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THERMAL RUNAWAY OF LTO AND NCA LITHIUM-ION BATTERIES IN A SEALED ENCLOSURE CONTAINING METHANE

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ABSTRACT

Lithium-Ion batteries (LIBs) have the potential to go into thermal runaway which introduces a new ignition source in hazardous environments such as gassy underground mines that may contain methane in the surrounding air. Researchers from the National Institute for Occupational Safety and Health (NIOSH) used an accelerating rate calorimeter (ARC) to induce thermal runaway in individual lithium-titanium-oxide (LTO) and lithium-nickel-cobalt-aluminum-oxide (NCA) LIB cells within a sealed enclosure with either no methane, a lean, a stoichiometric, or a rich methane-air mixture in the surrounding canister to determine if these LIB types would ignite the methane, causing an additive effect on overpressures. Canister pressures and maximum temperatures reached by the cells, surrounding air, and exhausted gases were measured in this study and remained consistent with varying methane concentrations.

INTRODUCTION

Because of their high energy density, lithium-Ion batteries (LIBs) have quickly become the industry standard in everything from power tools to battery electric vehicles [1]. A variety of different types and chemistries of LIBs are being used to power equipment in both surface and underground mines depending on the specific task needs [2]. While reducing the health hazards from exposing miners to diesel fumes [3], the adoption of LIBs introduces new hazard sources that miners and mining companies need to consider in order to ensure the safety of all personnel involved. LIBs have the potential to go into thermal runaway, producing a potential new ignition source in gassy underground mines that may contain methane in the surrounding air.

LIBs are already being used in a wide range of applications in the mining sector, and these include single-cell-powered equipment as well as larger, multi-cell equipment such as battery electric vehicles that replace diesel-powered equipment. Although effective at reducing miners' exposure to hazardous diesel emissions, LIBs are not without their own risks. Numerous LIB fires and/or explosion incidents have already been documented in consumer-level electronics as well as industrial applications including underground coal mines [4, 5, 6]. This, of course, is problematic in gassy underground mines because of the possibility for LIBs in thermal runaway to ignite methane. Previous research at the National Institute for Occupational Safety and Health (NIOSH) Pittsburgh Mining Research Division (PMRD) has shown that LIBs undergoing short-circuit-induced thermal runaway can ignite methane in a 20-liter chamber [7, 8]. Additionally, PMRD researchers have previously shown that LIBs were unable to ignite methane when in a sealed enclosure using iron phosphate (LFP) and nickel manganese cobalt (NMC) batteries [9] when thermal runaway was induced through heating.

Thermal runaway happens in a LIB when the internal exothermic reaction outpaces the battery's ability to externally dissipate heat, causing a rapid increase in cell temperature. The battery self-heats past the mechanical limits of its components, and internally generated gas increases the pressure within the cell causing it to rupture and vent the toxic and flammable gas [10]. Thermal runaway may produce pressures of several hundred bar [11]. Flammable gases produced by thermal runaway may mix with atmospheric oxygen, as well as ambient methane-air mixtures, and ignite. The explosive range of methane in air is 4.6% to 15.8% [12] and can be ignited through auto-ignition or hot surface ignition. Methane-air can also be ignited through electrical arcs and sparks; during testing, care was taken to ensure these were not a source of ignition in this experiment. The auto-ignition temperature range of a methane-air mixture is 601°C to 675°C [13], and the minimum hot surface ignition temperature is 931°C [14]. Different LIB chemistries tend to have different thermal runaway properties regarding the amount of gas released, the maximum temperature reached, and the maximum pressures reached. The major components of the released gases contain carbon monoxide, carbon dioxide, methane, and hydrogen in different percentages depending on the battery chemistry. Table 1 summarizes the thermal runaway characteristics of various cell types found in the literature. LCO refers to a lithium cobalt oxide cathode chemistry.

