Removal of Lithium from Firefighter Protective Clothing using CO2+ Cleaning Technology: Preliminary Test Results - Executive Summary

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Abstract

Lithium-ion or Li-ion batteries (LIB) are a major part of the energy future worldwide and incidents of LIB fires represent a new hazard to firefighters. LIB fires generate a range of toxic products of combustion, including but not limited to acids, soot, PAHs, toxic gases, cobalt, and lithium products. This study details preliminary testing of the effectiveness of the CO_2+ Cleaning System to remove lithium from test samples and loads designed to mimic firefighter gear. Tests were designed to use lithium carbonate as the lithium source. The testing protocol followed the National Firefighter Protection Association (NFPA) methods to the degree available, but modifications in analytical testing methods were observed. The results of this test showed an average lithium removal rate of about 80%, which closely match those from cobalt removals in earlier studies. While promising, more work will be done to refine the testing protocols and expand the number of LIB products of combustion examined.

Introduction

With the continued development of LIBs as an essential part of the electric vehicle market, fires involving these products have been shown to be hazardous for firefighters, as well as those involved in the fire incident. As the market for LIBs continues to grow very rapidly, the importance of impacts of products of incomplete combustion for LIB fires will be of great importance to firefighters and to those that care about them.

This paper summarizes initial testing conducted using the innovative CO_2+ Cleaning System, which has been shown to be very effective at removing organics, metals, and other contaminants of concern from firefighter turnout gear. This is the first test of CO2-based cleaning technology applied to LIB products of incomplete combustion.

Background

The main fuel in a LIB is an electrolyte, which is a solution consisting of organic solvent and inorganic salt. The most common solvents used in LIBs are ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, and combinations thereof. Lithium hexafluorophosphate ($LiPF_6$) is by far the most widely used electrolyte salt in LIBs. [1] Under normal conditions, the LIB is a closed system separated from air and designed to eliminate an explosion and fire incidents. However, if the system is opened through abuse, dangerous thermal runaway conditions can result. In combustion reactions, a thermal runaway releases byproducts that may ignite to cause smoke, heat, fire, and/or an explosion.

Three different thermal runaway gas explosion hazard scenarios can occur:

1. The flammable gas mixture is ignited soon after it is formed near the initiating module, such that there is only a minor deflagration and a subsequent fire.
2. Batteries in thermal runaway release flammable gases without igniting initially and a delayed explosion associated with the accumulation of additional flammable atmosphere then occurs.
3. There is an initial fire with accumulation of incomplete combustion products and possible fire suppression agent. Until something happens, e.g., oxygen addition to the rich gas mixture, to suddenly render the mixture ignitable.[2]

As reported by Johnplass et al [3] Golubkov et al [4], they analyzed the gas composition of the vented gas emitted from three different 18650 batteries showing generation of gases, including CO, CO_2, H_2, Ch_4, C_2H_4 and C_2H_6. All cells released high amounts of H_2 and hydrocarbons, which are highly flammable. The Occupational Safety and Health Administration

(OSHA) notes that combustion separates fluorine from lithium salts in the battery, which when mixed with water vapors, fluorine may produce hydrofluoric acid and is particularly hazardous because workers may not feel its effects until hours after skin exposure. [5]

Wang et al [1] and MacNeil et al [6] proposed decomposition reactions $Li_{0.5}CoO_2$ – a common charged positive electrode in LIBs reported – that would yield the starting LIB electrolyte, acid gases, PAHs, and metals. The likely lithium and cobalt products include: $LiPF_6$, $LiCoO_2$, Co_3O_4, CoO, Co, Li_2CO_3. LIB Fire Tests of Personal Protective Clothing (PPC) were conducted on Olsztyn, Poland 18 Sept 2021 using three different simulated photovoltaic (PV) module fires. [7] Using XRF analysis, one of the three tests showed both Lithium and Cobalt above detectable levels (<5 µg/gm), with test values of 35 and 24 µg/gm, respectively.

Test Objective and Approach

The objective of this test study is to identify the effectiveness of the CO2+ Cleaning System in addressing this challenge. Based on decades of experience in developing CO_2 cleaning systems, Cool Clean Technologies (CCT) in cooperation with its partner company Emergency Technical Decon (ETD) have developed a unique cleaning system utilizing liquid CO2 that provides superior cleaning and decontamination performance based on SVOCs, metals, and biologicals test results, and has been shown to be effective in removing per-and polyfluoroalkyl substances (PFAS) [8]. This preliminary study evaluates the effectiveness of CO_2+ Cleaning by quantifying removal of products of combustions from LIB fires present on firefighter protective clothing.

