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Further study of the intrinsic safety of internally shorted lithium and lithium-ion cells within methane-air

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Abstract

National Institute for Occupational Safety and Health (NIOSH) researchers continue to study the potential for lithium and lithium-ion battery thermal runaway from an internal short circuit in equipment for use in underground coal mines. Researchers conducted cell crush tests using a plastic wedge within a 20-L explosion-containment chamber filled with 6.5% CH_4-air to simulate the mining hazard. The present work extends earlier findings to include a study of $LiFePO_4$ cells crushed while under charge, prismatic form factor $LiCoO_2$ cells, primary spiral-wound constructed $LiMnO_2$ cells, and crush speed influence on thermal runaway susceptibility. The plastic wedge crush was a more severe test than the flat plate crush with a prismatic format cell. Test results indicate that prismatic Saft MP 174565 $LiCoO_2$ and primary spiral-wound Saft FRIWO M52EX $LiMnO_2$ cells pose a CH_4-air ignition hazard from internal short circuit. Under specified test conditions, A123 systems ANR26650M1A $LiFePO_4$ cylindrical cells produced no chamber ignitions while under a charge of up to 5 A. Common spiral-wound cell separators are too thin to meet intrinsic safety standards provisions for distance through solid insulation, suggesting that a hard internal short circuit within these cells should be considered for intrinsic safety evaluation purposes, even as a non-countable fault. Observed flames from a $LiMnO_2$ spiral-wound cell after a chamber ignition within an inert atmosphere indicate a sustained exothermic reaction within the cell. The influence of crush speed on ignitions under specified test conditions was not statistically significant.

Keywords

Batteries; Explosion protection; Fires; Hazardous areas; Intrinsic safety; Lithium-ion; Mining industry; Standardization

1. Introduction

Lithium-ion (Li-ion) batteries have become one of the most popular types of rechargeable battery for portable electronics. Li-ion technology provides enhanced energy storage capabilities that lengthen device runtime, shorten the recharge time, and extend the life of the battery. Beyond consumer electronics, Li-ion batteries are now growing in popularity for underground mine safety equipment such as cap lamps and communications and tracking

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equipment. Chemistry, performance, cost, and safety characteristics vary across lithium battery types. Portable electronics often use Li-ion batteries with lithium cobalt oxide ($LiCoO_2$) cathodes, which offer high energy density, but have well-known thermal runaway safety concerns. Safety concerns specific to underground coal mine fire and explosion hazards from $LiCoO_2$ cells were described previously (Dubaniewicz and DuCarme, 2013). A Li-ion powered Mine Safety and Health Administration (MSHA) permissible device was involved in a thermal event in an underground coal mine. An investigative report of the incident is not publically available.

Researchers with the National Institute for Occupational Safety and Health, Office of Mine Safety and Health Research (NIOSH, OMSHR) continue to study Li-ion battery thermal runaway potential in order to develop safety recommendations for underground coal mine applications.[1] The study includes an experimental evaluation of potential thermal runaway initiating events of cells placed within CH_4-air atmospheres to simulate a mining explosion hazard. The study focused on internal short circuits induced by external mechanical damage, with this failure mechanism known to produce thermal runaway in Li-ion cells. NIOSH researchers previously reported on a new method of inducing internal short circuit for thermal runaway susceptibility evaluation purposes that overcomes some limitations of the flat plate and nail penetration methods (Dubaniewicz and DuCarme, 2013). The present work extends earlier findings to include a study of:

- $LiFePO_4$ cells crushed while under charge.
- prismatic form factor $LiCoO_2$ cells.
- crush speed influence on thermal runaway susceptibility.
- primary, spiral-wound constructed $LiMnO_2$ cells.

2. Background/literature review

Li-ion thermal runaway hazards continue to be a concern. Wang et al., (2012) reviewed Li-ion battery fire and explosion accidents, and reported tens of thousands of mobile phone fires or explosions from various causes since 2006. They also listed several accidents involving large format $LiFePO_4$ batteries used in electric vehicles. Underwriters Laboratories (UL) (2013a) found that since March 2012, the Consumer Product Safety Commission (CPSC) documented 467 reported incidents that identified Li-ion cells as the battery type involved, with 353 of those being incidents involving fire/burn hazards. The UL report date suggests the CPSC incidents occurred within a period of slightly more than 1 year. The UL report emphasized the need to update existing standards and create new ones as our information and knowledge of potential Li-ion battery hazards increase. Li-ion battery failures grounded the Boeing 787 airliner fleet for several months over thermal runaway concerns with the batteries (NTSB, 2013). Li-ion or lithium cells were possibly linked to several cargo plane incidents, including two fatal crashes (GCAA, 2013) (Brett, 2011).

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[1] The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

Several studies suggest the need for more emphasis on the safety aspects of Li-ion technology. Barnett et al., (2013) assert that Li-ion battery safety issues are not met with the same scientific and technical rigor that apply to other aspects of Li-ion technology. Doughty and Roth (2012) propose that safety is often a property determined after the development phase of Li-ion technology, and that safety and thermal stability should become a prime consideration in the initial development and material selection phase. Roth and Orendorff (2012) reviewed research of nonflammable electrolytes, and contend that “electrolyte additives proposed to reduce gas generation and mitigate flammability have not gained much traction, in general, because of the tradeoff in performance.” UL notes that current safety standards do not address the potential impact of battery aging, and initial results have led the company to expand its safety research program. For example, UL (2013b) observed that aging adversely impacted the safety performance of a selected 2.8 Ah 18650 type $LiCoO_2$ cell.

Spiral-wound Li-ion cells use a thin separator material to insulate the anode from the cathode (Fig. 1). Physical damage to this separator causes an internal short circuit that may lead to catastrophic heating events. Some separator materials have shutdown properties that can provide a margin of safety against certain failure modes, including internal short circuits, that result in an elevated cell temperature. However, some potential safety issues remain. Baldwin (2009) reviewed separator materials and functions for lithium-based batteries used in aerospace missions, and suggests the shutdown mechanism would provide very little protection from an internal short circuit accompanied by a rapid internal heating rate. The thickness of commercial separator materials reviewed were <30 µm. Orendorff (2012) discussed challenges with designing safe Li-ion cell separators, including some tradeoffs between mechanical robustness and porosity/transport (performance) properties, primarily for large format cells. The thicknesses of four varieties of commercial separators reviewed were approximately 25 µm. Orendorff concluded that ceramic/polymer composites and high melting point polymer materials offer some improvement in thermal stability and abuse tolerance for Li-ion cell separators but, in general, there needs to be more evaluation work dedicated to quantifying the safety impact of new separators, particularly for large format cells.

Barnett et al., (2013) emphasize internal short circuit hazards from metallic dendritic growth through separators, where metal particles on (and possibly in) the cathode dissolve and plate out on the anode, growing back through the separator, leading to an internal short circuit. They note that ceramic layers are sometimes implemented as porous coatings on electrodes or as separators as a means of enhancing Li-ion battery safety. In limited testing of cells containing ceramic layers, they observed formation of internal shorts from dendritic growth, including internal short circuits that matured to thermal runaway.

