

Are Lithium Ion Cells Intrinsically Safe?

Thomas H. Dubaniewicz, Jr.

Lead Research Electrical Engineer
National Institute for Occupational Safety and Health
Office of Mine Safety and Health Research
626 Cochrans Mill Rd.
Pittsburgh, PA 15236, USA
tcd5@cdc.gov

Joseph P. DuCarme

Research Mechanical Engineer
National Institute for Occupational Safety and Health
Office of Mine Safety and Health Research
626 Cochrans Mill Rd.
Pittsburgh, PA 15236, USA
jld6@cdc.gov

Abstract – National Institute for Occupational Safety and Health (NIOSH) researchers are studying the potential for Li-ion battery thermal runaway from an internal short circuit in equipment approved as permissible for use in underground coal mines. Researchers used a plastic wedge to induce internal short circuits for thermal runaway susceptibility evaluation purposes, which proved to be a more severe test than the flat plate method for selected Li-ion cells. Researchers conducted cell crush tests within a 20-L chamber filled with 6.5% CH₄-air to simulate the mining hazard. Results indicate that LG Chem ICR18650S2 LiCoO₂ cells pose a CH₄ explosion hazard from a cell internal short circuit. Under specified test conditions, A123 Systems 26650 LiFePO₄ cells were safer than the LG Chem ICR18650S2 LiCoO₂ cells at a conservative statistical significance level.

I. INTRODUCTION

Gas or dust explosions are some of the greatest hazards faced by underground coal mine workers. Methane (CH₄) gas is released during the mining process and accumulates in areas that are not well ventilated. Coal dust accumulations can form explosive dust clouds when entrained into the air. CH₄ ignitions or explosives can disperse coal dust layers into the atmosphere that subsequently ignite and propagate as powerful explosions. Although fatal coal mine explosions in the US may be less frequent in modern times, they can account for large numbers of deaths, as sadly evidenced by the recent Upper Big Branch disaster, with 29 killed [1].

Mining equipment used in certain locations of underground coal mines where there is a normal risk of exposure to CH₄ must be approved as permissible by the Mine Safety and Health Administration (MSHA). The term “permissible” refers to equipment that meets specifications for construction and maintenance ensuring that such equipment will not cause a mine explosion or fire (30 CFR 75.2)[2]. Permissible equipment may be evaluated as Intrinsically Safe (IS). 30 CFR 18.2 interprets IS as incapable of releasing enough electrical or thermal energy under normal or abnormal conditions to cause ignition of CH₄ or natural gas and air of the most easily ignitable composition.

An MSHA-permissible cap lamp powered by a lithium ion (Li-ion) battery pack ignited a fire at the National Institute for Occupational Safety and Health (NIOSH) Pittsburgh Safety Research Coal Mine (SRCM) office building [3]. The newly purchased cap lamp was placed on a wooden pallet and caught fire overnight while on charge. Melted red plastic from the cap lamp battery enclosure was found spattered across the office, indicative of an explosive thermal runaway event. There was no indication of user abuse that might have contributed to the event. A definitive failure mechanism causing the fire was not determined. Concerns over fire and explosion hazards prompted MSHA to issue a Program Information Bulletin (PIB) regarding special precautions that should be observed when charging Li-ion batteries or equipment containing Li-ion batteries [4].

In recent years, NIOSH has been engaged in new technology development of mine communications and tracking equipment (CTE) to satisfy mandates of the 2006 Mine Improvement and New Emergency Response (MINER) Act. A consequence of the MINER Act is the proliferation of backup batteries in underground coal mines to power stationary CTE during mine emergencies that may involve ventilation disruption and CH₄ buildup. An additional fire or explosion hazard involves underground stationary CTE that is on charge and unattended for long periods of time, and may be exposed to CH₄ and/or coal dust under normal operation. Stationary battery-powered CTE in coal mines may also be susceptible to mechanical damage, such as from roof falls. The 2001 explosion disaster at the Jim Walter Resources #5 mine involved a battery damaged by a roof fall [5].

Most recently, the MSHA Approval and Certification Center is investigating a Li-ion powered cap lamp that caught fire in an underground coal mine. A written report of the incident was not publically available as of this writing.

NIOSH researchers are studying Li-ion battery thermal runaway potential of MSHA-permissible equipment in order to develop safety recommendations for underground coal mine applications. The study includes an experimental evaluation of potential thermal runaway initiating events of cells placed within CH₄-air atmospheres to simulate the mining 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. Researchers conceived a new method of inducing an internal short circuit for thermal runaway susceptibility evaluation purposes that was thought to overcome limitations of two other commonly used methods. This work summarizes literature findings and experimental observations from the first phase of the study, along with interim recommendations.¹

II. LITERATURE REVIEW

QinetiQ North America (QNA) [6] and Roth et al. [7] describe a three-stage thermal runaway process observed for certain Li-ion cell designs thought to achieve high levels of performance and safety. These high energy density devices contained electrodes separated by a polymer of perhaps a few tens of micrometers thick, immersed in a flammable organic electrolyte. Cathode and anode active materials begin to react exothermically with the electrolyte above a certain threshold temperature. If the heat is not dissipated, the temperature continues to rise above a certain onset temperature when the cell enters stage two, characterized by rapid heat release. Venting and release of smoke may occur during stage two. Additional heating causes the cell to enter stage three, in which high-rate cathode reactions cause the temperature to rise rapidly and flame or explosion to occur. This final stage is thermal runaway, which is characterized by a self-heating rate of 10 °C/min or more.

Standard UL 1642 [8] provides requirements for the construction, performance, testing, and marking of primary (nonrechargeable) and secondary (rechargeable) batteries containing lithium in various forms (metallic, alloy, or ion). Test evaluations include electrical, mechanical, and environmental tests. Mechanical integrity evaluations include a crush test, where samples of batteries are squeezed between two flat surfaces until 13 kN (3000 lbs) is reached, at which point the force is released. Battery safety standards IEC 62133 and UL 2054 specify a similar crush test [9]. The criterion for passing the UL 1642 crush test is that the samples shall not explode or catch fire. The UL 1642 interpretation of explosion is when the cell or battery contents are forcibly expelled and the cell or battery is torn or split into two or more pieces.

There have been numerous reported field failures of Li-ion battery-powered equipment. NIOSH previously contracted with QNA to perform a safety assessment of emergency backup batteries and battery charging systems for underground mining applications [6]. With regard to the Li-ion battery thermal runaway hazard, QNA concluded from Consumer Product Safety Commission recall data that more is required for acceptable safety than UL testing provides. To help address the mining safety issue, QNA discussed the

merits of experimental research to crush or puncture Li-ion cells within explosive CH₄-air atmospheres. Mikolajczak et al. [9] 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.