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

Cell Type	CO (%)	CO_2 (%)	CH_4 (%)	H_2 (%)	Peak T (˚C)	Reference
NMC	13.0	41.2	6.8	30.8	678	[15]
NMC	28.1	19.9	12.9	12.5	998	[16]
LFP	4.8	53.0	4.1	30.9	404	[15]
LFP	4.5	25.4	5.9	24.3	399	[16]
LCO/NMC	27.6	24.9	8.6	30.0	853	[15]
LCO	22.9	30.0	6.4	27.7	700	[17]
LTO	5.3	37.6	1.2	8.4	305	[16]
NCA	44.8	20.0	7.1	25.7	1075	[18]

The high volumes of vented gases lead to safety concerns for making battery enclosures that can withstand these thermal runaway conditions. The Mine Safety and Health Administration (MSHA) requires explosion-proof (XP) enclosures to be able to withstand an internal methane-air explosion and prevent ignition of a surrounding methane-air or coal dust environment (30 CFR 18 [19]). The minimum pressure that an XP enclosure must be able to withstand is 150 psig (10.3 barg), and the surface temperature must not exceed 150 °C (302 °F) under normal operation. During testing, if the internal enclosure exceeds a peak pressure of 125 psig (8.62 barg), the manufacturer must make structural changes to reduce pressure peaks to below 125 psig or conduct static pressure tests at a value of twice the highest explosion test peak pressure recorded. Previous research by Dubaniewicz et al. found the pressures generated by LIBs undergoing thermal runaway are greatly dependent on the free space within the enclosure and can far exceed pressure ratings of XP enclosures for well-confined batteries [11, 20].

For this study, researchers at NIOSH's PMRD investigated the overpressures generated within a sealed battery enclosure filled with an explosive methane-air mixture and a single LIB cell driven into thermal runaway using an accelerating rate calorimeter (ARC). Researchers induced thermal runaway in lithium-titanium-oxide (LTO) and lithium nickel cobalt aluminum oxide (NCA) LIBs within a sealed enclosure containing a methane-air mixture to see if this would lead to an increase in explosion overpressure generated by thermal runaway alone, similar to the previous testing with LFP and NMC chemistries [9]. Individual cells were forced into thermal runaway inside a tightly sealed enclosure with either no methane, a lean methane-air mixture, a stoichiometric methane-air mixture, or a rich methane-air mixture in the surrounding canister within NIOSH's ARC. Pressures generated by the battery going into thermal runaway as well as maximum temperatures reached by the cells, surrounding air, and exhausted gases were measured to see if the batteries were igniting the methane and causing an additive effect to overpressures. For all cell chemistries, the explosion overpressures remained consistent 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.

METHODS

NIOSH researchers used an Accelerating Rate Calorimeter (ARC) System (model EV+, Thermal Hazard Technology, Milton Keynes, United Kingdom) to induce thermal runaway through overheating LIBs. Individual LIB cells were sealed inside a custom-fabricated explosion containment canister and heated inside the model EV+ calorimeter. The canisters were made from a 6-in-long piece of 6-in-diameter schedule-80 pipe nipple sealed on both ends with caps. The interior volume of the canister was measured by filling it with water and was found to be 3,880 mL. Holes for pipe fittings were drilled through the top cap and fitted with battery leads, temperature probes, pressure transducers, the vacuum pump, a furnace ignitor, and a gas inlet valve for methane and air [Figure 1]. The cells were connected to the leads and a thermocouple, then sealed inside the canister [Figure 2]. Researchers used fully charged 18650 LTO (2.4V, 1300mAh) and 18650 NCA (3.7V, 3450mAh) cells. Each cell was cycled three times using an Arbin Multi-channel Potentiostat/Galvanostat (MSTAT, Arbin Instruments, College Station, Texas) system to ensure each had a measured discharge capacity of at least 95% of their rated capacity.

Researchers used compressed air to pressurize the canisters to 40 psig in order to verify the integrity of the seals and ensure pressure fittings would not leak. The canister was then evacuated using the ARC's vacuum pump and filled with methane and lab-grade compressed air to the selected methane-air concentrations through partial pressures measured by a 30-psia max pressure transducer. Initial testing was performed with various concentrations of methane without a battery to determine methane explosion pressures for this layout.

