Toxicology of the Lithium Ion Battery Fire

Captain Timothy J Vamosi, MSN-RN, EMTP

The Problem

- An irreversible thermal event in a lithium-ion battery can be initiated in several ways, by spontaneous internal or external short-circuit, overcharging, external heating or fire, mechanical abuse etc.

- The electrolyte in a lithium-ion battery is flammable and generally contains lithium hexafluorophosphate ($LiPF_6$) or other Li-salts containing fluorine.

- In the event of overheating the electrolyte will evaporate and eventually be vented out from the battery cells.

The Problem

- The gases may or may not be ignited immediately.
  - This leads to opportunity for exposures and contamination of persons

- In case the emitted gas is not immediately ignited the risk for a gas explosion at a later stage may be imminent.
  - This leads to thermal burns and exposure burns

- Li-ion batteries release a various number of toxic substances as well as e.g. CO (an asphyxiant gas) and CO_2 (induces anoxia) during heating and fire.
  - This is exposures causing an inability to process oxygen and/or the displacement of oxygen from the environment

The Problem

- At elevated temperature the fluorine content of the electrolyte and, to some extent, other parts of the battery such as the polyvinylidene fluoride (PVdF) binder in the electrodes, may form gases such as hydrogen fluoride HF, phosphorus pentafluoride (PF_5) and phosphoryl fluoride (POF_3).

- Compounds containing fluorine can also be present as e.g. flame retardants in electrolyte and/or separator, in additives and in the electrode materials, e.g. fluorophosphates, adding additional sources of fluorine.

The Problem

The decomposition of $LiPF_6$ (lithium hexaflourophosphate) is promoted by the presence of water/humidity according to the following reactions;

LiPF6→LiF+PF5 (1)

PF5+H2O→POF3+2HF (2)

LiPF6+H2O→LiF+POF3+2HF (3)

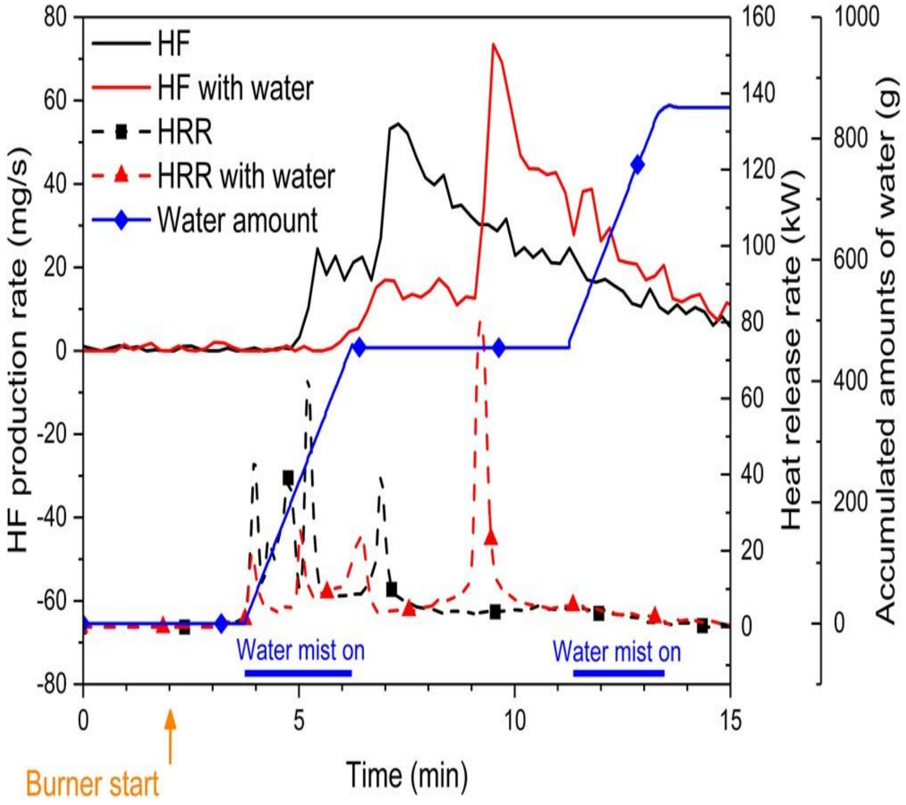
- Of these PF_5 (phosphorus pentafluoride) is rather short lived. The toxicity of HF (hydrogen fluoride) and the derivate hydrofluoric acid is well known while there is little toxicity data available for POF_3,(phosphoryl fluoride) which is a reactive intermediate that will either react with other organic materials or with water finally generating HF.

