NEW SCIENCE

SUSTAINABLE ENERGY

LITHIUM-ION

BATTERIES

- APPLYING FAULT TREE ANALYSIS METHODOLOGY
- INDENTATION INDUCED ISC TEST
- ADVANCING LITHIUM-ION BATTERY STANDARDS
- AGING EFFECTS ON LITHIUM-ION BATTERIES

JOURNAL ISSUE II
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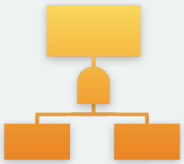
NEW CHALLENGES
CALL FOR NEW SCIENCE

Progress is an unstoppable, transformative force. New technologies, product advances and globalization are arriving one on top of another at a dizzying pace. Innovation makes us more efficient, more productive and more connected. But there is a cost, and that cost is risk. To help mitigate the emerging risks, UL is developing New Science. Through fundamental discovery, testing methodologies and equipment, procedures, software and standards, UL is creating new and important ways to make the world a safer place.

SUSTAINABLE ENERGY
LITHIUM-ION BATTERIES OVERVIEW

Our Lithium-ion Batteries journal covers four key subjects that demonstrate how UL is working to enhance the safety of lithium-ion batteries. Fault Tree Analysis is the foundation of how we approach lithium-ion battery safety — by identifying and understanding the root causes of failures. We found that one of the leading causes of failure is an internal short circuit (ISC), so we developed a simple and repeatable way to induce ISCs. The Indentation Induced ISC test enables us to study battery behaviors when an ISC occurs. This and related research has given us insights that we've used to update existing standards and create new ones to address the most recent applications of lithium-ion batteries. Finally, a new area of potential concern, Aging Effects, is a significant area we are focusing on, given the trend toward longer battery life and second-use applications for lithium-ion batteries.



APPLYING FAULT TREE ANALYSIS METHODOLOGY

INDENTATION INDUCED ISC TEST

ADVANCING LITHIUM-ION BATTERY STANDARDS

AGING EFFECTS ON LITHIUM-ION BATTERIES

WHY FAULT TREE ANALYSIS MATTERS

Several highly publicized fire, explosion and product recall incidents have raised concerns about the overall safety of lithium-ion batteries. There is an urgent need to understand the root causes of these incidents and to promote open cooperation between governmental research organizations, cell manufacturers, safety stakeholders and standards organizations to develop consensus-based updates to the safety standards. UL's innovative application of the Fault Tree Analysis methodology enhances our ability to identify and catalog the root causes of battery failures and to engage multiple organizations in dialogue to help improve battery safety.

There is an urgent need to understand the root causes of lithium-ion battery failures.

CONTEXT

Lithium-ion batteries are popular because they have several advantages relative to competing technologies: they generally have much higher energy density — the amount of energy they can store per kilogram of battery.[1] These batteries hold their charge, losing about 5 percent of their charge per month compared with a 20 percent loss per month for NiMH batteries,[2] and have no memory effect as other batteries do. This means that lithium-ion batteries do not have to be completely discharged before recharging.[3] These batteries can also last through hundreds of charge/discharge cycles.[4]

Lithium-ion batteries, however, are not flawless. There have been a number of failure incidents that have brought these batteries under intense governmental scrutiny.[5] These developments underscore the urgent need to understand the root causes and safety hazards associated with ISCs in lithium-ion cells and to update safety standards.

WHAT DID UL DO?

Given the importance of lithium-ion batteries to so many applications — from consumer electronics to transportation to stationary energy storage for energy utilities — UL has been conducting a broad range of research on different kinds of lithium-ion battery chemistries and formats. Specifically, we have been overseeing a variety of nondestructive analyses of lithium-ion batteries to understand structural elements and impedance, abuse tests to examine battery performance under "worst conditions," and material analyses to better understand how the different components and materials in lithium-ion batteries respond under various conditions.[6]

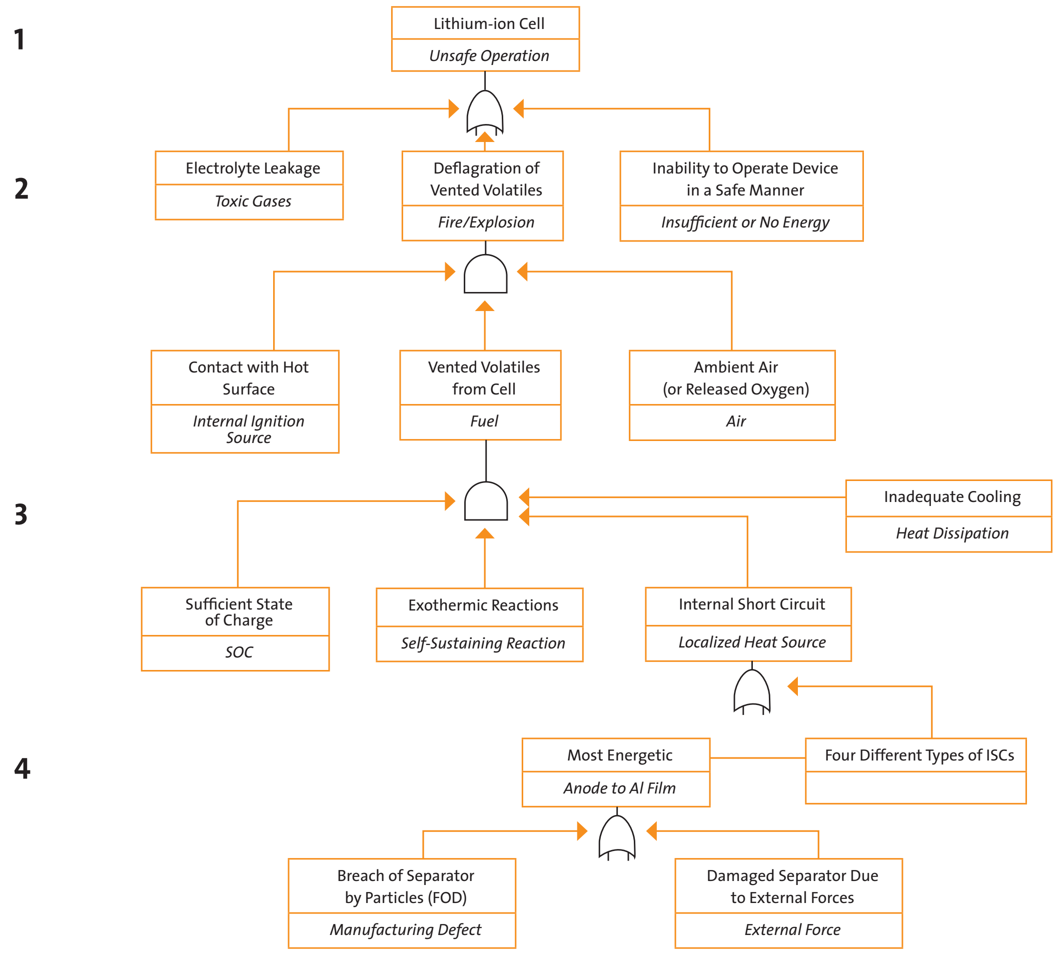
UL is also actively engaged in reviewing publicly available lithium-ion battery research, which shows a strong focus on understanding and mitigating cell failure modes involving internal short circuits (ISCs).[7] Although only brief accounts of field failures are available, a number have noted the presence of manufacturing defects that led to ISCs within the cell.[8] UL applied the Fault Tree Analysis methodology to the results of its battery safety research and field failure information to translate them into an accessible, logical format that identifies both the immediate and root causes of lithium-ion battery failures.