LIB-containing canisters were heated inside the ARC until the pressure transducer and thermocouples detected thermal runaway. The furnace ignitor was triggered post-thermal runaway to verify if the released gas and atmosphere was flammable inside the container after the test. A higher-speed (100 samples per second) pressure transducer, connected to an independent data acquisition system, was used to measure maximum pressures consistent with MSHA test procedures [21]. Temperatures were measured using thermocouples connected to the ARC.

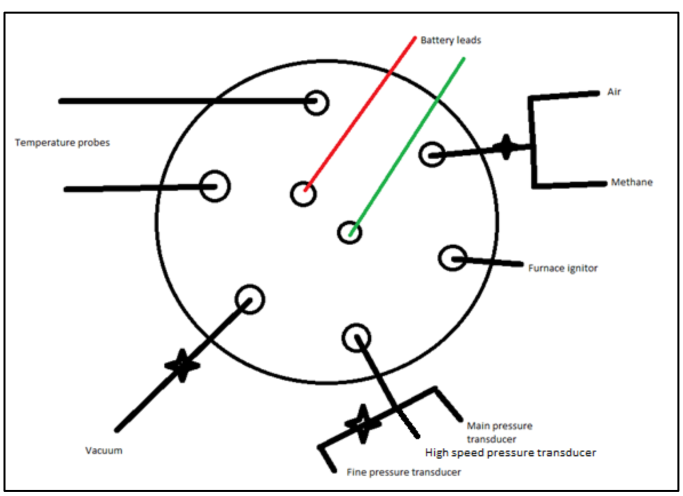


Figure 1. Canister cap layout with stars indicating where valves are located.

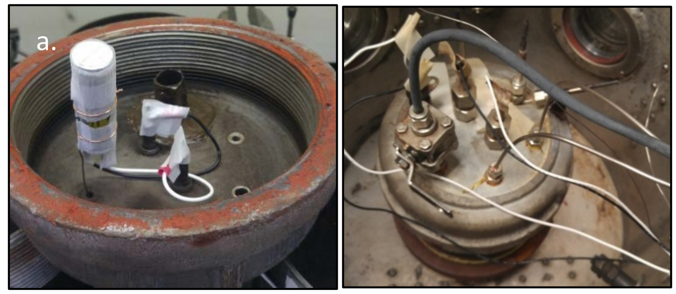


Figure 2. a) An LTO cell attached inside the lid of the canister and b) the sealed canister inside the ARC.

RESULTS AND DISCUSSION

Using the canister without a battery, researchers measured methane ignition pressures at various concentrations. The canister was first evacuated to the limit of the ARC's vacuum pump. Methane was injected to a specified voltage on the pressure transducer corresponding to the calculated percentage as determined by partial pressures. The canister was then filled back to one-bar pressure with lab-grade purified compressed air. The furnace ignitor was triggered for approximately five seconds, and researchers recorded the maximum pressure peak for each test. Figure 3 shows the methane curve with tests at 6% through 14% methane in air with each concentration being repeated three times.

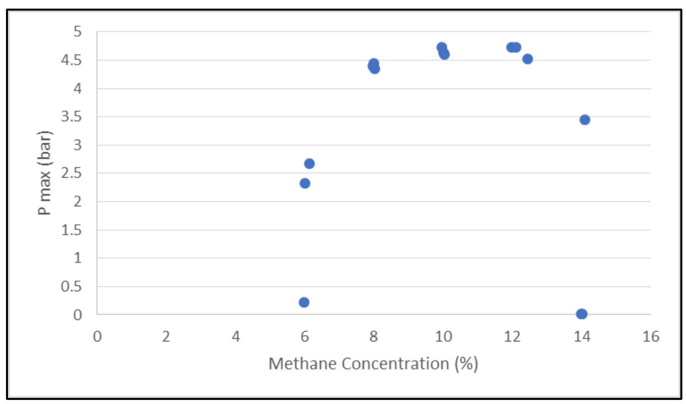


Figure 3. Methane explosibility curve generated in the 3,880-mL canister.

