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LITHIUM-ION BATTERY THERMAL RUNAWAY IN A METHANE-AIR ENVIRONMENT

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ABSTRACT

As lithium-ion batteries (LIBs) become more prevalent in the mining industry, new hazards of battery fire and explosion are emerging. Efforts must be taken to ensure that workers are safe from these new hazards, such as batteries undergoing thermal runaway in underground areas that may have explosive methane-air mixtures. Researchers at the National Institute for Occupational Safety and Health (NIOSH) investigated overpressures generated within a sealed battery enclosure filled with an explosive methane-air mixture and a single cell lithium-ion battery driven into thermal runaway using an accelerating rate calorimeter (ARC). For both iron phosphate (LFP) and nickel manganese cobalt (NMC) lithium-ion cells, the explosion overpressures remained unchanged with varying percentages of methane concentration in the atmosphere surrounding the cell. It's likely that the gases released from the battery undergoing thermal runaway caused an inert atmosphere within the sealed canister. The results from this study will help mining equipment manufacturers develop proper measures to keep miners safe while working with lithium-ion batteries in underground gassy mines.

INTRODUCTION

Lithium-ion batteries (LIBs) are already widely used for powering various consumer electronic products and are gaining more applications as electric vehicle use increases. As the mining industry transitions to using more LIB powered battery electric vehicles (BEVs) and equipment in both coal and metal/nonmetal operations, new unique hazards must be addressed to ensure workers remain safe. Due to their high energy density, LIBs are being applied in a wide range of applications in the mining sector [1]. Larger LIBs consisting of a higher number of cells are needed to power heavier equipment like BEVs to replace diesel-powered equipment whose emissions pose a health hazard. Diesel engines on mining equipment expose 28,000 miners, both above and below ground, to carcinogenic emissions on a yearly basis [2]. Although LIB-powered equipment eliminates this hazard, this equipment is not without its own risks.

There have been numerous fire and/or explosion accidents involving LIBs in both wearable devices and consumer electric cars that have been reported [3, 4], illuminating the safety concerns when adapting LIBs for underground use. Explosion hazards are an ever-present danger in gassy underground mines because of possible methane contaminated air and being literally surrounded by combustible material in the case of coal mines. Previous experiments at NIOSH's Pittsburgh Mining Research Division (PMRD) have shown that LIBs can ignite an explosive methane and air mixture when thermal runaway was induced through short circuiting the battery [5, 6]. The explosive range of methane in air is between 4.6% and 15.8% methane [7]. A methane-air mixture can be ignited through auto-ignition when the gas temperature is from 601°C to 675°C [8]. Methane-air may also be ignited by spark, flame, heated wire, hot gas, and hot surface. The reported minimum hot surface temperature for methane ignition is 931°C [9].

Thermal runaway in a LIB happens when an internal exothermic reaction outpaces the heat externally dissipated from the battery's exterior, leading to a rapid increase in internal cell temperature and pressure. The battery self-heats past the failure temperature of its internal components, causing the cell to rupture and vent toxic and flammable gases. Different LIB chemistries have different thermal runaway properties. Golubkov et al. [10] investigated the vented gas characteristics for three types of 18650 consumer LIBs in thermal runaway tests: lithium cobalt (LCO)/NMC blended, NMC, and LFP. Major gas components were analyzed for each, as well as peak cell temperatures and total volume of gas released. Table 1 summarizes these and the following cell thermal runaway gas composition tests. Somandepalli et al. [11] studied combustion hazards of thermal runaway failure of LCO pouch cells. In a previous study [12] at PMRD, experiments were conducted to study the vented gas during thermal runaway of three types of lithium-ion batteries: 18650 lithium titanate oxide (LTO), 18650 NMC, and 26650 LFP. These studies showed that the vented gas from the battery thermal runaway contains some flammable gases such as H_2, CO, and CH_4, and the vented gas itself from a lithium-ion battery thermal runaway may be flammable [13]. The vented gas could also contain a significant amount of CO_2 ranging from 19.9% to 53% in those studies. The peak cell temperature ranged from 305°C to 998°C.

Table 1. Thermal runaway gas compositions, gas volumes, and peak cell temperatures for various cell chemistries.

