Evaluation of Batteries for Safe Air Transport

Nicholas Williard 1,*, Christopher Hendricks 2, Bhanu Sood 2, Jae Sik Chung 3 and Michael Pecht 2

1 Schlumberger, Houston, TX 77004, USA
2 Center for Advanced Life Cycle Engineering, University of Maryland, College Park, MD 20742, USA; chendri1@calce.umd.edu (C.H.); bpsood@umd.edu (B.S.); pecht@calce.umd.edu (M.P.)
3 PCTEST Engineering Laboratory, Inc., Columbia, MD 21046, USA; anto@pctestlab.com

* Correspondence: nwilliard@slb.com; Tel.: +1-443-854-8444

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Abstract: Lithium-ion batteries are shipped worldwide with many limitations implemented to ensure safety and to prevent loss of cargo. Many of the transportation guidelines focus on new batteries; however, the shipment requirements for used or degraded batteries are less clear. Current international regulations regarding the air transport of lithium-ion batteries are critically reviewed. The pre-shipping tests are outlined and evaluated to assess their ability to fully mitigate risks during battery transport. In particular, the guidelines for shipping second-use batteries are considered. Because the electrochemical state of previously used batteries is inherently different from that of new batteries, additional considerations must be made to evaluate these types of cells. Additional tests are suggested that evaluate the risks of second-use batteries, which may or may not contain incipient faults.

Keywords: batteries; standards; transportation; public safety; aviation

1. Introduction

The shipment of lithium-ion batteries poses serious safety concerns especially during air travel. A short circuit in a single cell is capable of creating enough heat to result in cascading failures of adjacent batteries, leading to a catastrophic incident. While lithium-ion batteries are generally protected by redundant safety features and controlled by a battery management system (BMS) that prevents operation at excessive voltages and temperatures during use, the same protection is not practically implemented during transportation of lithium-ion cells. This is problematic when large quantities of batteries are shipped. Additionally, the increased use of lithium-ion batteries across many industries has resulted in the need for transporting degraded batteries for recycling or second-use applications. However, the risks associated with batteries that have prior usage histories are not well known, and the current regulatory requirements regarding second-use batteries are vague.

Safety concerns over the shipment of lithium-ion batteries were highlighted after a United Parcel Service cargo plane carrying a significant number of lithium-metal and lithium-ion batteries crashed in Dubai in September 2010. In July 2013, the United Arab Emirates General Civil Aviation Authority published its final report on the incident and concluded that flaming electrolyte from ruptured lithium cells resulted in the spread and sustainment of the fire [1]. In response to the questionable safety of lithium-ion batteries as cargo, the International Civil Aviation Organization (ICAO), a United Nations special agency, made several updates to their 2013–2014 Technical Instructions for the Safe Transport of Dangerous Goods by Air (Doc 9284) regarding the transport of batteries [2]. As large-format lithium-ion batteries were already under strict regulation, the changes in the document mainly addressed smaller battery types of less than 20 Watt-hours (Wh) per cell.
This paper provides a review of the current international regulations governing the shipment of lithium-ion batteries by air. The shipment of both new and degraded batteries is considered.

2. Current Regulations

The regulatory agency responsible for setting guidelines for the transport of lithium and lithium-ion batteries is the ICAO which is a United Nations (UN) special agency. This body works closely with the International Air Transportation Association (IATA), a trade association that represents 240 airlines. The ICAO’s practices regarding lithium-ion battery transportation have been adopted by all 191 member states including the U.S. Federal Aviation Administration (FAA) and the Civil Aviation Administration of China (CAAC). The five countries who have not yet adopted ICAO guidelines are Anguilla, Aruba, Bermuda, Christmas Island, and Turks and Caicos Islands. In 2014, the ICAO launched the “no country left behind” initiative to reach out to those countries that have not yet adopted the standards and to encourage consistent implementation of ICAO across all of its member states. The documents outlining the provisions for lithium and lithium-ion battery transport are the ICAO’s Technical Instructions for the Safe Transport of Dangerous Goods by Air [2] and the IATA’s Dangerous Goods Regulations [3].