Fault Tree Analysis is a symbolic logic analytical technique in which an undesired event is defined — in this case, a lithium-ion battery failure incident. The event is resolved through research into its immediate causes. The resolution of events continues until the root causes are identified at the appropriate level. A logical diagram, called a fault tree, is constructed that shows the logical event relationships.[9]

Fault Tree Analysis is a disciplined approach that provides a framework for the rigorous examination of a fault event (e.g., a battery failure incident). By employing this methodology, UL explicitly shows all the different relationships that are necessary to result in battery failure and gains an in-depth understanding of the logic and root causes of the incident.[10]

A Fault Tree Analysis has been developed to understand the possible causes of lithium-ion cell failures with a focus on incidents involving fire and explosion. The analysis presented here is for demonstration purposes only. Because of this, it captures the main points and is not developed in great detail. We conduct much more detailed analyses depending on the specific product and failure conditions.

Fault Tree Analysis of a lithium-ion cell that has become unsafe[11]



This specific fault tree depicts the following causal event relationships and logic:

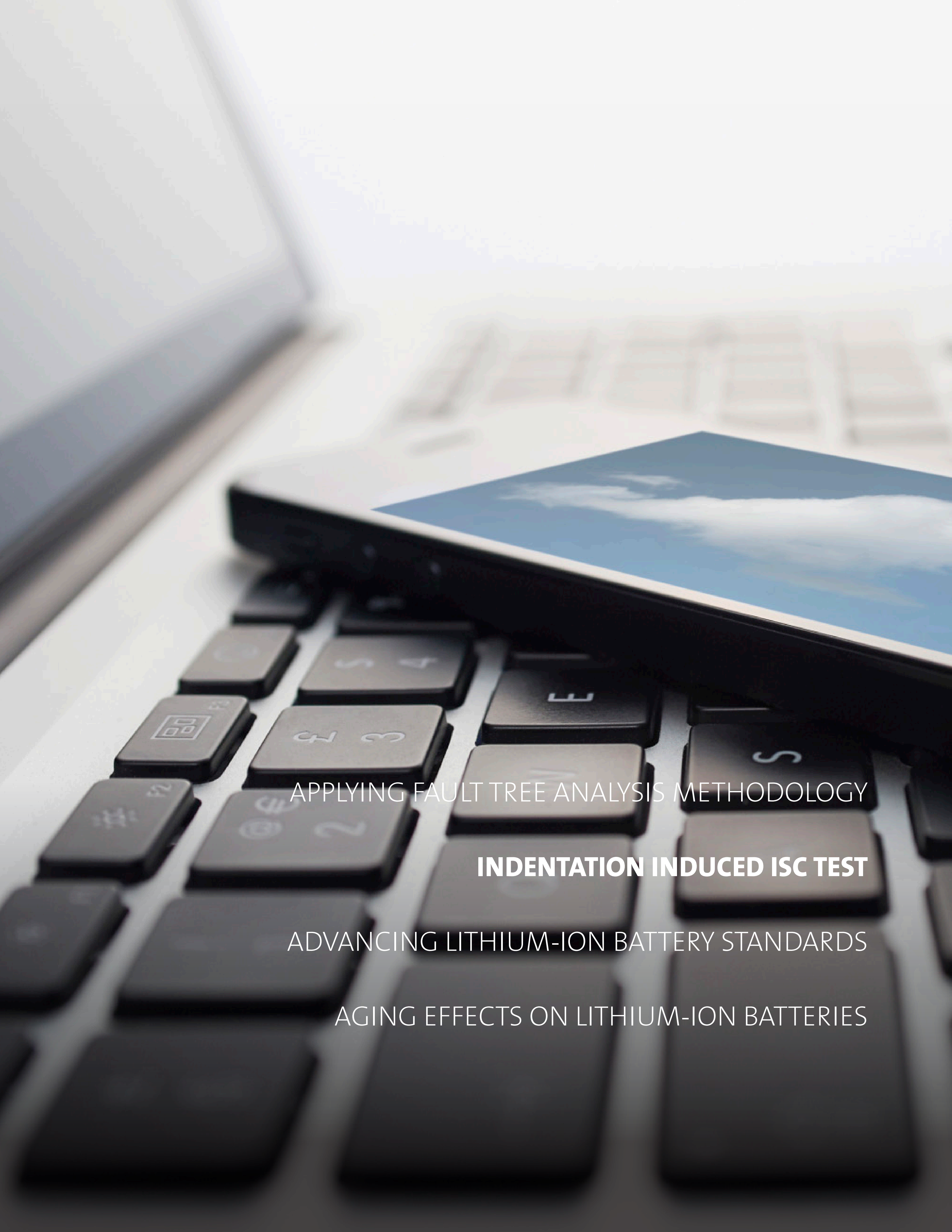
1. The principal event is the unsafe operation of the lithium-ion cell.
   - A few possible examples are an electrolyte leakage, which could release toxic gases, or the deflagration of vented volatiles, which could lead to fire/explosion or an inability to operate the safety-critical device that is powered by a lithium-ion cell.
2. Looking specifically at the hazard of deflagration of vented volatiles, three basic events are listed, which must ALL happen for a detonation to occur:
   - Ignition source: contact of the volatiles with a hot surface (or possibly the volatiles are already at a high temperature)
   - Fuel source: vented volatiles from the cell
   - Ambient air: oxygen needed to facilitate combustion (within the flammability limits)
3. Next, when the vented volatiles from the cell event are examined, four causal events are identified, each of which must occur for the volatiles to vent from the cell:
   - A sufficient state of charge of the cell (stored energy)
   - Exothermic reactions
   - An ISC to provide a pathway for charge flow that leads to a localized heat source
   - Inadequate cooling to provide sufficient heat dissipation

   When an ISC exists with a sufficient state of charge, then the charge flow results in localized heat generation. This will heat up the cell locally and possibly activate exothermic reactions among the active materials within the cell. If there is insufficient heat dissipation, then the heat generated by the exothermic reactions within the cell will feed back into the remaining materials that have not reacted, continuing the buildup of heat.
4. There are four different types of ISCs, and this fault tree focuses on the most energetic — anode to aluminum (Al) film (UL applies Fault Tree Analysis to the other ISC types as well) — and identifies two potential root causes of this type of ISC:
   - A breach of the separator by a particle, or foreign object damage, caused by a manufacturing defect
   - A damaged separator due to external forces

Our Fault Tree Analysis combines the results of several publicly available research studies and graphically depicts the causes and relationships between events that lead logically from a manufacturing defect or damage from an external force to the unsafe operation of a lithium-ion cell.