Researchers used the results from Figure 3 to select 6%, 10%, and 14% as the lean, near stoichiometric, and rich methane-air mixture concentrations for battery testing. A single LTO cell, charged to its full state of charge, was placed within the canister which was subsequently sealed and placed within the ARC. Using the same process as the methane-air ignition tests, the canister was filled with a mixture of air and methane. The canister was then heated by the ARC until the battery underwent thermal runaway, and the maximum pressures and temperatures were then measured. Batteries were also tested in a methane-absent atmosphere for comparison. Figure 4 shows the maximum overpressures reached when LTO cells underwent thermal runaway inside the canister at 0%, 6%, 10%, and 14% methane in air. The initial cannister pressure, as well as pressure generated from heating were subtracted in order to get the pressure generated only during thermal runaway. Tests were repeated three times at each concentration. A sample plot of the ARC measured pressure, cell temperature, gas temperature, and canister temperature is shown in Figure 5.

The LTO cells reached about one-bar overpressure during thermal runaway. The canister started at one-bar pressure and rose about one-bar during heating, so the maximum pressure inside the canister reached around three-bar for each test. The pressure generated by the LTO cells during thermal runaway were not significantly different between the different methane atmospheres and the methane-absent atmosphere (Table 2). No evidence for methane ignition by the LTO cells was observed since the pressures stayed well below those measured during the methane-air-only canister ignition tests. Upon conclusion of each test, researchers triggered the furnace ignitor for five seconds to check if the post-thermal runaway atmosphere was ignitable. Researchers did not observe any evidence of ignition, indicating that the gases released from the battery inerted the atmosphere mixture within the canister.

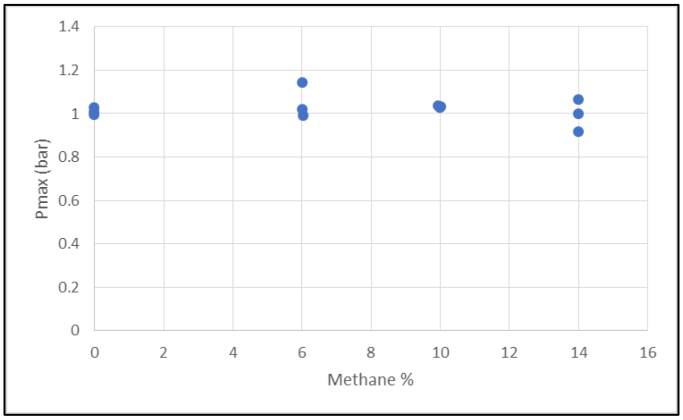


Figure 4. Maximum overpressures of LTO cells driven to thermal runaway within various methane concentrations.

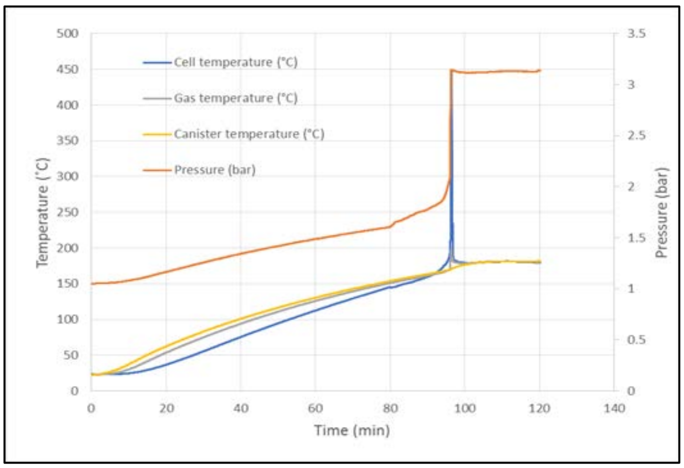


Figure 5. Time plots of gas, cell, and canister temperatures and canister pressure for an LTO cell within a 10% methane-air atmosphere.

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

% Methane-Air	0	6	10	14
NMC average peak pressure (bar)	8.95	8.59	8.92	9.22
LFP average peak pressure (bar)	2.30	1.42	1.13	2.55
LTO average peak pressure (bar)	1.01	1.05	1.03	0.99
NCA average peak pressure (bar)	9.02	9.42	9.85	9.22

Tests were then repeated using NCA cells instead of LTO cells. Once again, the canister was heated until cells underwent thermal runaway, and peak pressures and temperatures were recorded. The tests were repeated three times at each 0%, 6%, 10%, and 14% methane. Pressures generated by these tests are shown in Figure 6. A sample plot of the pressures and temperatures is shown in Figure 7.