Cell Type *[REF.]*	Gas V (L)	CO (%)	CO_2 (%)	CH_4 (%)	H_2 (%)	Peak T (°C)
NMC *[10]*	3.6	13.0	41.2	6.8	30.8	678
NMC *[12]*	11.1	28.1	19.9	12.9	12.5	998
LFP *[10]*	1.2	4.8	53.0	4.1	30.9	404
LFP *[12]*	3.3	4.5	25.4	5.9	24.3	399
LCO/NMC *[10]*	6.5	27.6	24.9	8.6	30.0	853
LCO *[11]*	2.5	22.9	30.0	6.4	27.7	700
LTO *[12]*	3.2	5.3	37.6	1.2	8.4	305

The Mine Safety and Health Administration (MSHA) requires explosion-proof enclosures to withstand an internal methane-air explosion and prevent ignition of an exterior methane-air environment (30 CFR 18 [14]). The enclosure must withstand a minimum pressure of at least 150 psig (10.3 barg). External surfaces of enclosures, under normal operation, shall not exceed 150 °C (302 °F). For required explosion testing [15], if any pressure peak exceeds 125 psig (8.62 barg), the manufacturer must either make constructional changes that will result in a reduction of pressure to 125 psig or less or conduct static pressure tests of the enclosure, with the enclosure withstanding a static pressure of twice the highest explosion test pressure value recorded.

Previous testing at NIOSH found LFP and NMC batteries enclosed in a sealed container under specified confinement conditions can generate pressures of 294 bar [16] and 101.6 bar [12], respectively, without the presence of methane. The 101.6 bar result for the NMC cell was obtained in an enclosure with a significant amount of free space; significantly higher pressures may be expected with well-confined cells. In this study, researchers conducted a series of experiments to investigate whether the presence of methane within a sealed enclosure increased the maximum overpressure that lithium-ion batteries generated while undergoing thermal runaway. Using an accelerating rate calorimeter (ARC), both NMC and LFP cells were tested within atmospheres containing methane concentrations ranging from 6 % to 14 % in air.

METHODS

Researchers fabricated an explosion containment canister from a 6” long piece of 6” diameter schedule 80 pipe nipple and two caps. The volume of the canister was measured by water displacement indicating a volume of 3,880 mL. Holes for pipe fittings were drilled through the top cap, and fittings were inserted for battery leads, temperature probes, pressure transducers, vacuum pump, an air/methane inlet, and a furnace ignitor [Figure 1]. Figure 2 shows a cell connected to the inside of the canister cap and the plumbing coming out of the cap after it has been sealed. The lithium-ion batteries were 26650 LFP cells rated at 3.8 Ah and 18650 NMC cells rated at 3.2 Ah. Each cell was conditioned prior to testing with three charge-discharge cycles using an Arbin Multi-channel Potentiostat/Galvanostat at manufacturers’ specifications. The cells had a measured discharge capacity of at least 95 % of their rated capacity.

Researchers used an ARC system from Thermal Hazard Technology (Bletchley, UK) to induce thermal runaway. Individual LIB cells were sealed inside a canister which was subsequently connected inside the model EV+ calorimeter inside the ARC. The integrity of the canister seals was verified prior to each test by pressurizing it to 40 psig and checking for leaks. The canister was evacuated using the ARC’s vacuum pump and refilled with the selected methane-air mixture using partial pressures for gas concentrations measured by the 30 psig maximum pressure transducer independent from the ARC system. Initial testing was done by igniting a series of selected methane-air mixtures inside the canister without a LIB to verify the experimental setup and determine methane explosion pressures for this specific layout.

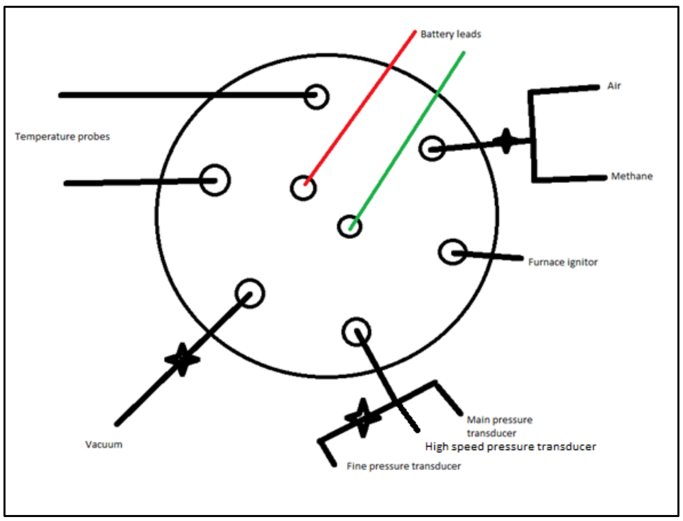


Figure 1. Canister cap layout with stars indicating where valves are located.

