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# Internal short circuit and accelerated rate calorimetry tests of lithium-ion cells: Considerations for methane-air intrinsic safety and explosion proof/flameproof protection methods

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ABSTRACT

Researchers with the National Institute for Occupational Safety and Health (NIOSH) studied the potential for lithium-ion cell thermal runaway from an internal short circuit in equipment for use in underground coal mines. In this third phase of the study, researchers compared plastic wedge crush-induced internal short circuit tests of selected lithium-ion cells within methane ($CH_4$)-air mixtures with accelerated rate calorimetry tests of similar cells. Plastic wedge crush test results with metal oxide lithium-ion cells extracted from intrinsically safe evaluated equipment were mixed, with one cell model igniting the chamber atmosphere while another cell model did not. The two cells models exhibited different internal short circuit behaviors. A lithium iron phosphate ($LiFePO_4$) cell model was tolerant to crush-induced internal short circuits within $CH_4$-air, tested under manufacturer recommended charging conditions. Accelerating rate calorimetry tests with similar cells within a nitrogen purged 353-mL chamber produced ignitions that exceeded explosion proof and flameproof enclosure minimum internal pressure design criteria. Ignition pressures within a 20-L chamber with 6.5% $CH_4$-air were relatively low, with much larger head space volume and less adiabatic test conditions. The literature indicates that sizeable lithium thionyl chloride ($LiSOCl_2$) primary (non rechargeable) cell ignitions can be especially violent and toxic. Because ignition of an explosive atmosphere is expected within explosion proof or flameproof enclosures, there is a need to consider the potential for an internal explosive atmosphere ignition in combination with a lithium or lithium-ion battery thermal runaway process, and the resulting effects on the enclosure.

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## 1. Introduction

Thermal events involving lithium-ion (Li-ion) battery-powered mine safety equipment prompted a safety research study by the National Institute for Occupational Safety and Health, Pittsburgh Mining Research Division (NIOSH, PMRD). Previous phases of the study (Dubaniewicz and DuCarme, 2013, 2014) demonstrated a potential methane ($CH_4$)-air ignition hazard from internal short circuit within selected Li-ion secondary and lithium primary cells, and a potentially safer Li-ion secondary cell that uses a lithium iron phosphate ($LiFePO_4$) cathode chemistry to weaken exothermic reactions within the cell. The potential for ambient explosive atmosphere ignition by li-ion cell thermal runaway was described in terms of cell chemistry (lithium cobalt oxide ($LiCoO_2$) for example), and spiral wound construction with a thin separator (Figs. 1 and 2). Researchers identified gaps in a revised Li-ion cell level safety standard and gaps in intrinsic safety standards, and provided recommendations for enhancing safety evaluation criteria. Recommendations to date have influenced revisions of the US adopted versions of the IEC 60079 series of explosion protected equipment standards.

This work reports findings and recommendations from the third and final phase of the study.[1] Samples of Li-ion rechargeable cells extracted from mine safety equipment, and higher-capacity $LiFePO_4$ cells, were evaluated by a plastic wedge crush-induced

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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.

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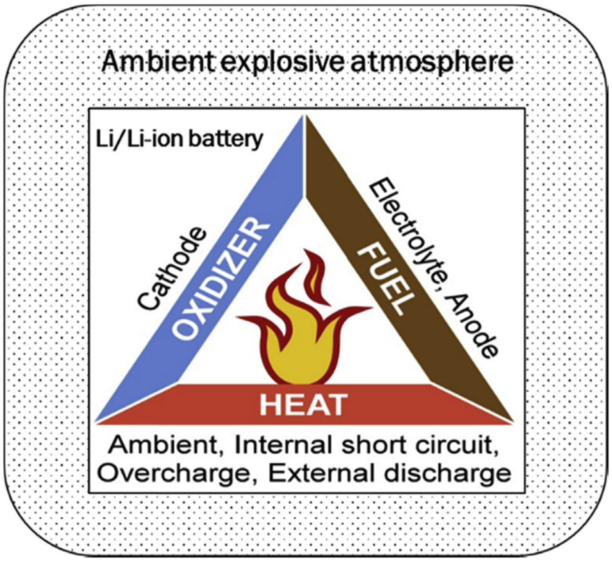


**Fig. 1.** Fire triangle representation of thermal runaway challenges with Li/Li-ion batteries used in explosive atmospheres.

internal short circuit and accelerated rate calorimetry (ARC) methods. Plastic wedge crush test results were mixed, indicating limited improvement to internal short circuit tolerance in Mine Safety and Health Administration (MSHA) approved intrinsically safe mine equipment. The larger-capacity $LiFePO_4$ cells were tolerant to the plastic wedge crush-induced internal short circuits, tested under manufacturer recommended charging conditions. ARC test results have safety implications for another explosion protection technique represented by MSHA compliant explosion proof enclosures and IEC 60079–1 compliant flameproof enclosures.

A literature review of sizeable lithium thionyl chloride ($LiSOCl_2$) primary (non rechargeable) cell ignitions suggests potential hazards for explosion protected equipment.

## 2. Background/literature review

The term “intrinsically safe” is appearing in battery safety literature as a term to describe various aspects of battery safety, and can be a source of confusion. The term was coined many decades ago by the explosion prevention community (Magison, 1998a), and the concept can be traced back to studies by what would become the United Kingdom Safety in Mines Research Establishment, following the 1913 Senghenydd colliery (coal mine) disaster. The Senghenydd disaster took the lives of 439 men and boys working in the mine, plus one rescuer (Redmayne et al., 1913). Dry cells (a battery) played a part in a suspected ignition source for the explosion, thought to involve a normally sparking and inductive signaling circuit. The battery met voltage safety limits for ignition prevention at the time; however, the influence of circuit inductance on spark ignition of explosive gas-air mixtures was not well understood. This possible ignition source was present in the Senghenydd mine even after a similar ignition source was positively identified for the 1912 Bedwas colliery fatal explosion (Redmayne et al., 1913) (Redmayne, 1913). Intrinsic safety is a protection technique for safe operation of electrical equipment in explosive atmospheres by limiting the energy available for ignition. The term “intrinsically safe” properly applies to systems, with fault tolerance as specified by applicable intrinsic safety standards.