Recent studies (Ong et al., 2010) (Zaghib et al., 2012) demonstrate some safety aspects of $LiFePO_4$ positive electrode materials compared to some other materials. The relative safety of $LiFePO_4$ is generally attributed to limited O_2 release upon high temperature decomposition. Previous research (Dubaniewicz and DuCarme, 2013) found that selected $LiFePO_4$ cells did not cause ignition when crushed within CH_4-air mixtures under specified test conditions. In the current study, additional tests were conducted to crush selected

$LiFePO_4$ cells while charging within normal charging conditions. These tests simulated a CH_4 ignition hazard involving underground stationary Li-ion battery-powered equipment that is on charge and unattended, while maintaining a single fault condition of a crush-induced internal short circuit.

NIOSH previously contracted with QinetiQ North America (QNA) to perform a safety assessment of emergency backup batteries and battery charging systems for underground mining applications (QNA, 2009). QNA reviewed safety aspects of several primary lithium cell chemistries, including $LiMnO_2$. The company reported that $LiMnO_2$ cells have shown resilience against many types of abuse testing, including short circuit, over-discharge, puncture, and crush. Overall, $LiMnO_2$ has been proven as one of the most robust primary cell types on the market today, still in use despite being one of the first-pioneered lithium technologies. Further, $LiMnO_2$ is one of the safest of Li technologies as long as the supplier is reputable and battery pack design has been appropriately tested. QNA concluded that $LiMnO_2$ is a good candidate power source for an underground primary-cell application. In the current study, researchers included a commercial $LiMnO_2$ cell marketed for intrinsically safe (IS) equipment, for evaluation as a potentially safe cell for powering IS mining equipment. An intrinsic safety evaluation test report for the cell was obtained for comparison purposes (DEKRA, 2011).

Li-ion cell vent gases may be flammable or inert, and the volume of vent gases from thermal runaway is substantial. Roth and Orendorff (2012) and Roth (2008) found that cell venting before thermal runaway is achieved may release flammable solvent vapor into the surrounding environment, which may then be ignited by an adequate ignition source. In contrast, they also found that the decomposition vent gases from Li-ion cells undergoing thermal runaway are not inherently combustible, and may act to inert the surrounding atmosphere. Further, thermal runaway typically produces high-rate gas generation from the decomposition of the organic solvents. Measurements of gas released from cells during thermal runaway using several different cathode materials showed “that the volumes of gas released at the end of the thermal runaway peak (typically 350 °C) were all nearly equal”, and approximately 1200 mL/Ah.

Standard IEC 62133 recognizes cell crushing as reasonably foreseeable misuse (IEC, 2012). IEC 62133 edition 2.0 contains revised crush test procedures. A new test provision indicates that once a 10% deformation with flat plates has occurred, the force is to be released. This new provision suggests that a cell may deform by 10% at forces significantly less than the 13 kN maximum force, at which point the force is released. Previous research (Dubaniewicz and DuCarme, 2013) found that a sample of cylindrical Li-ion cells crushed by flat plates deformed by approximately 18% without any adverse outcomes; similar cells readily ignited when crushed by a plastic wedge. IEC 62133 edition 2 has also eliminated a narrow side crush test of prismatic cells. Mikolajczak et al., (2011) demonstrated that crushing the edge of cells is more likely to cause cell thermal runaway than crush or penetration perpendicular to electrode surfaces, in agreement with findings by Maleki and Howard (2009). In the current study, researchers included a sample of prismatic cells to extend previous research to compare crush characteristics between a flat plate and a plastic wedge method.

Barnett et al., (2013) mention impact speed in a discussion of potential “gaming” of cell level safety standard tests. Crush or nail penetration speeds identified in the literature vary significantly. An amended 5th edition of the UN manual of tests specifies a 1.5-cm/s flat plate crush speed (UN, 2011). Neither IEC 62133 ed. 2.0 nor UL 1642 ed. 5 (UL, 2013c) specify a flat plate crush speed. The IEC 62133 ed. 2.0 forced internal short circuit test specifies a much slower 0.1-mm/s crush speed. A proposed UL indentation-induced internal short circuit test indicates a constant speed in the range of 0.01–0.1 mm/s (UL, 2013d). Spek and Hosseinifar (2012) discussed efforts to improve nail penetration test methods, and concluded that a 100-cm/s nail speed showed a strong tendency to produce adverse outcomes (100%, 6 samples) in large format Li-ion cells tested. Although not included in the conclusions, much slower nail speeds (1.1 cm/s) produced a similar rate of adverse outcomes (100%, 4 samples). Ichimura (2007) suggests that a slower nail penetration speed may produce more adverse results due to internal resistance considerations. Spotnitz and Franklin (2003) reported on nail tests performed by Dahn using 18650 $LiCoO_2$ cells. Using a nail with an embedded thermocouple, the nail temperature exceeded 600 °C when forced slowly into the cell to a depth of <4.5 mm. However, with a fast, deep nail penetration (7.5 mm), the nail temperature did not exceed 140 °C. Penetration speed was not specified. Based on Dahn's results, perhaps a sufficiently slow penetration may produce thermal runaway before maximum penetration is achieved, minimizing the influence of penetration depth. In testing reported here, interim results with a prismatic cell produced a limited number of ignitions, providing an opportunity to run another set of tests with similar cells using a different crush speed, to assess the influence of selected crush speeds using the Fisher's Exact Test (Rosner, 1990).

ACRI2001 (MSHA, 2008) and ANSI/ISA-60079-11 (ANSI/ISA, 2012) intrinsic safety standards provide requirements for separation distances through solid insulation. ACRI2001 stipulates a 0.5-mm minimum distance through solid insulation for voltages up to 60 V. If the separation between two conductors is less than one-third of this 0.5-mm value, ACRI2001 stipulates that the conductors are to be considered normally connected, if connection impairs intrinsic safety. Such shorting of conductors is not to be considered a fault in the analysis. That is, such a short is considered as a non-countable fault, allowing MSHA to apply up to two countable faults for intrinsic safety evaluation purposes. ANSI/ISA-60079-11 ANNEX F lists a 0.2-mm separation distance through solid insulation, for all over-voltages listed, for both “ia” and “ib” Levels of Protection. If separation distances are less than one-third of the values specified, they shall be considered as subject to non-countable short-circuit faults, if this impairs intrinsic safety. Neither ACRI2001 nor ANSI/ISA 60079-11 requirements for distance through solid insulation are currently applied to internal Li-ion cell constructions. These standards rely on other cell level standards to help ensure intrinsic safety in potentially explosive environments (Dubaniewicz and DuCarme, 2013).