IMPACT

UL is constantly seeking to improve the safety of lithium-ion batteries. This requires a systematic approach, an in-depth understanding of lithium-ion battery field incidents, and a focused effort in research and standards development to address the root causes of these incidents. The innovative application of Fault Tree Analysis to lithium-ion battery failures is the New Science that adds an extra dimension of rigor to UL's approach. It provides a transparent and detailed record of the analysis into the causes of battery failures, which makes Fault Tree Analysis an effective tool to communicate and build consensus, both within UL and with our various research partners and safety stakeholders. Fault Tree Analysis also helps us identify what new research is indicated — to explore and validate new potential causes of battery failures, as suggested by other research findings or field incidents. Fault Tree Analysis is central to how UL helps ensure lithium-ion battery safety.



APPLYING FAULT TREE ANALYSIS METHODOLOGY

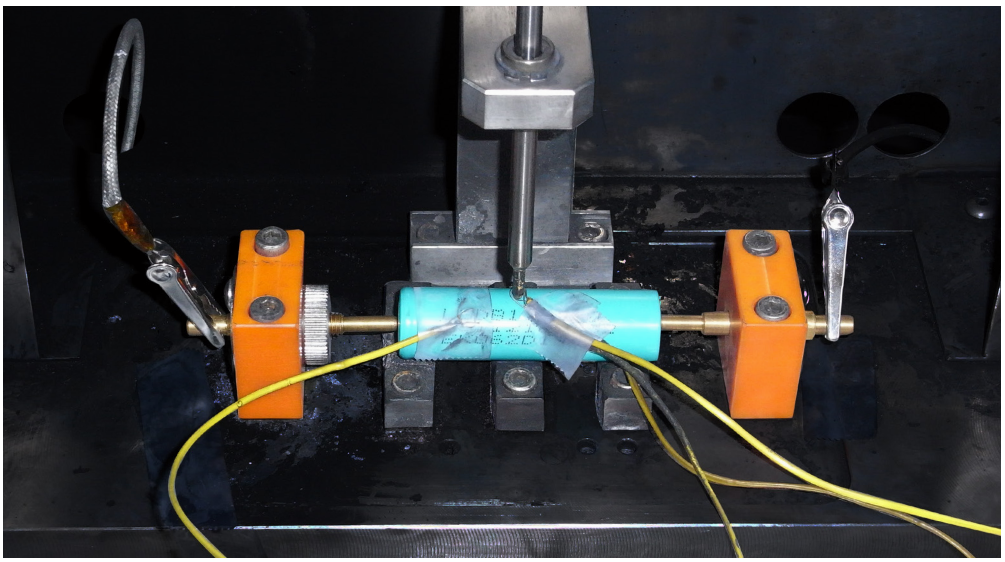
INDENTATION INDUCED ISC TEST

ADVANCING LITHIUM-ION BATTERY STANDARDS

AGING EFFECTS ON LITHIUM-ION BATTERIES

WHY THE INDENTATION INDUCED ISC TEST MATTERS

Driven largely by their long cycle lives, low self-discharge rates and high energy/power densities,[12] lithium-ion batteries are becoming an important sustainable energy technology. When considering reported incidents involving lithium-ion batteries, many cite internal short circuits (ISCs) as a possible intermediate cause for the overheating of the cell. Though other test methods exist to simulate ISCs in lithium-ion cells, the Indentation Induced ISC test was developed based on best-practice principles to provide a practical and simple method that is very suitable for battery safety standards. This test gives UL the ability to simulate how a lithium-ion cell behaves when subjected to an ISC condition, which will help mitigate the hazards of ISCs and support the safe commercialization of lithium-ion batteries.



UL developed the Indentation Induced ISC test to provide a practical and simple method for simulating ISCs in lithium-ion cells.

CONTEXT

The performance characteristics of lithium-ion batteries, coupled with the projected one-third decrease in their costs by 2017,[13] make them increasingly popular in a broad range of applications. For example, lithium-ion batteries now comprise in excess of 95 percent of mobile phone batteries worldwide.[14] Lithium-ion batteries are also used in a variety of consumer electrical and electronic devices (e.g., laptop computers, tablet computers and digital cameras), medical devices (e.g., patient monitors, handheld surgical tools and portable diagnostic equipment), industrial equipment (e.g., cordless power tools, wireless security systems and outdoor portable electronic equipment), automotive applications (e.g., electric vehicles), aerospace applications (e.g., aircraft and spacecraft), and energy (e.g., grid-connected electricity storage).[15]

Although lithium-ion batteries are designed with integrated passive safeguards and active safeguards for pack designs, these batteries have been involved in incidents involving overheating and fire that, while very rare, have put these batteries in the public spotlight.[16] In many cases, the battery failures were linked to ISCs that led to thermal runaway, resulting in the explosive release of energy along with fire. These incidents have provided an impetus for research aimed at understanding the causes of lithium-ion battery failures and guiding safer battery cell designs. The number of lithium-ion batteries in use, the complexity of the lithium-ion battery cells and the numerous usage conditions make the design of safe cells and the development of tests for battery safety standards extremely challenging.[17] These challenges underscore the need for a reliable ISC simulation method that helps improve product safety by ensuring that consensus-based battery safety standards effectively accommodate the rapidly changing state of lithium-ion cell design and applications.

WHAT DID UL DO?

UL invested research resources and collaborated with other organizations with the goal of developing a reliable and repeatable testing methodology that met two key criteria. First, the test needed to be able to generate a localized ISC within a closed cell that would simulate the conditions similar to those found in the field failures of lithium-ion batteries. Second, the new test needed to be acceptable for battery safety standards.

Our research resulted in the development of the innovative Indentation Induced ISC test. After demonstrating the potential of this testing method, we partnered with NASA and Oak Ridge National Laboratories (ORNL) to further develop the test approach. NASA already had its own ISC test method, but seeing the advances made in the UL test method, it adopted and fine-tuned the Indentation Induced ISC approach. This method is now part of NASA's battery qualification process for space applications. Next, UL collaborated with ORNL to extend the test setup to cover a variety of form factors.