Explosion proof and flameproof enclosures represent another common explosion protection technique for electrical equipment. An explosion proof or flameproof enclosure is an enclosure so constructed that, if ignition of an explosive atmosphere inside of the enclosure by electrical means does occur, the flame cannot propagate outside of the enclosure and spread to a surrounding explosive atmosphere (Magison, 1998b). Explosion proof and flameproof enclosures perform a similar safety function but differ in terms of design requirements.

The goal for explosion proof or flameproof enclosure standards is to produce enclosures that are strong enough to contain explosion pressures, with some additional factor of safety (Boring et al., 2005). MSHA's safety factor for explosion proof enclosures is based on a value of about 1.5 times the maximum pressure (104 psig, 7.17 bar) that can be realized from a $CH_4$-air ignition in a closed vessel, without the effects of pressure piling. MSHA requires explosion proof enclosures to be designed to withstand a minimum internal pressure of 150 psig (10.34 bar). More stringent internal pressure requirements may apply as determined by MSHA. The International Electrotechnical Commission Technical Committee 31 (IEC TC 31) maintains the IEC 60079-1 Flameproof standard. This standard uses a maximum recorded explosion pressure (reference pressure) for a specific enclosure to serve as the basis for defining the minimum pressure that the enclosure must be capable of sustaining. During prototype testing, the enclosure must be capable of withstanding pressures 1.5 times the maximum explosion (reference) pressure measured for that enclosure, 3.5 bar (50.76 psig) minimum.

The IEC 60079–1 edition 7 (IEC, 2014) specifies Li-ion secondary cells and lithium primary cells, including $LiSOCl_2$, subsequently placed within a flameproof enclosure as an acceptable explosion protection technique. The safety provisions for cells and batteries, provided in an annex, pertain to the prevention of electrolytic gas accumulation (usually hydrogen and oxygen), which is a hazard

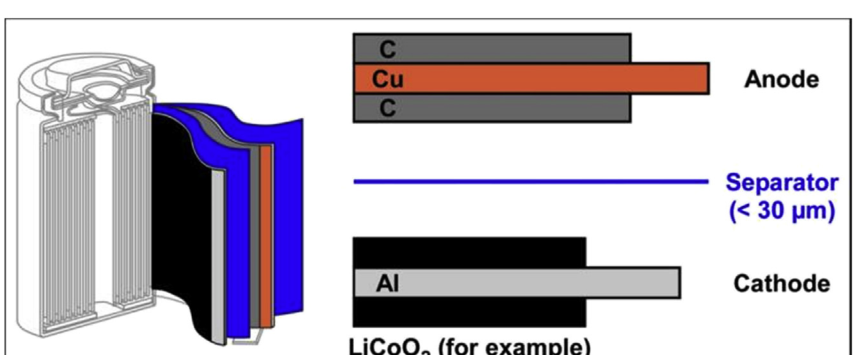


**Fig. 2.** A drawing of a common spiral-wound Li-ion cell construction with a thin separator material. The cell contents are immersed in a typically flammable electrolyte.

with more mature technologies such as lead acid batteries. There are no provisions in the standard for assessing potential overpressure contributions from lithium primary or Li-ion secondary cell ignitions.

ARC tests of lithium ion cells can provide cell ignition pressure data under controlled and reproducible conditions. ARC provides information about the thermal behavior of a substance as it is heated under near adiabatic conditions. The substance is heated in stages until very slow decomposition (or other reaction) is detected. The substance is then held under adiabatic conditions and the course of the decomposition (or other reaction) is monitored. ARC tests with Li-ion cells intentionally heat the cells to excessive temperatures to force thermal decomposition. Researchers continue to report significant Li-ion cell ignition pressures from ARC tests. Lu et al. (2013) performed a thermal hazard evaluation of $LiCoO_2$ and $LiFePO_4$ 18650 cells using an adiabatic calorimeter. The peak pressures for fully charged $LiCoO_2$ and $LiFePO_4$ cells were 116.44 bar (1630.15 psig) and 17.89 bar (250.42 psig), respectively. They concluded that the $LiFePO_4$ cell was safer than the $LiCoO_2$ cell, but cautioned that the $LiFePO_4$ cell produced a high temperature and pressure. The $LiCoO_2$ pressure result is consistent with ARC test results by other labs using relatively small volume chambers as reviewed previously (Dubaniewicz and DuCarme, 2013).

Sizeable $LiSOCl_2$ cell ignitions are violent and toxic. Jeevarajan and Winchester (2012) describe these cell ignitions in terms of explosive trinitrotoluene (TNT) mass equivalence. $LiSOCl_2$ battery ignitions have caused traumatic fatalities (Ducatman et al., 1988) (Conroe fire department, 2011). Levy and Bro (1994) describe other incidents. They also describe reduction products that may occur after cell discharge has been completed that can contribute to exothermic reactions. A sample of material safety data sheets for $LiSOCl_2$ cells warn against exposure to temperatures in excess of 150 °C (Tadiran, 2013) or rated temperature (Electrochem Solutions, 2013) due to unusual explosion and fire hazards. Sizeable $LiSOCl_2$ cells were not included in the NIOSH testing program due to concerns of exceeding the 21 bar (304.6 psig) pressure rating of the 20-L chamber, and toxicity and equipment corrosion considerations.

## 3. Methods and materials

### 3.1. Li-ion cells

Three different Li-ion cell models were studied in the present work.[2] All three models were spiral wound constructed. Samples of two of the cell models were obtained from battery packs of commercial mine safety equipment. One of these samples was obtained from cap lamps with MSHA approval # 6D-49-1 (CL cells). Another sample was obtained from personal dust monitors with MSHA approval # 19-A040002-0, (PDM cells). Cell specifications for these products were not publically available. The CL and PDM cells contained metal oxide cathodes. Their separators were dissimilar, judging by separator thickness measurements (Table 1). Compliance with all UL 1642 tests for the CL and PDM cells is assumed, including the flat plate crush test, based on MSHA intrinsic safety approval criteria that requires compliance with all UL 1642 provisions (MSHA, 2008).

The third cell model was K2 Energy 26650EV $LiFePO_4$ (K2 cells).

