LITHIUM CELL AND BATTERY STANDARD

Last updated: July 2019

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UNIVERSITY OF WATERLOO

1.0 PURPOSE

This standard provides handling, storage, creation, and disposal guidance for lithium batteries and cells.

2.0 SCOPE

This standard applies to any research work involving lithium cells or batteries at or on University of Waterloo campuses.

3.0 DEFINITIONS

Cell

A cell is a single encased electrochemical unit (one positive and one negative electrode) with a voltage differential across its two terminals.

Figure 1: Common examples of cells

Battery

A battery is two or more cells electrically connected together and fitted with devices such as a case, terminals, markings, and protective devices that it needs to function properly.

Figure 2: Examples of batteries

State of Charge (SOC)

SOC refers to the battery charge level.

4.0 BACKGROUND

4.1 LITHIUM BATTERY TYPES

Lithium batteries are grouped into two general categories, primary and secondary.

- Primary (non-rechargeable) lithium batteries are comprised of single-use cells containing metallic lithium anodes. Non-rechargeable batteries are referred to throughout the industry as “lithium” batteries.
- Secondary (rechargeable) lithium batteries are comprised of rechargeable cells containing an intercalated lithium compound for the anode and cathode. Rechargeable lithium batteries are commonly referred to as “lithium-ion” batteries.

Single lithium-ion 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. The lithiated metal oxide or phosphate coating on the cathode defines the “chemistry” of the battery. Lithium-ion 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-ion batteries varies from 18 ^{o}C to 145 ^{o}C. There are four basic cell designs; button/coin cells, polymer/pouch cells, cylindrical cells, and prismatic cells (see Figure 3).

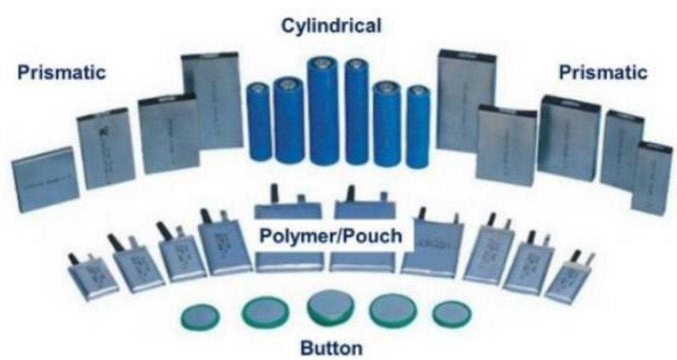

Figure 3: Typical Cell Designs

A lithium-polymer battery, or more correctly lithium-ion polymer battery (abbreviated as LiPo, LIP, or Li-pol) is a Li-ion battery in which the electrolyte has been "plasticized" or "gelled" through a polymer additive. Even with the gelled electrolyte added, a LiPo battery is essentially the same as a Li-ion battery. Both systems use identical cathode and anode material and contain a similar amount of electrolyte. LiPo batteries usually come in a soft package or pouch format, which makes them lighter and less rigid. LiPo batteries offer slightly higher specific energy and can be made thinner than conventional Li-ion batteries (see Figure 4).

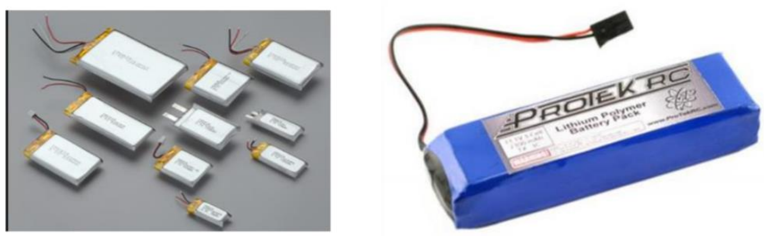

Figure 4: Examples of lithium-polymer (LiPo) batteries

In comparison to batteries of other chemistry types, Li-ion batteries possess a high energy density, they are relatively immune to memory effects, and they possess low self-discharge rates. Currently, their most common uses are for powering household and portable electronics (e.g. laptop computers and phones). However, because of these characteristics, researchers are finding other uses for them, such as electric vehicles or aerospace applications. Furthermore, they are becoming a common replacement for many applications that have been using historically lead acid batteries. The most common advantages and disadvantages of lithium-ion batteries are listed in Table 1.