The Indentation Induced ISC test is appropriate for cylindrical cells and other form factors, such as pouch and prismatic cells, with some variations in setup. In the test setup, the cell is placed in a holder that prevents its rotation or translation. An indenter with a smooth profile presses from above against the cell casing at a constant speed (0.01 – 0.1 mm/s). Test measurements include temperature of the casing surface at a point near the indentation site, distance traveled by the indenter (amount of cell casing deflection), applied force through the indenter and open circuit voltage. The cells can be at different states of charge (SOC) or stages of aging. The entire setup is placed in a chamber that allows for control of ambient temperature.[18]

As the indenter presses against the casing, layers of separator, anode and cathode immediately below the indentation region are deformed due to localized high curvature (Figure 1). The resulting high stress/strain will lead to a mechanical failure of the separator (with failure of the casing), allowing for direct contact between electrodes at a distance only a few layers below the casing surface (Figure 2).
The effect of the separator failure is a sudden alternate pathway for charge flow and a subsequent drop in the open circuit voltage (OCV) (Figure 3). For some cells, seconds after a measured drop in the open circuit voltage (100mV), there is a rapid increase in cell surface temperature (as high as 700°C) with an outcome involving explosive release of gases and generation of flames (Figure 4).[19]

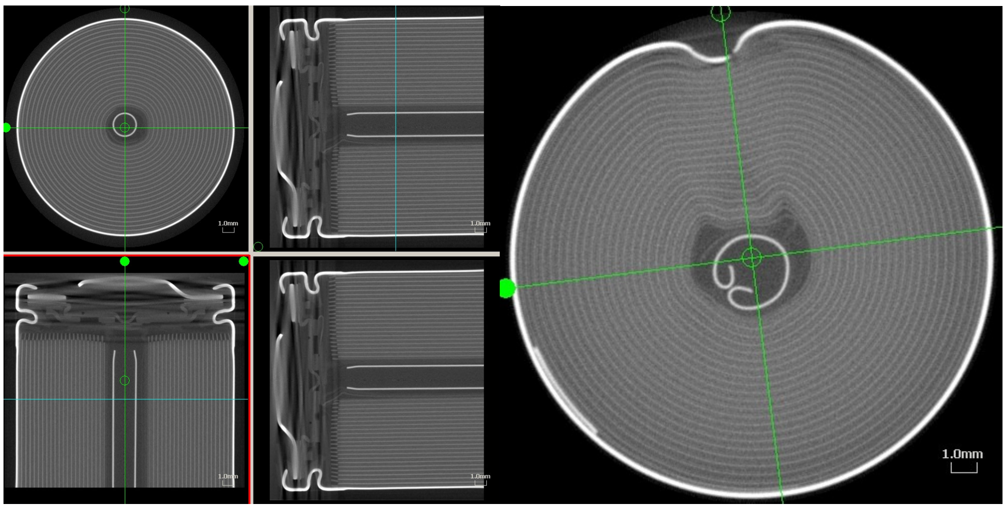


Figure 1 CT scan images of cylindrical lithium-ion cell prior to testing (left) and single CT scan image of cell after indentation (right)

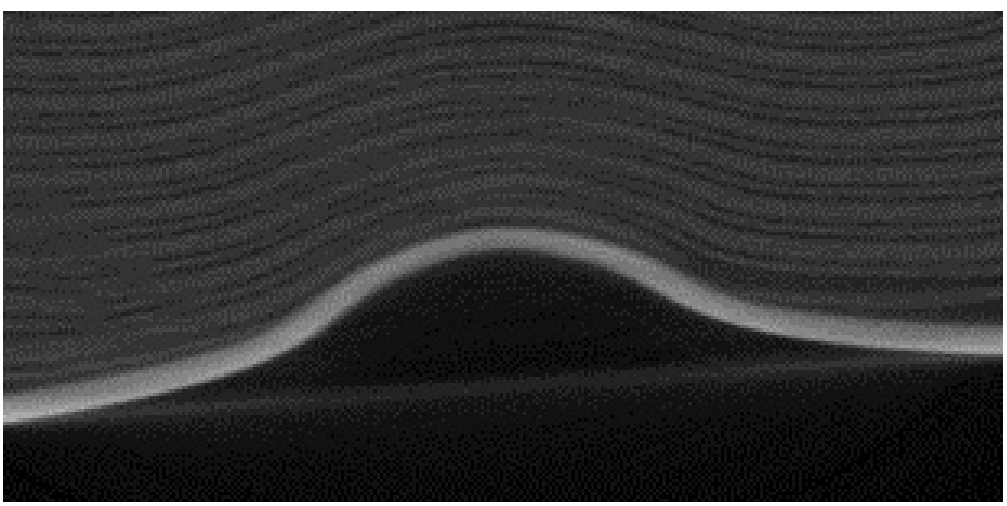


Figure 2 CT scan image of cell showing breakdown of layers directly below indentation region

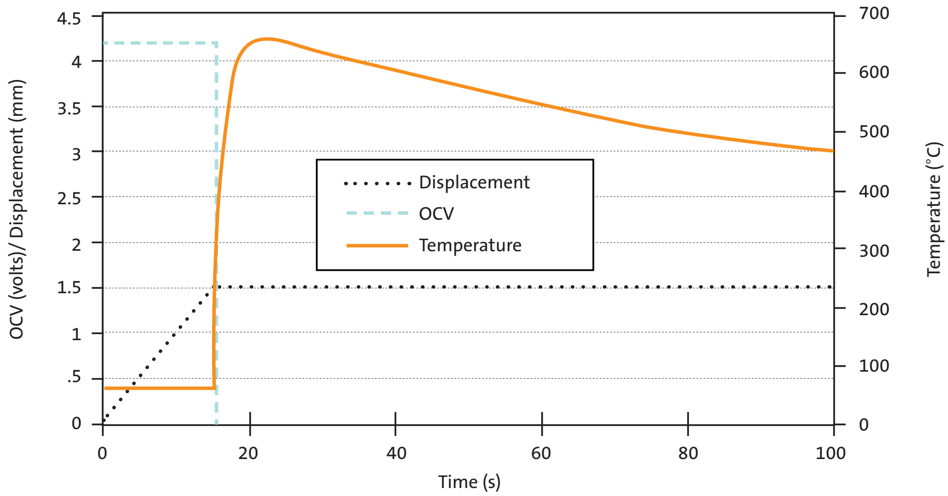


Figure 3 Measurements taken during the indentation test for a cell that is undergoing thermal runaway

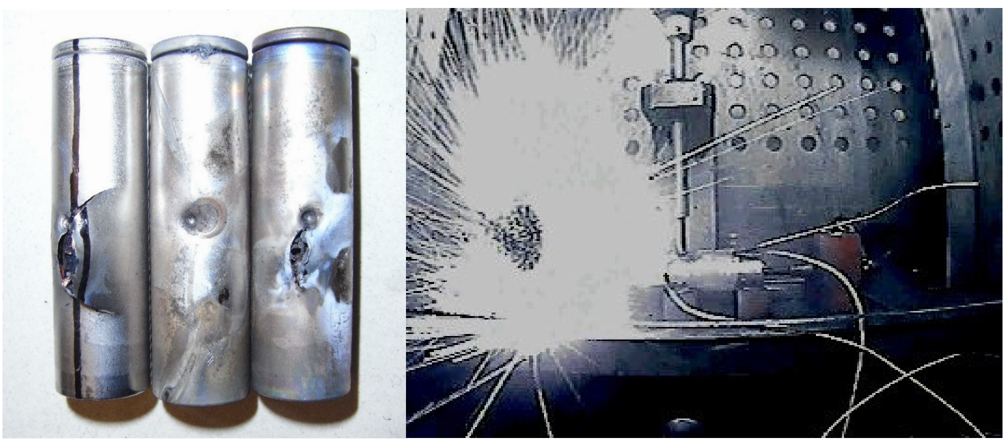


Figure 4 Picture of cells experiencing thermal runaway (left) and one example of explosive failure of lithium-ion cell during indentation test (right)

