香 港 大 學
THE UNIVERSITY OF HONG KONG

Lithium-ion and Lithium-polymer Battery Safety

1. Introduction

Lithium-based batteries have become the industry standard for rechargeable storage devices. They are common to University operations and used in many research applications. Battery fires and accidents are rare but the risk is increased where they are intensively used in research. Batteries remain safe as long as there are no defects and they are not damaged. Inexpensive batteries are not manufactured to a high standard and are more likely to exhibit manufacturing defects. Risks can be mitigated if the technology is well understood. This guidance provides information to help prevent fire, injury and loss of intellectual and other property.

Guidance

Lithium-based battery characteristics

Primary batteries are not rechargeable. Examples of lithium-based primary batteries are button cells and camera/smoke detector batteries. Primary batteries contain metallic lithium which reacts violently with moisture. The lithium is hermetically sealed within the rigid battery container. Fires involving primary lithium metal batteries are extinguished by smothering with a material such as sand bucket or a fire extinguisher that is rated for metal fires ie class D. Water is not an effective extinguishing material for primary lithium battery fires.

Secondary batteries can be recharged. Unlike primary lithium batteries, secondary lithium batteries do not contain metallic lithium, they contain an intercalated lithium compound (Lithium salt). It may be possible to extinguish fires involving secondary lithium-ion or lithium-polymer secondary batteries with carbon dioxide fire extinguisher or by smothering smothering with a material such as sand. **However in some cases fires may be impossible to extinguish.**

General features of lithium-based batteries

Lithium-based batteries have higher energy densities than batteries from earlier generations (up to 100 times higher). If more energy can be stored there is a greater risk that the energy will be unintentionally released in a way that causes harm. Single lithium-based batteries (also referred to as cells) have an operating voltage (V) that ranges from 3.6 – 4.2V. Lithium ions move from the anode to the cathode during discharge. The ions reverse direction during charging. Lithium-based batteries have electrolytes that are typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate. The flammability characteristics (flashpoint) of common carbonates used in lithium-based batteries vary from 18 to 145 degrees C.

Lithium-ion (LI-Ion) and Lithium-polymer (LiPo) batteries. The difference between lithium-ion and lithium-polymer batteries is the type of electrolyte used. Lithium-polymer batteries contain a micro porous gel electrolyte instead of a porous separator as found in lithium-ion. Standard lithium-ion batteries require a rigid case to press the electrodes together. Lithium-polymer batteries use laminated sheets that do not need compression. As a result they are available in a range of shapes and sizes.

Cylindrical

Prismatic

Pouch

Button Cells

LiPo batteries are used in many portable personal electronic devices – phones, tablets, laptops etc. As these devices normally include a battery management system that will suspend charging if detect anomaly, these devices are very low risk. Other than cell phones and tablets, most portable electronic/electrical devices operate above the normal operating voltage of single lithium-ion batteries (3.6 – 4.2V). For such devices, numerous cells connected in packs provide the desired voltage and capacity. Connecting cells in parallel increases pack amperage and discharge capacity. Connecting cells in series increases pack voltage. As an example, a 24V lithium-ion battery pack typically has six cells connected in series

Circuitry to monitor charging and discharging
Many battery packs or chargers have built-in circuitry used to monitor and control the charging and discharging characteristics of the pack.

As an example, circuitry will automatically manage the charging when the pack cells reach 4.2V and/or if the temperature exceeds a preset value. The circuits will shut down the pack if the cells discharge below a preset value (e.g., 3.3V per cell)

Lithium-based battery hazards

The main risk is fire as a result of their high energy density and use of a flammable organic electrolyte. This can lead to **Thermal Runaway** which is rapid self-heating from an exothermic reaction. Fire can result from

- Physical damage,
- Electrical abuse – short circuits or overcharging
- Exposure to elevated temperature
- Manufacturing defects such as imperfections or contaminants

Thermal runaway can spread to adjacent cells in a battery pack. When it starts flammable organic electrolyte vaporizes and the cell casing becomes pressurized. If the casing fails, flammable and toxic gases released. In the undamaged state cells do not contain particularly toxic materials, for example LiPF6 and organic carbonate electrolytes such as ethylene carbonate or diethyl carbonate. However, when burning starts compounds which are toxic and volatile can be produced including hydrogen fluoride and hydrogen cyanide. Thermal runaway can also lead to the evolution of flammable gases even if the battery itself is not burning.