Different classifications have been designated for lithium-ion cells and batteries transported individually (listed under UN 3480 in the UN regulations for Transportation of Dangerous Goods [2]) as opposed to cells and batteries transported inside a piece of equipment (UN 3481). A lithium-ion cell is defined as a single electrochemical unit consisting of an anode and a cathode inside a single encasing which exhibits a voltage differential across its two terminals. Lithium-ion batteries consist of multiple cells wired in series or parallel. In some cases, transport regulations for cells and batteries are slightly different. For lithium-ion batteries or cells transported individually, short-circuit protection is required. An external short circuit occurs when there is a low-resistance electrical connection between the negative and positive terminals of a battery. This condition can lead to rapid discharge and self-heating. When cells are transported individually, an electrically isolating material must be placed on the cell terminals to prevent a short circuit. This requirement can be fulfilled simply by sliding fitted plastic covers over each of the terminals, but cells may also be supplied with a short circuit protection circuit to break connection of the anode and the cathode if the discharge current exceeds a certain threshold.

When shipping multiple batteries or cells in bulk, each unit must be completely separated by a barrier and then placed in a “strong rigid outer packaging,” however, further specifications on the type of packaging that should be used are not provided and very often are decided by the shipper of the batteries. This can be a problem when the requirements are interpreted differently by shippers. The total package must be subjected to and pass a 1.2 m drop test and cannot weigh more than 10 kg. The package must contain documentation, including a shipper’s declaration that states “Dangerous Goods as per Attached Dangerous Goods Declaration (DGD)” or “Dangerous Goods as per Attached Shipper’s Declaration.” An additional document must be included that states:

“Package contains lithium-ion cells or batteries. Handle with care. When package is damaged can cause fire. Special procedures should be followed: inspect the package and arrange repack by qualified persons when required. Contact Nr: 00XX XXXX XXX XXX.”

The final package must include the label shown in Figure 1, with minimum dimensions of 120 mm wide and 110 mm high.
For cells or batteries shipped inside a device, external short-circuit protection is also required. The short-circuit protection of batteries in a device is described in special provision A164 [2] as “disconnection of the battery and protection of exposed terminals.” Any additional cells that may be included as spares should be individually wrapped. The specifications of the wrapping are not provided. The device must then be placed in an outer packaging, however, the UN provides no specifications for this packaging. The maximum number of cells or batteries per package is the number of cells required to power the device as well as two spare cells or batteries. The maximum weight of lithium-ion cells or batteries per package must not exceed 5 kg for passenger aircraft but may be up to 35 kg for cargo aircraft for cells greater than 20 Wh and batteries greater than 100 Wh. For documentation, the following statement must be placed on the waybill:

“Lithium ion Batteries in compliance with Section II of PI966.”

An additional document must be included that says:

“Package contains lithium ion cells or batteries. Handle with care. When package is damaged can cause fire. Special procedures should be followed: inspect the package and arrange repack by qualified persons when required. Contact Nr: 00XX XXXX XXX XXX.”

Manufacturers must certify that all cells or batteries that are shipped have been manufactured under a quality management program as specified in the Dangerous Goods Regulations (DGR) 3.9.2.6. Additionally, all cells and batteries must be tested in accordance with the UN’s Manual of Tests and Criteria, Part III, Subsection 38.3 [4] (DGR 3.9.2.6).

Compliance Tests

The UN’s Manual of Tests and Criteria lays out 8 tests that a rechargeable lithium-ion cell or battery must pass to satisfy regulatory guidelines and be cleared for air shipment. The first five tests must be sequentially performed on a single cell or battery without failure at any point during the tests. If the tests only involve cells, then each test must be repeated for 10 samples in a fully charged state and 10 samples in a fully discharged state. If the tests include batteries, then the tests must be performed on four fully charged batteries and four fully discharged batteries. The test sample requirements are outlined in Table 1.
Table 1. Summary of UN regulatory tests and required sample sizes.