Standard ANSI/ISA 60079-0 (ANSI/ISA, 2013) provides general requirements for explosion protection techniques covered by the ANSI/ISA 60079 series of standards. These are the US adopted versions of the IEC 60079 series of standards. ANSI/ISA 60079-0 indicates that additional consideration and additional testing may be required for equipment operating outside of normal air oxygen content, i.e., oxygen enriched atmospheres. Further, potential ignition sources from exothermic chemical reactions are not addressed by the standard, and equipment with such ignition sources should be subjected to a hazard analysis that identifies and lists all of the potential sources of ignition by the electrical equipment and the measures to be applied to prevent them from becoming effective. Ong et al., (2010) found that $LiCoO_2$ may release significant amounts of O_2 during thermal runaway decomposition. Ignition pressures on the order of 10.8 MPa (1560 psi) have been reported for certain spiral-wound $LiCoO_2$ cells (Jhu et al., 2011) (Yen et al., 2011). The excessive O_2 generation and the high thermal runaway pressures reported suggest that certain spiral-wound $LiCoO_2$ cells may be considered as strong oxidizers and potential exothermic chemical reaction ignition sources for ANSI/ISA 60079-0 purposes.

3. Methods and materials

NIOSH researchers conceived a new method of inducing internal short circuit for thermal runaway susceptibility evaluation purposes that was thought to overcome limitations of the flat plate and nail penetration methods (Dubaniewicz and DuCarme, 2013). The new method employs a 90° wedge-shaped plastic fixture in place of the UL flat plate to compress the cell. A plastic material was selected to minimize electrical and thermal energy dissipation by the test fixture itself. The wedge shape and point angle are designed to be robust enough to crush the cell without significant damage to the plastic wedge itself. A plastic fixture simulates external forces applied to plastic-wrapped or encased battery packs which are common (Mikolajczak et al., 2011). Numerous field failures have been linked to latent mechanical damage (Mikolajczak et al., 2011). Researchers also conducted a series of tests with flat plates to simulate the UL 1642 crush tests as an experimental control for tests with the plastic wedge. A hydraulic ram extension with a 13-mm-thick flat plate was fabricated from steel and used to perform these tests.

3.1. Methods

A custom hydraulic press (Fig. 2), designed and fabricated to fit inside a 20-L explosion-containment chamber, was used for these experiments. The press uses a small single-acting hydraulic cylinder with a 43-mm bore and 54-mm stroke. The cylinder ram is retracted by an internal spring when hydraulic fluid is released. A cutaway view of the press is shown below. The top and bottom plates are connected with a steel tube (not shown for clarity) that has access holes for installing the battery and plastic wedge or flat plate. A commercially available 0.75-kW hydraulic power unit supplies the hydraulic pressure, and the system relief valve is set to allow 13 kN of force at the cylinder ram. The press is controlled from a solenoid-operated four-way hydraulic valve. A bleed-in flow control is used to regulate the speed of the ram. The complete hydraulic system schematic is shown in Fig. 3.

Tests using the plastic wedge were completed at two different crush speeds. The nominal rates were 5 mm/s for the fast ram speed and 0.5 mm/s for the slow rate. Due to temperature and viscosity variations, the actual ram speed varies by a slight amount from test to test as documented in the Results section. Ram speed adjustment precision was limited with this setup because it is an open loop control system. Researchers investigated using a hydraulic cylinder with an internal linear variable differential transformer to enable closed loop control of the ram speed. Unfortunately, no such cylinder could be found that would fit inside the chamber. Viatran model 248 pressure transducer measurements were used to calculate cylinder force.

Cell crush tests were conducted within the 20-L chamber filled with 6.5% CH_4-air. The concentration of the gas-air mixture was determined by partial pressures and set to 100 kPa (14.5 psi) at room temperature. The CH_4 source purity was specified as 99.97%. Subsequent tests at 40 °C raised the chamber pressure slightly above atmospheric, and researchers bled off a small amount of gas to maintain 100 kPa (14.5 psi) after the temperature stabilized. The term "overpressure" refers to the peak chamber pressure above 100 kPa. A fan within the chamber provided mixing. Chamber headspace volume was approximately 18 L. Crush tests with the plastic wedge were conducted at 40 °C. Researchers waited at least 1 h after the cell surface temperature reached 38 °C before conducting ignition tests at 40 °C. Crush tests with flat plates were conducted at room temperatures per UL 1642. The rationale for chamber temperature selections was explained previously (Dubaniewicz and DuCarme, 2013). To determine if a flammable atmosphere was still present, a hot-surface furnace igniter placed inside the chamber was activated after tests that did not result in an ignition.

A personal computer-based Labview data acquisition program recorded cell voltages, pressure transducer signals, and thermocouple measurements. A chamber pressure transducer detected ignitions in conjunction with a high-speed video camera. The criterion for ignition was an overpressure of at least 50 kPa (7.25 psi), a value derived from previous explosibility research (Cashdollar and Hertzberg, 1985) (Cashdollar, 2000). Sapphire windows allowed viewing inside the chamber. A high-speed video camera (NAC model 512SC) recorded tests at 250 frames per second. A white LED fixture was placed within the chamber to provide illumination for video recording. An independent laboratory calibrated in-house multimeters and a thermocouple calibration cell traceable to the National Institute of Standards and Technology (NIST). A battery analyzer was calibrated by the manufacturer. Kapton tape was used to attach the thermocouple to the cell can, and to cover the bottom metal platen for insulation purposes.

A current limiting power supply (Acopian EP015MX500) was connected to selected $LiFePO_4$ cells for crush tests while under charge. These tests simulated a CH_4 ignition hazard involving underground stationary Li-ion battery powered equipment that is on charge and unattended. The power supply voltage was set to the maximum cell charge voltage recommended by the cell manufacturer. The test protocol called for limiting the power supply current to the maximum charge current recommended by the manufacturer, or 5 A, whichever amperage was less. The 5-A limit would maintain the charging circuit parameters within the safe region of the resistive circuit CH_4 ignition curves of ACRI2001 and ANSI/ISA 60079-11. The maximum recommended charge current for the selected $LiFePO_4$ cells exceeded 5 A, so the 5-A limit was selected for these tests. The charging parameters maintained the single fault condition of an internal short circuit induced by crush.

A Vencon UBA5 Battery Analyzer preconditioned and analyzed cells for testing (Table 1). A software package provided user configurable routines for constant current, constant voltage cycling, and for measuring resistance and capacity. The resistance routine uses a two-step DC measurement. Cell resistance was measured on fully charged cells.

Researchers disassembled a sample of each cell and measured the thickness of the cell separator using a scanning electron microscope (SEM) (Table 1).

3.2. Lithium-ion cells

A123 systems[2] model ANR26650M1A cylindrical 26650 format $LiFePO_4$ cells (M1A cells) were selected for crush tests while under charge. The M1A cells were conditioned prior to the test (Table 1) and fully charged before placing the cells in the 20-L chamber. The power supply was connected to the cell just prior to the crush test. The power supply was set to 3.8 V with a 5-A current limit. The M1A cells were purchased through a battery distributor.