Tobishima [10] reviewed Li-ion cell thermal runaway events, safety evaluation methods, and materials to improve thermal stability. When describing the UL 1642 crush test, Tobishima recommended an alternative test that was asserted to be harder to pass. One key feature of the alternative test was crushing the cell to less than half of its original thickness. The UL 1642 crush test does not specify a depth of crush.

Tobishima [10] described a nail penetration test, indicating it was a very important test for simulating internal short circuits linked to many actual accidents. However, some studies [9], [11]-[14] suggest that the nail test's ability to create thermal runaway from internal short may be defeated by the nail itself. Described weaknesses of the nail penetration test include thermal or electrical energy dissipation through the metallic nail alone, or through the metallic nail in contact with an exterior metallic cell can. Loud et al. [14] observed that a nail penetration test allowed gas and electrolyte to exit the cell at the point of penetration. Further, UL 1642 does not prescribe a nail penetration test.

Megerle et al. [15] demonstrated thermal runaway using an aggressive, iterative crush protocol. They observed that crush tests inducing case cracking generally produced less severe results than tests without case cracking.

Mikolajczak et al. [9] 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 [13]. Mikolajczak et al. [9] provided two explanations for the ease of producing thermal runaway from an edge crush, one relating to the inability to penetrate the separator in the case of the conventional crush test, and the other to electrical or thermal energy dissipation through a nail in the case of perpendicular metallic nail penetration. For cylindrical cells, the UL 1642 crush test is applied with the cell's longitudinal axis parallel to the flat plates only. The direction of force is perpendicular to the electrode surface within the cylindrical cell.

An apparently common safety misconception involves the crush test and internal shorting. Arora et al. [16] indicate that the standard cell crush test involves applying a force to the cell's enclosure until an internal short circuit is achieved. However, the UL 1642 crush test is stopped as soon as a predetermined force is applied without regard to achieving internal shorting. Mikolajczak et al. [9] found that when crush damage is perpendicular to the cell, it may not cause penetration of the separator, and thus, minimal or no internal shorting occurs.

UL 1642 [17] and IEC 62133 standard committees are considering a forced internal short circuit (FISC) test for

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.

inclusion in newer editions of UL 1642 and IEC 62133. The FISC test being considered for IEC 62133 [18] is based on FISC methods described in [19]. A nickel particle is inserted inside the cell and a press machine is used to compress the cell in an attempt to force the nickel particle to create an internal short circuit. The FISC test is stopped after a period of time once a voltage drop of at least 50 mV occurs, which is defined as attaining an internal short circuit. The FISC test is also stopped if the press force reaches 800 N for cylindrical cells or 400 N for prismatic cells, without creating an internal short. The acceptance criterion is no fire. Thus, the proposed FISC test procedures suggest that a cell may pass the test without exhibiting any indication of an internal short (press force limited), or by exhibiting limited shorting indicated by a voltage drop as small as 50 mV.

Balakrishnan et al. [20] reviewed safety mechanisms in Li-ion batteries. One such mechanism is a pressure relief vent often built into the cell. Under severe mechanical and electrical abuse conditions, the vent may provide a safe means of releasing internal pressure before the cell reaches excessively high temperatures. However, Roth et al. [7] described a thermal runaway process where cell venting may be followed by explosive decomposition. Because of the uncertainty surrounding the cell vent effectiveness, researchers used high speed video recordings in the NIOSH research study to observe the effectiveness of the cell venting process as the cell was crushed.

Thermal runaway susceptibility is dependent upon cell state of charge (SOC) and capacity. Cai et al. [12] reported on simulations and experiments of internal short circuits in Li-ion and Li-ion-polymer cells induced by “pinching” the cell between two metallic spheres. They found that the internal short circuit risk of thermal runaway increased with cell capacity and SOC for three types of prismatic form factor cells studied. White et al. [21] conducted Accelerating-rate Calorimetry (ARC) tests of selected 18650-type cells and observed that the onset temperature of a 2.1-Ahr LiCoO₂ cell at 82% SOC was comparable to that of a 1.1-Ahr LiFePO₄ cell at full SOC. They concluded that self-heating onset temperature and self-heating rate were functions of cell energy. In order to factor out these SOC and capacity dependencies, in the current study, researchers tested two cell designs of similar capacity, fully charged.

Several studies [9], [22] indicate that preheated cells are more susceptible to thermal runaway. Santhanagopalan et al. [22] developed an electrochemical thermal model and conducted experiments of Li-ion cell internal short circuits. The thermal model indicates that a cell passing a short circuit test at room temperature has a greater tendency towards runaway for higher values of the initial cell temperature. They reported that the margin for safety is reduced in a preheated cell. A short between lithiated (charged) anode material and an aluminum current collector produced the most heat of the short circuit scenarios studied. Mikolajczak et al. [9] explain that high ambient temperatures or adiabatic insulation will increase the likelihood that any given internal

fault can drive a cell to thermal runaway, and thus increase the energy available to heat the cell. IEC 60079-11 [23] and ACRI2001 [24] specify a maximum ambient temperature of 40 °C for IS evaluation purposes, unless otherwise specified. Thus, 40 °C may be considered within the specified ambient temperature range for “normal” operation of most IS equipment. 40 °C is below Li-ion cell self-heating onset temperatures [6], [7]. In contrast, the UL 1642 crush test is conducted at room temperature.

Some newer Li-ion chemistries are proving to be safer than others. QNA [6] reviewed ARC data for several different Li-ion chemistries, including data published by Roth [25]. LiMn₂O₄ and LiFePO₄ chemistries displayed higher onset temperatures than several others studied, showing they were more resistant to thermal abuse. The peak self-heating rate was lowest for the LiFePO₄ cell by a wide margin, leading QNA to conclude that LiFePO₄ cells were the safest on the market. A common LiCoO₂ cell chemistry was the least stable of those studied. QNA went on to recommend that either LiMn₂O₄ or LiFePO₄ may be sufficiently safe for underground coal mining applications. Chen and Richardson [26] describe the thermal stability of LiFePO₄ and its charged counterpart, FePO₄, as “remarkable” and instrumental in its commercialization as a Li-ion battery cathode material. Hund and Ingersoll [27] reported no sparks or fire from an over voltage charge abuse test of a LiFePO₄ cell. Scrosati and Garche [28] suggested that LiFePO₄ may be the cathode chemistry of choice for some hybrid electric vehicle (HEV) projects, for safety reasons. Based on these findings about potential safety benefits of LiFePO₄ chemistries, researchers included a commercial LiFePO₄ cell in the NIOSH research study for evaluation as a potentially safer cell for powering IS mining equipment.

