steel or metallic casing.

The high temperature of the material ejected, and the possibility of the ejected material igniting in the process, makes it a very capable ignition source for almost any potential target fuel within range.

For anyone unfortunate enough to be in range of the ejected material, the experience would be comparable to being the victim of napalm or white phosphorus.

Figure 7. Injured hand of a 3 year child watching videos when a laptop battery exploded. The hand had healed approximately 6 months at the time of the photo.

LITHIUM-ION CELLS AND THE FIRE INVESTIGATOR

It is becoming far more frequent that a Li-ion powered device, and/or the charger for the device, is found at a fire scene. As a fire investigator, it is imperative that a number of question be answered, and answered correctly, before reaching the conclusion that the fire or explosion incident being investigated is in fact the result of a Li-ion cell or battery failure. While some of these questions may seem basic, it is good practice to include them in your list.

- Was a battery, and/or battery powered device found in the area of origin?
- Does a witness place a cell or battery, and/or battery powered device in the area of origin?
- Was the cell, battery or device in fact a Li-ion cell or battery powered device?
- What type of Li-ion cell or battery was it?
- Did anyone witness the event as it occurred?

Figure 8. This Hoverboard caught fire as it was being removed from the box. (BGR.com)

- What state of charge was the cell or battery in at the time of the fire?
- Was the cell or battery in use and being discharged?
- Was the cell or battery being stored?
- How was it being stored?
- Was the cell or battery being charged?
- Was a single cell or a battery involved in the event?
- What was the state of the cell or battery after the fire?

  - Does the cell display signs of internal or external heating?
  - Did the cell rupture?
- Are there discernable fire patterns near the device, cell or battery which can be attributed to the failure of a cell?
- Are there discernable fire patterns on the device, cell or battery which can be attributed to the failure of a cell?
- Are there signs of arcing on the cell?
- Are there signs of external abuse on the cell or battery?

A fire investigator must learn to ask the right questions, in the right order. By doing so he or she can eliminate the impossible, and minimize the improbable. The investigator can then focus on the probable and hopefully avoid unnecessary paths of inquiry. While battery experts and sensitive, high powered scanners can extremely helpful when the answers are less clear cut, they are not always needed.

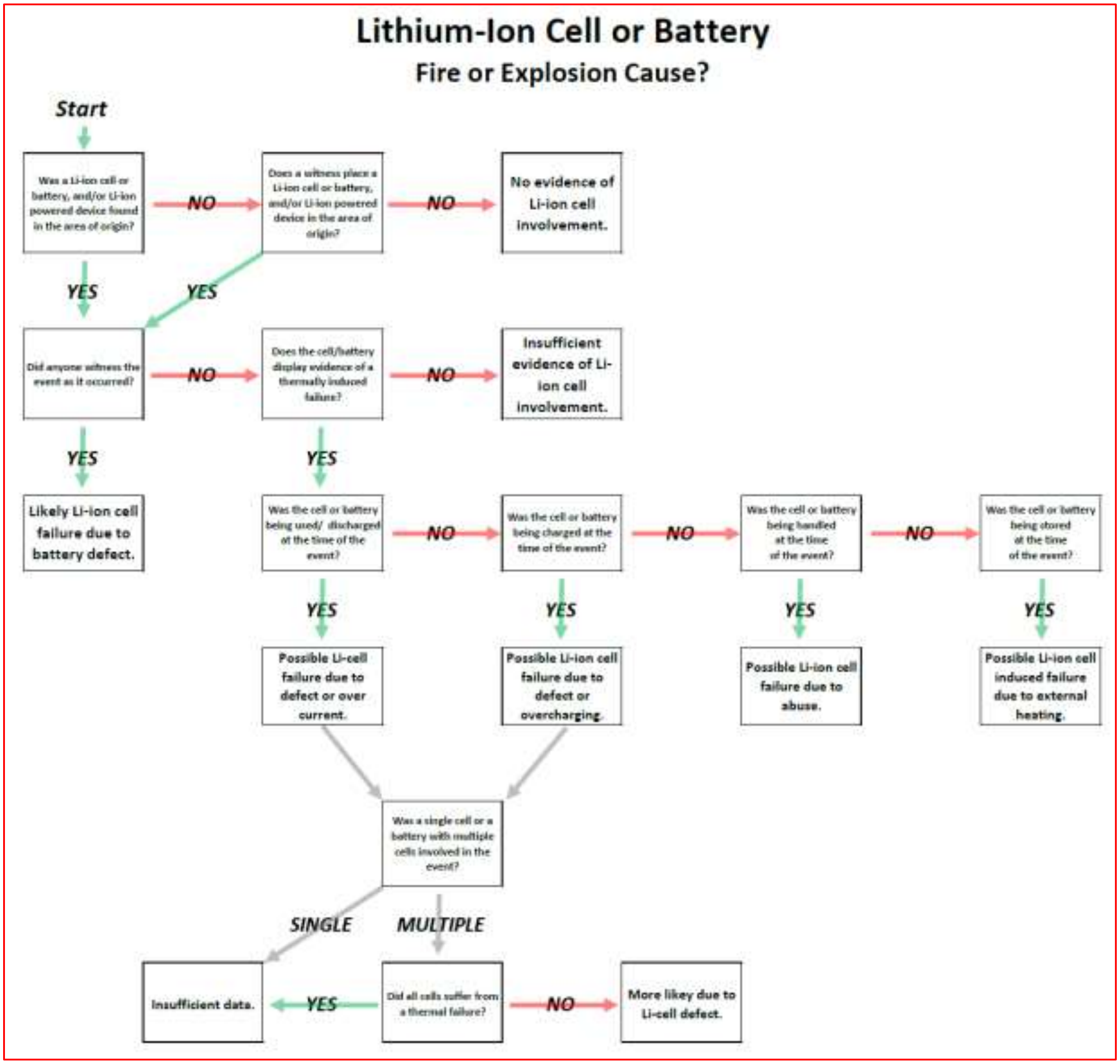

Figure 9. Simple Analysis Flow Chart.