A Saft MP 174565 Integration™ medium prismatic cell is marketed for use in potentially explosible atmospheres as compliant with the IEC 60079-11 intrinsic safety standard (class T4 assignment between −20 °C and +40 °C) (Saft, 2009). The medium prismatic spiral-wound cell features a $LiCoO_2$-based cathode and organic solvent electrolyte. Built-in redundant safety protections include a shutdown separator, circuit breaker, and safety vent. Both cell terminals are located at the top of the cell. Samples of the cells were purchased through a battery distributor. Received cells were specified by the battery distributor as MP 174565 (MP cells).

Saft FRIWO model M52EX cylindrical “C” format $LiMnO_2$ primary cells (M52EX cells) are designed to be in compliance with the IEC 60079-11 intrinsic safety standard (FRIWO, 2012) (Saft, 2012) (DEKRA, 2011). The spiral-wound constructed M52EX cell features several safety devices, including a shutdown separator and safety vent. A sample of M52EX cells were purchased through a battery distributor. Each cell had a label warning of fire, explosion, and severe burn hazard as well as do not recharge, crush, disassemble, heat above 100 °C, or incinerate. A cell was discharged for a capacity measurement (Table 1.). A separate cell was used for the resistance measurement. Neither of these two cells was crush tested.

Researchers purchased more cells of each type described above than tested. A random sequence generator provided a random set of serial numbers assigned to all purchased cells. Tested cells were a random sample of those purchased.

4. Results

4.1. M1A $LiFePO_4$ cells

Researchers conducted a series of ten plastic wedge crush tests of the fully charged M1A cells while connected to a charging circuit. The crush apparatus was placed in the 20-L chamber filled with 6.5% CH_4-air and the cell was maintained at 40 °C. Charge current was limited to 5 A to maintain charging parameters within the safe region of the IS resistive circuit ignition curves. The charging circuit was connected a few seconds before the crush. None of the M1A cells crushed under charge ignited the chamber atmosphere. High-speed

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[2] Mention of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH). In addition, citations to Web sites external to NIOSH do not constitute NIOSH endorsement of the sponsoring organizations or their programs or products. Furthermore, NIOSH is not responsible for the content of these Web sites. All Web addresses referenced in this document were accessible as of the publication date.

video showed all M1A cells rupturing and producing smoke near the point where the wedge penetrated the can (Fig. 4). Two cells ruptured such that the cells opened electrically within a few seconds and stopped the charge current; these two tests were repeated with other cells. The charge circuit was disconnected after 2 min accompanied by a significant cell temperature drop. These ruptured cells exposed the cell's internals and cooled relatively quickly compared to the MP and M52EX cells. One test produced a few luminous sparks without igniting the chamber atmosphere. Voltage and current time traces indicated that the cells hard-shorted before the cell ruptured. These tests produced chamber overpressures of <20 kPa (2.9 psi) when the cells ruptured (Table 2). The furnace igniter subsequently ignited the chamber atmosphere for all of these tests, confirming a flammable atmosphere was present.

4.2. MP prismatic $LiCoO_2$ cells

Researchers conducted three series of crush tests with the prismatic cells. The first series used flat plates to simulate the UL 1642 method as a comparison point for tests using the plastic wedge. The second series used the plastic wedge at a crush rate similar to that used for the flat plates. Interim results with this second series of tests produced a limited number of ignitions, providing an opportunity to conduct a third series of tests with a slower crush rate, to assess the potential influence of selected crush speeds using the Fisher's exact test.

4.2.1. MP cells, flat plates—Researchers conducted five flat plate crush tests using the Saft MP cells placed within 6.5% CH_4-air. These tests were conducted at room temperature per UL 1642. The crush was applied to the wide side of the cells using 13 kN cylinder force and approximately 6 mm/s crush speed. These flat plate tests produced no ignitions in five attempts. No cell venting, temperature increase, chamber overpressure, or voltage drop was apparent from the high-speed videos or sensor time traces. After a 5-min wait period, the chamber atmosphere was ignited by the furnace igniter for these flat plate tests, verifying a flammable atmosphere was present. The flat plate compressed the cells by approximately 4%. These flat plate tests provided some assurance that the MP cell samples were compliant with UL 1642 crush test requirements.

4.2.2. MP cells, plastic wedge—Researchers conducted a series of ten plastic wedge crush tests using the Saft MP cells placed within 6.5% CH_4-air at 40 °C ambient. The crush was applied to the wide side of the cells, with the wedge tip parallel to the top of the cells. The crush speed was approximately 6 mm/s and cell penetration was limited to approximately 66%. The cells hard-shorted to a voltage of <50 mV in all ten tests and ignited the chamber atmosphere in three of these tests. Table 3 lists summary data for the three chamber ignitions. The wedge tip penetrated the cell can for all tests. After a 5-min wait period accompanied by a significant temperature drop, the furnace igniter ignited the chamber atmosphere for cells that did not ignite the chamber atmosphere.

4.2.3. MP cells, plastic wedge, slower crush—The next series of ten tests with the Saft MP cells and plastic wedge used a slower crush speed of approximately 0.43 mm/s (avg. of crush speeds in Table 4.). The cells were placed within 6.5% CH_4-air at 40 °C. The crush was again applied to the wide side of the cells with the wedge tip parallel to the top of the cells (Fig. 5). Cell penetration was limited to approximately 66%. The cells hard-shorted to a negative voltage level in all ten tests. The wedge tip penetrated the cell can for all tests. Evidence of thermal runaway was observed in six of the ten tests, with cell can temperatures exceeding 372 °C and chamber overpressures exceeding the selected ignition criteria of 50 kPa (7.25 psi). Three of these thermal runaway events produced chamber overpressures ranging from 655 to 676 kPa. Three other thermal runaway events produced lower overpressures ranging from 65 to 72 kPa. The high-speed video recordings for the low overpressure thermal runaway events were obscured by smoke, but a bright flash was discernible through the smoke. The furnace igniter was unable to ignite the chamber atmosphere following the three lower overpressure thermal runaway events, indicating that there was no longer a flammable atmosphere within the chamber. The lower and higher overpressure thermal runaway events produced similar peak cell can temperatures.

Four of the slower crush tests produced no evidence of thermal runaway, with peak temperatures of <104 °C and chamber overpressures of <2 kPa. The high-speed video recordings were obscured by smoke without the bright flash observed for the six thermal runaway events. After a 5-min wait period accompanied by a significant temperature drop, the furnace igniter ignited the chamber atmosphere for these four tests, producing overpressures of 579–655 kPa (Table 4).

4.3. M52EX primary $LiMnO_2$ cells

Researchers next conducted a series of plastic wedge crush tests using the M52EX cells placed within 6.5% CH_4-air at 40 °C. The crush speed was approximately 0.6 mm/s and cell penetration was limited to approximately 66%. A slower crush speed was selected for this series because slower crush speeds produced twice as many ignitions as the faster crush speeds with the MP cells. The slower crush induced deeper voltage drops as well. The series was stopped after observing a fourth ignition in six tests per the testing protocol (Dubaniewicz and DuCarme, 2013). The cells hard-shorted to a voltage of <0.9 V for all tests. High-speed video showed fluid flowing from the negative terminal vent after internal shorting for all tests, and prior to ignition for tests that produced ignitions. Flame emanated from the negative terminal vent for one chamber ignition. Flames and sparks emanated from elsewhere through the cell can for the other three chamber ignitions. In one test the cell continued to emit flames and sparks through holes burned through the cell can (Fig. 6) after the chamber ignition, suggesting the cell was supplying its own oxygen source, as the chamber oxygen was mostly consumed by the chamber ignition. Another chamber ignition produced a relatively high 608 °C peak temperature with a 745 kPa chamber overpressure (Table 5). The cell contents were expelled during this test, likely allowing flame from the chamber ignition to heat the inner metal can surface in contact with the thermocouple.