The NCA cells followed the same general trend as the LTO cells, albeit at much higher pressures. Overpressures ranged from about 8 to 10.5 bar but do not show a clear indication that the atmosphere within the canister was being ignited based on added methane concentration, or lack thereof. Higher overpressures were measured with the separate high-speed pressure transducer than were measured with the ARC built-in transducer because of how fast the peak occurred and subsided with the NCA cells.

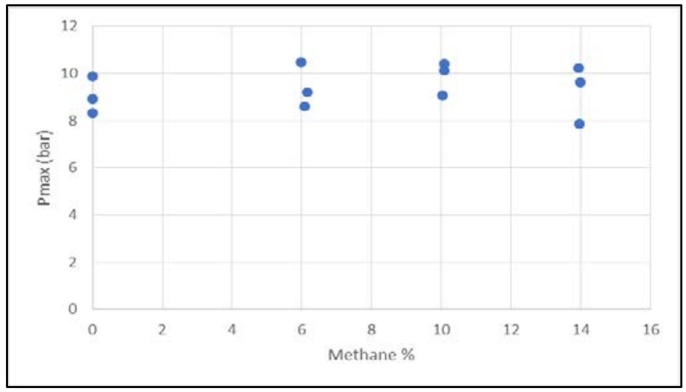


Figure 6. Thermal runaway overpressures of NCA cells at various methane concentrations.

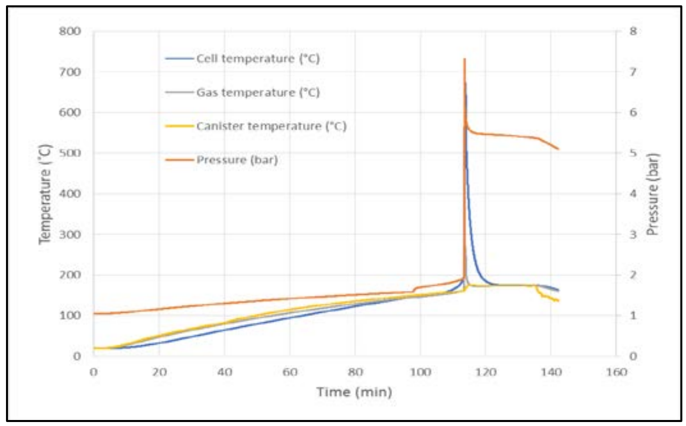


Figure 7. Time plots of gas, cell, and canister temperatures and canister pressure for an NCA cell within a 10% methane-air atmosphere.

When comparing the LTO and NCA cells to the previously tested 18650 NMC and 26650 LFP cells (Figure 8), the pressures generated by the LTO cells closely compare to the pressures generated by the LFP cells. Similar trends appear between the NMC and NCA cells. As discussed in a previously published work [9], the LFP cells had anomalous high peaks at 0% and 14% methane that researchers believe were caused by the vent failing, causing the cell contents to be ejected from its casing (Figure 9a). A similar incident occurred with the LTO cells (Figure 9b), but a corresponding high-pressure peak was not observed like it was in the LFP cells. Researchers believe this difference may be because of the manufacturer's inclusion of a burst disc on the bottom of the LTO cells that allowed pressure to alleviate before the battery failed completely. Table 2 shows the comparison in average maximum pressures at each methane concentration between the two battery chemistries tested and the two battery chemistries previously tested [9]. In all four chemistries tested, the concentration of methane in the canister did not make a significant difference in explosion overpressures when the batteries underwent heat-induced thermal runaway.