Magison [29] describes IS equipment and wiring as not capable of releasing sufficient electrical or thermal energy under normal or abnormal conditions to cause ignition of a specific hazardous atmospheric mixture in its most easily ignited concentration. Hazardous atmospheres in underground coal mines include CH₄-air mixtures and coal dust. MSHA requires [30] cap lamp components to comply with ACRI2001 [24] criteria for the evaluation and test of IS equipment. ACRI2001 contains provisions for lithium batteries, including a requirement that lithium batteries shall not explode or cause a fire when tested per UL 1642. MSHA relies on UL 1642 cell level evaluations to help ensure intrinsic safety in potentially explosive atmospheres.

Somewhat similar criteria for IS equipment used in other US industries is found in standard ANSI/ISA 60079-11. This is the US adopted version of the IEC 60079-11[23]. IEC 60079-11 recognizes that some lithium types of cells or batteries may explode. The standard notes that “Cells that comply with the requirements of UL 1642 or IEC 62133 or other relevant safety standards are considered to meet this requirement.” IEC 60079-11 permits battery packs containing serial and parallel configurations of Li-ion cells. All of these IS standards, national or international, for all applicable

industries, rely on other cell level safety standards for ensuring intrinsic safety of lithium battery-powered equipment used in potentially explosive environments. The IEC Technical Committee 31 has established a working group to address the safety of electrochemical cells and batteries in equipment for explosive atmospheres.

Several studies [31], [32] found that Li-ion cells can produce high explosion pressures. Over concerns regarding laboratory equipment damage and injury to staff, K. H. Yen et al. [31] studied explosive failures of Li-ion cells that may occur when subjected to typical safety standards abuse tests. The concern was prompted by a chemical hood that was destroyed by the blast pressure of failed cells. They conducted an over-temperature abuse test of a 2.6-Ahr Li-ion cell and measured 10.89 MPa (1580 psi) gage pressure in an adiabatic calorimeter as the cell temperature reached approximately 200 °C. Although not specified in the paper, a co-author indicated that the chamber volume was 17 mL. Jhu et al. [32] also studied the explosive failure of Li-ion cells placed within an adiabatic calorimeter. A fully charged 2.6-Ahr LiCoO₂ 18650 cell initiated self-heating at 129.1 °C, began thermal runaway at 160 °C, and peaked at 903 °C. Chamber gage pressure peaked at 10.797 MPa (1565.9 psi), which destroyed their chamber. Subsequent tests used a 150-mL expansion chamber to reduce peak pressures to protect the equipment and lab personnel. The 150-mL expansion chamber reduced the peak gage pressure to 2446 kPa (354.7 psi) during a test similar to the test that produced the 10.797 MPa gage pressure. Jhu et al. [32] concluded that an internal short circuit could lead to violent fire and explosion. With these safety concerns in mind, in the current study, researchers conducted cell crush tests within a 20 L chamber with no CH₄, and measured chamber pressures to assess the potential for personal injury.

III. METHODS

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. 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 over metal to minimize electrical and thermal energy dissipation by the test fixture itself. The wedge shape and point angle were selected because they were thought 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 [9]. 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.

Researchers designed and fabricated a custom crush fixture to fit inside a 20-L chamber for these experiments. The press uses a small single-acting hydraulic cylinder with a 43-mm bore and 54-mm stroke. The cylinder incorporates an

internal return spring; this retracts the cylinder ram when hydraulic fluid is released. A cutaway view of the press is shown in Fig. 1. The top and bottom plates are connected with a steel tube (not shown for clarity). This tube has access holes for installing the battery and Delrin® [33] plastic wedge. The wedge is made from a 12.7-mm-thick sheet of Delrin® by machining a 45° bevel on each side to create a 90° pointed edge. A commercially available 0.75-kW hydraulic power unit supplies the required flow. The system relief valve is set to produce 13 kN of force at the cylinder ram. The press is controlled from a solenoid-operated hydraulic four-way valve. A bleed-in flow control is used to regulate the speed of the ram and was set to about 5 mm/s. Viatran model 248 pressure transducer measurements are used to calculate cylinder force.

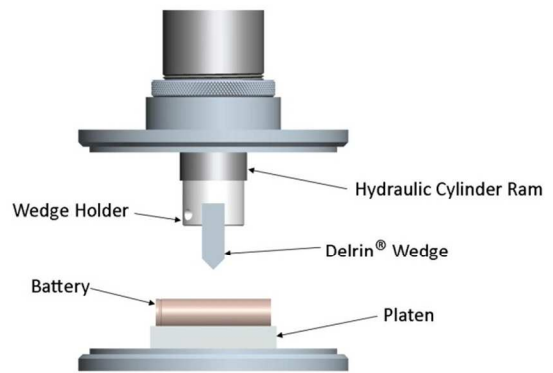


Fig. 1. Drawing of plastic wedge crush fixture with LG Chem cell.

The wedge and wedge holder were fabricated from Delrin® [33]. This material was selected for its mechanical, thermal insulating, and electrical resistance properties as well as its ability to be readily machined. This plastic has high mechanical strength and rigidity, excellent resistance to solvents and chemicals, and good electrical and thermal insulating characteristics. The material’s properties are listed in Table I. The wedge is considered a sacrificial element and a new one is installed for each test.

TABLE I. DELRIN® PROPERTIES AND CHARACTERISTICS

Property	Value
Yield Stress, MPa	71
Tensile Strength, MPa	96
Shear Strength, MPa	62
Tensile Modulus, MPa	3000
Surface Resistivity, Ω	>1E15
Thermal conductivity, W/m-K	0.33
Hardness, Rockwell M scale	92
Melt temperature, °C	>200

For all tests, the bottom platen was fabricated from steel and coated with an insulating paint. Its thickness was calculated to position the battery so that at full ram extension, the Delrin® wedge would penetrate about 66% into the battery’s diameter. Penetration was greater than 50% as recommended by Tobishima [10].

A ram extension with a 13-mm-thick flat plate was fabricated from steel and used to perform tests that simulated the UL 1642 crush test. The plate was also coated with an insulating paint. The extension length and bottom platen height were selected to allow only a slight clearance between them at full ram extension.

An IEC Ex certificate [34] for the manufacturer and model of cap lamp that caught fire at the NIOSH SRCM office [3] listed an LG Chem ICR18650S2 or a Sanyo UR 18650F cell as approved for use with the cap lamp. Samples of LG Chem model ICR18650S2, cylindrical 18650 format LiCoO₂ cells (LG Chem cells) were purchased through a battery distributor. Codes on the LG Chem cells indicated that they were manufactured seven years prior to these ignition tests. A specification sheet for the LG Chem cells [35] describes safety tests that the cell should pass, including a flat plate crush per UL 1642 and a nail penetration test. These tests were specified at room temperature. A123 systems² model 26650A, cylindrical 26650 format LiFePO₄ cells (A123 cells) [36] with similar rated capacity were selected for comparative testing and purchased directly from the manufacturer. A123 Systems indicated that the A123 cells were compliant with all UL 1642 single cell tests and were manufactured four years prior to these ignition tests. Newer versions of the LG Chem 18650 and A123 26650 cells have higher rated capacity.