There are a number of factors that influence the consequences of thermal runaway, including battery size, chemistry, construction (cell or pouch) and state of charge. If battery vents (no ignition of vented products) what is released is carbon dioxide, carbon monoxide, hydrogen and hydrocarbons. These materials flammable and represent fire and explosion risk. If the battery burns there is liberation of fluorine from the lithium salt. Fluorine then reacts with hydrogen to form hydrogen fluoride (HF) gas. **HF production is proportionate to the electrical energy stored (state of charge) of the battery HF is a particularly hazardous material.** HF gas dissolves in the mucus of the respiratory tract of anyone inhaling it, forming hydrofluoric acid. HF differs from other protic acids because it readily penetrates the skin and other tissues, causing the destruction of deep tissue layers. This process may continue for days if left untreated. **The practical implication of this is that injury becomes progressively more severe over time.** Inhaled hydrogen fluoride mist or vapor initially affects the nose, throat, and eyes. Lung injury may evolve rapidly or may be delayed in onset for 12 to 36 hours. Systemic poisoning can occur after lung exposure and depends on the ratio between body weight and lung surface area**.** The systemic effects of hydrogen fluoride are due to increased fluoride concentrations in the body which can change the levels of calcium, magnesium, and potassium in the blood..

Hydrogen cyanide (AC) is a systemic chemical asphyxiant. It interferes with the normal use of oxygen by nearly every organ of the body. Exposure to hydrogen cyanide (AC) can be rapidly fatal. It has whole-body (systemic) effects, particularly affecting those organ systems most sensitive to low oxygen levels: the central nervous system (brain), the cardiovascular system (heart and blood vessels), and the pulmonary system (lungs).

Hydrogen cyanide (AC) gas has a distinctive bitter almond odour (others describe a musty "old sneakers smell"), but a large proportion of people cannot detect it; the odour does not provide adequate warning of hazardous concentrations.

Good Battery Management

Procurement

- Purchase batteries from a reputable manufacturer or supplier
- Check that batteries conform to a recognized standard
- Avoid batteries shipped without protective packaging
- On arrival check that batteries are not damaged
- Safely dispose of any damaged batteries

Recognised Li-ion and Li-Po Safety Standards

China – CNCA Standards

- 0915 Lithium-ion batteries and battery packs for portable electronics. GB31241 "Safety Technical Specifications for Lithium-ion Batteries and Battery Packs for Portable Electronic Products" was implemented on 1 January 2024.
- 0914 Power Bank, mass does not exceed 18kg, containing lithium-ion battery and/or battery pack, removable power supply with AC and DC input/output. GB4943.1, GB31241
- 0807, 0907 Power adapter/charger for telecommunication terminal equipment. GB4943.1, GB/T9254.1, GB17625.1

International Standards

- IEC 62133, ANSI/UL 62133-2, CSA C22.2 No. 62133-2:20. For portable electronics. Addresses chemical hazards, electrical hazards, mechanical such as shock and vibration
- IEC 62619 Large format batteries, stationary applications include telecom, uninterruptible power supplies (UPS), electrical energy storage system, utility switching, emergency power, and similar applications. Motive applications include forklift trucks, golf carts, auto-guided vehicles (AGVs), railway, and marine — excluding road vehicles.
- UL 1642, UL 2054 Safety requirements for primary and secondary lithium battery cells used as a power source in electronic products
- UL 2580x, UL 2271 For use in electric vehicles
- UN DOT 38.3 and IEC 62281 for shipping (rather than using) Li-ion batteries

Standard for Battery Management System

- IEC 61508

The following guidance does not apply to manufacturer-supplied batteries inside portable or personal devices such as smartphones, laptops, tablets etc. as they incorporate a battery management system (BMS). Be sure to use the manufacture's recommended charging device.