The maximum temperature of the cells and canister atmosphere (Figure 10) follow a similar trend as maximum pressures with respect to the battery chemistries. The LTO cells closely aligned with the LFP cells, and the NCA cells resembled the previously tested NMC cells. The LTO cell surface and gas temperatures were below the 931 °C hot surface ignition and 601 °C auto-ignition temperature of methane-air. The NCA cell surface temperatures approached the 931 °C minimum surface temperature for hot surface methane-air ignition. NCA cell surface temperatures measured by Golubkov et al. (2015) [18] were above the minimum hot surface ignition temperature of methane. NCA thermal runaway should be considered as a potential ignition source for methane-air mixtures, but researchers did not see any indication that methane was ignited using this specific experimental setup. The low-temperature measurement for one of the LTO cells at 14% methane, in Figure 10a, is a result of the thermocouple slipping off the battery casing and measuring the gas temperature rather than the cell temperature.

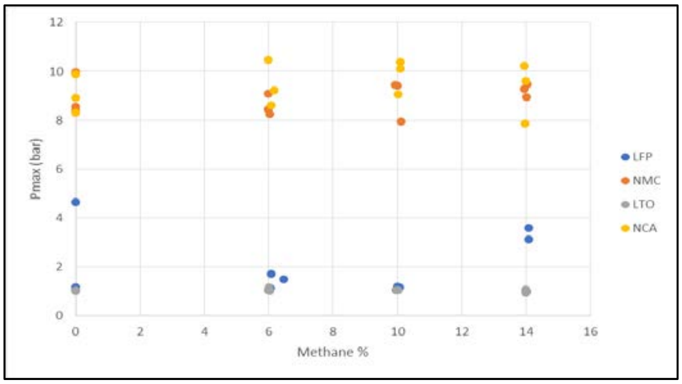
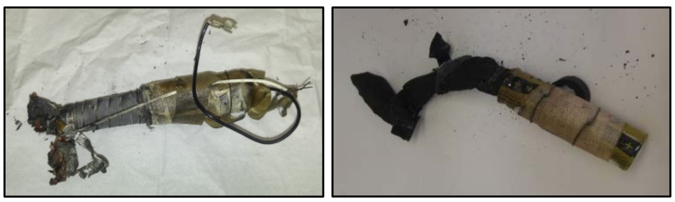
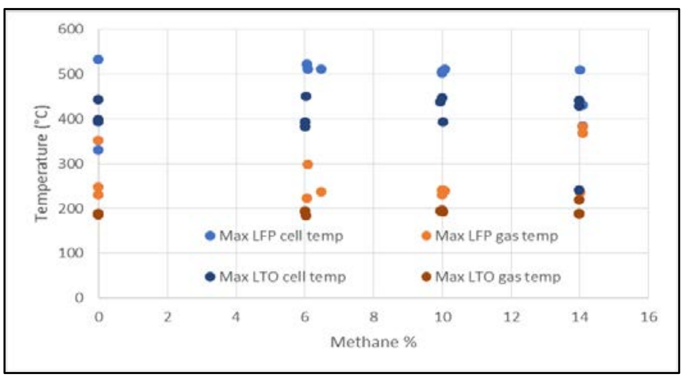


Figure 8. Comparison of maximum pressures of LFP, LTO, NMC, and NCA cells.

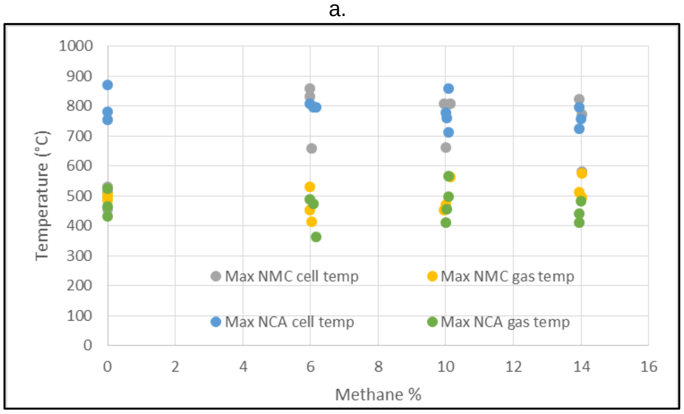


a. **b.**

Figure 9. a) an LFP cell and b) an LTO cell after ejecting their contents during thermal runaway.



a.



b.