The technical approach of this test is to use existing cleaning protocols specified in the National Fire Prevention Association (NFPA) 1851 2020 Standard Edition [9] combined with lithium analytical testing methodologies using CO_2-based cleaning process technology developed by the CCT. The NFPA is an international nonprofit organization devoted to eliminating death, injury, property, and economic loss due to fire, electrical and related hazards. The NFPA 1851-2020 Standard Edition specifies test protocols for evaluation of decontamination efficiencies for specified metals and SVOCs and defines test load characteristics for the decontamination efficiency evaluations. This study used NFPA-1851 testing protocols to conduct the lithium decontamination test evaluations. The use of this standard serves as a test baseline of which will be understood by persons in this field.

Experimental Methods

Test samples were prepared, surrogate garments were used, 40-pound ballast was used. As there are no 1851 standards detailing LIB combustion product analysis and testing protocols, the authors developed and modified the doping and analytical procedures following protocols used in other EPA test methods.

The experimental methods and analytical protocols used for these tests are as follows:

- Lithium carbonate Li_2CO_3 was used as the lithium analyte analyzed.
- Li_2CO_3 as Li was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES).
- Samples were 1”x2” (13 cm^2) pieces of Advance Tan outer shell fabric.
- Each sample was weighed to < 1 mg resolution.
- Target Li doping mass was 100 µg/sample or about 320 µg/gm.
- The analytical threshold level of this method was 13 µg/sample or about 42 µg/gm.
- Doped and blank samples were inserted into surrogate pants and coat samples per NFPA 1851-2020 specifications.
- Legend Technical Services of St. Paul, MN was used as the analytical lab for these tests.

The CO2+ cleaning system located in the ETD facility in Eagan, MN was used for these tests, shown in Figure 1. The system was programmed for a two-stage 18-minute wash cycle using the 'Outer Shell' program, which has a cycle duration of about 140 minutes. The test samples were inserted in the surrogate garments using procedures specified in NFPA 1851. At the completion of the cleaning cycle, the ballast and test garments were removed from the machine and the test samples were collected and inserted into clean labeled transfer tubes, which were subsequently returned to Legends Technical Services for analysis. The test was conducted on March 17, 2023.

Figure 1 – CO_2+ Cleaning System** located at **Emergency Technical Decon – Eagan, MN.

Results and Discussion

Following protocols developed for NFPA, a test was conducted to evaluate lithium removal efficiencies using Li_2CO_3 as an analyte. Samples from eight test samples were analyzed following protocols detailed above: sample blank samples, doped samples, and processed samples. The analytical results from these tests are summarized in Table 1.

Table 1 – Lithium Residuals from CO_2+ Cleaning

Sample ID	Sample Type	µg/sample
C2P2-01	Processed Sample	66
C2P3-02	Processed Sample	25
P2P2-03	Processed Sample	16
P2P3-04	Processed Sample	<13
C2P1-11	Processed Sample Blank	<13
P2P1-12	Processed Sample Blank	<13
TB1-09	Non-Processed Sample	100
TB2-10	Non-Processed Sample	100
Non-Detect Level determined to be < 13 µg/sample		

The results of processed samples show Li_2CO_3 residuals range from 66 µg/sample to a Non-Detect value of < 13 µg/sample. Because of the very wide range of values observed from these tests, both the low and high values are eliminated from process average evaluations. As a result of these test results, the average removal rate of lithium is 80% with a residual of µg/sample. Hence the process removed approximately 80 µg/sample.

Based on earlier studies of metals removal testing using the CO_2+ Cleaning process under a variety of operational scenarios, the average removal efficiency of the eight (8) most effective tests was 61%. [10,11] It is important to note that the removal efficiency of one of these metals – cobalt, a combustion product of LIB fires – had an average removal among those same eight (8) tests of 85% with a standard deviation of 8%. By combining the results from this study from those developed earlier, CO_2+ Cleaning shows evidence of being an effective cleaning process for lithium and cobalt compounds, common in many LIB fires. Further testing will evaluate cleaning efficiencies of both lithium and cobalt compounds in a single test matrix. As noted previously, each sample was 1"x2" or about 13 cm^2/sample or about 42 µg/gm, 8 times the detectable level 5 µg/gm [7] proposed earlier. This suggests that additional lithium testing requires a lower TLV than can be obtained with ICP-OES. Hence subsequent testing lithium testing will be conducted with the more sensitive Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) protocols or equivalent.

Further, it is recognized that the base analyte selected – Li_2CO_3 – may impact the results of this test as this compound is an oxidized form of lithium. There are other lithium products of incomplete combustion that should also be considered as each has a different solubility signature which impacts the potential cleaning efficiency in this process.

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