The Problem

- Commercial lithium-ion batteries can emit considerable amounts of HF during a fire and that the emission rates vary for different types of batteries.

- The use of water mist as an extinguishing agent may promote the formation of unwanted gases and limited measurements show an increase of HF production rate during the application of water mist, however, no significant difference in the total amount of HF formed with or without the use of water mist.

The Problem



- Significant amounts of HF, ranging between 20 and 200 mg/Wh of nominal battery energy capacity, were detected from the burning Li-ion batteries.

- The measured HF levels, verified using two independent measurement methods, indicate that HF can pose a serious toxic threat, especially for large Li-ion batteries and in confined environments.

The Problem

- If extrapolated for large battery packs the amounts would be 2–20 kg for a 100 kWh battery system, e.g. an electric vehicle and 20–200 kg for a 1000 kWh battery system, e.g. a small stationary energy storage.

- The immediate dangerous to life or health (IDLH) level for HF is 0.025 g/m^3 (30 ppm) and the lethal 10 minutes HF toxicity value (AEGL-3) is 0.0139 g/m^3 (170 ppm).

- The release of hydrogen fluoride from a Li-ion battery fire can therefore be a severe risk and an even greater risk in confined or semi-confined spaces.

Hydrogen Fluoride

- Hydrogen fluoride mixes readily with water forming hydrofluoric acid.
    - For all practical purposes, they are considered the same chemical.

- It has a strong irritating odor; however, odor should not be depended on to provide sufficient warning of exposure.

- It is considered a weak acid but is still extremely harmful due to its ability to penetrate tissue.

Hydrogen Fluoride

- Hydrogen fluoride/hydrofluoric acid can be absorbed systemically into the body by ingestion, inhalation, or skin or eye contact.

- Eye exposure to hydrogen fluoride/hydrofluoric acid is highly unlikely to result in systemic toxicity.

- Inhalation is an important route of exposure.

Hydrogen Fluoride

- There are two primary mechanisms through which HF acid causes tissue destruction.
- The first occurs due to the activity of corrosive hydrogen ion when using a high concentration of this acid (>50%) and is associated with cutaneous and ocular lesions, as well as digestive and respiratory mucous membrane damage.
- Corrosive burns are similar to those provoked by other acids: they occur immediately, with visible tissue destruction, grey areas, ulceration or necrosis, followed by intense pain

Hydrogen Fluoride

- The second is caused by cytotoxic fluoride anion responsible for local and systemic toxicity when HF acid products with high, as well as with low concentrations have been used.

- The fluoride ion is very small and diffuses readily in the aqueous media.

- Absorbed into the bloodstream, it is carried to all body organs in proportion to their vascularity and fluoride concentration in the blood.

- When reacting with cellular calcium and magnesium, forms insoluble chelates, CaF_2 and MgF_2, thus provoking local calcium depletion and inhibition of Na^+K^+ ATP-ase pump.

Hydrogen Fluoride

- Subsequently, the cell membrane’s permeability to potassium is increased resulting in local hyperkalemia.
- High lipid affinity induces liquefaction necrosis and cellular death, thus destructing the nerve and blood vessels, tendons, bone structures and all other tissues.
- These effects are due to the presence of fluoride ion and differ from other acids, in which the feature of the free hydrogen cations to provoke coagulative necrosis, which slows the further penetration into the tissues, is expressed.