5. Discussion

Mikolajczak et al, (2011) reported investigating hundreds of thermal runaway events from the field. These included numerous field failures caused by latent mechanical damage, particularly of soft pouch cells where mild mechanical damage did not cause immediate failure, but rather the cells failed during subsequent cycling. With numerous new reports of Li-ion field failures, UL emphasizes the need to update existing standards and create new ones as our information and knowledge of potential Li-ion battery hazards increase. Taken together, the new IEC 62133 edition 2 crush test provisions suggest that edition 2 provides less stringent crush hazard evaluation criteria than found in the previous edition. Flat plate tests with the prismatic cell reported here and with cylindrical cells reported previously (Dubaniewicz and DuCarme, 2013) produced no adverse results. Similar cells readily ignited the chamber atmosphere with the plastic wedge crush, using a fraction of the 13 kN force specified for the flat plate test. Field events and laboratory research suggest a need for a more invasive (e.g. wedge) crush test for cell level safety evaluations.

The fire triangle provides a simple model for describing thermal runaway events (Fig. 7). Li-ion cell elements that may contribute to thermal runaway are shown on the corresponding leg of the triangle. The three legs of the triangle are isolated by a thin separator within spiral-wound constructed cells. Spiral-wound cells also feature high current discharge, enhancing heat generation from internal short circuits. A Li-ion cell thermal runaway event may be prevented by removing any leg of the triangle.

The M1A cells crushed while under charge produced no chamber ignitions. A delithiated $LiFePO_4$ cathode produces relatively little O_2 upon thermal decomposition (Ong et al., 2010) (Zaghib et al., 2012), and thus inhibits the development of thermal runaway inside of the cell by weakening the oxidizer leg of the triangle. Other potential failure modes should be considered, as appropriate. Thermal events involving large format $LiFePO_4$ batteries have been reported (Wang et al., 2012). Larger capacity $LiFePO_4$ cells may produce correspondingly more O_2 and higher internal short circuit currents than smaller capacity cells that might favor an internal thermal reaction. As another example of a potential failure mode, a cell breach may expose electrolyte fuel vapors to oxidizing air, thus creating a flammable fuel-air mixture. Such a flammable mixture may be ignited by a competent ignition source. The ANSI/ISA 60079 series of explosion protection standards anticipate equipment exposure to flammable atmospheres, and provide design requirements that may serve to minimize the risk of ignition under a number of foreseeable fault conditions external to a $LiFePO_4$ cell. A multi-phase safety approach for large capacity Li-ion cells conceivably could provide a more robust cell-level safety solution. A weakly oxidizing cathode, flame retardant electrolyte and anode, and shutdown separator combined would help to minimize and isolate two legs of the triangle other than the heat source represented by the large electrical capacity.

Tests with the MP cells produced two types of thermal events characterized by higher or lower chamber overpressures. The lower overpressure events produced an inert atmosphere as verified by the furnace igniter. The lower overpressure events likely involved cell thermal runaway with vent gases of sufficient volume to inert the chamber atmosphere as described by Roth and Orendorff (2012) and Roth (2008). All thermal events produced peak cell can temperatures exceeding 327 °C and met the ignition criteria of a pressure rise of at least 50 kPa (7.25 psi).

Researchers used the Fisher's exact test to assess the potential influence of selected crush speeds (6.0 vs. 0.43 mm/s) on ignitions with the MP cells. The Fisher's exact test is used when data are analyzed in the form of a 2 × 2 contingency table and the expected value of at least one cell in the table is <5. The null hypothesis was that crushed cell samples using two different speeds were equally likely to ignite under otherwise similar test conditions. The selected alternative hypothesis was that the slower crush speeds were more likely to produce ignitions than the faster crush speeds, indicating the use of a one-tailed probability test. An SPSS statistical package computed Fisher's exact test p values using data listed in Table 6. The one-tailed p value for Table 6 data is 0.1849. Although twice as many thermal events were observed for the slower crush speeds, the influence of crush speed is not considered to be statistically significant for these tests. A wider variation in crush speeds conceivably may produce more significant results. The selected slower crush speeds were near the limit of the testing equipment.

M52EX cell intrinsic safety evaluations included a set of external short circuit tests (DEKRA, 2011). Eleven cells were subjected to external short circuit at various ambient temperatures ranging from −25 °C to +70 °C. The external short circuits produced maximum short circuit currents ranging from 30 to 70 A, with maximum cell temperatures ranging from 98 °C to 113 °C. No visible changes to the cells were reported (no “bombage,” bursting, damage, or leakage). By comparison, the plastic wedge produced short circuits within the M52EX cells, which then frequently ignited the chamber atmosphere.

Common Li-ion cell separators are less than 30 μm thick (Baldwin, 2009) (Orendorff, 2012). These separators are too thin to meet intrinsic safety standards provisions for distance through solid insulation (MSHA, 2008) (ANSI/ISA, 2012). Results reported here demonstrate that hard internal short circuits may impair intrinsic safety, and suggest that a hard internal short circuit within these spiral-wound Li-ion cells should be considered for intrinsic safety evaluation purposes, even as a non-countable fault. Results suggest that at least 4.8 Ah capacity for spiral wound $LiCoO_2$ cells and 5.1 Ah capacity for spiral wound $LiMnO_2$ cells may pose a thermal runaway hazard, even with a shutdown separator. Comparing the M52EX results with those from the DEKRA report indicate that external short circuits tests are not an adequate surrogate for evaluating internal short circuit hazards. Some steps are being taken to help address Li-ion thermal runaway hazards in explosion protection equipment design standards. The updated ANSI/ISA 60079-0 edition 6 indicates that the use of spiral-wound, lithium–cobalt-oxide cells is not recommended due to potential thermal runaway hazards resulting from internal short circuits.

6. Conclusions

A review of the safety research literature, field events, and laboratory testing suggest the need for a more invasive (e.g., wedge) crush test for cell level safety evaluations.

The plastic wedge crush was a more severe test than the flat plate crush with a prismatic format $LiCoO_2$ cell. The plastic wedge produced deeper penetration and lower impedance (hard) shorting while using a fraction of the applied force of the flat plates.

Testing reported here indicates that Saft MP 174565 and Saft FRIWO M52EX cells pose a CH_4-air ignition hazard from internal short circuit caused by crushing damage, even with shutdown separators.