<table>
<thead>
<tr>
<th>Test Cells</th>
<th>Batteries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altitude Simulation</td>
<td>10 fully charged cells</td>
</tr>
<tr>
<td>Thermal</td>
<td>10 fully discharged cells</td>
</tr>
<tr>
<td>Vibration</td>
<td>4 fully charged cells</td>
</tr>
<tr>
<td>Shock</td>
<td>4 fully discharged cells</td>
</tr>
<tr>
<td>External Short Circuit</td>
<td>Cells or batteries greater than 12 kg; 2 samples after 1 charge/discharge cycle and 2 samples after 25 charge/discharge cycles.</td>
</tr>
<tr>
<td>Impact</td>
<td>5 cells</td>
</tr>
<tr>
<td>Overcharge</td>
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<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Forced Discharge</td>
<td>10 fully charged cells after 1 charge/discharge cycle</td>
</tr>
<tr>
<td></td>
<td>10 fully discharged cells after 1 charge/discharge cycle</td>
</tr>
<tr>
<td></td>
<td>10 fully charged cells after 50 charge/discharge cycles</td>
</tr>
<tr>
<td></td>
<td>10 fully discharged cells after 50 charge/discharge cycles</td>
</tr>
</tbody>
</table>

In order to pass these tests the cells must not exhibit any of the following failure criteria. Mass loss must not exceed 0.5% for cells under 1 g, 0.2% for cells greater than 1 g and less than 75 g, or 0.1% for cells greater than 75 g. There should be no visible escape of electrolyte or other material (leakage). The cell should not vent, or release excessive internal pressure through its designed venting mechanism. The cell should not rupture, which is described as “the mechanical failure of a cell container or battery case induced by an internal or external cause, resulting in exposure or spillage but not ejection of solid materials.” The cell should never emit flames. Finally, the open circuit voltage must not fall by more than 10% of its voltage immediately prior to the test. The five tests are described below:

**Altitude simulation**: The altitude simulation test qualifies a cell or battery under low-pressure conditions such as those that may be experienced on board an aircraft. This test requires the cell or battery to be stored at a pressure of 11.6 kPa or less for at least 6 h without failure. The open-circuit voltage must not decline by more than 10% during the test.

**Thermal**: A temperature cycling test is implemented to assess the quality of the casing seal and the internal electrical connections. This test is conducted by storing the cell or battery at 75 °C for a minimum of 6 h followed by an additional 6 h of storage at −40 °C with no more than 30 min between the temperature extremes of both tests. This cycle is repeated 10 times.

**Vibration**: A cell or battery could be subjected to vibration loads during transport, leading to potential safety issues. This test is performed by vibrating the cell using a sinusoidal waveform with a logarithmic sweep from 7 Hz to 200 Hz and back in a 15 min time period. This is repeated 12 times for 3 different perpendicular mounting positions with one of the vibration directions perpendicular to the terminal face.

**Shock**: The shock test assesses the ability of the cell or battery to withstand large mechanical impacts during transport. This test is performed in a drop testing fixture, and the cell or battery should be subjected to a half-sine shock with maximum acceleration of 150 g, and a pulse duration of 6 ms. The test is repeated 6 times for three different mounting conditions for a total of 18 shocks. Each of the three mounting conditions should be mutually perpendicular axes.

**External short circuit**: The external short-circuit test simulates the cell or battery’s behavior under exposure of an external short circuit. This test should be performed at a temperature of 55 °C, and the external shorting resistance should be less than 0.1 Ω. This test is sustained for a 1-h period or until the
battery casing temperature has returned to a temperature of 55 °C. A battery failure must not occur during the 6 h period following the test.

The remaining three tests per the UN’s Manual of Tests and Criteria can be performed on a new cell or battery as follows:

**Impact:** The impact test is performed by placing the cell or battery on a flat surface and then placing a 15.8 mm diameter bar across the center of the cell or battery. A 9.1 kg mass is dropped from a height of 61 cm onto the cell or battery resulting in a kinetic energy of 54.4 J. Each cell or battery must meet the above-mentioned failure criteria, in addition to the requirement that the external temperature does not exceed 170 °C and there is no fire within 6 h after the test is performed. This test must be repeated five times with each of the cells or batteries at 50% of its rated state of charge (SOC).

**Overcharge:** The overcharge test evaluates battery safety when its voltage is taken above its maximum voltage limit. Cells that do not have explicit overcharge protection circuitry designed into them and that are to be used as part of a larger battery pack that affords such protection are exempt from this test. This test is performed by using a charging current that is two times the manufacturer’s recommended charging current. The overcharge voltage level is dependent on the maximum voltage limit of the cell or battery. If the test is for a single cell or a battery with a voltage less than 18 V, the overcharge voltage level is either two times the maximum voltage or 22 V, whichever is less. If the battery’s maximum voltage is greater than 22 V, the overcharge voltage level is 1.2 times the maximum voltage. The overcharge condition is held for 24 h in ambient temperature conditions, and should not result in fire during or within 24 h of the test. For batteries that weigh less than 12 kg, the test must be repeated for four samples after their first cycle and four samples after 50 charge/discharge cycles. For batteries that weigh more than 12 kg, two samples must be tested after the first cycle and two samples must be tested after 25 charge/discharge cycles.