Storage

Store primary and secondary batteries in separate locations. In the event of fire they require different types of fire extinguisher. Store batteries away from combustible materials. Remove batteries from devices for long-term storage. Store batteries between 20°C and 25°C. Avoid storage in a refrigerator as internal condensation can occur when moved to a different temperature environment. Separate fresh and depleted batteries (or keep a log). Avoid bulk storage in non-lab areas such as offices.

Visually inspect battery storage areas at least weekly. Charge batteries in storage to 50% capacity at least once every 6 months

Storage Containers.

All lithium batteries must be stored in a dedicated area clear of combustible materials. When more than a few lithium batteries must be kept within a given area, they should be stored in a vented metal flammable liquids or metal acid storage cabinet that is strictly dedicated to the storage of lithium batteries. No other hazardous or combustible materials shall be stored in or on the cabinet. The cabinet should help to contain a battery fire within the cabinet and prevent spread to the building or contents. Maintain at least 2-inches clearance around the cabinet. The cabinet vents must be kept open to allow fire-generated gasses to escape. Additional clearance from combustible materials must be provided around the vents. Label the outside of the cabinet to indicate that it contains lithium batteries.

Because of short-circuit risk from metal contact store in suitable container on shelf eg. insulated packaging, LiPo sack etc.

When only a few lithium polymer batteries are needed within a given location, storage within lithium battery safety bags/containers is recommended. They are usually labelled as LiPo Guard or LiPo Safe, etc. The storage bags/containers shall be stored in areas clear of combustible materials.

Charging

Do not attempt to charge a primary (disposable) battery. Store single use batteries apart from rechargeable batteries to prevent accidental charging (and to facilitate action in case of fire)

Let batteries cool to ambient temperature before charging. Charge or discharge battery to 50% capacity prior to long-term storage. Use chargers or charging methods specified by the battery manufacturer.

Remove batteries from charger promptly after charging is complete. Do not use a charger as a storage location. Charge batteries in a fire-retardant container such as a LiPo sack where practical. Do not overcharge (greater than 4.2V for most batteries) or over-discharge (below 3V) batteries.

An infra-red thermometer can be used to monitor battery temperature without need to contact the battery

If batteries emit an unusual smell, develop heat or change shape during charging or use, disconnect immediately and dispose.

Parallel Charging. Do not parallel charge batteries of varying age and charge status; chargers cannot monitor the current of individual cells and initial voltage balancing can lead to high amperage, battery damage, and heat generation. Check voltage before parallel charging; all batteries should be within 0.5 Volts of each other.

Handling and Use

Keep all flammable materials away from operating area. Handle batteries and or battery-powered devices cautiously to not damage the battery casing or connections. For soft LiPo casing batteries avoid sharps which could damage the casing. Keep batteries from contacting conductive materials, water, seawater, strong oxidizers and strong acids. **This includes metal jewelry and watches** that could cause a short circuit. Batteries can be used safely between -20°C and +60°C **IF** they are given time to reach the temperature of the environment where they will be used. Do not place batteries in direct sunlight, on hot surfaces or in hot locations. Allow time for cooling before charging a battery that is still warm from usage and before using a battery that is still warm from charging.

Inspect batteries for signs of damage before use. Never use and promptly dispose of damaged or puffy batteries.

Consider cell casing construction (soft with vents) and protective shielding for battery research and experimental or evolving application and use.

Transport

The following guidance does not apply to batteries inside portable or personal devices such as smartphones, laptops, tablets etc. as they incorporate a battery management system (BMS). Be sure to use the manufacture's recommended charging device.

Do not transport unpackaged/unsealed lithium-based batteries in a metal box or metal container - there is a risk of short circuit if they move within the container. Do not carry unpackaged/unsealed lithium-ion batteries in your pocket as keys or coins can cause batteries to short circuit. Transport lithium-ion batteries in the original container or a plastic or padded bag to prevent shock if dropped. Tape battery terminals to prevent exposed contacts and potential short circuiting. Avoid transporting fully charged lithium-ion batteries. Recommended level of charge for transport is approximately 30%.

Action in an Emergency

Follow these steps if there is evidence of a battery malfunction (e.g., swelling, heating, or irregular odors) Use personal protective equipment, such as gloves, goggles/safety glasses and lab coat. If batteries are showing evidence of thermal runaway failure, be very cautious because the gases may be flammable and toxic and failure modes can be hazardous.