Table 1: Common advantages and disadvantages associated with lihtium-ion batteries.

Advantages	Disadvantages
▪ High specific energy and high load capabilities ▪ Long cycle and extend shelf-life ▪ Maintenance-free ▪ High capacity, low internal resistance, good coulombic efficiency ▪ Simple charge algorithm and reasonably short charge times; ▪ Low self-discharge; less than half that of nickel-cadmium (NiCd) or nickel-metal hydride (NiMH) batteries	▪ Circuit protection requirement to prevent thermal run-away if stressed ▪ Degradation at high temperatures and when stored at high voltage; ▪ No rapid charge possible at freezing temperatures (< 0^{o}C or 32^{o}F) ▪ Severe transportation regulations required when shipping in larger quantities

Characteristics of specific lithium-ion batteries can also vary based on battery chemistry. This is highlighted in Table 2.

Table 2: Characteristics of different lithium-ion batteries

	LCO $LiCoO_2$	NCA $LiNiCoAlO_2$	NMC $LiMn_2CoO_2$	LMO $LiMn_2O_4$	LFP $LiFePO_4$	LTO* $Li_4Ti_5O_{12}$	Si/C*
Cathode	Lithium Cobalt Oxide	Lithium Nickel Cobalt Aluminum Oxide	Lithium Manganese Cobalt Aluminum Oxide	Lithium Manganese Spinel	Lithium Iron Phosphate	Lithium Titanate	Silicon Carbon Composite
Cell Voltage (100% SOC)	4.2V	4.0V	4.2V	4.2V	3.6V	2.8V	4.2V
Energy	++	+++	+++	+	++	-	+++
Power	++	+++	++	+++	++	+	++
Calendar Life	+	+++	+	-	++	-	-
Cycle Life	+	++	++	++	++	+++	--
Safety	+	+	+	++	+++	+++	+
Costs	-	+	++	++	+	-	++

4.2 BATTERY PACKS

Other than cell phones and tablets, most portable electronic devices operate above the normal operating voltage of single lithium-ion batteries (3.6–4.2V). In such devices, connecting numerous cells in packs provides the desired voltage and capacity. Connecting cells in parallel increases pack amperage and discharge capacity while connecting cells in series increases pack voltage. As an example, a 24V lithium-ion battery pack typically has six cells connected in series.

5.0 HAZARDS AND THEIR CAUSES

The most common hazards associated with lithium-ion battery handling, use, and storage are:

- Fires and explosions
- Venting of internal gases
- Leakage of cell electrolyte
- Rupture of battery case with exposure of internal components

These hazards present significant risk to workers and can be reduced if time is taken to understand the technology and the root cause of these events. The most common causes of lithium-ion battery related incidents stem from one of the three following conditions:

- Electrical abuse – overcharging and/or short circuits
- Overheating
- Mechanical abuse or internal contamination that causes a short circuit

5.1 ROOT CAUSES

5.1.1 OVERCHARGING AND RAPID CHARGING

In order for a battery to remain stable it should not be charged greater than its designed amount (overcharged), and it should not be charged too fast (should be limited to 8/10 of the rated current). Overcharging can cause metallic lithium to plate out onto to the anode without allowing the lithium ions to be absorbed back into it. Eventually this can cause a short circuit between internal battery components. Prolonged overcharging can also cause vapourization of the electrolyte and degradation of the cathode. This degradation forms carbon dioxide (CO_2). The result is the venting of the accumulated gases to release pressure. This can take the form in the release of gas, or as a catastrophic failure (explosion). Watch this short video of this phenomenon.

5.1.2 OVERHEATING

A battery can overheat due to various reasons. In some cases, it can be due to a short circuit, but in others, it may be due to poor storage practices. The following conditions are possible:

- Battery performance is reduced because increased temperature may increase the self-discharge rate of the cell. Overall, this can decrease the usable life of a cell.
- At high temperatures, the electrolyte can vapourize, which increases pressure within the cell, potentially causing an explosion or fire.