**Forced discharge:** The forced discharge test evaluates the ability of a cell or battery to withstand a forced discharge condition. This test is performed by connecting the cell or battery in series with a 12 V DC power supply with an internal current that matches the maximum discharge current recommended by the manufacturer. The test is defined by dividing the rated capacity by the test current applied. A fire should not occur during or within seven days of the test. This test must be repeated for ten fully charged samples and ten fully discharged samples after their first cycle, and then each of the ten samples should be tested again at a fully charged state and a fully discharged state after 50 charge/discharge cycles.

These tests help to identify cells or batteries that are unfit for air transport, however there are several noted improvements that can be made. Preconditioning recommendations would help ensure that all of the cells tested are in a comparable state. This could include placing a constant voltage trickle charge across each cell for a period of time to ensure that the open circuit potential reaches its specified value. The definition of cell or battery failure should include additional electrical measurements such as resistance and capacity in order to identify cell defects that are less obvious through observational criteria. Additionally, the required sample sizes for testing are not large enough to confidently represent large populations. However, requirements for large sample sizes can be a significant economic burden. In Section 4, a recommendation is given to reduce risk while maintaining a small sample size by hand picking cells or batteries that are most vulnerable to failure.

In the overcharge test, samples are required to be tested before and after 50 charge/discharge cycles however, the specifications for the charge/discharge cycles are not explicitly stated. The overcharge test is also conducted at ambient temperatures which does not represent an overcharge condition in the most extreme possible conditions. In the thermal test, temperature extremes can be separated by up to 30 min, however, the rate of temperature change in unheated sections of airplanes can be larger in magnitude. The impact test fails to capture the average impact force imparted onto the battery. In order to measure this force, the work-energy principle must be applied by also measuring the kinetic energy of the mass after impact. To do this, the distance traveled by the mass after impact...
should be measured. The standard should be modified such that the test achieves a constant impact force for all batteries to account for different geometries and materials. Finally, the addition of a moisture test and a puncture test would make the ICAO regulations more comprehensive and further reduce the risk of a catastrophic failure.

3. Hazards Associated with Degraded Batteries

The increased use of lithium-ion batteries in products such as electric and hybrid electric vehicles, E-bikes, and portable electronics results in vast quantities of used or degraded batteries. Wang et al. [5] estimated that 46 million kg of LiCoO$_2$ was used for fabricating 18650 cells in 2006, all of which will eventually require disposal or recycling. Automotive manufacturers generally suggest battery replacement when the battery’s capacity drops to 70%–80% of the original rated value. This leaves energy storage capabilities in degraded batteries with the possibility for second-use applications such as energy grid storage [6]. Other situations may arise where degraded cells or batteries must be tested to validate warranty claims or processed for recycling. In all these cases, the shipment and transport of degraded cells or batteries will be required.

Currently, there are two special provisions outlined by the UN for shipping degraded batteries:

- “Waste batteries and batteries being shipped for recycling or disposal are prohibited from air transport unless approved by the appropriate national authority of the State of Origin and the State of the Operator.” UN Special Provision A183.

- “Lithium batteries identified by the manufacturer as being defective for safety reasons, or that have been damaged, that have the potential of producing a dangerous evolution of heat, fire or short circuit are forbidden for transport (e.g., those being returned to the manufacturer for safety reasons).” UN Special Provision A154.

While a manufacturer may identify batteries as potentially defective, it is less clear whether a non-defective, degraded battery poses a safety risk. Saito et al. [7] found that degraded cells or batteries generate more self-heating at high rates of discharge due to the increase in internal resistance. Therefore, if a degraded battery experienced a short circuit, joule heating could pose a safety hazard. However, at the same time, degraded cells or batteries are able to store less energy, meaning that a potential thermal event would release less energy and could be less catastrophic. The specific materials used in the electrodes should also be identified and considered when evaluating the potential risk of degraded batteries. An electrode’s elemental composition and fabrication process can influence the risk of a cell failure. Kang et al. [8] showed that applying a thin coating of Al$_2$O$_3$ on a LiNiO$_2$ cathode improved thermal stability and suppressed oxygen gas evolution at high temperatures. Therefore, methods should be developed that evaluate if a previously used cell or battery is at a high risk of undergoing thermal runaway.

