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Safe application of lithium and lithium ion batteries

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English summary

The purpose of this report is to give a minimum of information for the safe use and assembling of batteries. The requirements for battery safety circuits are described as well as the most common use of devices such as fuses, thermal fuses and cut-off devices and safety valves as well as the rational for the use of diodes in battery protection.

A small chapter on the dimensioning of a battery for a defined use is also included.

The main goal is to ensure that the choice of cells and the assembling of cells into batteries are done according to best practices.

Sammendrag

Rapporten tar sikte på å gi et minimum av bakgrunn for sikker bruk av batterier, herunder hvilke sikringsmekanismer man kan forvente i cellene og hvilke tiltak man selv må ivareta. En beskrivelse av bruken av de viktigste komponentene som sikringer, dioder, termiske brytere og andre strømbrytere er gitt. Videre har man tatt med et lite kapittel om valg av batterityper.

Den overordnete målsetning er å sikre at valg av celler og sammensetningen av cellene blir slik at bruk av batterier har så lav risiko som mulig.

Content

Preface

The Norwegian Army was one of the first to use primary lithium batteries as these batteries had exceptionally good performance at low temperatures. As time went on, it also became clear that they also had other qualities, and after some battery fires and explosions in the late seventies and early eighties, FFI has been engaged in research on the safety of primary lithium batteries. This work was continued when the rechargeable lithium ion chemistries entered the marked in the nineties. FFI has also been involved as a battery user and developer of military equipment such as radios and autonomous underwater vehicles and as a consultant for the industry on battery safety.

There has been a more or less constant flow of reports on battery fires and battery explosions from all over the world. This is in spite of the continuous improvement in battery safety that has taken place since their introduction in the late seventies, the reason is of cause the enormous increase in their use

There are many applications where there is no realistic alternative to lithium batteries, but in most applications and where large batteries are involved, the consequences of a fire or explosion are unacceptable. This was the background for the cooperation between Statoil, Kongsberg Maritime, and the Norwegian Defense on battery safety. This was later expanded with Gassco, The Norwegian Coastal Administration (Kystdirektoratet), Directorate for Civil Protection and Emergency Planning (DSB) and Norsk Batteriretur to form Norwegian forum for battery safety. The secretary of the Forum is FFI and the Forums expenses are covered by the industry. Reports of incidents to the Forum are treated confidentially, but anonymous descriptions of events may be publicly reported in order to learn from the experiences. This confidentiality is considered essential in order to be informed of the incidents.

This report is a translation of the former FFI/Report 2010/00215 into English. A few changes and additions have also been made. The background for these reports is incidents that have been caused mainly by human errors and which would have been avoided given a better understanding of the batteries involved.