After the methane-air mixture was introduced into the canister, the ARC heated the canister containing the lithium-ion cell and methane-air mixture until thermal runaway was detected. A furnace ignitor inserted into the canister was used to attempt to ignite the canister atmosphere post-test to see if a flammable atmosphere remained. The furnace ignitor was also used as the ignition source for tests with methane-air only. A DATAQ Instruments model DI-720 data acquisition system recorded pressures at 100 samples per second, consistent with MSHA test procedures for explosion testing [15]. Temperatures and cell voltage were recorded by the ARC control and data acquisition software. Sensor data was imported into Microsoft Excel for data analysis.

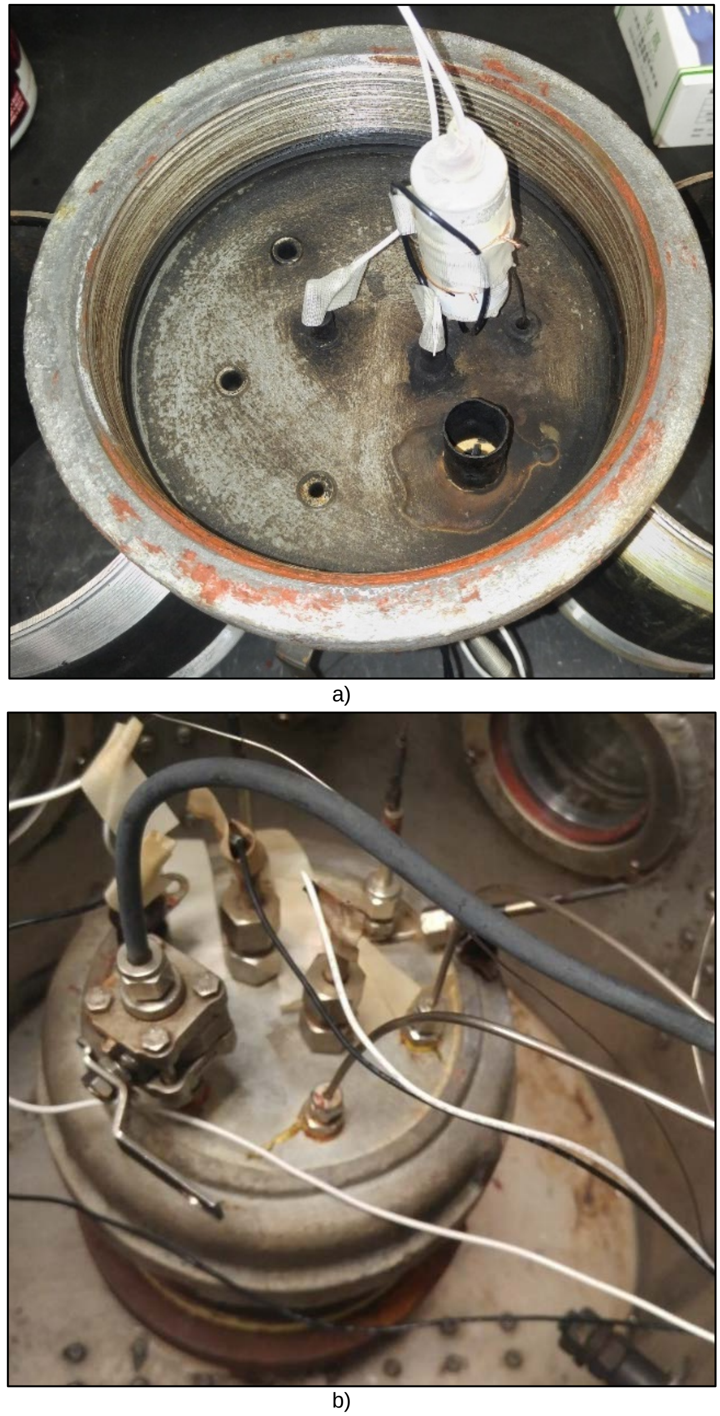


Figure 2. a) A battery attached inside the cap of the canister and b) the sealed canister connected inside the ARC.

