Removal of Lithium from Firefighter Protective Clothing using CO2+ Cleaning: Preliminary Test Results

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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 swatches 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 many industrial and commercial products including electric vehicles, fires involving these products have been shown to be quite hazardous for firefighters and 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 shown to be very effective at removing organics, metals, and other contaminants of concern from firefighter turnout gear. This is the first test of LCO2-based cleaning technology applied to firefighter turnout gear decontamination of 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] Key characteristics of stability of LIBs are:

- Flammable, poor thermal stability at moderately elevated temperatures,
- Likely vented out of battery upon overheating,
- Danger of fire under the effective of explosion energy,
- $LiPF_6$ is a hazardous substance:
    - Acute oral toxicity – causes severe skin and respiratory system burns and eye damage,
    - Chronic toxicity to organs through repeated or prolonged exposure.

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, i.e., LCO (Lithium Cobalt Oxide: $LiCoO_2$), NMC (Lithium Nickel Manganese Cobalt Oxide: $LiN\text{-}iMnCoO_2$) and LFP (Lithium Iron Phosphate: $LiFePO_4$). These batteries contain flammable materials in the form of Li, electrolytes, and graphite. When an 18650 battery is overheated or experiences a thermal runaway, the pressure inside the battery will increase. If the battery reaches around 150°C, a rupture disc will open and combustible gases, mists, and possible particles will then be vented into the surrounding atmosphere. They reported results on gaseous evolution from thermal runaway tests of three types of LIBs based on cathode materials. Tests show 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. Even though the gas could not burn in the inert atmosphere inside the reactor, the surface of the high-energy cells reached temperatures of up to 850 °C during the experiments.

The byproducts from a LIB combustion reaction are usually carbon dioxide and water vapor. In some LIBs, combustion can separate fluorine from lithium salts in the battery. If mixed with water vapors, fluorine may produce hydrofluoric acid, which is particularly hazardous because workers may not feel its effects until hours after skin exposure. [5]

Wang et al [6] proposed decomposition reactions $Li_{0.5}CoO_2$ – a common charged positive electrode in LIBs reported that the delithiated $Li_{0.5}CoO_2$ decomposes over 200°C and release O_2 as Eq. 1:

$$LiCoO_2 \rightarrow \tfrac{1}{2} LiCoO_2 + 1/6\ Co_3O_4 + 1/6\ O_2 \qquad \text{(Eq.1)}$$

In the present of solvent at elevated temperatures, Co_3O_4 could decompose to:

$$Co_3O_4 \rightarrow 3\ CoO + \tfrac{1}{2} O_2 \qquad \text{(Eq. 2)}$$

Which generates O_2 – a contributor to combustion reactions.

A second exothermic reaction is through the solid electrolyte interface (SEI) decomposing process, which is formed by stable layer, e.g., Li_2CO_3, and sub-stable layer, e.g., $(CH_2OCO_2Li)_2$ such as:

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + \tfrac{1}{2} O_2 \qquad \text{(Eq. 3)}$$

MacNeil et al [7] combined these reactions below showing likely products of thermal decomposition:

$$Li_{0.5}CoO_2 \rightarrow LiCoO_2 + 1/6\ Co_3O_4 \rightarrow \tfrac{1}{2} LiCoO_2 + \tfrac{1}{2} CoO \rightarrow Co + \tfrac{1}{4} Li_2CO_3 \qquad \text{(Eq. 4)}$$

Hence, to monitor the decomposition of LIBs in a fire situation, the above products are likely candidates in a chemical analysis in addition to 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. [8] Analytical samples were from all layers of contaminated jackets. Soot residues, total PAH values, and formaldehyde residues were quantified on the samples. For metals analysis, x-ray fluorescence (XRF) was used to detect cobalt and lithium residues on the samples. Two tests showed both lithium and cobalt below detectable levels (<5 µg/gm). However, the third showed test values of 35 and 24 µg/gm, respectively, on the test samples.

Test Objective and Approach

The objective of this test study is to identify the effectiveness of the CO_2+ Cleaning System in decontaminating firefighter gear exposed to LIB fire products of combustion. 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 CO_2 that provides superior cleaning and decontamination of SVOCs, PAH, metals, and biologicals, and has shown to be effective in removing per-and polyfluoroalkyl substances (PFAS) [9]. This study evaluates the effectiveness of CO_2+ Cleaning by quantifying removal of surrogate lithium products of combustions from LIB fires from test samples which mirror firefighter protective clothing.

The test approach is to use existing cleaning protocols specified in the National Fire Prevention Association (NFPA) 1851 standard [10] combined with lithium analytical testing methodologies using CO_2-based cleaning process technology developed by 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.