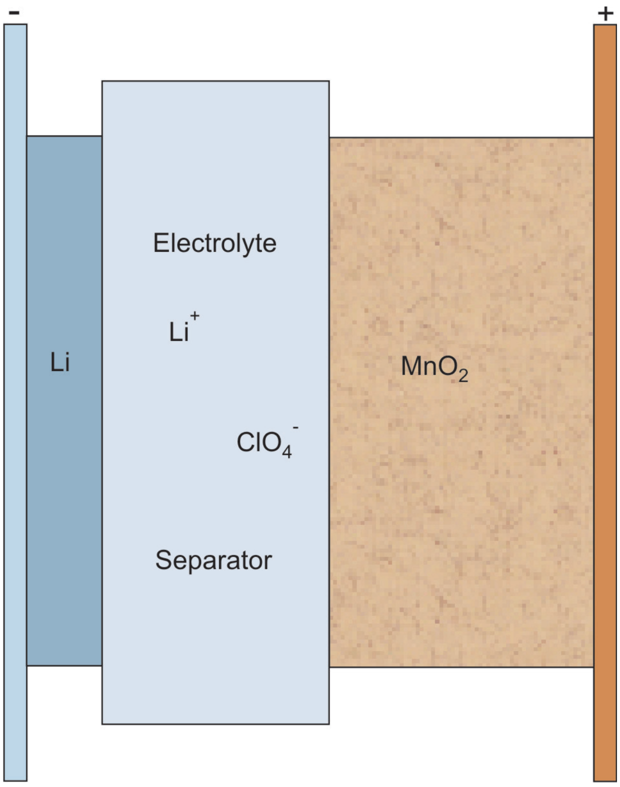
1 Introduction

Most batteries contain a fuel and an oxidant, the exception is metal / air batteries were the oxidant is oxygen in the air. (e.g. zink/air batteries for hearing aids). The fuel and the oxidant is mechanically and electrically separated by a separator wetted with electrolyte. The electrolyte conducts ions, but not electrons. Figure 1.1 shows the schematic design and figure 1.2 the construction of a button cell. The cathode is the positive electrode in the cell and connected to the positive terminal, the anode is the negative electrode in the cell and connected to the negative terminal.

When you discharge the battery, chemical energy is converted to electric energy: fuel is oxidized on the anode and oxidant reduced on the cathode. Electrons from the anode go through the load to the cathode. Because of the polarization on the electrodes (”voltage loss / overvoltage on the electrodes”) and the ohmic resistance of the battery components, some energy is also lost as heat. If you short circuit the battery, either internally e.g. because of a separator failure or externally, the chemical energy of the cell (reaction enthalpy) is converted to heat.

A **primary battery** is a battery that is not designed to be recharged after discharge whereas a **secondary battery** (also called an accumulator) can be recharged. The energy density (electric energy per weight of battery) of the traditional, water based batteries is of the order of 30 to 80 Wh/kg. In contrast the lithium ion secondary battery contains from 80 to 200 Wh/kg and the lithium primary battery from 200 to 600Wh/kg depending on design and chemistry.

The heat capacity of lithium batteries are typically ca 1 kJ/(K·kg). This is less than a half of the heat capacity of the water based batteries. Thus for the same amount of heat liberated, the temperature increase of a lithium battery will be twice as high assuming perfect thermal insulation (adiabatic process). Given that a battery has an energy density of 400Wh/kg (1440kJ/kg) and a heat capacity of 1 kJ/(K·kg), the adiabatic temperature increase will be 1440 K. The battery will of course disintegrate long before this temperature increase has been reached, but this calculation shows the damage potential of high energy batteries and the importance of good design to prevent this from happening.



Anode: $Li \Rightarrow Li^+ + e^-$

Cathode: $MnO_2 + Li^+ + e^- \Rightarrow LiMnO_2$

Cell: $Li + MnO_2 \Rightarrow LiMnO_2$

Fuel + oxidant => energy + products

Figure 1.1 Schematic description of a lithium manganese dioxide cell. Separator and cathode are both porous and filled with electrolyte. The electrolyte is a lithium salt dissolved in an organic liquid. (e.g. lithium perchlorate in tetrahydrofuran).

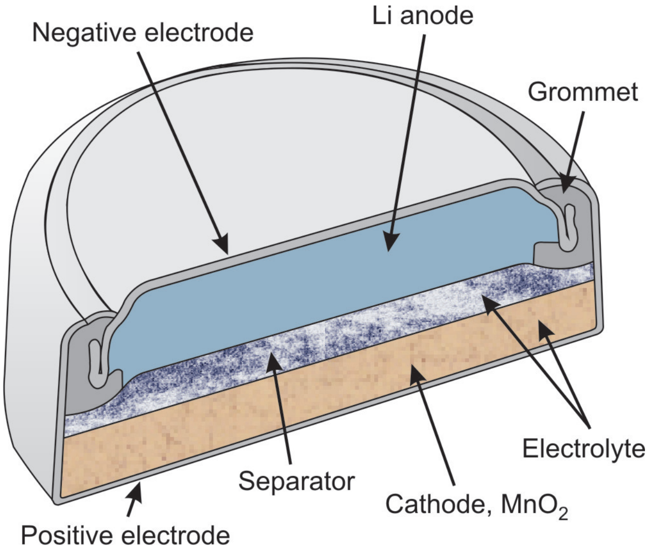


Figure 1.2 Lithium / manganese dioxide button cell.