5.1.3 SHORT CIRCUITS DUE TO MANUFACTURER CONTAMINATION

Dell and Apple had to recall almost six-million lithium-ion battery packs used in laptops because of internal contamination that caused heat related battery failures. The problem was that microscopic metallic particles (contamination) were somehow present in cells that caused a short circuit within the cell. This short circuit then caused an elevated self-discharge that in some cases caused heat generation and thermal runaway. The result was that the cell vented gases and sometimes flames. If the thermal runaway increases substantially, it can cause a chain reaction in neighbouring cells, which destroys the entire battery pack, sometimes in a catastrophic way (explosion).

5.2 HAZARDS

5.2.1 FIRES, EXPLOSIONS AND VENTING

Although cells are designed not to release their contents, the video in Section 5.1.1 demonstrates how this could happen. Many of the currently used Li-ion battery electrolytes are volatile, toxic, an irritant, corrosive, and/or flammable (Table 3). Leaking electrolyte from a Li-ion battery usually gives a sweet or ether-like odour.

Table 3: Typical solvents used in Li-ion battery electrolytes

Solvent	Hazard	Boiling Point (°C)	Vapour Pressure (mmgHg)
Dimethyl carbonate (DMC)	Flammable	90 – 91	40 – 42
Ethyl methyl carbonate (EMC)	Flammable, Irritant	107 – 110	8 - 18
Diethyl carbonate (DEC)	Flammable	125 – 129	8.1 – 8.3
Propylene carbonate (PC)	Irritant	242	0.03
Ethylene carbonate (EC)	Irritant	247 – 249	0.01
Dimethoxymethane (DMM)	Flammable, Irritant	41 – 42	300 – 330
1,2-Dimethoxyethane (DME)	Flammable, Toxic	84 – 85	44 – 58.6
1,2-Diethoxyethane (DEE)	Flammable, Toxic	121 – 122	44 – 58.4
Tetrahydrofuran (THF)	Flammable	64 – 66	25.9
1,3-Dioxolane	Flammable	74 – 78	127.5 – 130
Γ-Butyrolactone	Harmful	204 - 205	0.3

Many lithium salts have been researched for use in Li-ion batteries (see Table 4); most of them are known to be corrosive, toxic, or an irritant. Lithium hexafluorophosphate ($LiPF_6$) remains the most used salt for Li-ion batteries. Two well-known properties of $LiPF_6$ salt are its poor stability and reactivity with water. Upon contact with either atmospheric moisture or traces of water in the electrolyte, $LiPF_6$ undergoes hydrolysis forming hydrogen fluoride (HF), a very poisonous and corrosive substance both in gaseous and aqueous solution forms.

Table 4: Typical salts used in Li-ion battery electrolytes

Salt	Formula	Hazard
Lithium Hexafluorophosphate	$LiPF_6$	Corrosive, Toxic
Lithium Tetrafluoroborate	$LiBF_4$	Corrosive, Harmful
Lithium Hexafluoroarsenate	$LiAsF_6$	Toxic
Lithium Iodide	LiI	---
Lithium Trifluoromethane Sulfonate	$LiCF_3SO_3$	Irritant
Lithium Bis (Trifluoromethanesulfonyl) Imide	$Li(CF_3SO_2)_2$	Corrosive, Toxic
Lthium Perchlorate	$LiClO_4$	Oxidizer, Irritant
Lithium Bis(Oxalato)Borate	$LiB(C_2O_4)_2$	Irritant
Tetraethyl-Ammonium Tetrafluoroborate	$(C_2H_5)_4NBF_4$	Irritant, Harmful
Triethyl-Methyl-Ammonium Tetrafluoroborate	$(C_2H_5)_3CH_3NBF_4$	Corrosive, Harmful

In case of accidental release of the battery content, the operator may be exposed to one or more of the battery constituents. A list of generic constituents of a Li-ion battery is presented below (Table 5).

Table 5: Typical Li-ion battery constituents

Battery Component	Content (wt %)
Lithiated Metal Oxide	10 – 25
Organic Electrolyte	10 – 35
Inorganic salt in the electrolyte	1 – 5
Carbon, as Graphite	10 – 25
Copper (current collector)	1 – 10
Aluminum (outer jacket)	1 – 10

The composition may vary significantly between manufacturers. The chemical risks associated with the direct exposure to the substances contained in the battery are available in the Safety Data Sheet (SDS) of the corresponding battery. One must always refer to the manufacturer's battery SDS before its use.