**Table 1**
Cell conditioning summary data.

| | CL | PDM | K2 |
|---|---|---|---|
| Cell can type | 18650 | 18650 | 26650 |
| Charge, discharge voltage | 4.2, 3.0 | 4.2, 3.0 | 3.65, 2.5 |
| Rated capacity (Ah) | 2.35 | 2.3 | 3.2 |
| Measured discharge capacity (% rated) | >98% | >99% | >95% |
| Measured separator thickness (μm) | 40 | 25 | 25 |

The K2 cells were selected for testing because they have a higher capacity rating than previously tested $LiFePO_4$ cells.[3] The K2 cell samples were purchased directly from the manufacturer. All cells were conditioned prior to testing with at least three charge discharge cycles (Table 1).

### 3.2. Crush test methods

Efforts to develop methods to induce an internal short circuit with a plastic wedge inside the 20-L chamber containing 6.5% $CH_4$-air were described previously (Dubaniewicz and DuCarme, 2013, 2014). Fig. 3 is a drawing of the plastic wedge crush test fixture and Fig. 4 shows it being prepared for installation within the instrumented 20-L chamber. The press uses a small single-acting hydraulic cylinder that is small enough to fit inside the chamber. The press was set to produce up to 13 kN of force at the cylinder ram, similar to the maximum force of the UL 1642 standard flat plate crush test. All crush tests were conducted at 40 °C at least 1 h after reaching 38 °C. The crush speed was set to <1 mm/s. The chamber provided approximately 18 L of open head space with the crush fixture installed. A thermocouple was attached to the cell can using kapton tape approximately 1.3 cm (0.5 in) from the end of the can opposite of the vent. Kapton tape covered the bottom metal platen for insulation purposes. 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). The term “overpressure” refers to the peak chamber pressure above 100 kPa. A furnace igniter 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. The CL cells were tested under fully charged

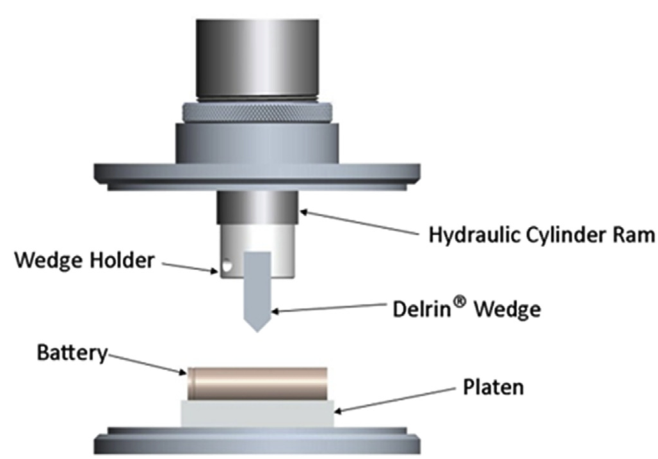


**Fig. 3.** Drawing of the plastic wedge crush test fixture.

[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.

[3] The nominal capacity of the M1A cells tested previously was 2.3 Ah.

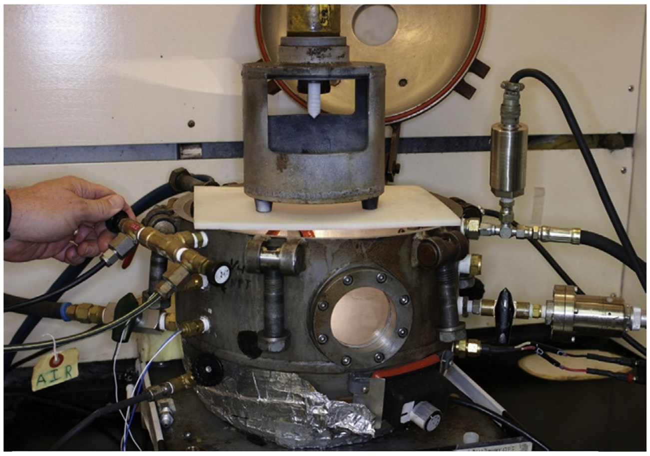


**Fig. 4.** Photograph of the wedge crush test fixture prepared for placement within the 20-L chamber.

conditions only as these tests confirmed a 6.5% $CH_4$-air ignition hazard (See Section 4 Results). The PDM cells did not ignite 6.5% $CH_4$-air while fully charged, so an additional series was conducted with fully charged cells under charging conditions of 4.2 V and current limit of 2.3 A. This 1C charge condition is non-abusive for common metal oxide cells. The K2 cells were tested fully charged under charging conditions of 4.1 V and current limit of 3.2 A. The K2 cell charging parameters were based on cell manufacturer maximum recommendations.

### 3.3. ARC test methods

ARC tests were performed by AllCell Technologies (AllCell) using NIOSH researcher-provided Li-ion cells and charging instructions. The cells were ARC tested at full charge. The ARC pressure chamber had an internal volume of 353 mL and was purged with nitrogen. A thermocouple was attached to the cell under several layers of kapton tape applied to the entire cell for insulation purposes (Fig. 5). The calorimeter used the standard heat-wait-seek procedure that is traditionally used to characterize energetic chemical reactions. The temperature is increased in steps, and at each step, the self-heat rate of the sample is monitored to see if it exceeds the specified threshold. For the NIOSH tests, AllCell selected a 5 °C step beginning at 50 °C. The onset of thermal runaway was defined by AllCell to occur when the cell self-heating rate reached 0.03 °C/min. Cell voltage, cell temperature, and chamber pressure (absolute) were recorded as a function of time. The time to maximum self-heating rate was taken as the time between the peak self-heating rate and the onset temperature. The difference between the peak and onset temperature is a measure of the adiabatic temperature rise.