As summarized by Young [11] typical turnout gear is comprised of three distinct layers: the thermal liner, the moisture barrier, and the outer shell. Maintenance and repair of turnout gear is also governed by the NFPA 1851, which mandates that an advanced inspection of all personal turnout gear ensembles and ensemble elements be conducted at a minimum of every 12 months or whenever routine inspections indicate that a problem may exist. Further, the NFPA standard [10] recommends that firefighter gear and its elements be subjected to advanced cleaning when they are soiled or contaminated and/or not less than twice per year. Stull [12] identifies key contaminants commonly found on firefighter turnout gear and the importance of proper decontamination procedures to protect the health of the firefighter and details the steps necessary to validate cleaning effectiveness.

Experimental Methods

LIB combustion product cleaning efficiency testing using the CO_2+ Cleaning system largely followed the protocols identified in NFPA-1851. Test samples were prepared, surrogate garments were used, and 40-pound ballast was used. As there are not 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.

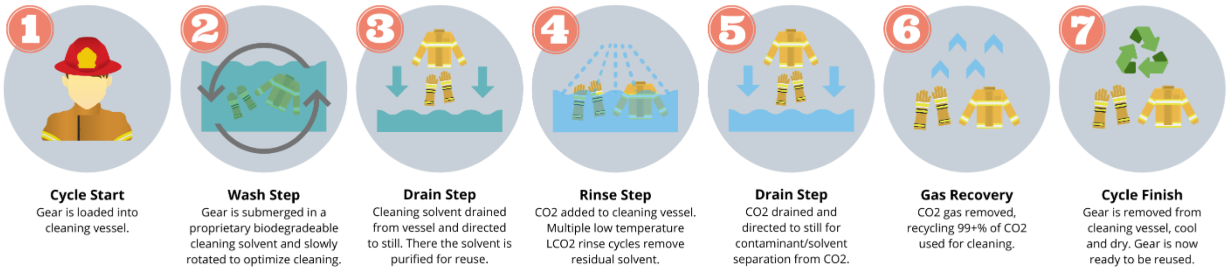
Several important analytical assumptions needed to be made for these tests.

1. Which form(s) of lithium should be examined?
    a. As noted above, LIB combustion products containing lithium can be quite varied and in a wide range of concentrations.
    b. Possible lithium compound LIB combustion products cited above are: $LiPF_6$, $LiCoO_2$, Li_2CO_3.
    c. Others have identified lithium-hydride LiH as the tracking analyte to be used.
2. What concentration of lithium should be applied?
    a. The concentration to be applied should be sufficient to provide a good signal for effective analytical quantification.
    b. Represents an approximate level of contamination expected from an LIB fire incident.
3. Which analytical method should be used to evaluate lithium compound presence?
    a. Taking these issues into consideration the experimental methods and analytical protocols used for these tests are as follows:
        i. Li_2CO_3 with a purity > 98% was used as the lithium analyte.
        ii. The doping solvent was created by diluting the solid to a 10,000-ppm solution in nanopure water.

iii. 50 µL of the doping solvent onto the samples and allowed them to dry.
iv. Li_2CO_3 as Li was analyzed using ICP-OES according to EPA method 6010D.
v. Samples were 1” x 2” (13 cm^2) pieces of Advance Tan outer shell fabric.
vi. Each sample was weighed to < 1 mg resolution.
vii. Target Li doping mass on the sample was 100 µg/sample or about 320 µg/gm.
viii. Analytical threshold level of this method was 13 µg/sample or about 42 µg/gm.
ix. Doped and blank samples were inserted into surrogate pants and coat samples per NFPA 1851 specifications.
x. Legend Technical Services of St. Paul, MN was used as the analytical lab.

The CO_2+ Cleaning System located in the ETD facility in Eagan, MN was used for these tests, shown on the next page 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 entire process is laid out in Figure 2. The test samples were inserted in the surrogate garments using procedures specified in NFPA 1851 – see Figure 3. 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 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.



1 **Cycle Start**
Gear is loaded into cleaning vessel.

2 **Wash Step**
Gear is submerged in a proprietary biodegradeable cleaning solvent and slowly rotated to optimize cleaning.

3 **Drain Step**
Cleaning solvent drained from vessel and directed to still. There the solvent is purified for reuse.

4 **Rinse Step**
CO2 added to cleaning vessel. Multiple low temperature LCO2 rinse cycles remove residual solvent.

5 **Drain Step**
CO2 drained and directed to still for contaminant/solvent separation from CO2.