5.2.2 GAS EMISSIONS (VENTING)

The main consequences of a thermal run-away are the emission of heat and gas which is flammable. Some cell designs include a specially designed vent that opens and releases gases. In some cases, this vent can become obstructed or may not open correctly, which may result in battery bulging, hissing or rupturing of the enclosure (Figure 5). When cells, such as pouch cells, do not include a specific vent, gases may be released at weak points in the external pouch.

Figure 5: Swollen lithium-ion pouch batteries

The release of vented gases avoids the catastrophic failure of the cell containment structure but creates a new hazard associated with the toxicity and flammability of the vented gases. Gas release depends on the battery composition and state of charge (SOC); the higher the SOC, the larger the amount of gases released. A general list of potential gases emitted during a thermal run away of a Li-ion battery is provided in Table 5, with indications of their relative concentration.

Table 6: Potential gases emitted during a Li-ion battery thermal run-away

Battery Component	Content (wt %)	Hazard
Carbon Dioxide	~ 30	Asphyxiant
Hydrogen	~ 30	Flammable
Carbon Monoxide	20 – 25	Flammable, Toxic
Methane	5 – 8	Flammable
Ethylene	3 - 8	Flammable
Ethane	1 - 3	Flammable
Propylene	1 - 3	Flammable
C4s and others	< 1	Flammable
Hydrogen Fluoride	0.3	Corrosive, Toxic

The gases released by a venting Li-ion cell are mainly carbon dioxide (CO_2) and hydrogen (H_2). Other gases that form through heating are vaporized electrolyte, consisting of ethylene and/or propylene along with combustion products of organic solvents. If a Li-ion battery hisses, bulges or release any gases:

1. Move the device away from flammable materials and place it on a non-combustible surface or outdoors to let gases vent.
2. If not possible or too dangerous, evacuate the room and label "DO NOT ENTER".
3. Allow sufficient time for the room ventilation to ventilate any gases released.

Most of the gases reported in Table 6 are flammable. In addition, carbon monoxide and some other gases can also pose significant health hazards.

6.0 TYPICAL BATTERY PROTECTION MECHANISMS

Battery packs can be equipped with several different types of protection systems. In larger or more complex battery packs (like for vehicles), protection systems would include a primary system that monitors a cell and the entire pack state of charge (SOC) and temperature. The primary system would also limit the rate of charge and discharge of the cells in order to prevent overcharging or dangerous discharge. A secondary system is sometimes also employed which shuts down the pack if the primary system fails. The last safety system is simply a venting system that allows overpressures to be released in a safe manner.

7.0 STORAGE AND USE BEST PRACTICES

7.1 PROCUREMENT

Purchase batteries from a reputable manufacturer or supplier.

- Avoid batteries shipped without protective packaging (i.e., hard plastic or equal)
- Inspect batteries upon receipt and safely dispose of damaged batteries.

7.2 STORAGE

- Store batteries away from combustible materials.
- Remove batteries from the device for long-term storage.
- Store the batteries at temperatures between 5°C and 20°C (41°F and 68°F).
- Separate fresh and depleted cells (or keep a log).
- If practical, store batteries in a metal storage cabinets.
- Avoid bulk-storage in non-laboratory areas such as offices.
- Visually inspect battery storage areas at least weekly.
- Charge batteries in storage to approximately 50% of capacity at least once every six months.
- Store primary and secondary batteries apart from one another.

7.3 HANDLING AND USE

- Handle batteries and or battery-powered devices cautiously to not damage the battery casing or connections.
- Keep batteries from contacting conductive materials, water, seawater, strong oxidizers and strong acids.
- Do not place batteries in direct sunlight, on hot surfaces or in hot locations.
- Inspect batteries for signs of damage before use. Never use and promptly dispose of damaged or puffy batteries.
- Keep all flammable materials away from operating area.
- Allow time for cooling before charging a battery that is still warm from usage and using a battery that is still warm from charging.
- Consider cell casing construction (soft with vents) and protective shielding for battery research or evolving application and use.