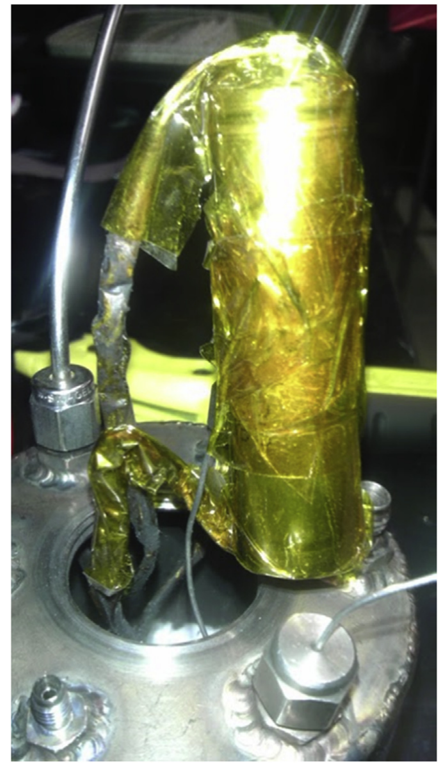

**Fig. 5.** Photograph of a kapton tape wrapped Li-ion cell prepared for placement within the AllCell ARC test chamber.

**Fig. 6.** Photograph of a ruptured CL cell that ignited the 20-L chamber atmosphere with a partially melted plastic wedge.

## 4. Results

### 4.1. Plastic wedge crush tests

Plastic wedge crush test results were mixed, with one cell model igniting the chamber atmosphere while the two other cell models did not. Figs. 6–8 show examples of crushed cells, and summary data are provided in Tables 2 and 3. For all tests, the plastic wedge induced internal short circuits using forces significantly less than the maximum force specified for the UL 1642 flat plate test. An internal short circuit was produced in all tests as determined from voltage, current, and temperature time traces (Figs. 9–12). The crush speeds were maintained at < 1 mm/s. The CL cells produced chamber ignitions in three of ten plastic wedge crush tests. For the three chamber ignitions, the CL cell can ruptured on the negative terminal side, opposite of the vent. Table 2 lists summary data for the CL cell chamber ignitions. Measured cell can temperatures were lower than the thermal runaway or $CH_4$-air flame temperatures due to the insulating nature of the can, kapton tape, and separation distance between the thermocouple and short circuit. The PDM cells and K2 cells did not ignite the chamber atmosphere in any tests as summarized in Table 3. Chamber overpressures were well below the selected

**Fig. 7.** Photograph of a crushed PDM cell that did not ignite the 20-L chamber atmosphere with a plastic wedge. The cell short-circuited internally.

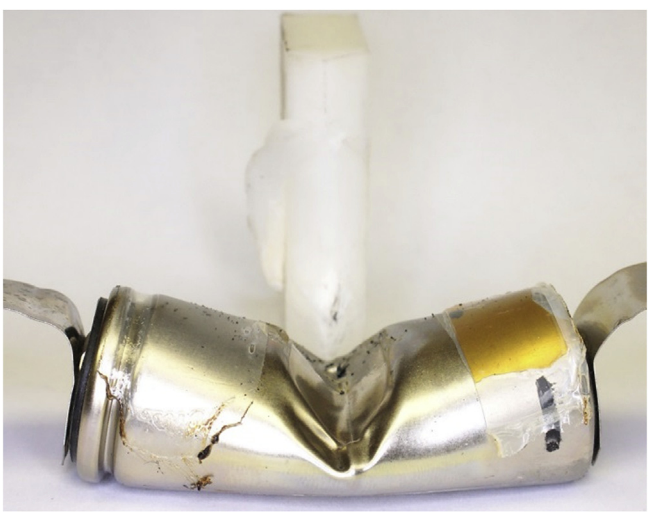

**Fig. 8.** Photograph of a crushed K2 cell that did not ignite the 20-L chamber atmosphere with a partially melted plastic wedge. The cell short-circuited internally.

**Table 2**
Summary data of three CL cell plastic wedge crush tests that produced 20-L chamber ignitions, 6.5% $CH_4$-air, 40 °C.

| | |
|---|---|
| Cylinder force at short circuit kN (lbf) | 2.94 to 4.39 (662–987) |
| Crush speed avg. (range) mm/s | 0.7 (0.67–0.75) |
| Chamber overpressure kPa (psi) | 510 to 676 (74–98) |
| Peak cell can temperatures °C | 383 to 397 |

ignition criterion of at least 50 kPa (7.25 psi). The K2 cells exhibited higher temperatures than the other cells, suggesting enhanced tolerance to higher internal temperatures. Subsequent chamber ignitions by a furnace igniter verified that an explosive atmosphere remained in the chamber.

Figs. 9–12 provide time traces of data for a few typical plastic wedge crush tests. Comparing Figs. 9 and 10, the CL cell voltage decayed to zero within seconds after shorting whereas the PDM cell voltage rebounded after the initial short. The PDM cells (Figs. 10 and 11) exhibited a secondary temperature rise after the wedge was retracted, possibly due to additional internal shorts introduced as the wedge moved. This secondary temperature rise occurred with all PDM cell crush tests but did not occur with the CL or K2 cells. The voltage rebound and secondary temperature rise indicate incomplete discharge after the initial internal short circuit, suggesting that the PDM cells may have contained a shutdown separator.

Fig. 11 shows the temperature response of a representative PDM cell that was crushed while subjected to a current-limited charge of 4.2 V and 2.3 A. The cell accepted an external charge for approximately 5 s, after which the charge circuit opened for the duration of the test. The resistance to the external charge ranged from approximately 0.5 to 0.9 Ω. The open circuit response suggests the activation of a charge current interrupting device within the PDM cell.

Fig. 12 shows the temperature response of a representative K2 cell that was crushed while subjected to a current-limited charge of 4.1 V and 3.2 A. The cell accepted charge for slightly less than 50 s, at which point the charge circuit opened for a few seconds. The peak rate of temperature rise occurred during the open circuit period, suggesting that the cell heating was primarily driven by an internal short circuit. After the open circuit period the cell again accepted charge with a resistance of approximately 0.3 Ω for the duration of the test. The location of this reconnection to the charge circuit is unknown. The lack of apparent influence on cell temperature suggests that the reconnection may have been shorted through the cell can.

### 4.2. ARC tests

Figs. 13–15 provide time traces of AllCell measured data for each cell model subjected to an ARC test. The sealed chamber pressure rose above atmospheric as the chamber was heated prior to cell venting. Two abrupt chamber pressure events occurred with each cell, the first due to cell venting and the second to thermal runaway. Peak pressures and pressure rates occurred with thermal runaway (Table 4.). A brief endothermic cell temperature response was detected shortly after cell venting for the three cells. The CL cell thermal onset coincided with venting.