Hydrogen Fluoride

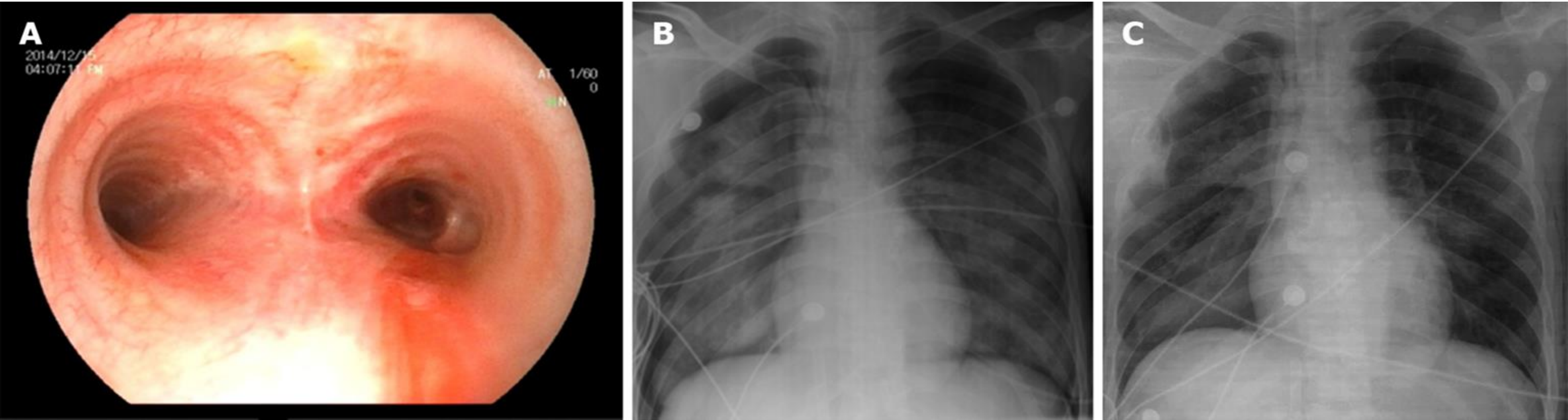
Eye Exposure

- Mild: Rapid onset of irritation and reversible clouding (opacification) of the surface of the eye (cornea).
- Severe (e.g., with exposure to liquid hydrogen fluoride/hydrofluoric acid): Rapid onset of pain, redness and damage to the surface of the eye (cornea), sloughing of the cornea, swelling, and progressive damage and scarring leading to permanent clouding (opacification) of the cornea, which may occur immediately or be delayed for several days after exposure.
- Permanent visual defects are more likely with severe exposures.
- Eye exposure to vapor may cause delayed findings of eye and mucous membrane irritation; more serious eye injury is possible following exposure to concentrated vapor.

Hydrogen Fluoride

Inhalation Exposure

- Mild: Irritation of the moist linings of the nose and throat (mucous membranes), possible burns, cough, narrowing of the large airways (bronchoconstriction), and difficulty breathing or shortness of breath (dyspnea).
- Severe: Immediate narrowing and swelling of the throat, upper airway obstruction, accumulation of fluid in the lungs (pulmonary edema), and partial or complete lung collapse.
- Whole-body (systemic) effects are likely, including low blood levels of calcium and magnesium (hypocalcemia and hypomagnesemia), high blood levels of potassium (hyperkalemia), low blood pressure (hypotension), abnormal or disordered heart rhythms (dysrhythmias), accumulation of acid in blood and tissues (metabolic acidosis), involuntary muscle contractions, seizures, and death.



Hydrogen Fluoride

Dermal Exposure

- Concentrations < 20%: Redness (erythema), pain, and serious injury (possibly delayed for 24 hours and often reported after significant tissue injury has occurred).
- Concentrations 20-50%: Redness (erythema), pain, and serious injury (possibly delayed for 24 hours and often reported after significant tissue injury has occurred).
- Concentrations > 50%: Immediate redness (erythema) and severe, throbbing pain; rapid tissue destruction (whitish discoloration followed by blistering (vesication)); and acute whole-body (systemic) effects (including lung damage).
- Exposure of more than 1% of the body’s surface area may lead to systemic toxicity.

Hydrogen Fluoride

- Initial treatment is primarily supportive.

- It includes monitoring of signs and symptoms of whole-body (systemic) toxicity, which can be fatal.

- Rapid decontamination and use of a fluoride binding agent are critical.

- Treatment is a continuum of care: removal from site, followed by rapid decontamination, followed by rapid treatment with a fluoride binding agent.