Certain use conditions predispose cells or batteries to undergo thermal runaway. Thermal runaway is perpetuated by an internal short circuit, which generates self-heating and causes the volatile electrolyte solvents to undergo exothermic reactions. If the temperature of the cell exceeds the melting point of the separator (e.g., 115–135 °C for polyolefin materials), further exothermic reactions can increase the cell’s temperature, generate gases, and cause the battery to vent flammable electrolyte and gases [9]. Internal short circuits can be introduced into a cell in a number of ways, and all possible causes must be considered when determining if a degraded battery should also be considered a safety hazard.

3.1. Current Collector Corrosion and Dissolution

Shu et al. [10] observed corrosion of copper current collectors in electrolyte solvent solutions after 30 days of storage. This was attributed to trace amounts of water, which resulted in the formation of hydrofluoric acid within the cell. When a cell or battery is left in storage for an extended period,
the copper current collector is susceptible to corrosion. Free copper particles within a cell or battery could eventually result in short-circuiting between the electrodes, especially if the cell or battery is put back into operation. Additionally, when the cell’s voltage falls below 1.5 V, the copper current collector becomes unstable in the organic carbonate solvent and can dissolve \cite{11,12}. Any cell or battery that has been left in storage and has a terminal voltage below the minimum voltage specified by the manufacturer needs to be assessed for potential copper corrosion and dissolution prior to shipping. Further research into the extent of copper dissolution under various storage conditions would assist in determining the risk that overdischarged cells or batteries pose.

### 3.2. Separator Shrinkage

The separator plays a key role in cell or battery safety as it prevents the anode and the cathode from short-circuiting. It is typically composed of single or multilayer polyolefin sheets, with the most common materials being polyethylene (PE) and polypropylene (PP). For polyolefin materials, thermally induced separator shrinkage occurs at approximately 110 °C, with the coverable area of the separator reducing by as much as 14% \cite{13,14}. If the separator shrinks and exposes the edges of the electrodes, short-circuiting can occur and could elevate the risk of a catastrophic failure. Batteries designed for higher-temperature applications may use a solid electrolyte, such as Li$_2$S-P$_2$S$_5$ \cite{15}, or an Al$^{3+}$ doped LiGe$_2$(PO$_4$)$_3$ (LGP) \cite{16}, for improved ionic conductivity, in which case separator shrinkage is not an issue. The type of separator used in a degraded battery should be known before it is cleared for shipping. If a battery is known to have been stored at temperatures exceeding 90 °C, or if the storage/usage history of a battery is not known, then a representative sample should be disassembled and the separator inspected. Separators showing signs of shrinkage should be considered defective for safety reasons.

### 3.3. Contamination

Contamination due to poor quality control during the manufacturing process has been linked to battery overheating. In 2006, Sony recalled 4.1 million Dell laptop batteries due to contamination issues \cite{17}. Metal particles found within the cells were causing a puncture in the separator, leading to short-circuiting between the anode and the cathode. Metal contamination within a cell is often a result of spattering during current collector tab welding, but it can also be introduced due to poor environmental controls during assembly \cite{18}. Moisture contamination is also a concern as it has been shown to result in the formation of hydrofluoric acid in lithium-ion cells containing LiPF$_6$ electrolytes \cite{19}. Hydrofluoric acid can then etch cell materials, leading to rapid degradation or a short-circuit failure if stray metallic particles are dispersed throughout the cell.

One of the biggest challenges in battery reliability is the detection of trace contamination in assembled cells. Often, contamination issues are not highlighted until after failures have been observed. Any cell or battery that has an open recall for issues regarding contamination should be considered defective for safety reasons. When contamination particles result in internal short circuits, rapid self-discharge of the cell or battery is observed. Products that exhibit a self-discharge rate more than 1.5 times faster than what was described by the manufacturer should be considered defective for safety reasons.