The CL and PDM cells exhibited voltage dropout occurring near 107 °C whereas the K2 cell exhibited voltage dropout near 162 °C. The voltage dropout occurred hours before the thermal onset for the CL and PDM cells, suggesting the activation of a current interrupting device within the cells caused by external heating. Complete voltage dropout for the K2 cell coincided with cell venting, after thermal onset.

Table 4 lists ARC test summary data for the three Li-ion cell models. The K2 cell exhibited a relatively high onset temperature, low peak temperature, low peak pressure rate, and longer time to peak self-heat rate—all indicators of a less reactive chemistry than the other two cells. However, once forced to ignite, the K2 cell did produce a significant chamber pressure that was similar to the other two cells. The larger size of the K2 cell may allow it to contain larger amounts of active material that could contribute disproportionately to the measured ignition pressure compared to the smaller CL and PDM cells. The PDM cell ARC test peak temperature, peak pressure rate, and time to peak self-heat rate suggest a slightly less reactive chemistry than the CL cell, or perhaps a more effective thermal arrest mechanism due to a shutdown separator. The measured pressure for all three cells within this nitrogen purged 353-mL chamber exceeds minimum pressure containment requirements for explosion proof and flameproof enclosures by a significant margin.

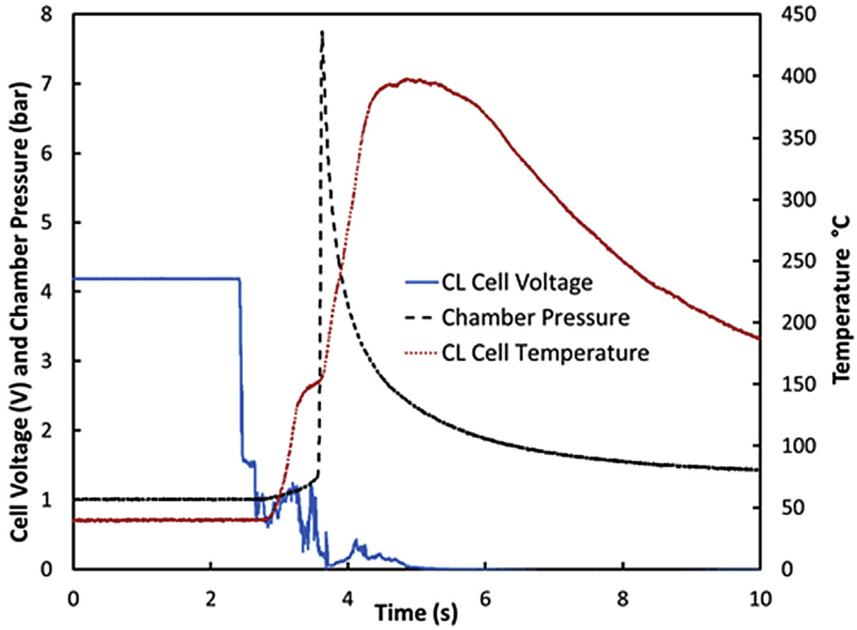


**Fig. 9.** Time traces of cell voltage, temperature, and chamber pressure during a CL cell plastic wedge crush that ignited the 20-L chamber atmosphere. The cell was obtained from an intrinsic safety evaluated cap lamp.

**Table 3**
Summary data of plastic wedge crush tests that did not produce 20-L chamber ignitions, 6.5% $CH_4$-air, 40 °C.

| | CL | PDM | PDM | K2 |
|---|---|---|---|---|
| Number of tests | 7 | 10 | 10 | 10 |
| Charging parameters | – | – | 4.2 V, 2.3 A | 4.1 V, 3.2 A |
| Cylinder force at short circuit kN (lbf) | 1.85 to 3.67 (417–826) | 2.05 to 3.47 (462–779) | 2.14 to 3.26 (481–732) | 3.03 to 6.36 (681–1430) |
| Crush speed avg. (range) mm/s | 0.71 (0.64–0.8) | 0.67 (0.61–0.82) | 0.73 (0.66–0.79) | 0.64 (0.47–0.72) |
| Chamber overpressure kPa (psi) | <0.69 (0.1) | <0.69 (0.1) | <0.69 (0.1) | 2.76 (0.4) |
| Peak cell can temperatures °C | 103 to 119 | 102 to 121 | 102 to 115 | 138 to148 |
| Furnace igniter overpressure kPa (psi) | 496 to 517 (72–75) | 496 to 565 (72–82) | 496 to 524 (72–76) | 551 to 655 (80–95) |

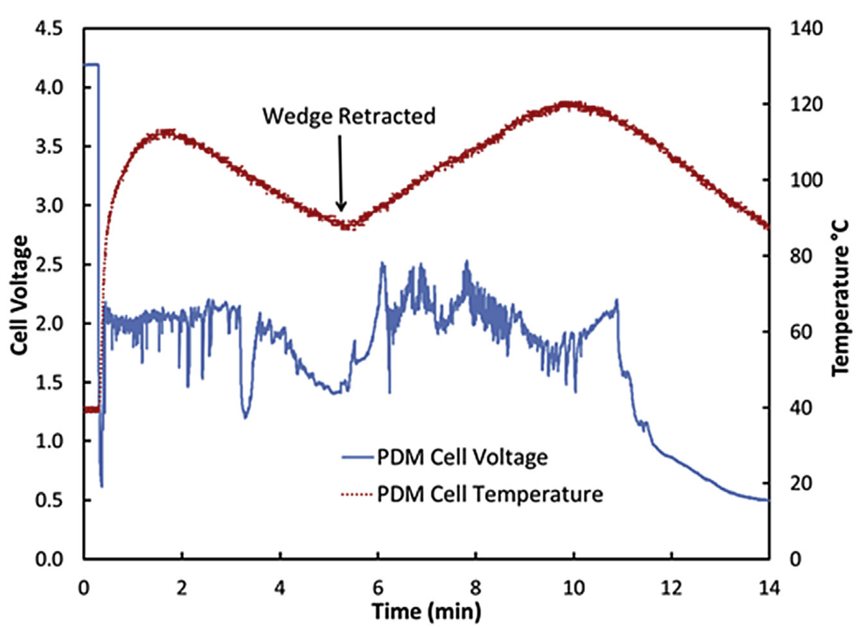


**Fig. 10.** Time traces of cell voltage and temperature during a PDM cell plastic wedge crush test that did not ignite the 20-L chamber atmosphere. A secondary temperature rise began with wedge retraction.