Given a sufficiently high temperature locally in the cell, exothermal reactions can take place leading to a further increase in the temperature. One obvious reaction is the direct reaction between the fuel and the oxidant, but other reactions may also take place in the cell. Normally metallic lithium is covered with a thin film (solid electrolyte interface, SEI). This film conducts lithium ions, but not electrons and protects the metal against a direct reaction with the electrolyte. If the metal melts however, the film may break and a direct reaction between lithium and the electrolyte may take place. In batteries where the electrolyte is also the oxidant (such as thionyl-, sulfuryl- and sulfur dioxide batteries), the heat of reaction is large and very violent explosions have been observed. Lithium melts at 180ºC and has a density of only 700kg/m^3. When it melts, it floats to the top of the cell and short the cell. Polypropylene and polyethylene are both common separator materials and melt (and shrink) at a lower temperature. This may also result in internal shorts. It is observed experimentally that explosions are common if you exceed the melting temperature of lithium in cells that do not have safety valves.

Other exothermal reactions of concern are reactions between the active material in the electrodes and the electrolyte. Examples are the reduction of the electrolyte by the anode and oxidation of the electrolyte by the cathode in lithium ion when the cells are heated or overcharged.

The temperature in the cell is a function of the rates of heat generation and removal. Small batteries and cells have larger surface area relative to volume and give off heat more easily. Thus the problem of heat transport and battery temperature increases with the size of the battery. As the potential for rapid heat generation also increases with the current capability of the cell, high rate batteries are generally of more concern than low rate batteries.

Batteries of questionable quality have been observed in the market lately. Dubious quality is not easy to reveal by testing: As an example: The normal frequency of development of internal shorts in cells is of the order of 1 ppm from reputable producers. An increase by a factor 1000 could be a catastrophe for the reputation of the battery user, but the cost of the test of the large number of cells needed in order to reveal this in advance, would have been prohibitive. In the end, battery selection must be based on trust to the producer and on an evaluation of the safety built into the cells and batteries.

It should also be taken into consideration that many lithium and most lithium ion batteries contain a flammable electrolyte. Thus they may be considered as any other container of flammable liquid. If they are heated sufficiently the electrolyte will vaporize and vent and if ignited, the vapor will burn. Thus, even if the battery is in the discharged state, it is not harmless.

Last but not least, some lithium chemistries contain components that are considered corrosive, toxic or environmentally harmful.

2 Cell geometries

Mechanically cells are of four main types: Prismatic, spirally wound, ”bobbin” and button cells. For high rate batteries it is important that the internal resistance is as low as possible. This is achieved by reducing the distance between the electrodes as much as possible (thus thin separators) and to use thin electrodes in order to increase the active electrode area. In order to increase the conductivity of the electrodes, they are pressed onto metal current collectors and when the active material has a low conductivity, carbon is added to the active material in order to increase the conductivity. High rate cells are either spirally wound or prismatic.

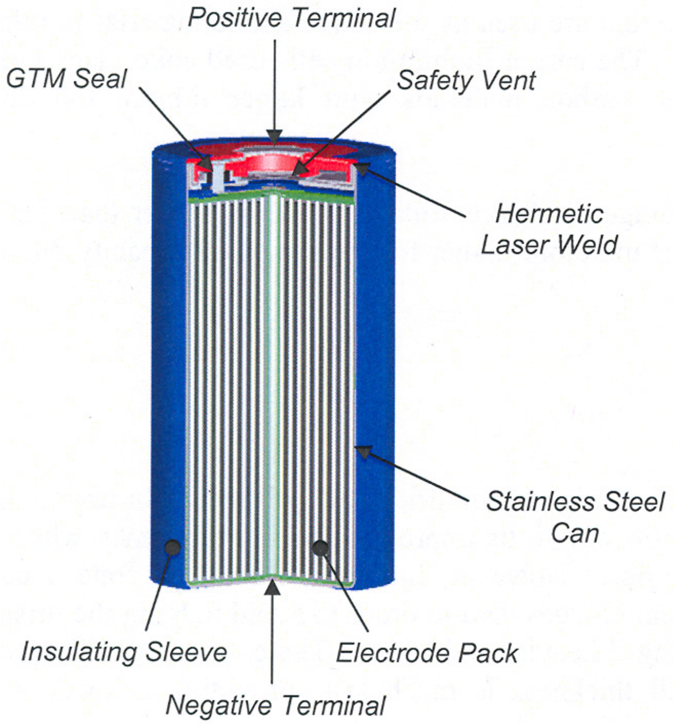


Figure 2.1 Spirally wound cell (lithium ion cell from AGM Ltd).