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

Researchers calculated that the volume of gas released from the LTO and NCA cells reached to as high as 3.9 L and 10.3 L, respectively, based on the canister size and pressures generated. When researchers activated the furnace ignitor within the canister after the cells had undergone thermal runaway, no additional pressure peaks were observed. This indicates that the atmosphere inside the canister was no longer explosible after the batteries had released their gas. The methane, carbon monoxide, and carbon dioxide released from the cell by thermal runaway likely diluted the atmospheric oxygen within the canister, causing the atmosphere to become inert.

CONCLUSIONS

A series of accelerating rate calorimeter (ARC) tests were conducted to determine if thermal runaway by LTO and NCA cells can ignite an explosive methane-air atmosphere within a sealed battery enclosure. Neither of these LIB chemistries were able to ignite the methane as researchers did not see any indication of higher peak explosion pressures based on methane concentration in the atmosphere surrounding the cell under specified test conditions (i.e., sealed within a limited volume enclosure). Using an independent ignition source post-thermal runaway, NIOSH researchers were also unable to ignite the methane, indicating that the gases released during thermal runaway likely created an inert atmosphere inside this specific enclosure. The results from this research will help mining equipment manufacturers properly address new safety hazards and develop measures to keep miners safe while working with lithium-ion-battery-powered equipment 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.

REFERENCES

1. GMG (2018). Recommended Best Practices for Battery Electric Vehicles in Underground Mining – 2nd Edition. Global Mining Guidelines Group document No.: 20180621_UG_Mining_BEV-GMG-WG-v02-r01. Retrieved August 2021 from https://gmggroup.org/guidelines/.

2. Unwin, J. (2019). In Charge: The Battery Technologies Leading the Way in Mining. Mining Technology. Retrieved August 2022 from https://www.mining-technology.com/analysis/in-charge-the-battery-technologies-leading-the-way-in-mining.

3. NIOSH (2017). Mining project: Advanced strategies for controlling exposures to diesel aerosols. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. Retrieved August 2021 from https://www.cdc.gov/niosh/mining/researchprogram/projects/project_DieselAerosols.html.

4. OSHA (2019). Preventing Fire and/or Explosion Injury from Small and Wearable Lithium Battery Powered Devices. Safety and Health Information Bulletin. U.S. Occupational Safety and Health Administration, Arlington, VA, USA. Retrieved August 2021 from https://www.osha.gov/sites/default/files/publications/shib011819.pdf.

5. NTSB (2020). Safety Risks to Emergency Responders from Lithium-Ion Battery Fires in Electric Vehicles. Safety Report NTSB/SR-20/01 PB2020-101011. U.S. National Transportation Safety Board. Washington, D.C., USA. Retrieved August 2021 from https://www.ntsb.gov/safety/safety-studies/Documents/SR2001.pdf.

6. Gillis, L. (2019). December Fire at Red Lake Mine Raises Red Flags About Lithium-Ion Batteries. Northern Ontario Business. Retrieved August 2022 from https://www.northernontariobusiness.com/industry-

news/mining/december-fire-at-red-lake-mine-raises-red-flags-about-lithium-batteries-1440101

7. Dubaniewicz, T.H., DuCarme, J.P. (2014). Further study of the intrinsic safety of internally shorted lithium and lithium-ion cells within methane-air. J. Loss Prev. Process Ind. 32: 165-173. Retrieved August 2021 from http://www.ncbi.nlm.nih.gov/pmc/articles/PMC4485987/.

8. Dubaniewicz, T.H., DuCarme, J.P. (2016). Internal short circuit and accelerated rate calorimetry tests of lithium-ion cells: Considerations for methane-air intrinsic safety and explosion proof/flameproof protection methods. J Loss Prev Process Ind. 43: 575–584. Retrieved August 2021 from https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5040472/.

9. Rayyan, N., Dubaniewicz, T.H., Yuan, L., Brown, C., Soles, J., Thomas, R. (2022). Lithium-Ion Battery Thermal Runaway in a Methane-Air Environment. SME Annual Meeting, Feb. 27 – Mar. 02, 2022. Salt Lake City, Utah. Preprint 22-112.