- Disconnect the battery (if possible).
- Remove the battery from the equipment/device (if possible).
- Place the battery in a robust, fire-proof container away from combustibles.
- Secondary (rechargeable) Lithium batteries do not contain lithium metal so it is not necessary to consider as a metal fire Use a CO_2 or dry powder fire extinguisher.
- Fire involving primary (single use) Lithium batteries should be considered as a metal fire – smother with sand bucket or use class D fire extinguisher

In some cases it may be impossible to extinguish a fire, as the cellular design of batteries prevents entry of fire extinguishing materials. Even if a fire is extinguished, thermal runaway can still occur releasing flammable gases which ignite or explode with they encounter another source of ignition. Preventing fire from starting by good battery management is the best strategy.

Discharging a damaged or suspect battery

As the level of risk in terms of potential Hydrogen Fluoride (HF) production correlates with level of charge, it is better to attempt to discharge a battery when it becomes defective.

- Choose a well ventilated area away from flammable materials
- Place the battery in a robust metal or hard plastic bucket
- Fill bucket with 3% salt water solution (sodium chloride or common salt). It is important that there is much greater salt water volume than battery volume, so that any heat produced during discharge will be absorbed and dissipated by a large volume of salt water
- After 2 days in salt water the battery will be discharged
- Alternatively remove them from device, place in fire resistant container (e.g. metal drum) with sand or other extinguishing agent until discharged
- Check with multimeter that 0V produced. Repeat discharge step if voltage still detected.

Circumstances which led to battery accidents at MIT and HKU

- batteries left on chargers for extended times
- unattended charging
- incompatible chargers
- failure of one set of output sockets of a charger designed to charge two battery packs simultaneously
- cheap knock-off batteries
- shorts from improperly wired or isolated connections.

Conclusion – Lithium-based battery Hazards

Lithium-based batteries are quite safe

Lithium-based batteries integral to portable electronic hand-held devices are particularly safe, though not completely risk-free.

However if damaged or used without proper care, they can overheat, ignite, and burn aggressively.

Lithium-based battery users must be acquainted with their unique vulnerabilities

The most important safety consideration for lithium-ion and lithium-polymer batteries is to aim to prevent fire starting rather than attempting to deal with a fire once it has started.

When using batteries treat them as if they will ignite at any time.

Even though the odds are remote, if each battery is segregated from combustible materials during storage, charging, and in use, in the rare possibility that a fire does occur, the odds are better that it will be limited to the battery itself.

Additional Resources

CROSS Topic Paper: Fire Safety Concerns with lithium-ion batteries
https://www.cross-safety.org/uk/safety-information/cross-topic-paper/fire-safety-concerns-lithium-ion-batteries
https://www.cross-safety.org/uk/safety-information/cross-safety-report/fire-safety-risks-lithium-ion-batteries-1058

University of Washington Lithium Battery Safety:
https://www.ehs.washington.edu/system/files/resources/lithium-battery-safety.pdf

University of Pennsylvania Lithium Battery Safety:
https://ehrs.upenn.edu/sites/default/files/2021-02/Lithium%20Battery%20Safety%20Program%202021.pdf

New Jersey Institute of Technology Battery Safety
https://www.njit.edu/environmentalsafety/sites/njit.edu.environmentalsafety/files/General%20Lithium%20Ion%20Battery%20Safety.pdf

Massachusetts Institute of Technology (MIT) Battery Safety
https://ehs.mit.edu/wp-content/uploads/2019/09/Lithium_Battery_Safety_Guidance.pdf

CNCA announcement on Li-ion battery safety standards
https://www.cnca.gov.cn/zwxx/gg/2023/art/2023/art_9b1f71e55d06483d9cbdd35e791a4e60.html

(English version) https://www.tuvsud.com/en/e-ssentials-newsletter/consumer-products-and-retail-essentials/e-ssentials-3-2023/china-announcement-of-compulsory-product-certification-management-for-lithium-ion-batteries

Li-ion tamer guide to certification standards for Li-ion batteries
https://liiontamer.com/wp-content/uploads/Top-11-Lithium-Ion-Battery-Regulations.pdf