Under specified test conditions, A123 systems ANR26650M1A $LiFePO_4$ cells produced no chamber ignitions while under a charge of up to 5 A. These tests simulated a potential CH_4 ignition hazard involving underground stationary Li-ion battery powered equipment that may short circuit internally under normal charging conditions. Other potential failure modes should be considered, as appropriate.

The influence of crush speed on ignitions under specified test conditions was not statistically significant. A wider variation in crush speeds conceivably may produce more significant results. The selected slower crush speeds were near the limit of the testing equipment.

Common spiral-wound cell separators are too thin to meet intrinsic safety standards provisions for distance through solid insulation. Results with selected $LiCoO_2$ and $LiMnO_2$ spiral-wound cells demonstrate that hard internal short circuits may impair intrinsic safety as described within the ACRI2001 and ANSI/ISA 60079-11 standards, and suggest that a hard internal short circuit within these spiral-wound Li-ion and lithium cells should be considered for intrinsic safety evaluation purposes, even as a non-countable fault.

The literature indicates that spiral-wound $LiCoO_2$ cells may produce significant amounts of oxygen and high pressures during thermal decomposition, suggesting that these cells may be considered as potentially strong oxidizers and exothermic chemical reaction ignition sources for ANSI/ISA 60079-0 purposes. Observed flames from a $LiMnO_2$ spiral-wound cell after a chamber ignition within an inert atmosphere indicate a sustained exothermic chemical reaction in this cell as well. $LiFePO_4$ cells may offer a safer alternative due to limited oxygen release upon thermal decomposition.

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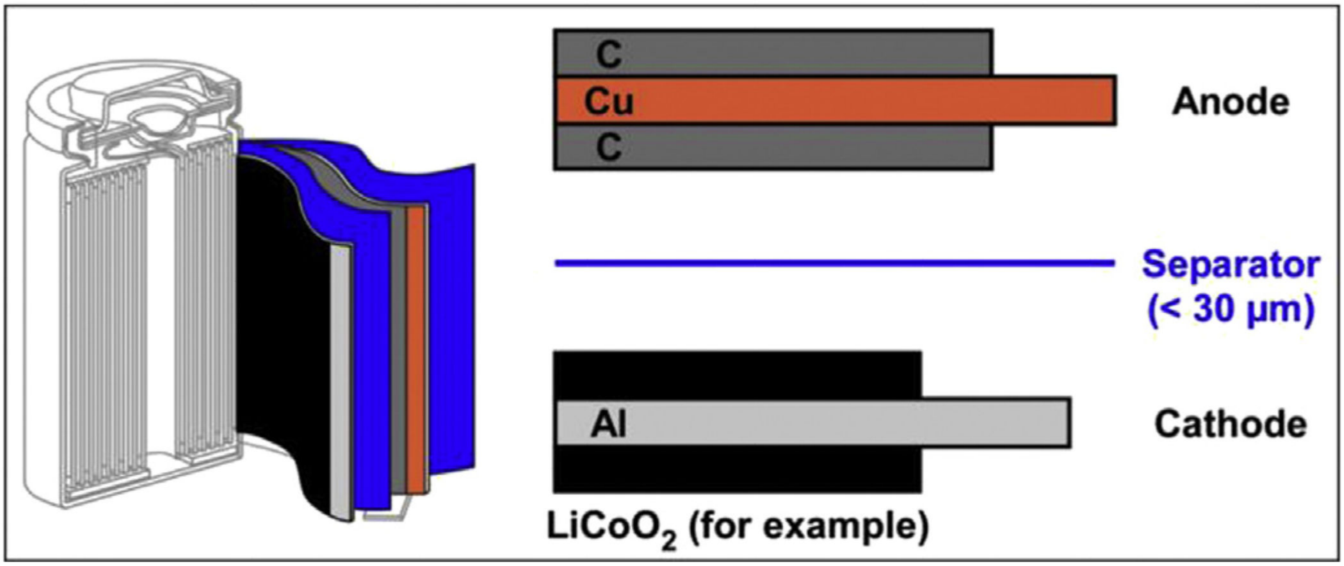

Fig. 1.

A drawing of a common spiral-wound Li-ion cell construction with a thin separator material.

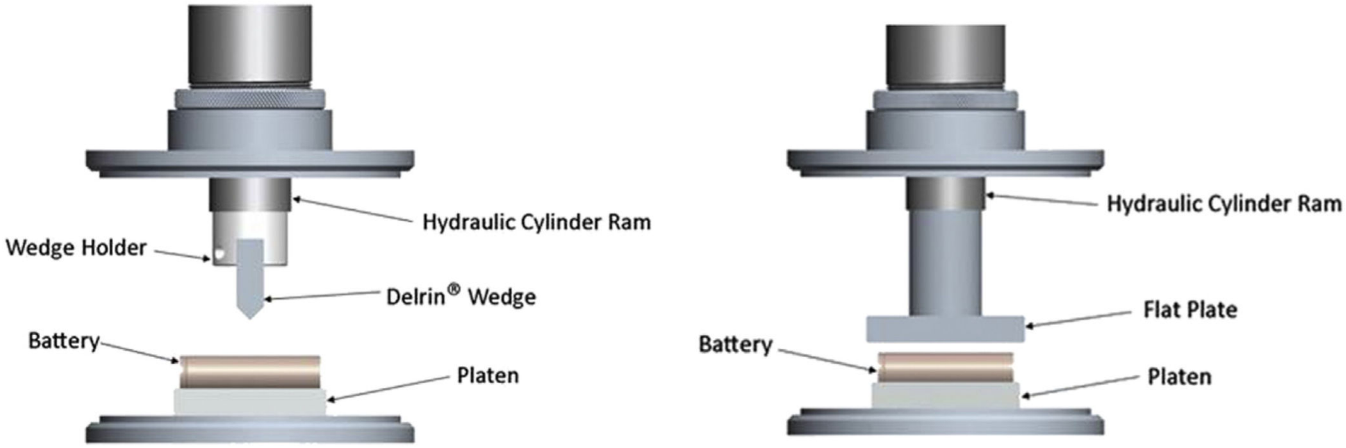

Fig. 2.
Drawings of the plastic wedge and flat plate crush test fixtures.