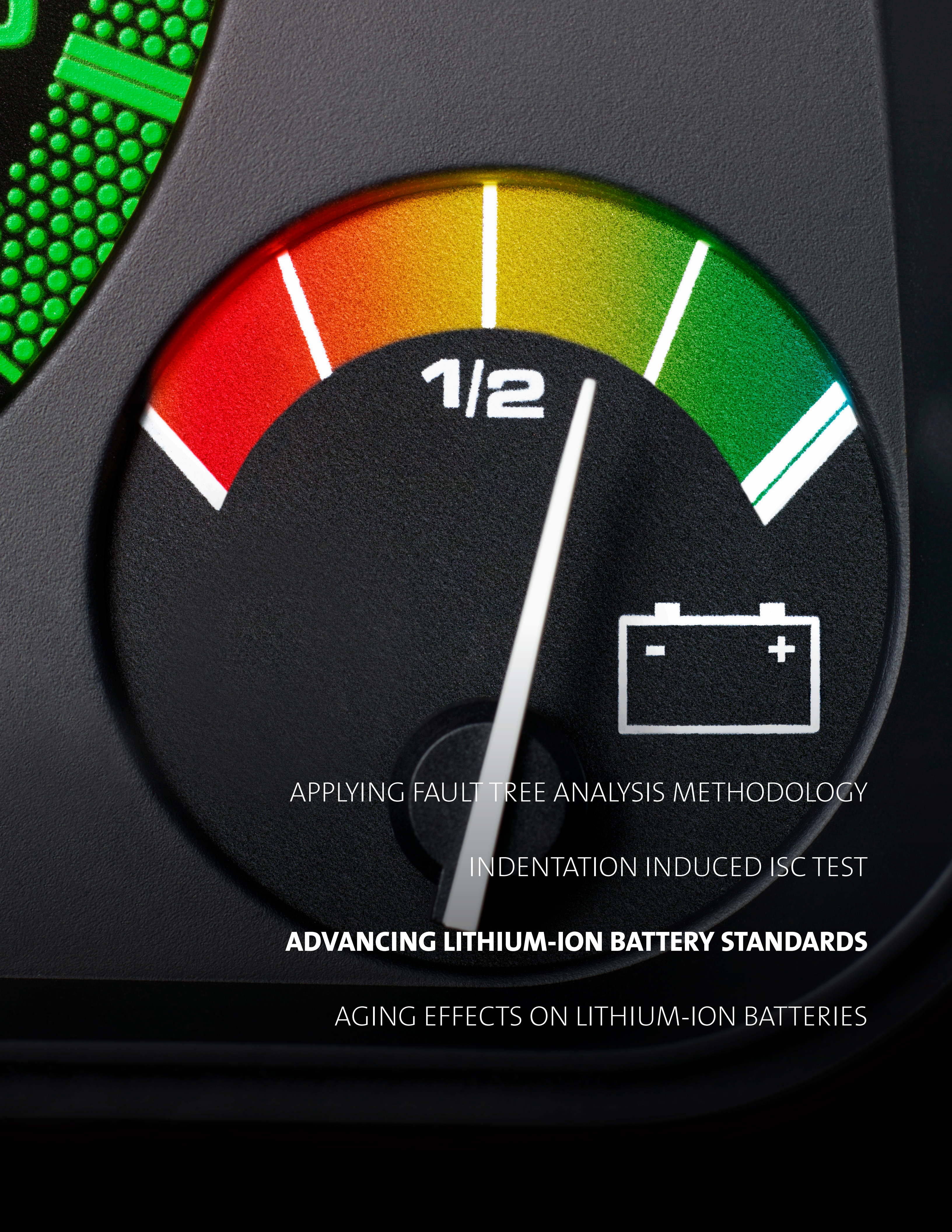
Risk is typically measured in terms of the severity of failure multiplied by the probability of failure. In forcing a failure, the Indentation Induced ISC test is basically measuring the severity of cell failure. As noted above, NASA uses this technique in its screening of commercial off-the-shelf (COTS) rechargeable batteries for space applications. Cells that do not perform well under this type of test would then be subjected to a more stringent secondary testing schedule to help establish the probability of ISC cell failure.[20]

Today, UL is developing tests and standards for applications involving cell safety through battery system safety. The focus is on refining large-format lithium-ion battery standards (UL 2580 for electric vehicles, UL 2271 for light electric vehicles and UL 1973 for light electric rail and stationary applications — for more information, please refer to the third article in this journal, "Advancing Lithium-ion Battery Standards"), revising cell requirements to address specific applications, verifying cell operating regions, ensuring that battery systems maintain safe cell operating regions, and exploring system failure mode effects analysis (FMEA) and functional safety.[21]

IMPACT

Research at UL, along with collaborations with well-known battery safety research laboratories, has resulted in the development of the Indentation Induced ISC test. This testing approach shows promise as a candidate for battery safety standards, most likely as a screening test. To date, analysis of results from cells subjected to the Indentation Induced ISC test shows a correlation between test performance (observed severity of failure) and a variety of cell parameters, including energy density, thermal stability of active materials and cell chemistry.[22]

With recalls and other safety issues related to lithium-ion batteries still making headlines, there is a heightened need for the kind of open and cooperative dialogue UL and other key stakeholders are engaging in to share information on the failure modes of lithium-ion cells and to help develop and refine ISC tests for consensus-based safety standards.[23] We are committed to evolving standards to help drive the safe use of lithium-ion batteries as their applications expand to more and more industries and products. As the leading organization for lithium-ion battery safety testing, UL is focused on the full range of battery chemistries and designs, including different materials, component-level characterization at the cell level and highly integrated battery systems. We will continue to dedicate significant resources to battery safety research and will continue to actively improve existing standards and develop new ones.



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WHY ADVANCING LITHIUM-ION BATTERY STANDARDS MATTERS

The use of lithium-ion batteries is on the rise, with the market expected to double globally by 2016.[24] With new uses and potential safety hazards, it is therefore important to update existing standards and create new ones as our information and knowledge increase. In this way, we can maximize the safety of lithium-ion batteries as well as safeguard the adoption of new applications and uses of these batteries.

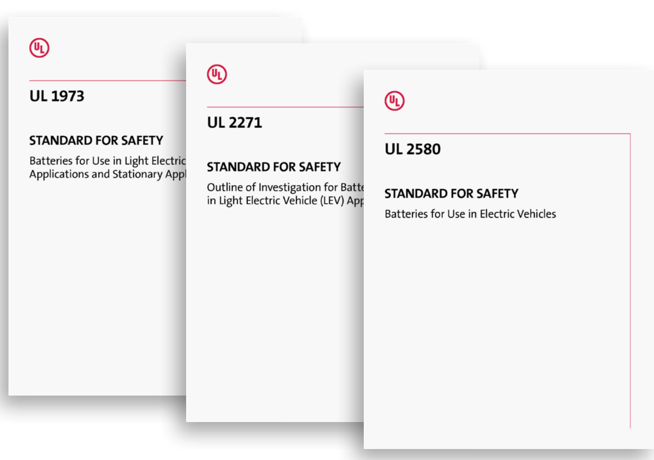
CONTEXT

In recent years there have been reports of field failures involving lithium-ion batteries. These range from failures in 2006 of laptops powered by lithium-ion batteries to cargo plane fires involving bulk transport of lithium-ion cells.[25] Since March 2012, the Consumer Product Safety Commission documented 467 reported incidents that identified lithium-ion cells as the battery type involved, with 353 of those being incidents involving fire/burn hazards.[26] Further, in 2013 there were two reported incidents related to lithium-ion batteries employed in the Boeing 787 aircraft, in which flames were seen coming from an auxiliary power unit (APU) battery and/or odd smells were detected in the cockpit and cabin.[27]

Dangers related to lithium-ion batteries include fire, explosion, electric shock and hazardous material exposure.