Figure 2.1 shows a lithium ion cell (courtesy of AGM Ltd). GTM, ”glass to metal” is a hermetic penetrator (a metal pin through a glass insulator, the seal is welded to the can). The hermetic design secures against water vapor and oxygen penetrating into the cell and is generally used in professional equipment. The fuel is lithium intercalated in carbon, the oxidant lithium cobalt oxide and the electrolyte a solution of lithium salt in a mixture of organic esters. In order to absorb volume changes of the active components during use, all metal can cells contain a void volume. Thus the pressure increase caused by a expansion of the active mass will be minor and the pressure in the cell determined by the vapor pressure of the electrolyte and thus by the cell temperature.

Low rate cells are cells designed for low current over long time. In such cells, thicker electrodes are used such as in button cells and bobbin cells. Because these cells use a smaller part of the cell volume for inert components such as electrolyte, separators and current collectors, they usually have a higher specific energy at low current than high rate cells. Figure 2.2 shows a bobbin cell.

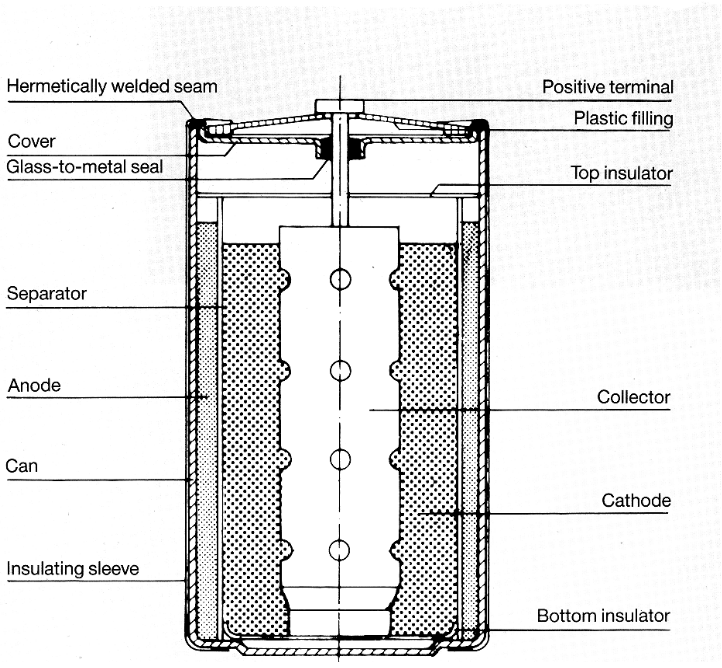


Figure 2.2 Bobbin cell. (lithium thionyl chloride cell from Tadiran).

Bobbin cells are used in primary batteries, mainly in lithium thionyl chloride cells. The figure 2.2 shows one such cell. The anode is a cylinder of lithium, the cathode a porous bobbin of carbon and a binder and the oxidant thionyl chloride ($SOCl_2$). The electrolyte is lithium aluminum chloride dissolved in thionyl chloride. Thus the electrolyte functions both as electrolyte and as oxidant (”liquid cathode”). The internal resistance of this cell design is fairly high and these cells are typically used for long term applications (months to many years).

Prismatic geometry is used in lithium (ion) polymer cells and in some large lithium ion cells. Figure 2.3 shows some prismatic polymer cells and batteries from Kokam. Polymer cells have their name from the electrolyte which is in the form of a polymer. Most are a hybrid form where a gel is made from a polymer and a conventional electrolyte based on carbonate esters and lithium hexafluorophosphate. The cells are usually packed in a metalized plastic film not very different from a vacuum packed coffee bag. Swelling of the cells during use is not uncommon and sufficient space must be allocated in the battery compartment. Leakage of electrolyte is easily smelled as the esters have a strong smell. The main advantage of the design is low weight and low cost.