Ignition experiments were conducted in a 20-L test chamber which can be used at initial pressures that are below, at, or above atmospheric as long as the maximum explosion pressure is less than 2100 kPa (305 psi). The CH₄-air concentration was set to 6.5% by volume per IEC 60079-11 provisions for testing potential thermal ignition sources in mines. The concentration of the gas-air mixture was determined by partial pressures and set to 100 kPa (14.5 psi) at room temperature. The CH₄ 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 after the temperature stabilized. Heat tape was wrapped around the exterior of the chamber. A fan within the chamber provided mixing. A furnace heating element placed inside the chamber was used to ignite the atmosphere after tests that resulted in non-ignitions, confirming that a flammable atmosphere was present.

Researchers conducted cell crush tests with no CH₄ in the 20-L chamber and measured chamber pressures to assess the potential for personal injury [31], [32]. Open head space volume inside the chamber was estimated to be 18 L, taking

into account the Li-ion cell, press, fan, and white LED fixture.

Chamber instrumentation included a gas pressure transducer (Viatran model 218-28) and a 30-AWG, 0.25-mm-diameter (0.01-inch-diameter) K type thermocouple attached to the surface of the Li-ion cell. IEC 60079-0 [37] considers surface temperature of equipment under test as stabilized when the rate of temperature rise falls to 2 K/hr. Researchers waited at least 1 hr after the cell surface temperature reached 38 °C before conducting ignition tests at 40 °C.

The thermocouple was inserted underneath plastic wrapping around the LG Chem cell; against the metallic can about 1.3 cm (0.5 inch) from the cell end opposite the vent. Cardboard insulation around the A123 cell was removed, and the thermocouple was taped against the metallic can about 1.3 cm from the cell end opposite the vent.

The chamber pressure transducer detected ignitions in conjunction with a high speed video camera. The criterion for ignition was a pressure rise of at least 50 kPa (7.25 psi), a value derived from previous explosibility research [38], [39]. 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. Cell venting observed prior to ignitions in this study indicated that the cell vent was not effective protection. Ignitions saturated (whited-out) the video recordings whereas non-ignitions did not.

A personal computer-based Labview data acquisition program recorded cell voltages, pressure transducer signals, and thermocouple measurements. Data acquisition was initiated by a signal from the hydraulic solenoid-operated four-way valve. An independent laboratory calibrated in-house multimeters traceable to the National Institute of Standards and Technology (NIST). Thermocouple measurements were checked in-house using a thermocouple calibration cell.

A Vencon UBA5 Battery Analyzer preconditioned and analyzed cells for testing. 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.

Researchers used the Fisher's exact test [40] to assess the relative safety between two cell designs. The null hypothesis was that crushed samples of two different Li-ion cell designs were equally likely to ignite under similar test conditions. A maximum of 10 tests were planned for a particular cell design. Only a cell design that produced 0 ignitions in 10 attempts was to be considered as a safer cell candidate. The alternative hypothesis under this scenario was that the alternative cell design was more likely to ignite than the safer cell candidate. There was no possibility that the alternative cell design would be observed to be less likely to ignite, indicating the use of a one-tailed probability test. This implied that at least 4 ignitions in 10 attempts with another cell design would be needed to produce a conservative one-

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.

tailed significance value of $p < 0.05$ —that is, a less than 0.05 probability that the observed ignitions and non-ignitions came from the same underlying population, thus rejecting the null hypothesis. The cell designs could then be considered independent from an ignition standpoint, under specified test conditions, at a conservative significance level. A test series with a particular cell design was ended when either 4 ignitions were observed or a total of 10 cells were tested. A series was stopped after 4 observed ignitions to save wear and tear on the chamber instrumentation. An SPSS statistical package computed Fisher’s exact test p values using ignition and non-ignition data listed in a 2 by 2 table such as that shown in Table V. The test assumes random sampling; a random sequence generator provided a random set of serial numbers assigned to cell samples.

IV. RESULTS

A. Cell Conditioning

Cells were conditioned within manufacturer’s recommendations [35], [36] at room temperature (Table II). Cells were cycled through at least 3 charge-discharge cycles using a constant current, constant voltage routine. Measured discharge capacity was slightly below rated, and resistance measurements were slightly above rated. A123 Systems indicates that Li-ion cells may show certain shelf life or calendar-related aging effects where impedance grows with time and capacity is lost over time. Additionally, internal resistance and capacity measurement protocols may influence results. The capacities of the two cell designs were similar and greater than 95% of rated (MSHA recommends battery replacement when capacity fades to 80% of rated [4]). The cells were given a final top-off charge prior to ignition tests.

TABLE II. CELL CONDITIONING SUMMARY DATA

	LG Chem	A123
Charge, discharge voltage	4.2, 3.0	3.8, 2.0
Charge or discharge constant current (A)	1.075	3.0
End charge current (mA)	50	50
Rated capacity (Ahr)	2.2	2.2
Measured discharge capacity (% rated)	> 95%	> 96%
Rated impedance @ 1 kHz (mΩ)	90	8
Measured resistance range (mΩ)	113 to 135	25 to 43
Cell age when tested (years)	7	4

B. Plastic Wedge vs. Flat Plate Methods

The plastic wedge and UL simulated flat plate methods were compared in CH₄-air ignition tests using the LG Chem cells. The cell was maintained at room temperature for the flat plate tests per UL 1642, and at 40 °C for the plastic wedge tests per IEC 60079-0 and ACRI2001. The chamber contained 6.5% CH₄-air at 100 kPa. The cylinder force for both the wedge and flat plate were set to 13 kN per UL 1642. The plastic wedge tests were stopped after obtaining four ignitions. The flat plate produced no ignitions in ten attempts (Table III). The chamber atmosphere was ignited by the

furnace element for these 10 flat plate tests, verifying a flammable atmosphere was present. The flat plate compressed the cells about 18%.

TABLE III. FLAT PLATES VS. PLASTIC WEDGE, 6.5% CH₄-AIR IGNITION TESTS, LG CHEM CELLS.

	Ignitions	No ignitions	Totals
Plastic wedge, 40 °C	4	3	7
Flat plates, 25 °C	0	10	10
Totals	4	13	17

Video recordings showed non-luminous material ejecting from the cell vent prior to the four LG Chem cell CH₄-air ignitions. Three of the four cells ruptured and spewed luminous sparks from the side of the can close to the plastic wedge, after initial cell venting and prior to ignition (Fig. 2). The fourth can did not rupture on the side but spewed sparks from the cell vent, after initial cell venting and prior to ignition. Ignitions saturated (whited-out) the video recordings.