### 3.4. Dendrite Growth

Lithium plating can occur on the surface of battery electrodes and cause internal short circuits \cite{20}. The lithium plating side-reaction occurs when the potential difference between the electrode and electrolyte (over-potential) drops below zero, preventing the intended lithium intercalation reaction and resulting in a surface layer of metallic lithium. The over-potential can fall below zero when a cell or battery has been charged at high current rates or at low temperatures \cite{21}. When the surface of an electrode has undergone lithium plating, there is a risk of lithium dendrite formation. Lithium dendrites have the potential to puncture the separator and result in an internal short circuit and
catastrophic failure. The formation of lithium dendrites can be partially reversed though a controlled
discharge to facilitate re-intercalation [22]. However, detection of lithium plating is a challenge for
BMSs, most of which use phenomenological-based models or equivalent circuit models to estimate the
internal state of the cell or battery. Because most BMSs do not explicitly model the physical phenomena
that occur in a cell or battery, lithium plating is typically not detected until there is a noticeable drop in
performance or a thermal event. Any battery that has operated under high charge/discharge rates or
in subzero working environments should be subjected to a 0.5C complete discharge to assure that no
plated lithium exists on the electrode surfaces.

4. Suggested Pre-Shipping Tests

The safety regulatory tests outlined in Section 2 do not provide a reliable claim to safety if the cells
have undergone some prior use in-between the time they were first tested and when they were shipped.
The usage history may dampen or exacerbate safety risks depending on the specific application where
the batteries were used. For example, batteries that were used to operate an unmanned aerial vehicle
are likely to have undergone significant shock and vibrational loads as compared to batteries used in
more stationary applications. Batteries that were used in the oil and gas industry are likely to have
been subjected to higher pressures and temperatures than batteries used in consumer electronics. Large
mechanical loads can result in cracking or flaking of the electrode material and have the potential to
allow loose particles to form an internal short circuit. However, batteries that have lost capacity but
were not exposed to heavy loading during usage may be more benign as they are no longer capable of
storing as much energy as they were in their unused state.

To properly evaluate the air transport risks of second-use batteries, samples should undergo a
rigorous but timely set of tests. These tests are designed specifically to identify and evaluate any safety
risks in a population of cells.

4.1. Disassembly

In many cases, complete cell or battery usage histories are not available for determining the
transport risks. However, a cell disassembly can be performed on selected samples known to have
undergone the same field conditions as the remainder of the lot. Disassembly can be performed
according to the guidelines outlined by Williard et al. [23]. The state of the disassembled cell can
be assumed to represent the rest of the batteries under consideration if chosen correctly. In order to
maximize safety, the cells exhibiting the greatest degradation (measured by capacity, internal resistance,
and impedance) should be tested. Bulging of the cell’s casing is often an indication of gas generation
associated with degradation or abuse, therefore, bulging cells should also be selected. To obtain a
conservative overview of a cell population, the cell with the most degradation by capacity, internal
resistance, or impedance, and the cell displaying the most bulging (as indicated by the cell thickness)
should be selected for disassembly.

When a cell is disassembled, the current collector should be inspected for signs of pitting corrosion
and the separator should be inspected for shrinkage or puncture. The dimensions of the separator
should be larger than the contact area between the anode and the cathode.

Issues involving possible contamination can be investigated using microscopy. The surface of
the electrodes should be examined for evidence of foreign particles dispersed throughout the cell. All
current collector tab connections should be investigated for the presence of weld splatter, and the full
electrode should be scanned by optical microscopy to identify obvious metallic contamination. Lithium
plating and dendrite growth may be harder to observe through optical microscopy and instead can
be viewed with scanning electron microscopy (SEM). Zier et al. [20] developed a method to enhance
observation of lithium plating by dyeing electrodes with OsO₄. This allowed a clearer observation
of metallic lithium in a back-scattering image. If the battery has fallen below 2 V, the presence of
free copper should also be investigated. While energy dispersive spectroscopy (EDS) can be used to
identify high concentrations of metallic copper, additional methods are needed to properly quantify
the amount of free copper in the battery. X-ray photoelectron spectroscopy (XPS) can be used to study the surface of the electrodes and combined with depth profiling to study beyond the surface.