Figure 2.3 Prismatic polymer cells and batteries.

3 Safety mechanisms

Cells and batteries should be equipped with a number of safety measures in order to avoid that a battery failure or a user failure results in a safety incident. Both production quality and safety measures varies between the different producers, thus it makes no sense to say that e.g. sulfur dioxide cells are safer than iron disulphide cells etc.

Depending on the system, different safety measures are used on the cell level, the battery level and for large systems on the system level.

3.1 Cell level

Safety valve
The safety valve is often just a weakening in the can or lid that opens when the internal pressure exceeds a certain limit. Depending on the composition of the electrolyte the opening temperature is selected so that the vapor pressure exceeds the opening pressure of the valve well below the melting point of lithium for lithium primary cells. A correctly designed valve ensures that all volatile components have left the cell before exothermal reactions can take place.

In a lithium ion cell with cobalt oxide cathode, the cathode / electrolyte reaction is very exothermal and it is imperative that the electrolyte has evaporated before any reactions between the electrode materials and the electrolyte takes place. In primary batteries (such as Li / thionyl chloride, Li / sulfuryl chloride and Li / sulfur dioxide) the electrolyte is also oxidant, as mentioned earlier. A cell ventilation with these chemistries is unpleasant as the vapors are both very irritating and corrosive, but the alternative, a violent explosion is much worse.

Pressure switch

Some cells contain a current interrupt device (CID) that activates if the internal pressure exceeds a set limit. This type of CID is irreversible. See figure 3.1.

Fuses

Common melting fuse: This CID interrupts the current if the current exceeds a set level. (More precisely is the activation depending on both time and current level). Activation of a fuse is irreversible.

Polymer fuse (Polymer positive resistance coefficient resistor, PPTC): The resistance (R) increases very rapidly above a certain temperature. The PPTC reacts on temperature and indirectly also on current via resistive heating ($I^2 \cdot R$). This fuse is reversible. If the load is removed and the fuse cooled down, the cell is operational.

Thermal Cut-Off device (TCO)

A TCO is a CID that disconnects irreversibly if the temperature exceeds the melting point of the fuse wire. The maximum current for the component should not be exceeded as this may result in a premature opening. A common cut-off temperature is 93°C.

Shunt diodes

Some cell types have a habit of exploding if over-discharged. (If the polarity of the cell is reversed, unwanted chemical reactions may take place). The cell reversal voltage can be limited by placing a diode parallel to the cell. Figure 3.1 shows the design of the cell protection in a lithium sulfuryl chloride cell. The diode limits the reverse voltage to ca 0.3V (Schottky diode). There is some discussion whether or not shunt diodes always increase safety; a leaking diode may also pose a problem.

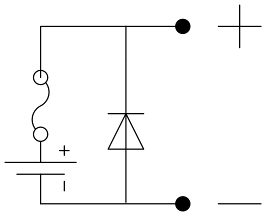


Figure 3.1 Schematic of cell with internal fuse and shunt diode (e.g. Electrochem CSC 93).

Series diodes

Some primary cells may explode if recharged. To protect against charging, a diode is serially connected to the cell. In a string of cells, one diode is sufficient. (string = series connection). In order to reduce the voltage loss, Schottky diodes are commonly used in spite of their relatively low breakdown voltage.

Electronic cell protection circuits

Most lithium ion and lithium polymer cells (secondary batteries) will be destroyed if discharged below a minimum voltage or recharged above a maximum voltage. Typical figures are 2.5V and

4.3V. In order to avoid this, many producers integrate an electronic protection circuit into the cell in order to protect against overcharge (which also may lead to fire), over-discharge and over-current. This protection is not always visible, but may be integrated e.g. in the lid of the cell. Integrated circuits for this purpose are available from a number of suppliers. Lately also microcontrollers have been designed for this purpose, making available data such as cumulative charge taken from the cell, state of charge (SOC), state of health (SOH), cell temperature etc. This also makes it possible to protect from being charged by a "non-recognized charger" in order to avoid the use of "pirated" batteries and chargers. At present, this technology is used in consumer equipment such as cameras and mobile phones. An international standard for smart batteries exists as well. See http://smartbattery.org/ for details.