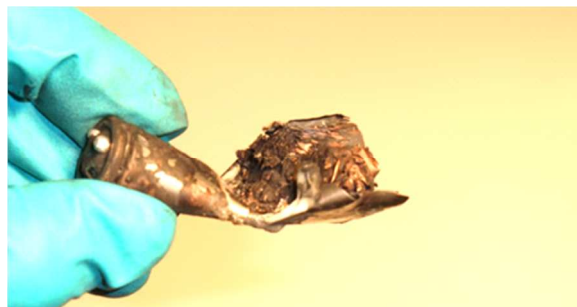


Fig. 2. Ruptured LG Chem cell crushed by the plastic wedge that ignited 6.5% CH₄-air.

Figs. 3-5 show time traces for an LG Chem cell CH₄-air ignition, crushed by the plastic wedge at 40 °C. Fig. 3 shows the cell yielding and hard shorting at cylinder forces significantly less than 13 kN. Figs. 4-5 show pressure and temperature peaks from 6.5% CH₄-air ignition occurring shortly after the hard short. Summary data for the four LG Chem cells that ignited CH₄ are listed in Table IV. Measured cell can temperatures were lower than the thermal runaway or CH₄-air flame temperatures due to the insulating nature of the can, plastic cover, and separation distance between the thermocouple and short circuit.

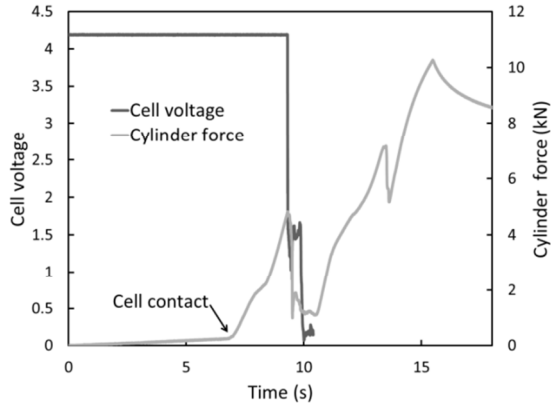


Fig. 3. Graph showing that an LG Chem cell hard shorted as the plastic wedge applied force reached 4.75 kN (1065 lbs).

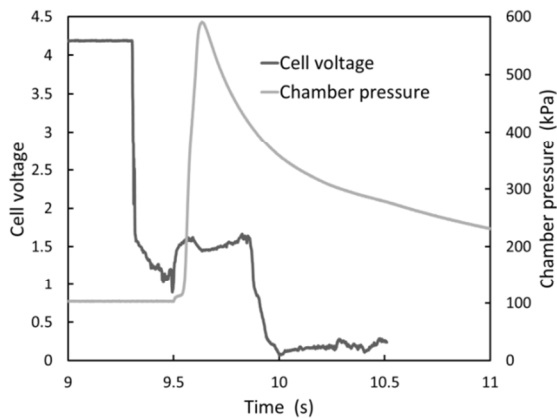


Fig. 4. Graph showing that an LG Chem cell hard shorted prior to 6.5% CH₄-air ignition indicated by 586 kPa (85 psi) peak chamber pressure.

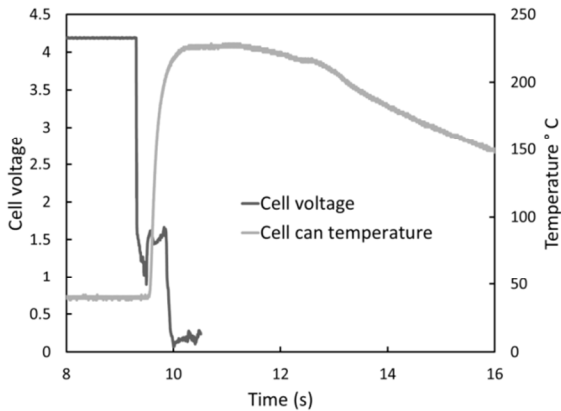


Fig. 5. Graph showing that an LG Chem cell hard shorted and the cell can surface temperature reached 221 °C during a 6.5% CH₄-air ignition.

TABLE IV. CHAMBER SENSOR SUMMARY DATA, 6.5% CH₄-AIR IGNITIONS, LG CHEM CELLS, PLASTIC WEDGE, 40 °C.

Cylinder force at ignition, kN (Lbs)	4.75 to 5.96 (1068 to 1340)
Peak chamber pressure, kPa (psi)	586 to 738 (85 to 107)
Peak cell can temperature, °C	221 to 360

Three LG Chem cell plastic wedge tests at 40 °C did not produce ignitions (Fig. 6). These cells were hard shorted to a few tenths of a volt within a few seconds after wedge contact. The wedge tip penetrated the can in two of the three cells. There were no measurable chamber pressure increases. Peak cell can temperature measurements ranged from 84 to 103 °C. The temperatures decayed over a 5-minute waiting period, after which the test was terminated and the chamber atmosphere was ignited by the furnace element, verifying a flammable atmosphere was present.

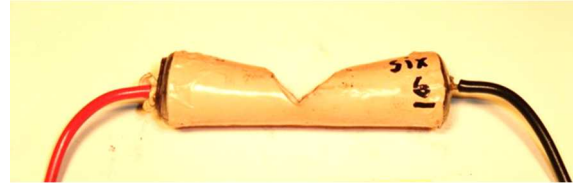


Fig. 6. Photograph showing an LG Chem cell crushed by the plastic wedge that did not rupture nor ignite 6.5% CH₄-air at 40 °C ambient temperature. The cell hard shorted.

The LG Chem cell flat plate tests produced no CH₄-air ignitions, no measurable cell can temperature increases, and no apparent cell venting as observed from the video. Seven of the flat plate tests produced no cell voltage drops. Three tests showed evidence of soft shorting; producing voltage drops of 22 mV or less. A cell voltage and cylinder force time trace for one of the three soft shorts is shown in Fig. 7. Researchers stopped the press extension temporarily when 13 kN was reached. Fig. 7 shows that the cylinder force decayed over time because of internal hydraulic system leakage. Researchers then retracted the cylinder after a short period of time. These three cells returned to their pretest voltage as the plate was retracted. Two of the three cells self-discharged completely and the third discharged by 1 V overnight without going into thermal runaway.