6 **Gas Recovery**
CO2 gas removed, recycling 99+% of CO2 used for cleaning.

7 **Cycle Finish**
Gear is removed from cleaning vessel, cool and dry. Gear is now ready to be reused.

Figure 2 – CO_2+ Cleaning process used for testing samples visualized in steps.

Results and Discussion

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

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.

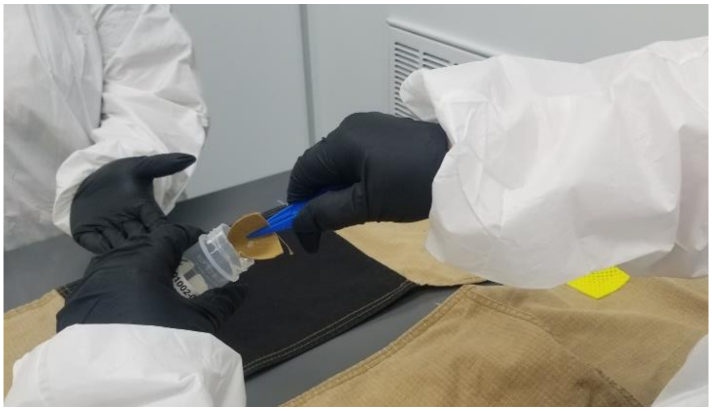


Figure 3 – Lithium doped sample

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%. [13,14] 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 [8] 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.

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		

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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References

1. Wang, Qingsong, Jinhua Sun and GuanQuan Cho, Lithium-Ion Battery Fire and Explosion, Fire Safety Science – Proceedings of the Eight International Symposium, pp. 375-382, International Association of Fire Safety Science, 2002.
2. Zalosh, Robert, Pravinray Gandhi, Adam Barowy; Lithium-ion energy storage battery explosion incidents; Journal of Loss Prevention in the Process Industries; 72 (2021) 104560.
3. Johnsplass, Jonathan, Mathias Henriksen, Knut Vågsæther, Joachim Lundberg and Dag Bjerketvedt; Simulation of burning velocities in gases vented from thermal run-a-way lithium-ion batteries; Proceedings of the 58th SIMS; Sept 25-27, Reykjavik Iceland; DOI: 10:3384/ecp17138157.
4. Golubkov, Audrey W, David Fuchs, Julian Wagner, Helmar Wiltsche, Christoph Stangl, Gisela Fauler, Gernot Voitic, Alexander Thalera and Viktor Hacker; Thermal-runaway experiments on consumer Li-ion batteries with metal-oxide and olivin-type cathodes; RSC Adv.,2014,4,3633.
5. Preventing Fire and/or Explosion Injury from Small and Wearable Lithium Battery Powered Devices, OSHA Safety and Health Information Bulletin SHIB 06-20-2019.
6. Wang, Qingsong, Jinhua Sun and GuanQuan Cho, Lithium-Ion Battery Fire and Explosion, Fire Safety Science – Proceedings of the Eight International Symposium, pp. 375-382, International Association of Fire Safety Science.
7. MacNeil, D.D., and J. R. Dahn; The Reactions of $Li_{0.5}CoO_2$ with Nonaqueous Solvents at Elevated Temperatures; Journal of The Electrochemical Society, Volume 149, Number 7, 2002.
8. Szmytke, Ewelina, Dorota Brzezinska, Waldemar Machnowski and Szymon Kokotet; Firefighters' Clothing Contamination in Fires of Electric Vehicle Batteries and Photovoltaic Modules – Literature Review and Pilot Test Results; Int. J. Environ. Res. Public Health 2022, 19, 12442, Pages 7-15.
9. Sorbo, N.W., CO2+ Cleaning Technology: An Innovative and Effective Cleaning Solution for Firefighter Gear Cleaning; Cool Clean Technologies / Emergency Technical Decon, January 2023.
10. NFPA 1851 – Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting, 2020.
11. R. Young, Understanding Turnout Gear, Fire Apparatus and Emergency Equipment, 10/1/2010, https://www.fireapparatusmagazine.com/ems/understanding-turnout-gear/.
12. Stull, J.O.; "PPE: How Clean is Clean"; Fire Engineering – PPE Supplement, January 2018; www.FireEngineering.com.
13. Sorbo, N.W.; "Firefighter Turnout Gear SVOC Cleaning Efficiency of CO2-Based Cleaning Process Compared to Traditional Water-Based Cleaning Methods", Cool Clean Technologies, October 2020.
14. UL Laboratories NFPA 1851 Compliance Test Data, January 2021, January 2023.