RESULTS AND DISCUSSION

Researchers measured methane-air ignition pressures as a function of methane concentration within the 3,880 mL canister prior to conducting tests with the LIB cells (Figure 3). The canister was evacuated to a minimal pressure determined by the limit of the vacuum pump. It was then filled with methane to a specified concentration determined by partial pressures and subsequently filled the rest of the way to a one-bar pressure using lab-grade purified air. Researchers triggered the furnace ignitor for approximately 5 seconds and recorded the maximum pressure peak for each concentration. Tests were repeated three times for each methane-air concentration.

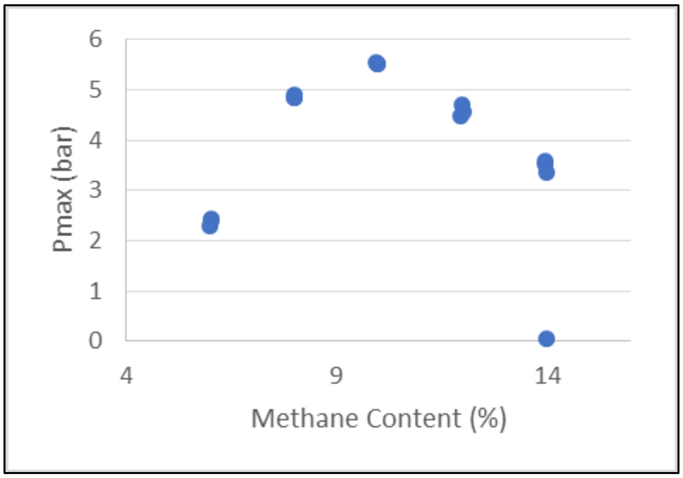


Figure 3. Methane explosible range in the 3,880 mL canister.

Based on the results in Figure 3, researchers selected 6 % (lean), 10 % (near stoichiometric), and 14 % (rich) methane-air mixtures for the battery tests. An NMC cell was put into the canister with a concentration of methane and heated until it underwent thermal runaway. The maximum pressure was recorded and compared to an NMC cell undergoing thermal runaway in a methane-absent atmosphere. A sample plot of the canister pressure, canister temperature, gas temperature, and cell temperature for an NMC cell with 10 % methane-air is shown in Figure 4. Methane-air tests with NMC cells were repeated three times for each concentration of methane, and the maximum pressures were plotted in Figure 5.

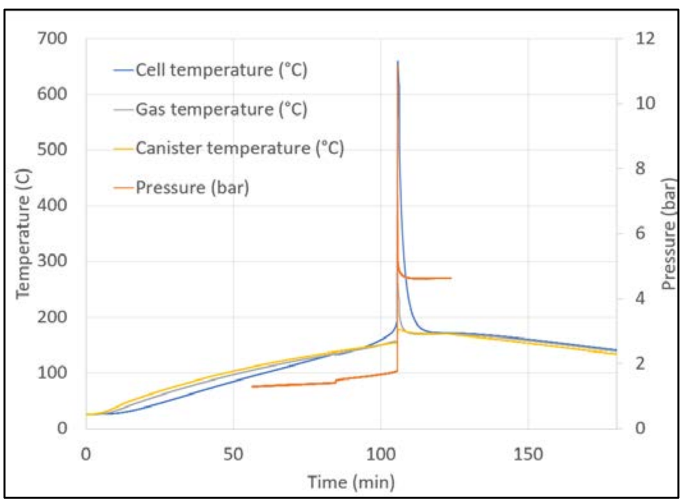


Figure 4. Time plots of gas, cell, and canister temperatures and canister pressure for an NMC cell within a 10% methane-air atmosphere.

For the NMC cells, the pressures generated during thermal runaway in a methane-containing environment did not significantly differ from those in a nonmethane-containing environment (Figure 5 and Table 2). Also, only a single pressure peak was apparent in the time plots; a second pressure peak may have indicated separate ignition of the surrounding atmosphere. From this, researchers did not see evidence that the methane was being ignited by the NMC cell undergoing thermal runaway inside the container.