Dangers related to lithium-ion batteries include fire, explosion, electric shock and hazardous material exposure (vented toxic gases, leaked electrolytes).

With the electric vehicle market aggressively growing, the worldwide capacity for lithium-ion batteries for this mode of transportation will multiply tenfold by 2020.[28] UL — along with various other industry stakeholders, including manufacturers and industry associations — has been prioritizing the updating of existing standards and advancing the creation of new standards.



WHAT DID UL DO?

The Standards Today

UL 1642 covers secondary (rechargeable) lithium-ion cells and primary (non-rechargeable) cells and batteries. Lithium primary cells have metallic lithium or lithium alloy anodes. Lithium-ion cells do not contain metallic lithium and typically have lithiated graphite at the negative electrode and a lithium metal oxide or phosphate at the positive electrode. Batteries may consist of a single cell or two or more cells connected in series or parallel — both with and without protection and control circuitry. UL 1642 includes the following tests: short circuit, abnormal charging, forced discharge, vibration, shock, crush, cell impact, temperature cycling, heating, altitude simulation and projectile/fire exposure.

Battery safety standards[30]

TEST	CERTIFICATION					SELF DECLARATION								
	UL 1642	UL 2054	UL SUBJECT 2271	UL 2580	UL 1973	IEC 62133	IEC 62281*	NEMA c18.2 M, Pt2	SAE J2929	UN Pt.III, S 38.3	IEEE 1625*	IEEE 1725*	JIS C8714*	SBA S1101*
External short circuit	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Abnormal charge and overcharge	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Forced discharge & overcharge	x	x	x	x	x	x	x	x	x	x				x
Crush	x		x	x	x	x	x	x	x	x			x	
Impact	x						x	x		x				x
Shock	x		x	x	x	x	x	x	x	x				
Vibration	x		x	x	x	x	x	x	x	x				
Heating	x					x		x			x	x	x	
Temperature cycling	x		x	x	x	x	x	x	x	x				
Low pressure	x					x	x	x		x				
Projectile and external fire	x			x	x						x	x		
Drop		x	x	x	x	x		x	x		x	x	x	x
Continuous low-rate charging						x								
Molded casing heating test		x	x	x	x	x		x						
Insulation resistance			x	x		x			x	x				
Internal short circuit or internal fire test	in progress			x	x	x							x	x

*Note: These are certification-related standards.

UL 2054 covers secondary (rechargeable) and primary (non-rechargeable) cells (chemistries include nickel [Ni-Cad, Ni-MH], alkaline, carbon zinc and lead acid) for portable applications. It also covers battery packs for portable applications and for all types of cells, including lithium-ion and lithium primary. UL 2054 includes short circuit, abnormal charging, abusive overcharge, forced discharge, limited power source, battery pack component temperature, battery pack surface temperature, 250 N steady force, mold stress relief and drop impact. UL 2054 also requires the lithium-ion cells to comply with UL 1642.[29]

At the cell level, UL is working on developing a new internal short circuit (ISC) test method for inclusion into UL 1642.

What's Changing

At the cell level, UL is working on developing a new internal short circuit (ISC) test method for lithium-ion cells for inclusion in the lithium battery safety standard UL 1642. The test, which is referred to as an "indentation induced internal short circuit" (IIISC) test:

- Causes an ISC by creating a small localized defect in the cell separator (limited to only the surface layer of the electrode)
- Induces failure of the cell for cylindrical, prismatic and pouch format cells
- Is sensitive to design changes that affect the cell safety performance
- Is a method suitable for standards testing[31]

There are also improvements to ongoing product criteria and quality requirements.[32] At the cell level, UL 1642 now includes the cell safe operating region parameter requirements for lithium-ion cells, and UL 2054 now includes requirements that the battery pack maintain cells within the cell safe operating region parameters.

There is also greater attention to application-specific design challenges, abuse conditions and improvements to the certification process.[33]

Large-format Focused Standards

In addition to updates to UL 1642/UL 2054, UL is working on large-format focused standards, including UL 2271 and revisions to UL 2580 and UL 1973, given the growing global market needs. When UL 2271 is published, all three will be American National Standards Institute (ANSI) standards.

UL 2580 covers safety (electric shock, mechanical hazards, toxic and combustible releases) of electrical energy storage assemblies (EESAs) for on-road vehicles and industrial off-road vehicles. The standard is not chemistry-specific and includes batteries, electrochemical capacitors, and hybrid combinations of batteries and electrochemical capacitors. The standard also includes safety requirements for cells and electrochemical capacitors used in the EESAs.

A safety analysis of electric energy storage assemblies such as a failure mode and effects analysis (FMEA) is required as well as specific construction requirements and tests, including electrical, mechanical, environmental and production tests.[34]

The UL 2580 test program includes short circuit, overcharge, overdischarge, humidity/isolation resistance, thermal control failure, temperature cycling, drop, vibration endurance, mechanical shock, rotation, crush, immersion, fire exposure, temperature and imbalanced charge tests.[35]

UL 2271 covers batteries, electrochemical capacitors and hybrid EESAs for use in light electric vehicles (LEVs). Heavy-duty industrial trucks are outside the scope of this standard (their EESAs are covered under UL 2580, above). Construction criteria are similar to UL 2580 with some exceptions, including:

- Enclosure relative thermal index (RTI) minimum of 80°C
- IP3X accessibility (tool as persons may be more exposed to these EESAs compared with UL 2580 types)
- Battery more apt to be user-removable for charging or replacement and may have handles
- Cell criteria same as proposed for UL 2580

For all of these standards, UL is including cell safety requirements to address a variety of emerging needs.