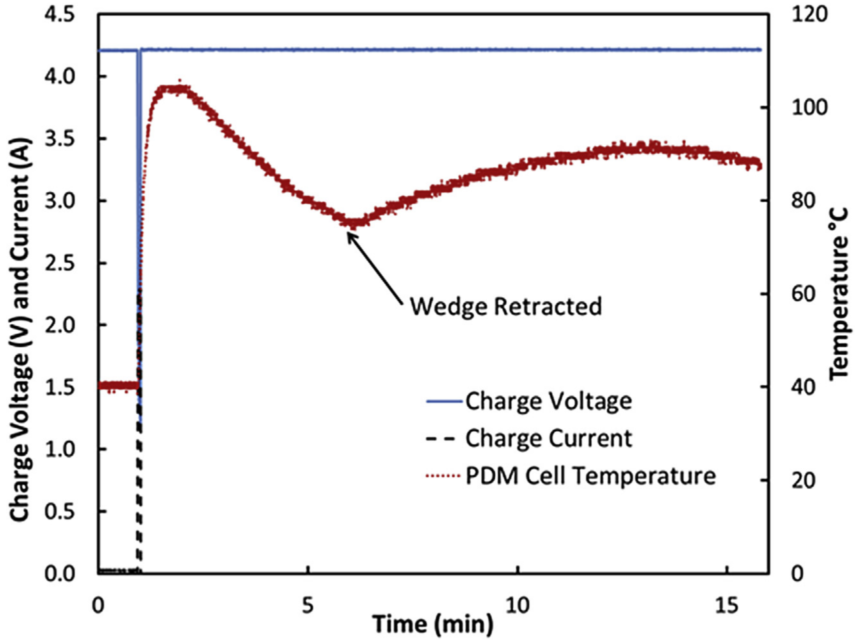


**Fig. 11.** Time traces of charge voltage, current, and cell temperature during a PDM cell plastic wedge crush test that did not ignite the 20-L chamber atmosphere. The open circuit after the initial short circuit suggests the activation of a charge current interrupting device within the cell. A secondary temperature rise began with wedge retraction.

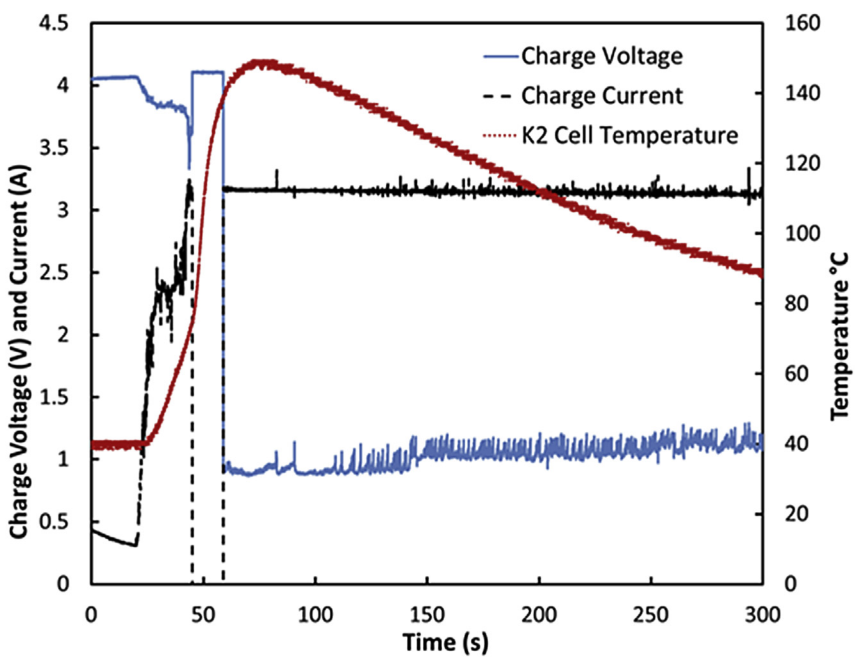


**Fig. 12.** Time traces of charge voltage, current, and cell temperature during a K2 cell plastic wedge crush test that did not ignite the 20-L chamber atmosphere. Maximum temperature rise (slope) occurred during open circuit conditions.

## 5. Discussion

The plastic wedge produced internal short circuits for all crush tests attempted under the NIOSH study reported here and previously (Dubaniewicz and DuCarme, 2013, 2014). All of these plastic wedge tests used only a fraction of the force specified for the UL flat plate crush test.

The plastic wedge crush tests revealed some functional characteristics of these cells. The PDM cells exhibited a voltage rebound as the cells were crushed and then a secondary temperature rise after the wedge was retracted. This voltage rebound and secondary temperature rise did not occur with plastic wedge crush tests of the CL or K2 cells. The voltage rebound and secondary temperature rise indicate incomplete discharge after the initial internal short circuit, suggesting that the PDM cells may have contained a shutdown separator. The two cells models (CL and PDM) obtained from approved mine safety equipment exhibited different internal short circuit behaviors. Results suggest that cells that do not exhibit internal short circuit characteristics consistent with a shutdown separator may meet existing requirements for intrinsically safe