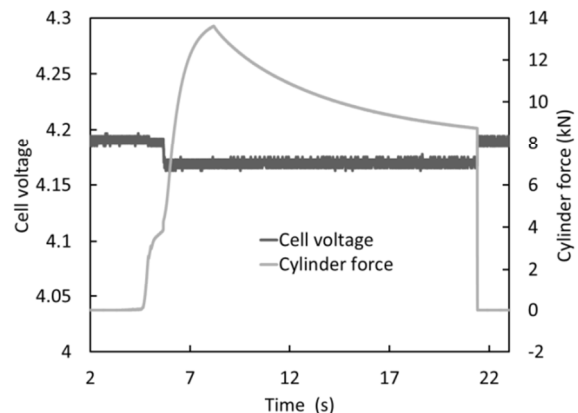


Fig. 7. Time traces of cell voltage and flat plate applied force showing that a soft short appeared and disappeared as the plate was extended and retracted.

C. A123 26650 vs. LG Chem ICR18650S2 Cells

Researchers conducted ten 6.5% CH₄-air ignition tests using the A123 cells and plastic wedge at 40 °C. None of the

A123 cells ignited the chamber atmosphere. Video showed all A123 cells rupturing and producing smoke near the point where the wedge penetrated the can (Fig. 8). These tests produced chamber overpressures of 3.8 kPa (0.58 psi) or less when the cells ruptured, indicating the chamber atmosphere did not ignite. The furnace igniter subsequently ignited the chamber atmosphere for all of these tests, confirming a flammable atmosphere was present. Table V lists A123 and LG Chem cell test data in the Fisher’s exact test two by two format. The one-tailed p value for Table 5 data is $p = 0.015$. The two cell designs can be considered independent from an ignition standpoint at a significance level of $p < 0.05$ as discussed above.

TABLE V. LG CHEM CELLS VS. A123 CELLS, 6.5% CH₄-AIR IGNITION TEST RESULTS, PLASTIC WEDGE, 40 °C.

	Ignitions	No ignitions	Totals
LG Chem cells	4	3	7
A123 cells	0	10	10
Totals	4	13	17

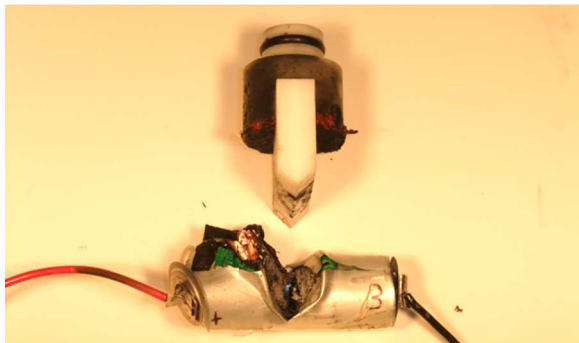


Fig. 8. Ruptured A123 cell crushed by a plastic wedge that did not ignite 6.5% CH₄-air.

D. Cell Crush Tests with No CH₄

An LG Chem cell and A123 cell were each tested without CH₄ in the chamber using the plastic wedge at 40 °C. The LG Chem cell went into thermal runaway and the A123 cell did not. The ruptured A123 cell produced a 2 kPa overpressure and a peak can temperature of 86 °C. The LG Chem cell thermal runaway produced 482 kPa (70 psi) chamber peak pressure (Fig. 9), 284 °C peak can temperature, and the high speed video recording was saturated.

V. DISCUSSION

ACRI2001 IS evaluations and ANSI/ISA 60079-11 level of protection “ia” evaluations take into consideration up to 2 countable faults. Two-countable-faults-evaluated IS equipment is permitted for use in coal mines by MSHA, and in other industrial hazardous locations per the National Electrical Code, Articles 500 and 505 [41]. Mikolajczak et al. [9] indicate that some field failures involved mechanically induced cell internal short circuits. Stationary battery-powered CTE in coal mines may be susceptible to

mechanical damage, such as from roof falls. For the NIOSH study, researchers charged cells within manufacturer’s recommendations and kept the ambient temperature within the normal range for IS evaluations. Tests reported here simulated a single, foreseeable internal short circuit fault from an external crush. The number of faults considered was not excessive relative to IS evaluation criteria.

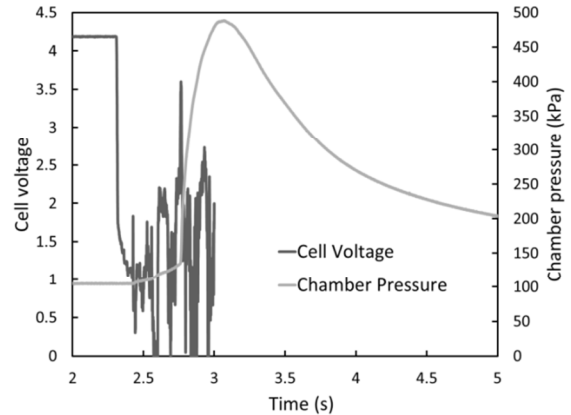


Fig. 9. An LG Chem cell crushed by the plastic wedge went into thermal runaway and produced 482 kPa (70 psi) peak chamber pressure with no CH₄ in the chamber.

There was a clear distinction between ignitions and non-ignitions in all tests. Cell ignitions produced pressures in excess of 480 kPa, and non-ignitions produced pressures well below the 50 kPa threshold criterion. Furnace igniter ignitions produced pressures in excess of 510 kPa, and verified that a flammable atmosphere was maintained in the chamber for all cell crush tests that did not result in ignition of the chamber atmosphere.

The LG Chem cells readily ignited CH₄-air whereas the A123 cells did not ignite in any tests. The LG Chem cells were tested at 100% SOC, but different results may be obtained if cell SOC were limited to significantly lower values. The Fisher’s exact test results indicate that the two cell designs can be considered to be independent from an ignition standpoint at a conservative significance level. The A123 cells were the safer of the two cell designs, under specified test conditions.

Ignition by a heated surface is a function of the heat source dimensions [42]. Auto ignition temperature (AIT) usually refers to ignition temperature obtained within a heated vessel, where the atmosphere is heated through the surrounding vessel walls. Heated wire, rod, or tube ignition temperatures are normally much higher than heated vessel AITs. Some CH₄-air ignition temperature data are listed in Table VI. CH₄-air AIT is significantly higher than AITs for some typical Li-ion electrolyte components summarized by [9]. Mikolajczak et al. [9] indicate that temperatures produced by cell thermal runaway reactions are considered sufficient to cause hot surface ignition of flammable mixtures, but do not reach levels that will cause the melting of pure copper (1080 °C). In some cases, very small points of pure copper, nickel,

or steel melting were found within a cell, attributed to internal electrical arcing or shorting [9]. By comparison, Kuchta [42] lists a 1220 °C ignition temperature for CH₄-air ignited by a heated nichrome wire. CH₄-air ignition temperatures are significantly higher than those for many industrially important explosive atmospheres [43]. Results reported here should not be considered conservative for explosive atmospheres with lower igniting temperatures than CH₄-air.