Implications for FireFighting/Rescue Tactics

- Due to the severity of the toxins released firefighting must be completed with exposure and contamination in mind
  - I.E. - Full PPE and SCBA in place at all times; distance tactics and First Responder Decon

- Rescues of persons exposed to off gassing or by-products of combustion may require decontamination; speciality care facilities; interaction with receiving hospitals

Thermal Burns

- This burn pattern was caused by the thermal runaway of two 18650 cells in the patient’s pocket.
- The patient reached cross-body and was able to remove the fiery device from his left pocket, burning his right hand in the process.
- These thermal burns have been found in reviews of vape and cell phone incidents to be often a mixture of partial and full thickness burns, commonly requiring intensive and definitive treatment in the hospital.

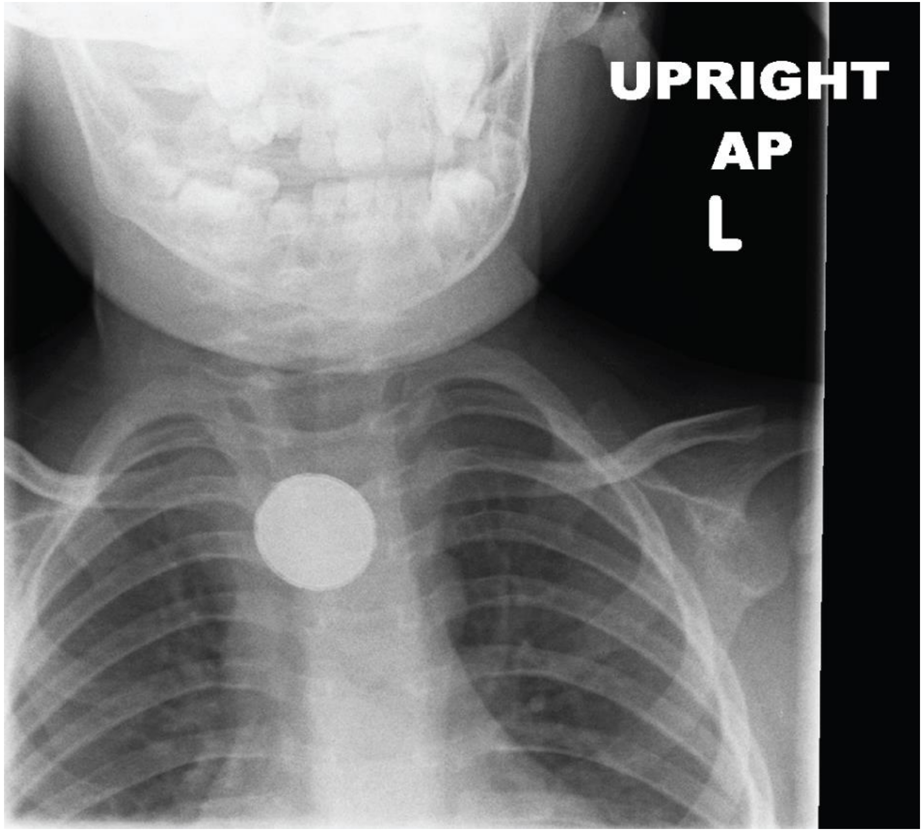
Thermal Burns

Initial assessment of injuries should accompany the Advanced Trauma Life Support guidelines; serum levels of lithium, cobalt, and manganese should be checked and elevated levels should be monitored; patients should be monitored for signs of metal toxicity; wound should be extensively debrided and irrigated to remove any residual materials; and litmus test should be performed to check for alkali pH prior to irrigation with water or other aqueous solutions.