The test program for UL 2271 has some differences from UL 2580 due to application and includes the following:[36] short circuit, overcharge, overdischarge, humidity/isolation resistance, thermal control failure, temperature cycling, vibration, drop, mechanical shock, rotation, crush, immersion, temperature and imbalanced charge tests.[37]

UL 1973 covers electric energy storage systems (EESSs) for stationary applications such as photovoltaic (PV), wind turbine storage or uninterruptable power supply (UPS) applications. UL 1973 also covers EESSs for use in light electric rail (LER) applications and stationary rail applications. As with UL 2580 and UL 2271, UL 1973 includes construction criteria and tests.[38]

UL 1973 includes short circuit, overcharge, overdischarge, imbalance charge, dielectric voltage withstand, continuity, temperature, failure of thermal stability system, temperature cycling, vibration endurance, shock, drop, enclosure, water exposure, and external fire and internal fire tests.[39]

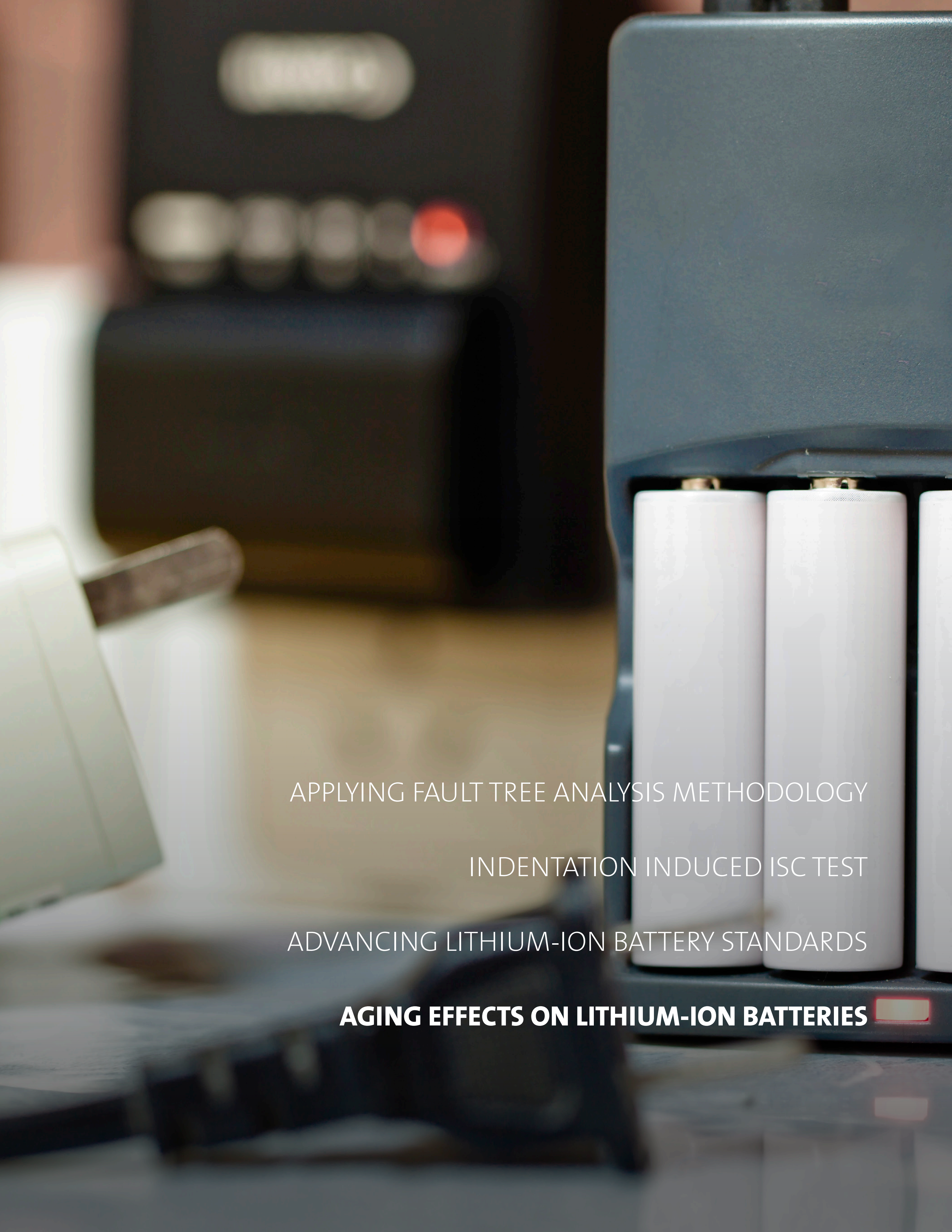
Updates to lithium-ion battery safety standards

STANDARD/ SCOPE	WHAT'S CHANGING	REGULATORY ENVIRONMENT
UL 1642 Primary and secondary lithium cells	New internal short circuit (ISC) test method under development Ongoing improvements to product criteria and certification requirements Cell safe operation region parameter requirements for lithium-ion battery cells	Voluntary
UL 2054 Household and commercial batteries, includes lithium batteries, portable applications	Requirements that battery packs maintain cells within the cell safe operating region parameters	Voluntary
UL 2580 EESAs for on road vehicles and off road industrial vehicles	Revising cell requirements to address specific applications Verifying cell operation region Ensuring system maintain cell operating region System failure mode and effects analysis/Functional Safety Ongoing improvements to testing protocols	Voluntary (NFPA 505)
UL 2271 EESAs for light electric vehicle (LEV) applications	Revising cell requirements to address specific applications Verifying cell operation region Ensuring system maintain cell operating region System failure mode and effects analysis/Functional Safety Ongoing improvements to testing protocols	Voluntary
UL 1973 EESAs for stationary and light electric rail applications	Revising cell requirements to address specific applications Verifying cell operation region Ensuring system maintain cell operating region System failure mode and effects analysis/Functional Safety Ongoing improvements to testing protocols	Voluntary, NEC and other installation codes

For all the above standards, UL is including cell safety requirements to address specific applications, verify cell operating regions, help ensure that systems maintain cell operation region, require a system FMEA and, if necessary, evaluate functional safety.[40]

IMPACT

UL is continuing to advance safety by developing updates to existing standards and creating new standards when information, research and consensus are complete. These standards and UL's leading role comprise the New Science that is spearheading the important role lithium-ion batteries play today and in the future, while helping ensure their safe continued use, adoption and expansion.



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WHY STUDYING AGING EFFECTS ON LITHIUM-ION BATTERY SAFETY MATTERS

Today, lithium-ion batteries are increasingly being used for longer periods. Many lithium-ion cells are recycled and reused, while others are used in applications — such as electric vehicles and stationary energy storage — with an expected battery life ranging from five to 20 years. These longer-term uses are important because field failures of lithium-ion batteries, though rare, are highly publicized and suggest that some failure mechanisms may be dependent on how the state of the lithium-ion cell changes over time. Equally important is the fact that current safety standards do not address the potential impact of battery aging.

CONTEXT

Some of the most common and well-known uses of lithium-ion batteries are in consumer electronics, where the expected battery life — whether for a single-cell pack in a cellphone or a six- to 12-cell pack in a laptop computer — is one to three years.[41] In contrast, batteries used in electric vehicles (EVs) and hybrid electric vehicles (HEVs) are expected to have a five- to 15-year battery life, while those used in stationary energy storage applications are expected to have a 10- to 20-year life.[42] In addition, while lithium-ion battery recycling is still in its infancy, the market is projected to grow to $2 billion by 2022.[43] This translates to approximately 10 percent of the 2022 lithium-ion battery market. And now emerging are "second life" uses of lithium-ion batteries, typically from EVs or HEVs. The automobile industry generally defines "end of life" as the point in time when a lithium-ion battery has lost 20 percent of its original energy storage capacity or 25 percent of its peak power capacity — a milestone that is typically reached at 200,000 miles or 2,000 charging cycles.[44] Second-life applications include resale of the highest-quality used lithium-ion batteries for EVs and HEVs, particularly those used in urban areas, and for stationary energy storage in grid applications, either repacked into larger installations (at the megawatt level) or simply used as they are.[45] Whether in first or second life in EVs or stationary energy storage, lithium-ion batteries are being used for longer periods and over more cycles than ever before.