TABLE VI. SELECTED CH₄-AIR IGNITION TEMPERATURES (°C)

AIT (800 mL vol.) [44]	Heated air jet (1 cm dia.) [42]	Heated nichrome wire (0.1 cm dia.) [42]
600	1040	1220

The flat plates produced no hard shorts within the LG Chem cells at 13 kN applied force, and a few observed soft shorts returned to pretest voltage after the plate was retracted. These flat plate tests provided some assurance that this particular sample of cells was compliant with UL 1642 crush test requirements, as specified [35].

The plastic wedge produced hard shorts in all tests reported here with relative ease. The wedge crushed the cell to less than half of its original thickness as recommended by Tobishima [10], using a fraction of the applied force specified in UL 1642. Researchers limited wedge penetration to approximately 66% of the cell diameter. The pointed edge of the wedge overcame the difficulty of penetrating the separator as described by Mikolajczak et al. [9]. The applied pressure did not damage or melt the wedge tip significantly in tests that did not produce ignition. The plastic wedge tip melted during tests that produced ignitions. A plastic fixture simulates external forces applied to plastic wrapped or encased battery packs which are common [9]. The plastic wedge crush method does not compensate for potential heat dissipation through a cell's metallic can. The plastic wedge minimizes energy dissipating effects of the test fixture itself, compared to metallic nails. Safety standards organizations may wish to consider the plastic wedge crush test, in response to field failure reports involving external mechanical damage [9].

The UL 1642 interpretation of explosion is when the cell or battery contents are forcibly expelled and the cell or battery is torn or split into two or more pieces. The A123 cells pressed by the wedge ruptured and produced smoke, but did not ignite the chamber atmosphere. These results suggest that ignition of the explosive atmosphere in question may be a more appropriate failure criterion using the plastic wedge, for IS evaluation purposes.

The MSHA-approved Li-ion cap lamp battery contains a multi-cell battery pack within a sealed plastic enclosure. The LG Chem cell thermal runaway test with no CH₄ in the chamber produced a significant chamber peak pressure of 482 kPa (70 psi). Although the peak pressure was orders of magnitude less than reported by [31]-[32], the chamber

provided about 18 L of head space to allow expansion and reduce peak pressure. Peak pressures will be significantly higher than found in this study within significantly smaller volume, sealed enclosures, under otherwise similar test conditions.

Observed thermal runaway with the LG Chem ICR18650S2 cells fully charged and not charging suggests that the field failure of the MSHA-approved cap lamp in the NIOSH Pittsburgh SRCM office conceivably could have involved an internal short circuit cell fault while under normal charge, and not necessarily a charging fault.

Results suggest the plastic wedge test should be a more severe test than the nail penetration test specified in [35], potentially due to elevated ambient temperatures and the electrical and thermal insulating properties of the plastic.

VI. CONCLUSIONS

Intrinsically safe evaluated equipment powered by LG Chem ICR18650S2 LiCoO₂ cells pose a CH₄ explosion hazard from cell internal short circuit.

Under specified test conditions, the A123 26650A LiFePO₄ cells were safer than the LG Chem ICR18650S2 LiCoO₂ cells at a conservative statistical significance level. Other potential failure modes should be considered, as appropriate.

Intrinsically safe evaluated equipment powered by cells with similar form factor, chemistry, and charge capacity to the LG Chem ICR18650S2 should be reevaluated per an appropriate cell internal short circuit test within suitable atmospheric conditions (gas mixture and ambient temperature).

There was a clear distinction between ignitions and non-ignitions in all tests. Ignitions and non-ignitions produced chamber pressures well above and well below the threshold criterion, respectively.

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

Vents in the LG Chem ICR18650S2 cells were not reliable protection against thermal runaway in the plastic wedge tests. Venting was observed prior to ignition in all LG Chem cell tests that produced ignitions.

The LG Chem ICR18650S2 cell thermal runaway test with no CH₄ in the chamber produced significant chamber pressures with relatively large head space volume.

ACKNOWLEDGMENT

The authors gratefully acknowledge S. Gallagher and L. J. McWilliams for help with the statistical analysis.

REFERENCES

- [1] Fatal Underground Mine Explosion, April 5, 2010, Upper Big Branch Mine-South, Performance Coal Company Montcoal, Raleigh County,