Thermal Burns

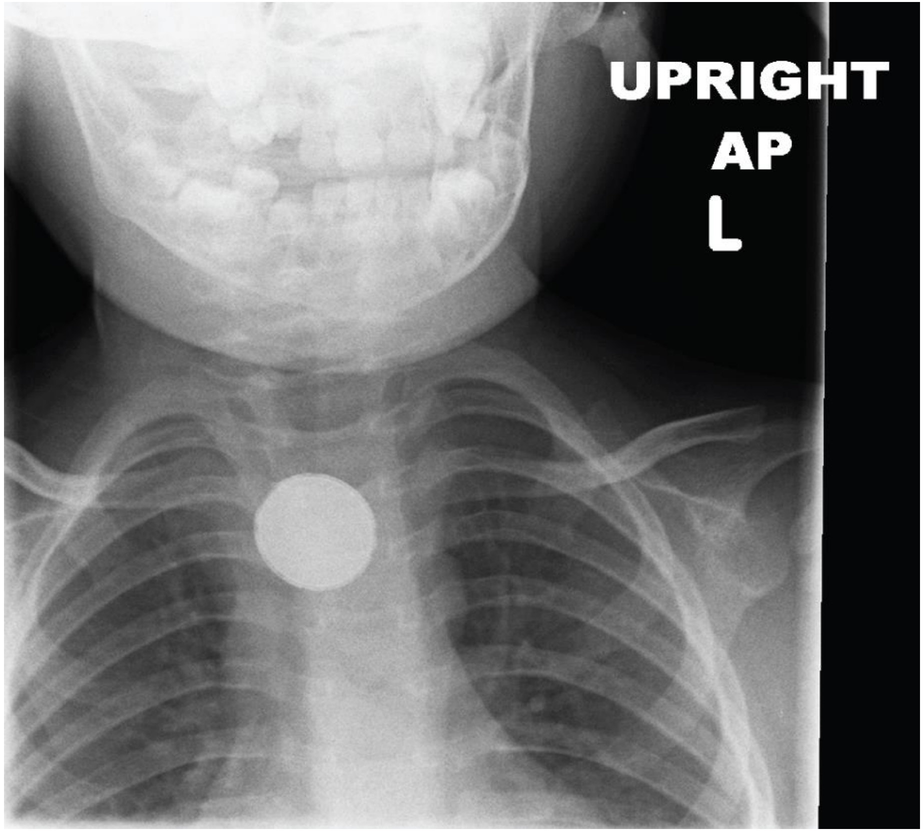
- CRITICAL BURNS
  - If < 20 minutes by ground, transport to a level 1 or 2 trauma center (level 1 or 2 pediatric trauma center for pediatrics).
  - If < 20 minutes by ground from a level 3 trauma center and no level 1 or 2 (level 1 or 2 pediatric trauma center for pediatrics) within 20 minutes, transport to a level 3 and/or consider air ambulance, if available.
  - If > 20 minutes by ground to a level 1, 2 or 3 trauma center, activate air ambulance, if available.

Pediatric Consideration



- Between 1999 and 2019, the United States National Poison Data System reported a 66.7% increase in yearly ingestion of button batteries (6.98 to 10.46 per million population) and a 10-fold increase in complications (0.77% [*n* = 76] to 7.53% [*n* = 551]).
- Button batteries can cause substantial tissue damage within 2 hours of ingestion.
- Lithium batteries (given their high voltage) and those 20 mm or larger (which are likely to become lodged in the esophagus) are most dangerous, especially in children younger than 6 years.
- Complications include gastrointestinal perforation, aortoesophageal fistulas and strictures.

Pediatric Consideration



Honey should be administered before the patient reaches the hospital, and sucralfate when in hospital within 12 hours of battery ingestion, to mitigate tissue injury while awaiting possible definitive management.

Animal studies have shown that these treatments result in fewer full-thickness injuries and less extension of injury.

Honey can be given at 10 mL every 10 minutes for children older than 1 year (up to 6 doses) and sucralfate can be given at 1 g every 10 minutes (up to 3 doses).

Injuries from button battery ingestion can occur despite removal of the battery; injuries such as strictures and fistulas have been reported weeks to months after removal.

Caregivers should monitor for symptoms including gastrointestinal bleeding and vomiting.

Hydrogen Fluoride

- Hydrogen Fluoride
  - Hydrogen fluoride goes easily and quickly through the skin and into the tissues in the body. There it damages the cells and causes them to not work properly.
  - The seriousness of poisoning caused by hydrogen fluoride depends on the amount, route, and length of time of exposure, as well as the age and pre existing medical condition of the person exposed.
  - Breathing hydrogen fluoride can damage lung tissue and cause swelling and fluid accumulation in the lungs (pulmonary edema).
  - Skin contact with hydrogen fluoride may cause severe burns that develop after several hours and form skin ulcers.
  - Hydrogen Fluoride diluted in water becomes Hydrofluoric Acid.

Considerations

- As we saw earlier there are many other byproducts of combustion and off gassing that should be considered when a response to LIB fires is required

- More research is needed to continue on the potential risks of exposure from these types of fires and their impact on the fire service and the community

- More research is needed on the consequences of LIB fires impact on PPE, PPE and personnel decon, industrial decon

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