10. Chen, S., Wang, Z., Wang, J., Tong, X., Yan, W. (2020). Lower Explosion Limited of the Vented Gases from Li-Ion Batteries Thermal Runaway in High Temperature Condition. Journal of Loss Prevention in Process Industries. 63. 103992. Retrieved August 2021 from https://doi.org/10.1016/j.jlp.2019.103992.

11. Dubaniewicz, T.H., Barone, T.L., Brown, C.B., Thomas, R.A., (2022). Comparison of thermal runaway pressures within sealed enclosures for nickel manganese cobalt and iron phosphate cathode lithium-ion cells. Journal of Loss Prevention in the Process Industries 76:104739. Retrieved August 2022 from https://doi.org/10.1016/j.jlp.2022.104739.

12. Coward, H.F., Jones, G.W., (1952). Limits of flammability of gases and vapors. U.S. Bureau of Mines Information Circular No. 503. 155 pp. Retrieved August 2021 from https://www.osti.gov/biblio/7355338.

13. Kundu, S., Zanganeh, J., Moghtaderi, B. (2016). A Review on Understanding Explosions from Methane-Air Mixture. Journal of Loss Prevention in Process Industries. 40. 507-523. Retrieved August 2021 from https://doi.org/10.1016/j.jlp.2016.02.004.

14. Ungut, A., James, H. (2001). Autoignition of Gaseous Fuel-Air Mixtures Near a Hot Surface. IChemE Symposium Series No. 148, pp. 487-192. Retrieved August 2021 from https://www.icheme.org/media/10183/xvi-paper-38.pdf.

15. Golubkov, A.W., Fuchs, D., Wagner, J., Wiltsche, H., Stangl, C., Fauler, G., Voitic, G., Thaler, A., Hacker, V., (2014). Thermal-Runaway Experiments on Consumer Li-ion Batteries with Metal-Oxide and Olivin-type Cathodes. RSC Advances 4, 3633-3642. Retrieved August 2021 from https://pubs.rsc.org/en/content/articlehtml/2014/ra/c3ra45748f.

16. Yuan, L., Dubaniewicz, T. H., Zlochower, I., Thomas, R., Rayyan, N. (2020). Experimental Study on Thermal Runaway and Vented Gases of Lithium-Ion Cells. Process Safety and Environmental Protection. 144 (2020) 186-192. Retrieved August 2021 from https://doi.org/10.1016/j.psep.2020.07.028.

17. Somandepalli, V., Marr, K., Horn, Q., (2014). Quantification of Combustion Hazards of Thermal Runaway Failures in Lithium-Ion Batteries. SAE Int. J. Alt. Powertrains 98–104. Retrieved August 2021 from https://www.jstor.org/stable/26169043.

18. Golubkov, A.W., Scheikl, S., Planteu, R., Voitic, G., Wiltsche, H., Stangl, C., Fauler, G., Thaler, A., Hacker, V., (2015). Thermal Runaway of Commercial 18650 Li-ion Batteries with LPF and NCA Cathodes – Impact of State of Charge and Overcharge. RSC Advances 2015, 5, 57171. Retrieved August 2022 from https://doi.org/10.1039/C5RA05897J.

19. 30 CFR. (2018). Code of Federal Regulations, Mineral Resources, Parts 1 to 199, U.S. Department of Labor, Mine Safety and Health Administration, Arlington, VA, USA. Retrieved August 2021 from https://arlweb.msha.gov/regs/30cfr/.

20. Dubaniewicz, T.H., Zlochower, I., Barone, T., Thomas, R., Yuan, L. (2021). Thermal Runaway Pressures of Iron Phosphate Lithium-Ion Cells as a Function of Free Space Within Sealed Enclosures. Mining, Metallurgy & Exploration 38:539–547. https://doi.org/10.1007/s42461-020-00349-9.

21. MSHA (2005). REQUIREMENTS FOR EXPLOSION TESTING PER 30 CFR, 18.62, ASTP 2137. U.S. Department of Labor, Mine Safety and Health Administration, Arlington, VA, USA. Retrieved August 2021 from https://arlweb.msha.gov/TECHSUPP/ACC/StandardTestProcs/ASTP2137.pdf.