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

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ABSTRACT

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

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1. Introduction

Lithium-ion (Li-ion) batteries have become one of the most popular types of rechargeable battery for portable electronics. Li-ion technology provides enhanced energy storage capabilities that lengthen device runtime, shorten the recharge time, and extend the life of the battery. Beyond consumer electronics, Li-ion batteries are now growing in popularity for underground mine safety equipment such as cap lamps and communications and tracking equipment. Chemistry, performance, cost, and safety characteristics vary across lithium battery types. Portable electronics often use Li-ion batteries with lithium cobalt oxide ($LiCoO_2$) cathodes, which offer high energy density, but have well-known thermal runaway safety concerns. Safety concerns specific to underground coal mine fire and explosion hazards from $LiCoO_2$ cells were described previously (Dubaniewicz and DuCarme, 2013). A Li-ion powered Mine Safety and Health Administration (MSHA) permissible device was involved in a thermal event in an underground coal mine. An investigative report of the incident is not publically available.

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

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

2. Background/literature review

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

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

Spiral-wound Li-ion cells use a thin separator material to insulate the anode from the cathode (Fig. 1). Physical damage to this separator causes an internal short circuit that may lead to catastrophic heating events. Some separator materials have shutdown properties that can provide a margin of safety against certain failure modes, including internal short circuits, that result in an elevated cell temperature. However, some potential safety issues remain.

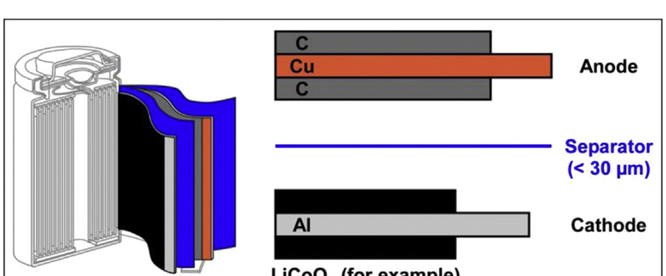

Fig. 1. A drawing of a common spiral-wound Li-ion cell construction with a thin separator material.

Baldwin (2009) reviewed separator materials and functions for lithium-based batteries used in aerospace missions, and suggests the shutdown mechanism would provide very little protection from an internal short circuit accompanied by a rapid internal heating rate. The thickness of commercial separator materials reviewed were <30 μm. Orendorff (2012) discussed challenges with designing safe Li-ion cell separators, including some tradeoffs between mechanical robustness and porosity/transport (performance) properties, primarily for large format cells. The thicknesses of four varieties of commercial separators reviewed were approximately 25 μm. Orendorff concluded that ceramic/polymer composites and high melting point polymer materials offer some improvement in thermal stability and abuse tolerance for Li-ion cell separators but, in general, there needs to be more evaluation work dedicated to quantifying the safety impact of new separators, particularly for large format cells.

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

Recent studies (Ong et al., 2010) (Zaghib et al., 2012) demonstrate some safety aspects of $LiFePO_4$ positive electrode materials compared to some other materials. The relative safety of $LiFePO_4$ is generally attributed to limited O_2 release upon high temperature decomposition. Previous research (Dubaniewicz and DuCarme, 2013) found that selected $LiFePO_4$ cells did not cause ignition when crushed within CH_4-air mixtures under specified test conditions. In the current study, additional tests were conducted to crush selected $LiFePO_4$ cells while charging within normal charging conditions. These tests simulated a CH_4 ignition hazard involving underground stationary Li-ion battery-powered equipment that is on charge and unattended, while maintaining a single fault condition of a crush-induced internal short circuit.

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

Li-ion cell vent gases may be flammable or inert, and the volume of vent gases from thermal runaway is substantial. Roth and Orendorff (2012) and Roth (2008) found that cell venting before thermal runaway is achieved may release flammable solvent vapor into the surrounding environment, which may then be ignited by an adequate ignition source. In contrast, they also found that the decomposition vent gases from Li-ion cells undergoing thermal