LFP cells were then tested using the same experimental procedure and methane concentrations. Maximum pressures were plotted in Figure 6. Most of the LFP cells followed the same general trend as the NMC cells; however, two tests at 14 % methane and one at 0 % methane had elevated thermal runaway pressures. Most LFP tests showed an obtuse curve pressure response (Figure 7a), whereas the three elevated pressure tests had a sharper peak at thermal runaway (Figure 7b). Upon inspection of the batteries after the three elevated pressure tests, researchers found that the cells had ejected their contents through the vent in the cell casing (Figure 8). The vents apparently activated at a higher internal pressure for these tests. The no-methane data was combined with data from Dubaniewicz et al. [16] and plotted in Figure 9. The plot shows a consistent trend between thermal runaway pressure and the amount of free space/cell volume (R^2 > 0.95). For the LFP cells, the pressures generated during thermal runaway in a methane-containing environment did not differ significantly from those in a nonmethane-containing environment (Figure 6 and Table 2). Also, only a single pressure peak was apparent in the time plots; a second pressure peak may have indicated separate ignition of the surrounding atmosphere. Researchers did not see evidence that the methane was being ignited by the LFP cell thermal runaway inside the canister.

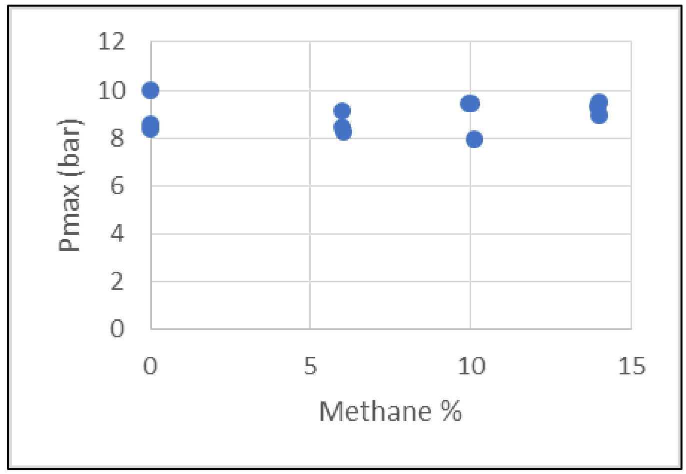


Figure 5. Maximum pressures of NMC cells driven to thermal runaway within various methane concentrations.

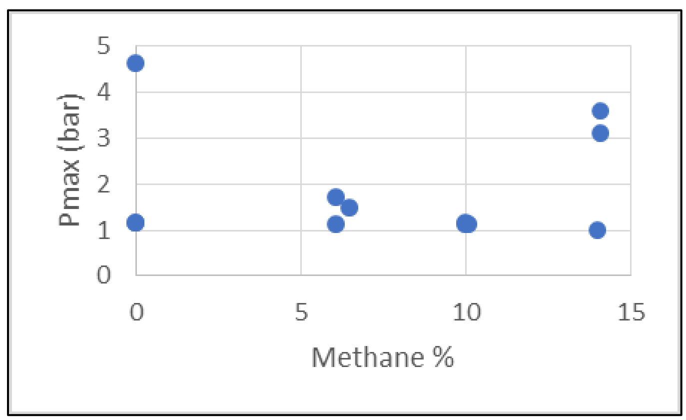
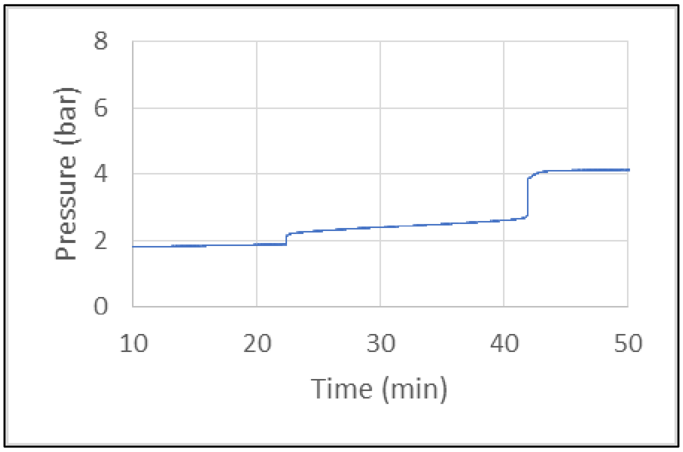


Figure 6. Thermal runaway pressures of LFP cells at various methane concentrations.