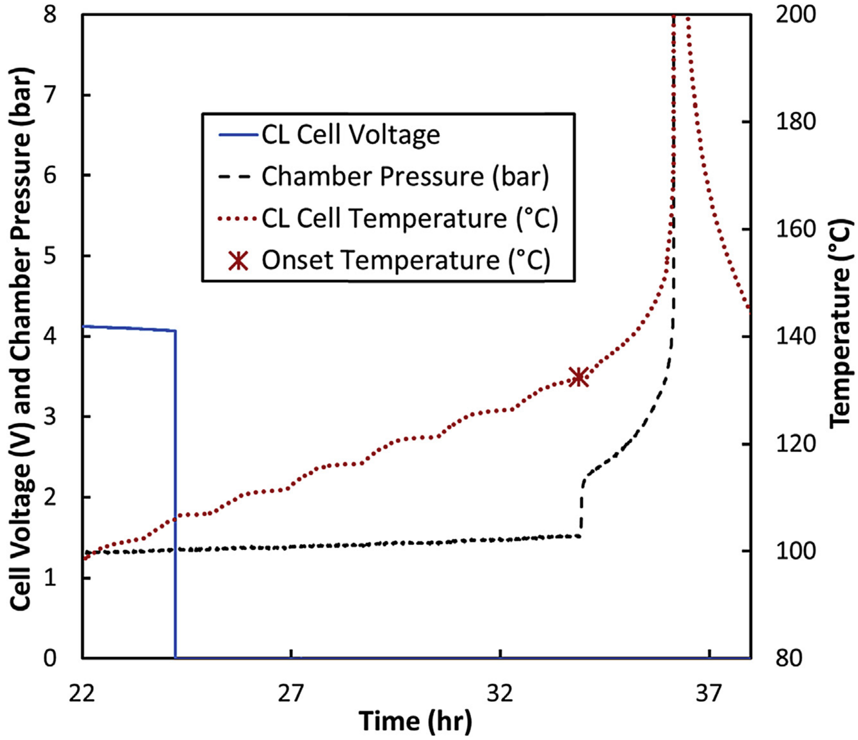


**Fig. 13.** Time traces of cell voltage, temperature, and chamber pressure during the CL cell ARC test. Chamber pressure exceeded explosion proof and flameproof enclosure minimum pressure design criteria by a significant margin.

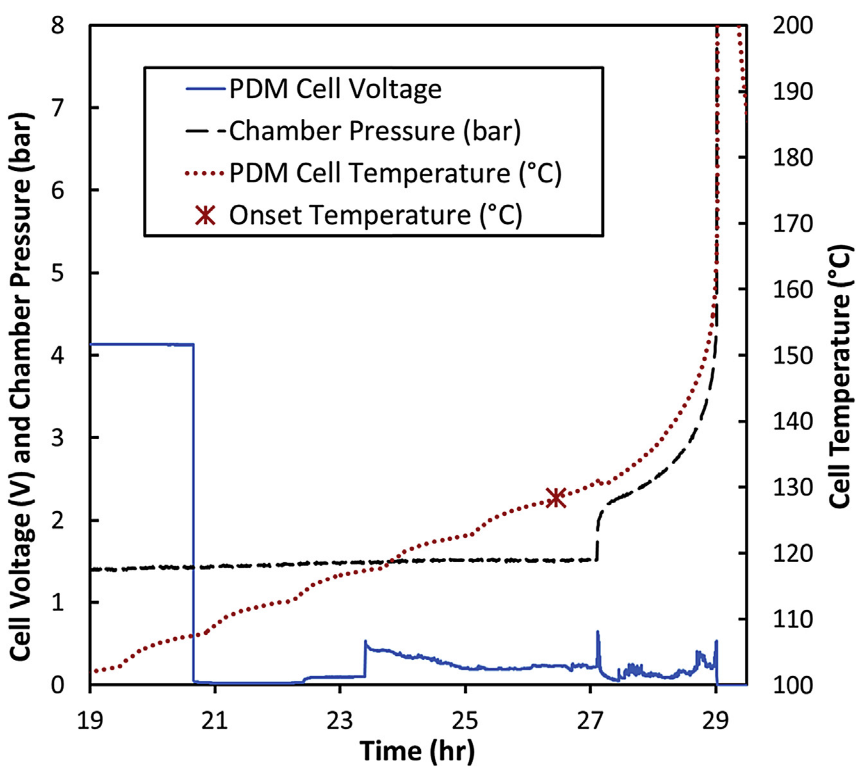


**Fig. 14.** Time traces of cell voltage, temperature, and chamber pressure during the PDM cell ARC test. Chamber pressure exceeded explosion proof and flameproof enclosure minimum pressure design criteria by a significant margin.

evaluated equipment.

The ARC tests produced chamber pressures significantly higher than the 20-L chamber crush tests. The difference is attributed to the larger headspace and less adiabatic test conditions within the 20-L chamber. For the 18650 cell types, the ratio of chamber internal vol. to cell vol. was approximately 20 for the AllCell chamber

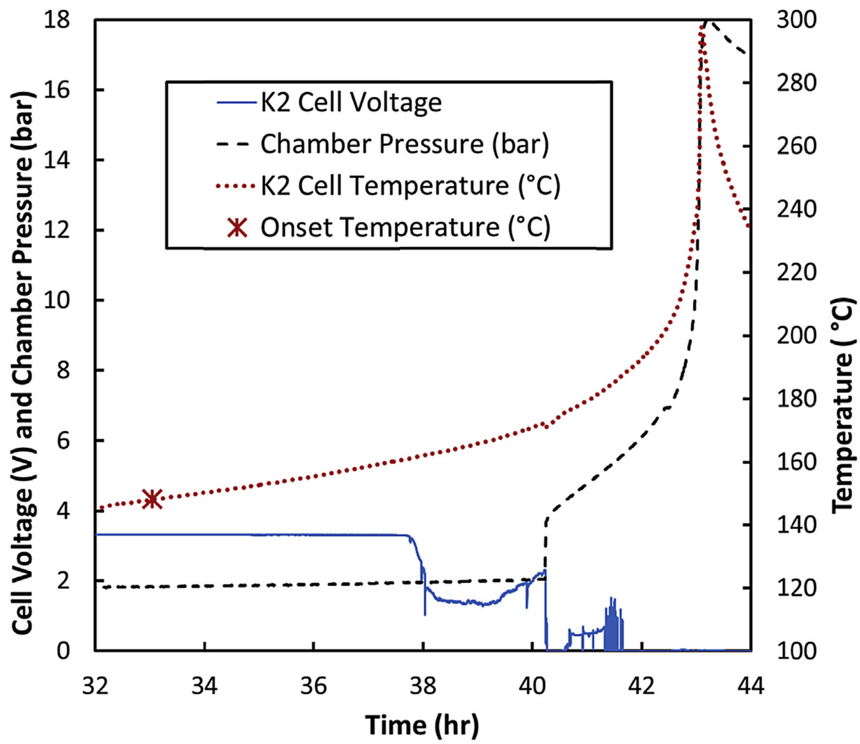


**Fig. 15.** Time traces of cell voltage, temperature, and chamber pressure during the K2 cell ARC test. Chamber pressure exceeded explosion proof and flameproof enclosure minimum pressure design criteria by a significant margin.