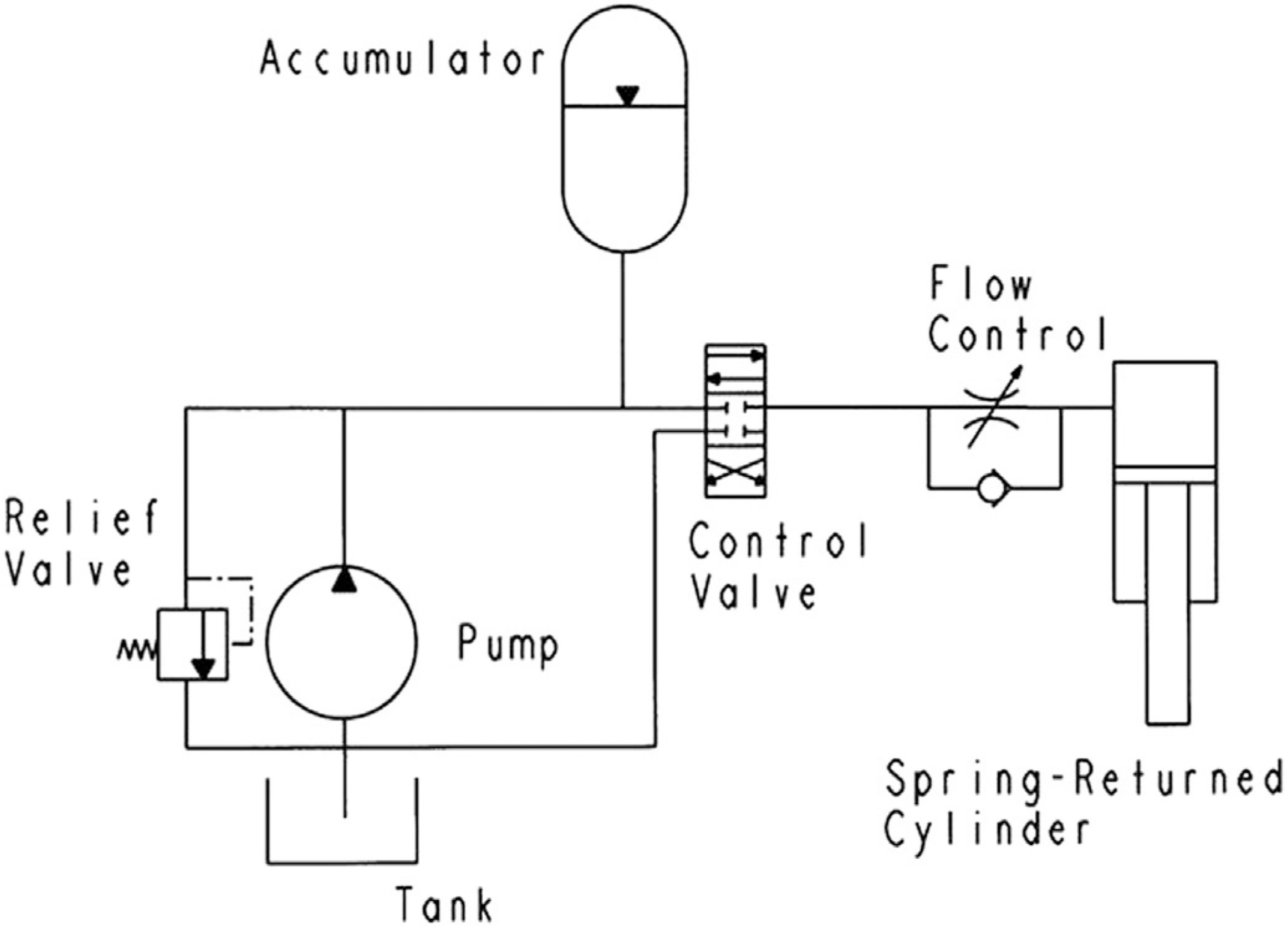

Fig. 3.

Hydraulic schematic.

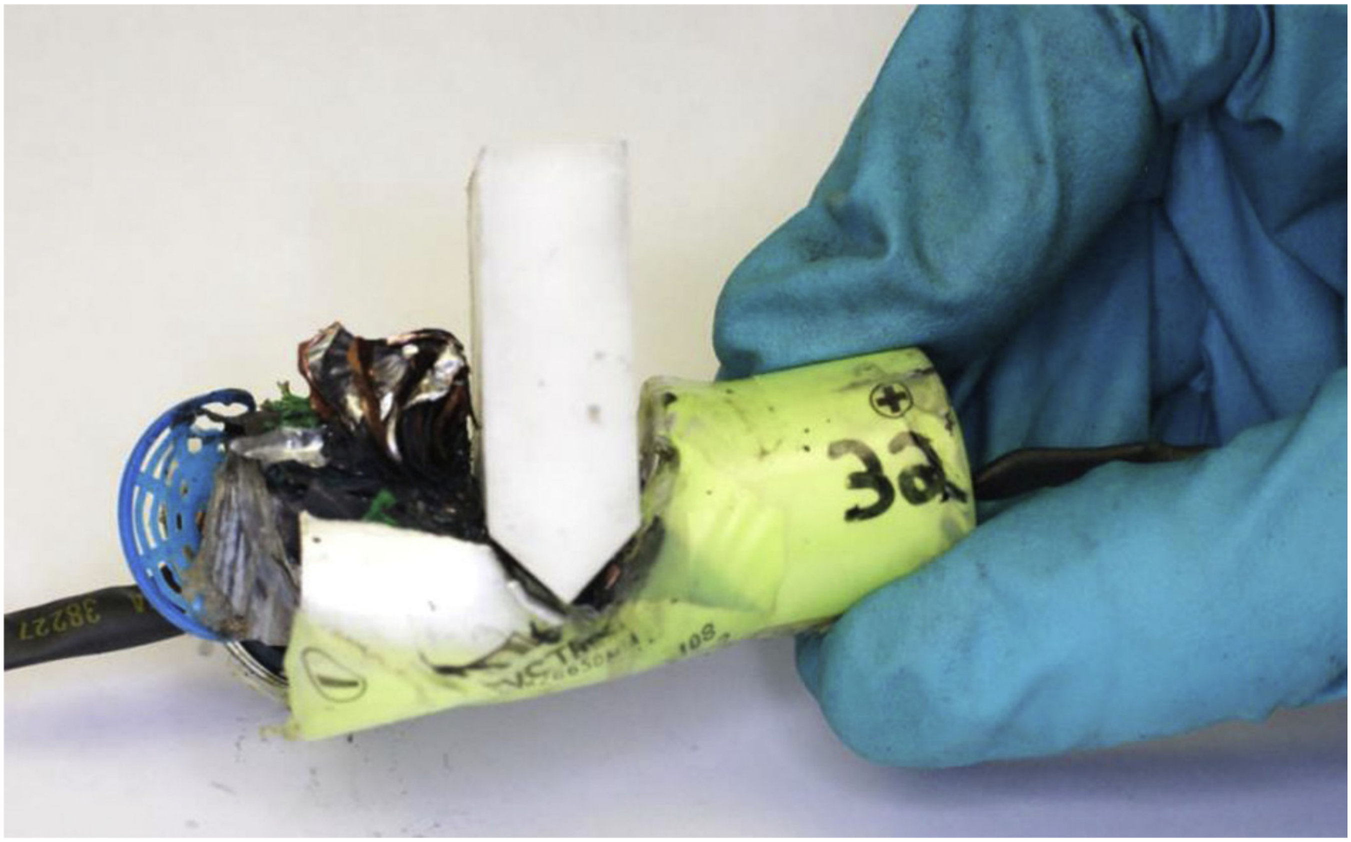

Fig. 4.

An M1A cell crushed under charge ruptured but did not ignite the chamber atmosphere.