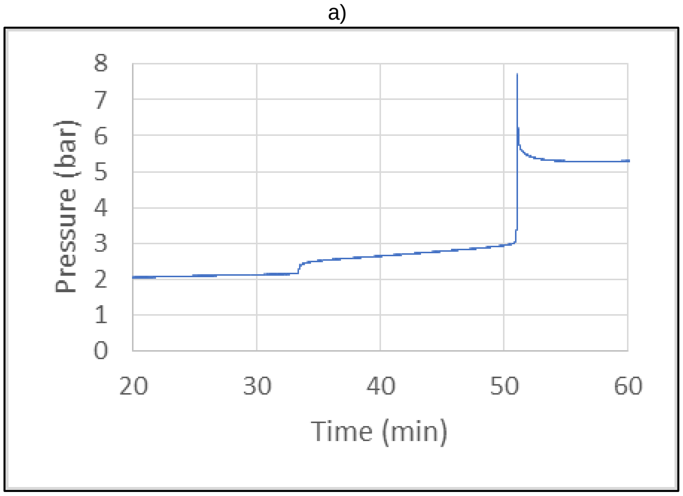
Table 2. Average peak pressures of NMC and LFP cell thermal runaways within selected methane-air mixtures.

% methane-air	0	6	10	14
NMC avg. peak pressure (bar)	8.95	8.59	8.92	9.22
LFP avg. peak pressure (bar)	2.30	1.42	1.13	2.55

Examining the maximum temperatures of the cells and canister atmosphere (Figure 10), the LFP cell surface temperatures were below and the NMC cell surface temperatures were near the 931 °C minimum temperature for methane-air hot surface ignition [7]. Likewise, the LFP cell gas temperatures were well below and the NMC gas temperatures were near the 601 °C autoignition temperature of methane-air [6].



a)



b)

Figure 7. Sample of LFP battery thermal runaway without methane within the canister with a) obtuse pressure peak at 42 min and b) sharp pressure peak at 51 min.

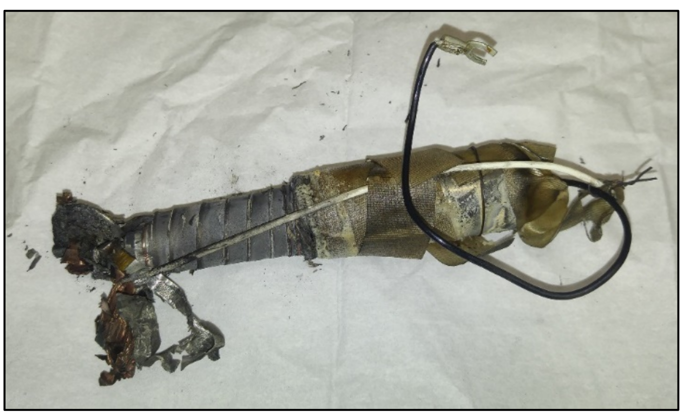


Figure 8. LFP cell after ejecting its contents during one of the elevated peak pressure tests.

When researchers activated the furnace ignitor within the canister post thermal runaway, no additional pressure peaks were observed, indicating that the atmosphere within the canister had become inert. Previous experiments by Yuan et al. [12] measuring the amount of gas produced found 11.1 L from the NMC cells and 3.3 L from the LFP cells composed of methane, carbon monoxide, and carbon dioxide (Table 1). Similarly, the calculated volume of gas released during the methane-air tests above ranged from 6.5 L to 10.5 L for the NMC cells and 3.1 L to 5.4 L for the LFP cells. The dilution of the atmospheric oxygen by these thermal runaway gases released likely caused the atmosphere to become inert.