The use of electronics in batteries has been a mixed blessing; battery failures caused by the failure of protection circuits are not uncommon. And as most of the protection circuits are powered by the battery they protect, they limit the allowable storage time of rechargeable batteries before a recharge of the battery must take place. An alternative to electronic protection does not exist however, as exemplified by some battery manufacturers refusing to sell unprotected batteries.

Separator

The separator in the cell is an extremely important component both with respect to safety and to the electric performance of the cell. Its purpose is to make sure that electronic contact between anode and cathode do not take place even under harsh conditions of shock, vibration and temperature variations and at the same time have the least possible resistance to ion transport through the membrane. Common is one or more layers of a porous material in a thickness of 20 to 100µm. Most are made from polymers such as polyethylene and polypropylene, but in order to increase the temperature resistance, inorganic materials may also be used. Some separator materials shrink (contract) if heated above a certain temperature. This may result in an internal short. A shut-down separator has the property of closing the pores above a certain temperature. This increases the internal resistance of the cell, reducing the cell current. The process is irreversible.

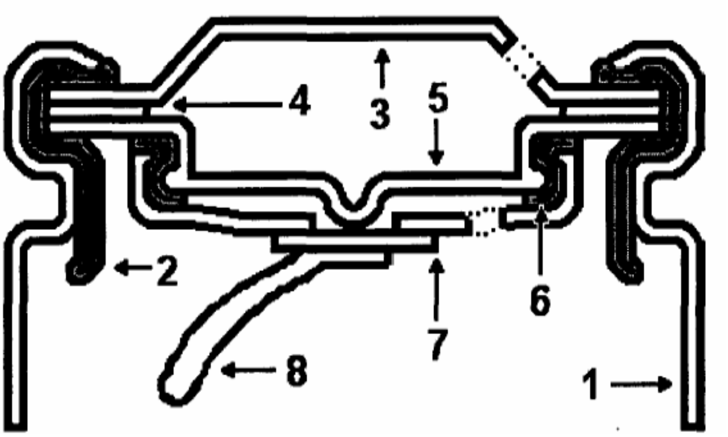
Part of the large increase in the specific energy of lithium ion batteries over the last years has been achieved through reductions in the separator thickness. This reduction has at the same time made the cells more vulnerable for foreign matter penetrating the separator and shorting the cell.

Seals

Low cost cells usually have a crimp seal; a plastic gasket seals the cell. Depending on the seal quality, electrolyte vapours leak out and water and oxygen leak in to the cell and reduces the calendar life of the cell. Contamination of the atmosphere by electrolyte vapour may also be a problem in completely sealed environments e.g. in submarines.

GTM seals are used in welded cells. They give a hermetic seal. Some GTM seals have also been used as a safety valve as they crack and open under pressure. Compared to other valve designs, they are of low cross-section and may have poor reproducibility.

Figure 3.2 shows the safety mechanisms in the top of a typical cell with crimp seal for consumer application (e.g. laptop PC):



1	Can
2	Insolating gasket (”crimp seal”)
3	Top (positive connection)
4	Disk shaped polymer fuse (PTC),
5	CID (moving part, activated by pressure)
6	Insulator
7	CID (stationary part)
8	Connection to the cathode (positive electrode)

Figure 3.2 Top of a typical 18650 lithium ion PC cell. Diameter 18mm. (From E Darcy et al, Proceedings of the 43rd Power Sources Conference, pp 15-18, 2008).

Please note that if you fill the void in the valve (between 3, 4 and 5) with a moulding compound, it will no longer function as intended.

3.2 Battery

3.2.1 Nomenclature

Capacity and energy content: The capacity of a cell is the charge (in coulombs or ampere hours (Ah)) that can be drawn from a fully charged cell before the cell voltage falls below a set limit. (e.g. discharged to 0.9V for a NiMH cell or down to 2.75V for a lithium ion cell). Energy content is the energy (in joule (J) or watt hours (Wh)) the battery can deliver before the cell voltage falls below a set limit. Both cell capacity and energy is dependent on the current load as well as the temperature during discharge and usually both decrease with increasing current and decreasing temperature. Thus the figures should be given under well defined discharge conditions.