Lithium-ion batteries are increasingly used for longer periods due to recycling, reuse or applications with longer expected battery lives.

A common belief about lithium-ion batteries is that they become more safe over time, primarily because aging tends to degrade performance with batteries losing some of their energy storage capacity as well as some of their efficiency in discharging energy. It would seem to make sense that a battery with less energy stored and a more limited ability to discharge that energy would be a lower risk and that over time the potential severity of failures would decrease. A contrary hypothesis about lithium-ion batteries is that the degradation of lithium-ion battery materials through aging would give the batteries a higher risk of failure.

The safety of lithium-ion batteries encompasses both the frequency and severity of failure. Given the trend toward longer lithium-ion battery usage and reuse cycles, UL believed that the effects of aging on lithium-ion battery safety should be studied to understand how aging mechanisms affect battery failure.

WHAT DID UL DO?

UL developed a first-stage research study to understand what was suggested in the field failures. The initial research focused on one commonly used lithium-ion cell type: the 18650-type lithium-ion battery with a lithium cobalt oxide (LiCoOx) chemistry and 2,800 milliamp hours (mAh) energy storage capacity.[46] The plan was to conduct tests on the batteries at 25°C and 45°C over 50, 100, 200, 300, 350 and 400 charging cycles. The research included nondestructive analysis, abuse tests and material analysis to investigate the potential correlation between the mechanism of aging on materials and a cell's tolerance of abuse conditions.[47]

UL aging effects research[48]

TECHNIQUE		PURPOSE
Material Analysis	Scanning Electron Microscope (SEM)	Observe the change of morphology of electrode surface, such as particle size, distribution of active material, binder, conductive carbon, coating layer, thickness, etc.
	Energy Dispersive X-ray (EDX)	Analyze the elements of battery materials (electrodes, separator) to obtain the composition change of battery materials
	X-ray Diffraction (XRD)	Observe the crystal structural change of electrode
	Fourier Transform Infrared (FTIR)	Analyze the surface chemistry, mainly SEI layer, of electrode
	Differential Scanning Calorimetry (DSC)	Evaluate the change of thermal stability of the electrode materials
	Raman Spectroscopy	Observe the structural change of electrode materials
	X-ray Photoelectron Spectroscopy (XPS)	Analyze the surface chemistry, mainly SEI layer, of electrode
	Pyrolysis Gas Chromatography/ Mass Spectroscopy (GC/MS)	Analyze the thermal decomposition mechanism for active materials
Nondestructive Test	Electrochemical Impedance Spectroscopy (EIS)	Analyze the internal resistance change
	Computed Tomography (CT) Scan	Investigate the internal physical structure, such as valve, electrode packing and alignment
Abnormal Test	Indentation Induced Internal Short Circuit (IIISC)	Evaluate the battery behaviors when localized internal short circuit occurs
	Vibration	Evaluate the behavior of the battery upon vibration after charging/ discharging cycles
	Hot Box	Evaluate thermal stability of battery
	Overcharge	Evaluate the battery behavior under overcharging condition

Our innovative research into the effects of aging on lithium-ion batteries identified two critical safety concerns.

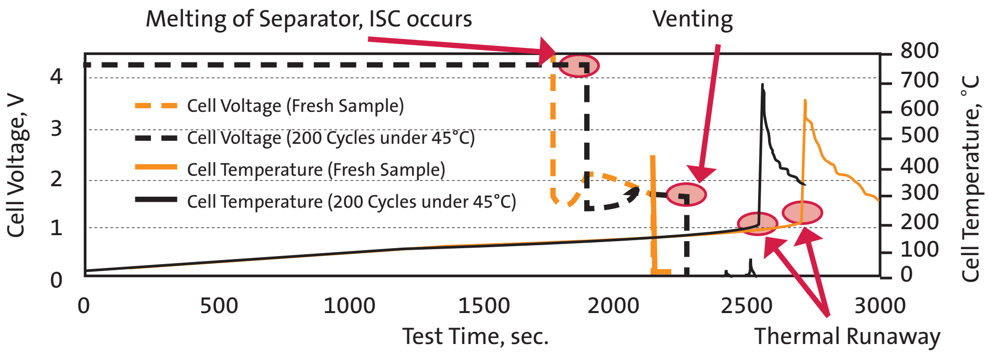
The first safety concern is the polarization effect on aged batteries, which can be detected from temperature and cell voltage profiles during overcharging. When polarization occurs in a battery, a higher voltage plateau can usually be observed under charging, while a lower voltage plateau can be observed under discharging. Further, an increased thermal effect, which is also a potential safety concern, results from the increased cell impedance and the decay of charging and discharging efficiency.

An increased thermal effect can also lead to a greater risk of side chemical reactions that are unfavorable to the safety performance of a lithium-ion battery. For example, the solid electrolyte interface (SEI) usually works as the protective layer to prevent the electrolyte material from further interaction with the electrode in a lithium-ion cell.[49] However, SEI is thermally unstable and can decompose at 60°C in some specific situations.[50] And the failure of SEI may become the root cause that eventually leads to a catastrophic thermal runaway.[51]

Another critical safety concern that our research identified is the thermal stability of active materials in aged batteries. Based on the result of the "hot box" test, thermal runaway was triggered earlier in aged samples. In aged cells, separator melting and venting were delayed when compared with that of a fresh cell during the test. Data from a differential scanning calorimeter suggests that heat-generating reactions with the cells occur earlier for an aged cell.[52]

The cell aged for 400 cycles shows a much more violent explosion than cells aged for less than 300 cycles.

Hot Box Test on fresh and aged 18650-type lithium-ion cells [53]



The results of electrochemical impedance spectroscopy and material analysis provide both indirect and direct evidence that the bulk composition of active materials does not change in aged cells. Instead, the composition and crystalline structure in the interfaces of active materials show significant changes in aged cells versus fresh cells. The implication here is that the aging effect primarily occurs near the surface region of active materials in the tested cells, which is also the region where the process of ion exchange occurs.

IMPACT

UL's research to assess the effects of aging on lithium-ion battery safety is still in its early stages. However, based on the results to date, we are expanding our research program. In order to establish more general results, the research will move beyond the single chemistry studied so far into other common cell chemistries, such as NMC (lithium nickel manganese cobalt oxide) and LFP (lithium iron phosphate).[54] The research will also be extended over more cycles and conducted on large-format lithium-ion battery systems such as those used in electric vehicles and stationary energy storage applications. Once the full impact of aging on lithium-ion battery safety is determined, UL will update the relevant safety standards to reflect the findings and to help ensure the safe use of lithium-ion batteries over time and across applications.

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