4.2. Thermal and Mechanical Stress Testing

Incipient faults within a cell may not be easily detectable under low-stress conditions. However, applying thermal and mechanical loads to a battery can help to identify issues that are not otherwise apparent through typical voltage or resistance measurements. Situations may arise during usage wherein developing faults such as lithium dendrites, small tears in the separator, or disintegrated shards from current collectors greatly increase the risk of a short circuit but have not actually resulted in a bridge between the anode and the cathode. One way to identify if these situations are present within a battery is to apply thermal and mechanical loads to the battery at incremental levels until the battery has undergone failure. The magnitude of the external load that results in the failure, as well as the nature of the failure itself, can be used to identify if the risk of a used battery has increased or decreased during its operational life. Degraded batteries under incremental loading can be benchmarked against the same type of batteries in an unused condition to determine if the temperature or amount of external pressure that causes failure has decreased. Additionally, if batteries in an unused state undergo failure without outgassing, or expelling of flaming electrolyte, then the used cells should undergo failure in a similar way. Catastrophic failures can be an indication that incipient faults have developed during usage. In keeping line with previous UN test sample sizes for pre-shipping tests, ten representative samples should be selected from a group of batteries to undergo temperature stress testing, and ten samples should be selected to undergo mechanical testing. This allows conservative testing without being an overly economic burden on entities shipping batteries. Additionally, four cells in an unused state should be procured from the manufacturer. These cells should be subjected to the same temperature and mechanical tests as the used cells. The purpose of the unused cells is to set a benchmark for evaluating degradation.

Temperature stress testing should be performed in two different ways; the first method evaluates the properties of cell as a whole, while the second evaluates the safety properties of the materials themselves. In the first temperature stress test, eight cells should be selected from a group of batteries with similar usage histories. Measurements of DC resistance, open-circuit voltage, discharge capacity, and weight should be taken at the beginning of the test and after each incremental temperature exposure. The cells are then placed in a thermally controlled chamber, brought to 0 °C, and held at that temperature for 1 h. After 1 h of low-temperature exposure, cell measurements are taken and the temperature is increased to 30 °C and held for 1 h. This process is repeated up to 150 °C or until the cell undergoes failure, which is defined in the same way as the safety regulatory tests outlined in Section 2. If failure occurs in the degraded cells more than 60 °C lower than observed in the unused cells, the degraded cells should be considered defective for safety reasons.

Differential scanning calorimetry (DSC) analysis on the cathode and anode materials has proven to be effective for evaluation of electrode safety. DSC methods are described by Wen et al. [24]. DSC is performed by heating a sample and then measuring the temperature required to heat an electrode sample as compared to some reference material. This experiment identifies the specific temperatures at which thermally induced reactions occur in the electrode materials themselves. It also gives an indication of how much heat is released during an exothermic decomposition reaction. The results of DSC for degraded cells should be compared against the results of DSC for unused cells to evaluate if the activation temperatures for exothermic reactions within a cell have decreased as a result of usage. To fully evaluate the safety of a cell, additional samples should be subjected to different pressure conditions to observe how lithium ion dynamics is influenced by external press [25]. Pressure testing and cell characterization below ambient conditions can be performed inside a sealed low-pressure chamber, while high pressure testing can be simulated using compressive loads. The low-pressure testing is similar to the altitude test described by the UN standards, however, the test begins at standard altitude and pressure, and drops at certain pressure intervals until a near-vacuum state is
reached. During pressure testing, low-current-rate pulsed charge/discharge cycles are performed at each pressure level with a rest period in-between each pulse. This charge/discharge profile is identical to that required to perform galvanostatic intermittent titration technique (GITT) [26], which can allow for electrochemical safety characterization as described in the following section.

To evaluate high-pressure tests, compressive loading is applied to simulate hydrostatic loading. True hydrostatic loading can be achieved by testing a battery within a fluid at specified depths; however, capacity leakage may occur due to the conductivity of the fluid between the two terminals of a submerged battery. During compressive loading, low-current-rate pulsed charge/discharge cycles are performed in the same way as they are during low-pressure testing in order to electrochemically characterize the cell.