Because the electric properties of cells and batteries are linearly scalable, a very convenient unit for cell current is the C unit. 1C correspond to the nominal capacity of the battery divided by 1 hour. Thus a 5Ah battery that is discharged with 10A is discharged at 2C. Similarly a 70 Ah battery discharged with 3.5A is discharged at 0.05C, often also written as C/20.

Battery: A battery is a connection of one or more identical elements (According to IEC a cell is a battery if it has terminals for connection and a label giving type and polarity).
Parallel connection: If you have 5 cells in parallel in a battery, the battery voltage equals the cell voltage, but the capacity has been increased by a factor 5. The internal resistance of the battery has been decreased with a factor 5 and the battery can deliver 5 times more current than the cell. A parallel connection of n cells is written **nP**.
Series connection: Similarly gives a battery made from 5 serially connected cells 5 times the cell voltage, but the capacity is the cell capacity and the internal resistance is 5 times the cell resistance (neglecting connections). A series connection of n cells is written **nS**.

A **4S3P** connection (figure 3.3) means 3 strings, each of 4 cells in series. The strings are then connected in parallel. A typical 10.8V / 10Ah PC battery may be made from 12 UR18650F cells each 2.5 Ah in a **4P3S** connection. **4P3S** implies that 4 and 4 cells are connected in parallel, then the parallel connected units are serially connected. See figure 3.4. Ignoring the diodes, the energy content (in Wh) is equal for the two batteries, only determined by the number of cells (12), but their electrical and safety properties are different

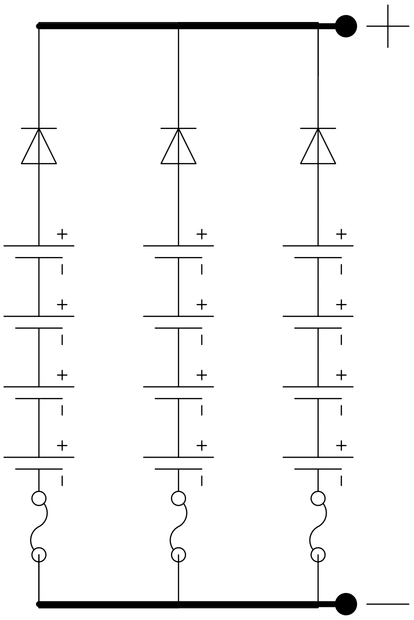


*Figure 3.3 **4S3P** connection of cells in a primary battery with polymer fuses and series diodes. Usually also a TCO and a fuse will be added to the circuit.*

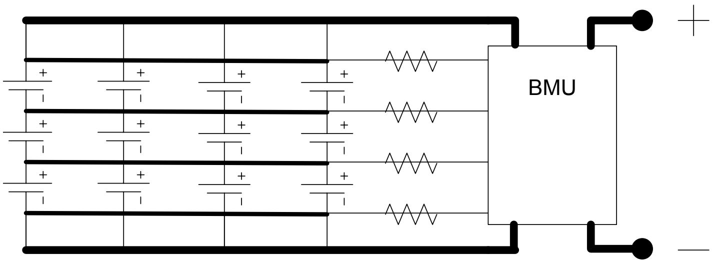


*Figure 3.4 **4P3S** connection of cells with electronic battery management unit (BMU). The cell voltages are measured via resistive sense inputs that ensure a low current in the sense leads in the event of a circuit failure. The BMU also measures battery current and temperature and breaks the current if any measurements are outside set limits.*

Calendar life and cycle life: The end of life of a battery is usually defined as when the battery capacity has fallen below 80% of its original capacity. The cycle life is based on the number of charge / discharge cycles the battery has been exposed to. Unless well defined, both figures can be totally meaningless. Calendar life depends on the storage conditions (mainly temperature and humidity and for secondary batteries also the state of charge). The cycle life depends in addition on the current during charge and discharge, temperature, and depth of discharge. Not only has the battery capacity changed with age but the internal resistance usually also increases with time. For some applications this may well be the life limiting factor.

A useful figure for cycle count can be the total charge delivered by the battery divided its nominal capacity.