Figure 10. Charger/battery remains in the area of origin. Found to be Ni-Cad battery, not Li-ion.

Figure 11. Remains of laptop battery from in a fire scene. Each Li-ion cell displays a different degree of damage.

The preceding list of questions is designed to gather data and form hypotheses. The answers will not always give a direct answer to the question: Was a Li-ion battery failure the cause of the fire or explosion? For that answer, we may need to gather more data, and likely perform some very in depth laboratory examinations.

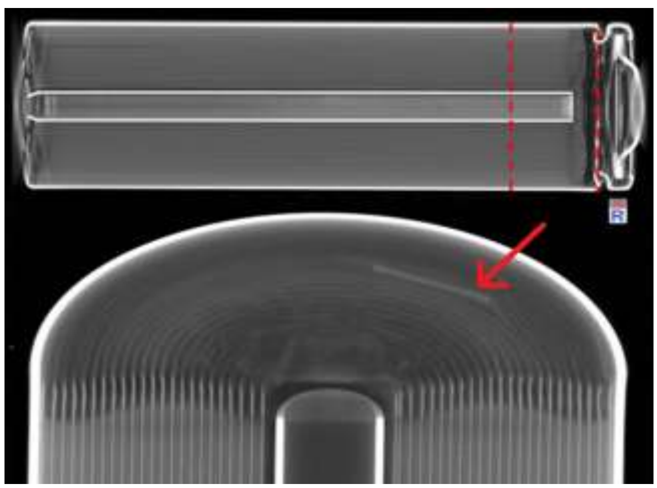

Figure 12. CT scan of Li-ion 18650 cell.
(Exponent Engineering image)

Beyond basic visual observation, other investigative technologies may be necessary to make any conclusions. These include, but are not limited to:

- Microscopy and photo-microscopy give the investigator ability to see and photograph minute details not visible to the naked eye.
- X-rays can be useful for examining damaged cells, but far more useful for examining un- or less damaged exemplar cells from the same battery pack.
- Energy Dispersive X-ray Spectroscopy (EDS) analysis may detect dispersion of core materials on or beyond the cell casing or the powered device. [16]
- Scanning Electron Microscopy (SEM) may detect flaws beyond light based microscopy.
- CT (Computed Tomographic) scanning, or CAT Scanning, can find flaws inside of incident or exemplar cells. [17]

While many of these technologies have price tags far beyond the grasp of the average fire investigator, labs are available that can provide the services for a fee. The investigator and/or the client must evaluate the need for such services, their probability of gaining useful information, and the cost of the service.

COMING TO YOUR CONCLUSIONS

All possible, or at least practical, attempts should be made to gather evidence and information. The investigator can then complete the analysis and begin to form his conclusions.

Based upon the evidence, data, information and witness statements the investigator can determine whether a lithium-ion cell, battery or device was involved, ignited or caused the fire or explosion event being investigated. The level of certainty of the conclusions can also be established.

According to <u>NFPA 921 Guide for Fire and Explosion Investigation</u>, the level of certainty falls in two categories.

(1) ***Probable****. This level of certainty corresponds to being more likely true than not. At this level of certainty, the likelihood of the hypothesis being true is greater than 50 percent.*

(2) ***Possible****. At this level of certainty, the hypothesis can be demonstrated to be feasible but cannot be declared probable. If two or more hypotheses are equally likely, then the level of certainty must be "possible."*

While this may be the current standard for presenting evidence in court proceedings, the conscientious investigator should strive for a higher standard, and make sure he can back up his conclusions. By using the correct methodology, asking the right questions, and using the right tools, perhaps the bar can be raised when it comes to investigating fires where Li-ion batteries are involved.

CONCLUSION

In order to come to the proper conclusions concerning the involvement and causation of a fire or explosion by a lithium-ion battery or device, the fire investigator must have a thorough though not necessarily exhaustive knowledge of the chemistry, construction, behavior, use and potential abuse of Li-ion batteries. Simply finding a Li-ion cell, battery or powered device is not sufficient.

Using the proper fire investigation methodology, asking the right questions, and forming the right hypotheses can go a long way towards including or excluding Li-ion devices as a potential ignition and/or first fuel source.

Confirmation of hypotheses linking Li-ion cells to causation can range from the simple (a witnessed event) to extremely complex and intensive laboratory examinations.

It must be acknowledged that some of the technology available for laboratory examination is beyond the means of the average fire investigator. This does not, however, necessarily exclude the investigator from forming hypotheses and opinions about the roll of Li-ion products in a fire or explosion event.

An investigator must be aware of his own skills, knowledge, training, and limitations. He or she must be cognizant of when his or her talents are sufficient, and when additional expertise must be sought.

ABOUT THE AUTHORS

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ENDNOTES

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