Fig. 5.
An MP cell crushed by the plastic wedge at a slower speed that produced a lower overpressure thermal event. The cell swelled significantly.

Fig. 6.

An M52EX cell crushed by the plastic wedge that ignited the chamber atmosphere with two holes burned through the side of the cell can.

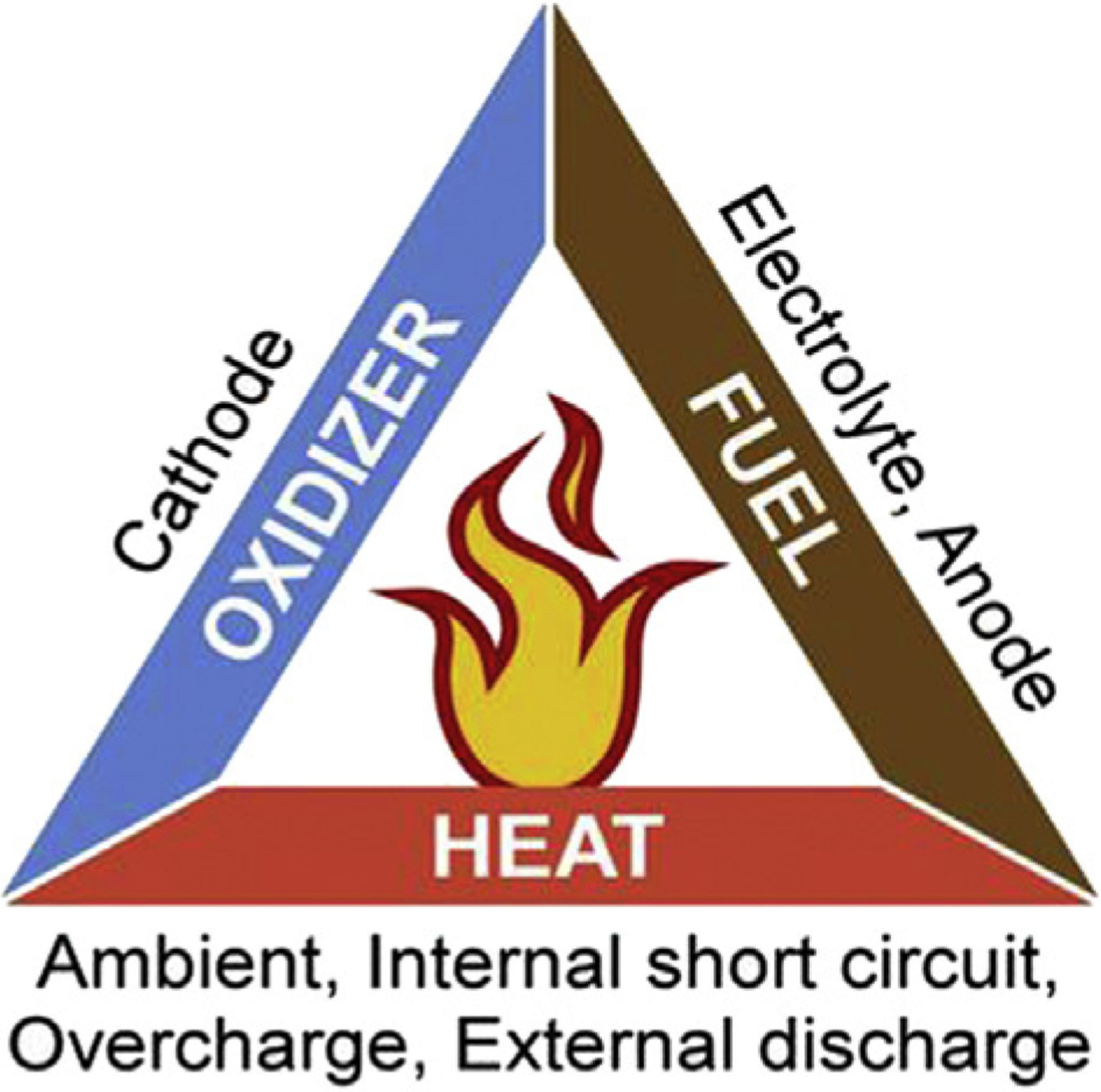

Fig. 7.

Fire triangle analogy for Li-ion cell thermal runaway.

Table 1

Cell specifications and conditioning summary data.

	M1A	**MP**	**M52EX**
Charge, discharge voltage	3.8, 2.0	4.2, 2.5	–, 2.0
Charge or discharge constant current (A)	3	2.4	0.2
End charge current (mA)	50	50	–
Rated capacity (Ah)	3.2	4.8	5.1
Measured discharge capacity (% rated)	>100%	>96%	101.7%
Measured resistance range (mΩ)	23 to 29	41 to 51	120
Measured separator thickness (μm)	20	20	40

Table 2

Summary data, M1A cells crushed under charge, plastic wedge, 40 C, 6.5% CH_4-air non-ignitions.

Cylinder force at short circuit kN (lbf)	1.83 to 3.18 (411–716)
Crush speed avg. (range) mm/s	3.9 (3.0–5.3)
Chamber overpressure kPa (psi)	<20 (2.9)
Peak cell can temperatures °C	67 to 174

Table 3

Summary data, MP cells, plastic wedge, 6 mm/s crush speed, 40 °C, 6.5% CH_4-air ignitions.

Cylinder force at short circuit kN (lbf)	6.72 to 7.65 (1510–1720)
Crush speed avg. (range) mm/s	6.0 (4.8–7.3)
Chamber overpressure kPa (psi)	648 to 696 (94–101)
Peak cell can temperatures °C	327 to 510

Table 4

Summary data for MP cells crushed by the plastic wedge, slower crush speeds.

	Higher pressure thermal runaway	Lower pressure thermal runaway	No thermal runaway
Cylinder force at short circuit kN (lbf)	6.54 to 7.30 (1470–1640)	7.03 to 7.87 (1580–1770)	6.72 to 7.78 (1510–1750)
Crush speed avg. (range) mm/s	0.33 (0.2–0.46)	0.49 (0.44–0.58)	0.46 (0.3–0.66)
Chamber overpressure kPa (psi)	655 to 676 (95–98)	65 to 72 (9.4–10.4)	<2 (0.3)
Furnace igniter overpressure kPa (psi)	–	–	579 to 655 (84–95)
Peak cell can temperatures °C	390 to 427	372 to 423	102 to 104

Table 5

Summary data, M52EX cells, plastic wedge, 40 °C, 6.5% CH_4-air ignitions.

Cylinder force at short circuit kN (lbf)	3.49 to 4.27 (784–960)
Crush speed avg. (range) mm/s	0.58 (0.52–0.69)
Chamber overpressure kPa (psi)	421 to 745 (61–108)
Peak cell can temperatures °C	340 to 608

Table 6

Fisher's exact test comparison of crush speed influence on ignition using the MP cells.

MP cells	Ignitions	No ignitions	Totals
Slower crush	6	4	10
Faster crush	3	7	10
Totals	9	11	20