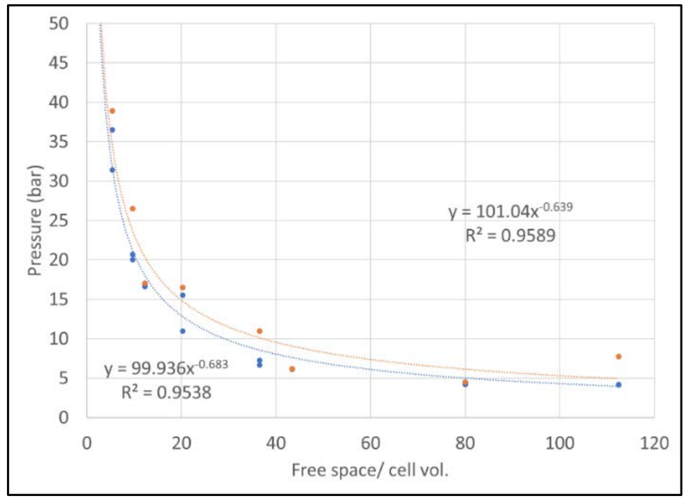
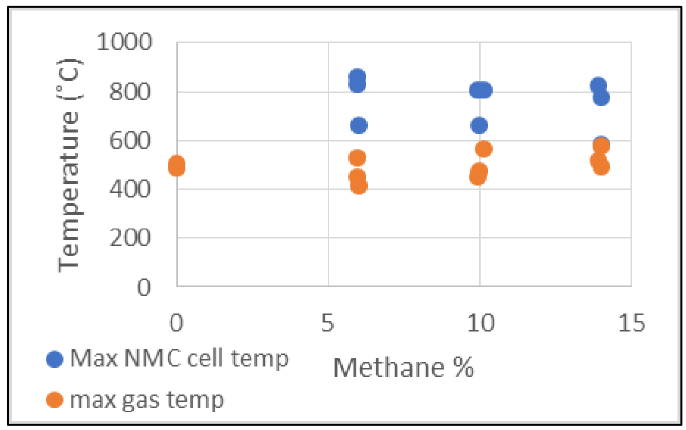
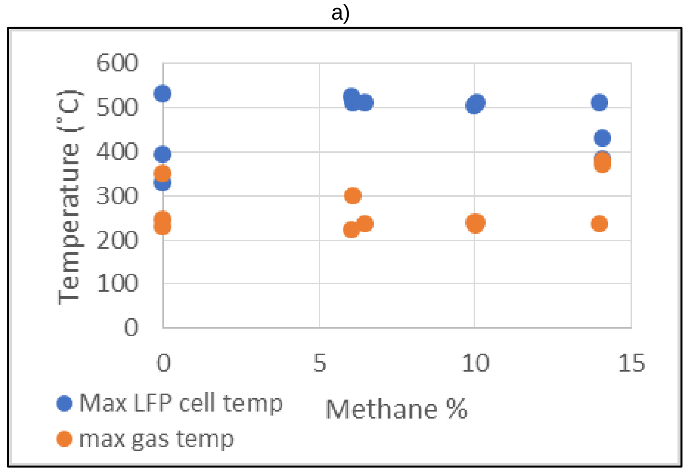


Figure 9. No-methane test pressures plotted with previous LFP free-space pressure tests from Dubaniewicz et al. [16]. All tests at each free space / cell volume ratio were analyzed together (blue) and maximum pressures were analyzed separately (orange).



a)



b)

Figure 10. Maximum cell and atmosphere temperatures of cells undergoing thermal runaway in methane-air of a) NMC cells and b) LFP cells.

CONCLUSIONS

A series of experiments were conducted to investigate if a LIB's thermal runaway can ignite an explosive methane-air mixture in a sealed battery enclosure using an ARC with either an NMC or LFP LIB cell. For both of these LIB cell chemistries, thermal runaway overpressures remained unchanged with varying percentages of methane in the atmosphere surrounding the cell. Neither of the LIB cell chemistries tested were able to ignite the selected methane-air atmospheres under specified test conditions. An independent ignition source (a furnace ignitor) was unable to ignite the atmospheres post-test, indicating that the atmosphere was inert. Significant amounts of CO_2, CH_4, and CO can be released from a cell undergoing thermal runaway. It is likely that the gases released from the cell undergoing thermal runaway dilute the atmospheric oxygen enough to create an inert atmosphere within this particular canister. These results can help mining equipment manufacturers and mine safety personnel develop explosion prevention and control measures for LIBs used in underground gassy mines.

DISCLAIMER

The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention. Mention of any company or product does not constitute endorsement by NIOSH.

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