7.4 LI-ION CHARGING GUIDELINES

- Do not draw current from the battery while charging. Drawing current while charging may confuse the charger;
- Charge at a moderate temperature; never charge at freezing temperature;
- A Li-ion battery does not need to be fully charged; a partial charge is better. Not all chargers apply a full topping charge and the battery may not be fully charged when the “ready” signal appears; a 100% charge on a gauge may not reflect reality;
- Discontinue using a charger and/or battery if the battery gets excessively warm;
- Never charge a primary (disposable lithium or alkaline) battery; store one-time use batteries separately.

- Only use chargers specified by the manufacturer of the battery to charge a battery.
- Remove cells and pack from chargers promptly after charging is complete. Don't use the charger as a storage location.
- Charge and store batteries in a fire-retardant container like a high quality Lipo Sack when practical.
- 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.
- Do not overcharge (greater than 4.2V for most cells) or over-discharge (below 3V) cells.

7.5 DISPOSAL

For disposal requirements of lithium and lithium-ion batteries, please refer to the UW Hazardous Waste Standard.

7.6 TRANSPORTATION

Lithium batteries are designated as a Dangerous Goods under the Transportation of Dangerous goods. Before shipping, or transporting lithium or lithium ion batteries, please refer to Transport Canada.

7.7 EMERGENCIES

7.7.1 FIRES AND OVERHEATING

If a Li-ion battery overheats, hisses, or bulges, immediately move the device away from flammable materials and place it on a non-combustible surface. If possible, remove the battery and put it outdoors to burn out. Simply disconnecting the battery from charge may not stop its destructive path.

A small Li-ion fire can be handled like any other combustible fire. For best results, use a foam extinguisher, CO_2, ABC dry chemical, powdered graphite, copper powder, or soda (sodium carbonate). If the fire occurs in an airplane cabin, the FAA instructs flight attendants to use water or soda pop. Water-based products are most readily available and are appropriate since Li-ion contains very little lithium metal that reacts with water. Water also cools the adjacent area and prevents the fire from spreading. Research laboratories and factories can also use water to extinguish Li-ion battery fires.

CAUTION – with primary cells (Lithium-metal batteries) only use a Class D fire extinguisher, as lithium-metal batteries contain large amounts of lithium which will react violently with water.

With all battery fires, allow ample ventilation while the battery burns itself out.

8.0 LITHIUM BATTERY SYSTEM DESIGN GUIDANCE

Lithium battery system design is a highly interdisciplinary topic that requires qualified designers. Best practices outlined in IEEE, Navy, NASA, and Department of Defense publications should be followed. Battery selection, protection, life, charging design, electric control systems, energy balance of the system, and warning labels are examples of topics that require thoughtful consideration. Systems designed for mobile applications should apply best practices to ensure appropriate safeguards are in place. Designs should include a hazard assessment that identifies health, physical and environmental hazards, with all hazards appropriately mitigated through engineering and administrative controls. Examples of baseline criteria for system design include:

- Failure scenarios, including thermal runaway should be considered during design and testing so that a failure is not catastrophic.
- Maintain cells at manufacturers' recommended operating temperatures during charging or discharging.
- Size/specify battery packs and chargers to limit the charge rate and discharge current of the battery during use to 50% of the rated value (or less).
- Practice electrical safety procedures for high capacity battery packs (50V or greater) that present electrical shock and arc hazards. Use personal protective equipment (PPE) and insulate or protect exposed conductors and terminals.

9.0 REFERENCES AND PUBLICATIONS

- Lithium Batteries – Concordia University
- Lithium Battery Safety – University of Washington
- Battery University – Safety Concerns
- Consumer Product Safety Commission – Battery Safety Alerts
- Consumer Product Safety Commission – Recall List
- IEEE, A Guide to Lithium Battery Safety
- IEEE Standard 1679.1-2017 "Evaluation of Lithium-based Batteries in Stationary Applications"
- Navy Lithium Battery Safety Program – Technical Manual (S9310)
- Navy High-Energy Storage Systems Safety Manual (SG270)
- NFPA Lithium Ion Hazard and Use Assessment
- NFPA Lithium Ion Hazard and Use Assessment IIB
- NFPA Lithium Ion Hazard and Use Assessment III
- SFPE Lithium-Ion Battery Hazards

10.0 TRAINING RESOURCES

https://mediaex-
server.larc.nasa.gov/Academy/Play/c95968b350924eac9ee304f52f1f282f1d