- West Virginia. U. S. Dept. of Labor, Mine Safety and Health Administration, Arlington VA, Report of Investigation, Dec. 2011.
- [2] 30 CFR. Code of Federal Regulations, Mineral Resources, parts 1 to 199. Available: <http://www.msha.gov/30CFR/CFRINTRO.HTM>
- [3] D. Snyder, "Considerations for C&T Battery Safety," *Coal News*, vol. 6 (8), Aug. 2009, p. 38
Available: http://www.coalnews.net/images/pdf/CoalNews_0809.pdf
- [4] "Charging of Lithium Ion or Lithium Polymer Batteries," PROGRAM INFORMATION BULLETIN NO. P11-12, U.S. Department of Labor, Mine Safety and Health Administration, Arlington, VA, 2011
- [5] Fatal underground coal mine explosions, September 23, 2001, No. 5 Mine, Jim Walter Resources, Inc. Alabama. CAI-2001-20 through 32. U.S. Department of Labor, Mine Safety and Health Administration, Report of Investigation, 2002.
- [6] "Performance and Safety Investigation of Emergency Backup Batteries and Battery Charging Systems for Underground Mining Applications - Volume 1," QinetiQ North America / Foster Miller Inc., Waltham MA. Rep. DNSH-090162-1883. Sep. 2009. Available by request from: OMSHR@cdc.gov.
- [7] E. P. Roth, C. C. Crafts, D. H. Doughty, J. McBreen, "Advanced Technology Development Program for Lithium-Ion Batteries: Thermal Abuse Performance of 18650 Li-Ion Cells," Sandia National Laboratories, Albuquerque, NM. SAND2004-0584. Mar. 2004.
- [8] *UL 1642 Underwriters Laboratories Inc. Standard for Safety – Lithium Batteries Edition 4*, Sep. 2005.
- [9] C. Mikolajczak, M. Kahn, K. White, R. T. Long, "Lithium-Ion Batteries Hazard and Use Assessment Final Report," The Fire Protection Research Foundation, Quincy, MA. July, 2011.
- [10] S. Tobishima, "SECONDARY BATTERIES – LITHIUM RECHARGEABLE SYSTEMS – LITHIUM-ION I Thermal Runaway," In *Encyclopedia of Electrochemical Power Sources*, J.Garche, Ed., Amsterdam: Elsevier, 2009, pp. 409-417.
- [11] M. Ichimura, "The safety characteristics of lithium-ion batteries for mobile phones and the nail penetration test," in *Telecommunications Energy Conference, INTELEC 2007. 29th International*, pp. 687-692.
- [12] W. Cai, W. Wang, H. Maleki, J. Howard, E. Lara-Curzio, "Experimental simulation of internal short circuit in Li-ion and Li-ion polymer cells," *J. Power Sources*, vol. 196 (2011), pp. 7779-7783.
- [13] H. Maleki, J. N. Howard, "Internal short circuit in li-ion cells," *J. Power Sources*, vol. 191 (2009), pp. 568-574.
- [14] J.Loud, S.Nilsson, and Y.Du, "On the Testing Method of Simulating a Cell Internal Short Circuit for Lithium Ion Batteries" IEEE 17th Annual Battery Conference on Applications and Advances, Long Beach CA, 2002, pp. 205-208.
- [15] Megerle, M., Kelley, A., Mikolajczak, CJ. Effect of cell state-of-charge on outcome of internal cell faults: preliminary report. Exponent Failure Analysis Associate, Inc., August 6, 2004. Available: http://www.prba.org/prba/publications/battery_studies_and_reports/Default.aspx
- [16] A. Arora, N. K. Medora, T. Livernois, J. Swart, "Safety of lithium-ion batteries for hybrid electric vehicles," In: *Electric and Hybrid Vehicles, Power Sources, Models, Sustainability, Infrastructure and the Market*, Elsevier B.V., UK, 2010, pp. 463-491.
- [17] L. B. Florence, M. Tabaddor, "Challenges for safety standards for lithium ion cells," Battery Safety 2011. Presentations from a meeting held 9-11 Nov. 2011, Las Vegas, NV. Knowledge Press Inc. (2011)
- [18] *IEC 62133 ed.2, Final Draft International Standard (FDIS). Secondary cells and batteries containing alkaline or other non-acid electrolytes*. Oct. 2011
- [19] *JIS C 8714 Safety tests for portable Lithium Ion secondary cells and batteries for use in portable electronic applications. Japanese Industrial Standard*. The Battery Association of Japan. 2007
- [20] P. G. Balakrishnan, R. Ramesh, T. P. Kumar, "Safety mechanisms in lithium-ion batteries," *J. Power Sources*, vol. 155 (2006), pp. 401-414.
- [21] K. White, Q. Horn, S. Singh, R. Spray, N. Budiansky, "Thermal Stability of Lithium-ion Cells as Functions of Chemistry, Design and Energy," International Battery Association-Pacific Power Sources Conference, Presentations from a meeting held Jan. 2010, Kona Hawaii
- [22] S. Santhanagopalan, P. Ramadass, J. Z. Zhang, "Analysis of internal short-circuit in a lithium ion cell," *J. Power Sources*, vol. 194 (2009), pp. 550-557.
- [23] *IEC 60079-11 Ed. 6.0 Explosive atmospheres - Part 11: Equipment protection by intrinsic safety "i"*, June 2011.
- [24] *Criteria for the Evaluation and Test of Intrinsically Safe Apparatus and Associated Apparatus (ACRI2001)*, U.S. Department of Labor, Mine Safety and Health Administration, Triadelphia, WV, 2008.
- [25] E. P. Roth, "Abuse Response of 18650 Li-Ion Cells with Different Cathodes Using EC:EMC/LiPF6 and EC:PC:DMC/LiPF6 Electrolytes" *ECS Trans.*, vol. 11 (19), pp. 19-41, 2008.
- [26] G. Chen, T. J. Richardson, "Thermal instability of Olivine-type LiMnPO₄ cathodes," *J. Power Sources*, v. 195 (2010), pp. 1221-1224.
- [27] T.D. Hund, D. Ingersoll, "Selected Test Results from the LiFeBatt Iron Phosphate Li-Ion Battery," Sandia National Laboratories, Albuquerque, NM. SAND2008-5583. Sep. 2008.
- [28] B. Scrosati, J. Garche, "Lithium batteries: Status, prospects and future," *J. Power Sources*, vol. 195 (2010), pp. 2419-2430.
- [29] E. C. Magison, *Electrical Instruments in Hazardous Locations 4th Edition*, Research Triangle Park, NC: ISA, 1998, pp. 341-413.
- [30] "Policy to Determine Compliance with 30 CFR 19.7(e) and 19.4(a)," APOL 2204. U.S. Department of Labor, Mine Safety and Health Administration, Arlington, VA, 2007
- [31] Kai-Hsiang Yen, Mahmood Tabaddor, Yi Ying Chiang, Li-Ju Chen, and Carl Wang, "Estimation of explosion pressure for abused lithium ion cells," 44th Power Sources Conference 2010. Proceedings of a meeting held 14-17 June 2010, Las Vegas, NV. Curran Associates, Inc. (Mar. 2011)
- [32] C.Y. Jhu, Y. W. Wang, C. M. Shu, J. C. Chang, H. C. Wu, "Thermal explosion hazards on 18650 lithium ion batteries with a VSP2 adiabatic calorimeter," *J. Haz. Materials*, vol. 192 (2011), pp. 99-107.
- [33] "Product and Properties Guide - Delrin" DuPont Engineering Polymers, Wilmington, DE, 2000.
- [34] *IECEX Certificate of Conformity* No. IECEx FTZU 08.0001, Feb. 2008.
- [35] "PRODUCT SPECIFICATION - Rechargeable Lithium Ion Battery Model : ICR18650 S2 2200mAh," LG Chem, Seoul, Korea, 2003. Available: http://18650.cn/uploads/PDF/LG/Cylindrical/LG_Li-Ion_ICR18650S2.pdf
- [36] Proper operation of A123 Systems high power Lithium-ion cells summary usage and care guidelines, A123 Systems, Watertown MA, MD000003-02, Oct. 2006
- [37] *IEC 60079-0 Ed. 6.0 Explosive atmospheres - Part 0: Equipment - General requirements*, 2011.
- [38] K.L. Cashdollar, M. Hertzberg, "20-Liter explosibility test chamber for dusts and gases," *Review of Scientific Instr.*, vol. 56 (1985), 596-602.
- [39] K. L. Cashdollar, "Overview of dust explosibility characteristics," *J. Loss Prev. Proc. Ind.*, vol. 13 (2000), pp.183-199.
- [40] B. Rosner, *Fundamentals of Biostatistics*, 3rd edition, PWS-Kent Publishing Company, Boston MA, 1990, p. 341
- [41] *NFPA 70 National Electrical Code 2011 Edition*, Quincy, MA: National Fire Protection Association, 2010.
- [42] J. M. Kuchta, "Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries – A Manual, Bulletin 680" U.S. Dept. of the Interior, Bureau of Mines, Pittsburgh, PA. 1985.
- [43] M. W. Earley, *National Electrical Code Handbook Twelfth Edition*, Quincy, MA: National Fire Protection Association, 2011.
- [44] C. Robinson, D. B. Smith, "The auto-ignition temperature of methane," *J. Haz. Materials*, vol. 8, (1984), pp. 199-203.