**Table 4**
AllCell ARC test summary data for three Li-ion cell models.

| Cell model | Onset temp. (°C) | Peak temp. (°C) | Adiabatic temp. Rise (°C) | Time to peak self-heat rate (hr) | Peak pressure (bar) | Peak pressure rate (bar/min) |
|---|---|---|---|---|---|---|
| CL | 132.3 | 389.7 | 257.4 | 2.18 | 19.89 | 86.5 |
| PDM | 128.3 | 334.4 | 204.9 | 2.26 | 20.99 | 57.7 |
| K2 | 148.1 | 297.9 | 148.7 | 9.57 | 18.02 | 3.35 |

compared to a value of approximately 1000 for the NIOSH 20-L chamber.

The latest revision of the IEC flameproof standard identifies lithium and Li-ion batteries within flameproof enclosures as a suitable explosion protection method for explosive atmospheres. ARC tests of certain Li-ion cells suggest that thermal runaway of these cells can induce pressures that exceed minimum explosion proof or flameproof enclosure pressure ratings by a wide margin. ARC test temperatures may approximate a high-temperature atmosphere within an explosion proof or flameproof enclosure from an expected internal ignition of an explosive atmosphere. Because ignition of an internal explosive atmosphere is expected, there is a need to consider the potential for the ignition to initiate a thermal runaway process and the resulting pressure or sustained combustion of the common-cause event. For cell ignition assessment purposes, the cell temperature should be considered to be raised to the maximum allowable before ignition of the explosive atmosphere.

Certain lithium metal and Li-ion cell chemistries can sustain an exothermic reaction over a period of time within an inert atmosphere. Thus, in addition to excessive overpressure, conceivable lithium or Li-ion large format battery ignition concerns within explosion proof or flameproof enclosures include transmitting hot gases through explosion proof/flameproof gaps or excessive enclosure external surface temperatures.

Potential ignition mechanisms for sizeable $LiSOCl_2$ cells should be considered carefully before they are used in explosion protected equipment. For example, $LiSOCl_2$ cells with a spiral wound construction may contain thin separator materials that are susceptible to internal short circuit failure modes for intrinsic safety evaluation purposes (Dubaniewicz and DuCarme, 2014). Exposure to flame temperatures within explosion proof or flameproof enclosures is another potential ignition mechanism for $LiSOCl_2$ cells of any construction. Discharged cells may contain products that can contribute to exothermic reactions as described by Levy and Bro (1994); potential ignition mechanisms for partially or fully discharged $LiSOCl_2$ cells should also be considered.

The 20-L chamber crush tests used a lean 6.5% $CH_4$-air mixture for thermal threshold ignition purposes per IEC 60079–0. Threshold thermal ignition levels for mixtures of $CH_4$ plus cell vent gases with air are unknown. Additional cell internal short circuit research using other $CH_4$-air mixtures is warranted for mining equipment intrinsic safety purposes. Direct ignition of stoichiometric $CH_4$-air in explosion proof or flameproof chambers containing lithium or Li-ion cells, and vice versa, is warranted for enclosure integrity investigation purposes.

Li-ion battery packs commonly employ a battery management system (BMS) that performs electronic and software-controlled safety functions. For explosion proof or flameproof applications involving a BMS, there is a need to consider the potential for an explosive atmosphere ignition within the enclosure to adversely impact or negate BMS safety functions.

With regard to the adoption of new lithium or Li-ion battery technologies for any explosion protection technique (intrinsic safety, flameproof, etc.), the IEC TC31 committee should perform a systematic evaluation of foreseeable failure modes that may result in ignition of the batteries as well as the explosive atmosphere. Systematic safety evaluations should occur before adoption of new technologies into the safety standards—with lessons from Senghenydd and Bedwas not to be forgotten.

## 6. Conclusions

The plastic wedge produced internal short circuits for all crush tests attempted under the NIOSH study reported here and previously. Observed ignitions of the chamber atmosphere by the Li-ion cells from the approved cap lamp are cause to reiterate a previous recommendation (Dubaniewicz and DuCarme, 2013) that intrinsic safety evaluated equipment powered by cells with similar form factor, chemistry, and charge capacity should be reevaluated per an appropriate cell internal short-circuit test within suitable atmospheric conditions (gas mixture and ambient temperature). Under specified plastic wedge test conditions, cells from the approved personal dust monitor did not ignite the 20-L chamber atmosphere. Other potential failure modes should be considered, as appropriate. The two cells models exhibited different internal short circuit behaviors.

Under specified plastic wedge test conditions, the K2 Energy 26650EV cells with a $LiFePO_4$ cathode also did not ignite the 20-L chamber atmosphere. The K2 cell capacity was the largest of the $LiFePO_4$ cells tested under the three phases of the study. Other potential failure modes should be considered, as appropriate.

The literature indicates that $LiCoO_2$ cell ARC ignition pressures within relatively small chambers may exceed explosion proof and flameproof enclosure minimum internal pressure design criteria by a wide margin. Within a nitrogen-purged 353-mL chamber, AllCell ARC tests with the CL, PDM, and K2 cells produced chamber pressures exceeding explosion proof and flameproof minimum pressure design criteria by a significant margin. Ignition pressures within a 20-L chamber were relatively low, with much larger head space volume and less adiabatic test conditions.

The literature indicates that sizeable $LiSOCl_2$ cell ignitions can be especially violent and toxic. Potential ignition mechanisms for sizeable $LiSOCl_2$ cells should be considered carefully before they are used in explosion protected equipment.

The IEC 60079–1 edition 7 standard specifies Li-ion secondary cells and lithium primary cells being subsequently placed within a flameproof enclosure as an acceptable explosion protection technique. Because ignition of an explosive atmosphere is expected within explosion proof or flameproof enclosures, there is a need to consider the potential for an internal explosive atmosphere ignition to initiate the lithium or Li-ion battery thermal runaway process, or a battery thermal runaway that may ignite an explosive atmosphere within the enclosure, and the resulting effects on the enclosure from the combined events. These potential series of events should be considered as a common-cause condition for equipment assessment purposes.

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