4.3. Electrochemical Characterization

The tests outlined in the UN’s *Manual of Tests and Criteria* [4] specify a number of electrical and mechanical tests that must be performed in order to certify that a cell or battery is safe for air transport. While these tests cover a broad range of possible scenarios, they do not address situations in which multiple stresses occur at the same time. For example, an external short-circuit test and a low-pressure test are specified, but these tests are not performed together. During transport at high altitudes, if there is an external short circuit of a cell or battery, it is likely that it will occur in a low-pressure environment. It is unclear from these tests if a low-pressure environment would increase the risk of battery failure during a short-circuit event, vibration, or shock. Therefore, the true safety performance of a lithium-ion cell or battery during air transport is not completely tested.

One approach to address the concerns that multiple stress factors impact the safety of cells or batteries being transported by air would be to perform all the permutations of the eight tests together. However, this would require an infeasible number of tests to complete the certification of any particular cell or battery and would place an enormous burden on battery manufacturers and certification agencies. Rather than perform all of these tests, the relationship between thermal and mechanical loads on the electrochemical performance of batteries should be characterized and understood. Best practices can then be developed based on an understanding of the interactions between external stresses and the internal electrochemical phenomena that could lead to a thermal runaway or catastrophic failure.

To obtain information on how a cell or battery will behave under different loading scenarios, physical parameters should be measured to understand how they change in relation to each other under different stress conditions. One parameter of importance is a battery’s diffusion coefficient. When performing compression or low-pressure testing on batteries, the voltage is typically monitored as a means to qualify a pass or fail. However, the voltage in a battery under a mechanical load does not undergo a significant change unless a short circuit actually takes place. This prevents batteries from being evaluated with a high level of granularity and instead just produces a binary pass-or-fail result. By determining how the diffusion of a battery changes under different loading conditions and at different levels of usage, the health and relative safety can be much better quantified.

Wu and Chiang [27] showed that the high rate of discharge properties of a battery is mainly limited by the diffusion of lithium ions inside a battery. Decreased lithium diffusion caused by temperature or pressure could result in a battery not being capable of delivering a high current discharge. If the cause of the high current discharge is an external short circuit and the diffusion of lithium is being hindered by some external pressure (or lack of external pressure in low altitudes), internal heating could occur faster than if the battery was at atmospheric pressure. By increasing or decreasing external pressure to a magnitude that induces cell failure, and then measuring and relating lithium diffusion to the corresponding pressure, lithium diffusion can be used as a metric to determine a cell’s risk for failure. This analysis can become critical in determining a cell’s risk during air transport.
5. Conclusions

The battery literature contains a wealth of knowledge regarding the potential safety hazards of both new and used lithium-ion batteries; however, this knowledge has not been fully incorporated into the safety standards. The packaging requirements and safeguards that are used for bulk shipments of lithium batteries on commercial planes do not adequately help to manage all risks hazards. The chain reaction initiated by internal short circuit, puncture, or other types of damage in a single lithium battery can be hazardous as the fire propagates from one package to the next. This propagation can occur due to improper packaging. New ICAO proposals and guidelines for bulk shipments call for inserting gels or other types of cooling agents between batteries or power packs. If adopted, the changes would lead to higher costs and extra weight for shippers. The current safety tests cover a broad range of possible scenarios, however, these tests do not address situations in which multiple simultaneous stresses act on the battery.

While reducing the SOC of batteries prior to shipping reduces the energy released during a battery thermal runaway event, it poses a few problems. If the batteries are shipped long distances under a wide range of ambient conditions, the batteries are at higher risk of self-discharging to unsafe levels. The development of stringent functional requirements for batteries to identify and mitigate all risks (even for batteries that have undergone previous use) is the most effective way of qualifying batteries to be shipped on-board air transport vessels. If not performed properly, the cells could experience performance degradation as a result of shipping and storage at low SOCs.

New methodologies for assessing the safety of batteries are needed. Given that it is not practical to disassemble a representative sample of batteries prior to shipment, a rapid, nondestructive assessment of batteries and their risk of catastrophic failure are needed to economically ship batteries in a safe manner. This communication summarizes the physical causes of failure and motivates the development of best practices for testing and evaluating battery transport safety.

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Abbreviations

The following abbreviations are used in this manuscript:

BMS Battery management system
ICAO International civil aviation organization
IATA International air transportation association
FAA U.S. federal aviation administration
UN United nations
DGR Dangerous goods regulations
SOC State of charge
LiCoO$_2$ Lithium cobalt oxide
PE Polyethylene
PP Polypropylene
DSC Differential scanning calorimetry
GITT Galvanostatic intermittent titration technique
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