In addition to the changes mentioned above, catastrophic cell failures may take place in a battery (i.e. internal short or open circuit, or soft shorts increasing rate of self discharge or electrolyte leakage).

3.2.2 Lithium metal primary battery design practice

It is common practice to assemble the battery of series connected strings where each string has a fuse in the negative lead and a diode in the positive lead to protect against charging. If more than one string is used, the strings are parallel connected after the diodes and fuses as shown in figure 3.3. Direct parallel connection of primary cells should be avoided!

Unless polymer fuses (PTC) are used, some other form of over-temperature cut-off is mandatory. This may be a TCO mounted with good thermal contact to the battery cell. Verify that the TCO or PTC is rated for the maximum battery voltage.

Cables should be fused as close to the battery as possible. If sense leads are used, they shall be protected against shorts with resistors close to the cell. (Shorts of sense cables to cell cans are a familiar cause of battery fires). The cables should be of high quality and it is recommended that the insulation has a high temperature rating e.g. PTFE or similar. Note that for some applications, halogen containing insulation (e.g. PVC, PVDF etc) is prohibited.

The battery pack shall be rugged with respect to shock and vibration. If the cells are potted, make sure that the potting does not affect the safety valves in the cell.

The battery container shall be rugged and designed so that a cell vent, fire or explosion does not result in high velocity fragments.

The temperature of the battery is a function of the ambient temperature, heat generation within the battery, heat capacity and conductivity and heat loss to the surroundings. Thus size, geometry and material selection and design is important. If anywhere within the battery the melting temperature of lithium (180ºC) is exceed, an explosion may be the result.

For large batteries a Battery Management Unit, "BMU" is recommended. If a temperature anywhere in the battery, battery current or voltage is outside the acceptable windows, the battery is disconnected. ("Life support" systems are never disconnected, but the system must give an alarm).

3.2.3 Secondary batteries

Electric energy put into the battery during charge is
Either converted into **chemical energy** and stored
Or converted in to **heat**
Or both
A charge current I will also result in resistive heat generation ($R \cdot I^2$), where R is the internal resistance of the battery. Changes in entropy $T\Delta S$ also result in heat consumption or production, but the amount of heat is usually too low to be of any safety concern.

Heat is also generated if one substance is generated at one electrode and consumed at the other electrode. A familiar example is the generation of oxygen (O_2) on the positive electrode and its subsequent removal by reduction to water at the negative electrode.
This reaction protects valve regulated lead acid batteries (VRLA), NiCd and NiMH batteries during over-charge, given that the battery temperature can be kept at an acceptable level.

At present, no similar reaction exists for lithium ion batteries. Overcharge always results in chemical changes that destroy the battery and in the worst cases, results in fire or explosion.

A significant difference between batteries made from cells with aqueous electrolyte such as NiCd and NiMH and batteries made from lithium ion cells is that lithium ion cells should always be equipped with an electronic protection circuit. This circuit disconnects the cell if the cell voltage exceeds a maximum cell voltage, falls below a minimum voltage or if the cell temperature or cell current exceeds set values. A certain element of redundancy is recommended and common practice is to use two-fault tolerant design.

3.2.4 Cell connections and routing of cables

Short between cables and cell cans are common causes of battery failure. A short to the cell can may bypass the internal safety device in the cell. Especially rechargeable batteries may have a long life and robust design with respect to mechanical abuse (shock and vibration) is mandatory.

Spot welding is recommended and soldering to a cell wall should never be done. Most cells can be delivered with solder tags if necessary. For some applications, non-magnetic cells must be used. They may be assembled using strips of austenitic stainless steel.

3.2.5 Battery containers

The required strength and ventilation of the battery container depends on the type of battery and its application. Cells with aqueous electrolyte will always give off some hydrogen which may make the atmosphere within the container explosive unless the container is vented. The problem increases with increasing temperature and is caused by the corrosion of the anode in the cell. This is the case for NiCd, NiMH, lead acid, Leclanché and alkaline cells.
In order to keep the hydrogen concentration in air below 4% (LEL, lower explosive limit) a minimum ventilation of the battery compartment will be required.

Normally lithium or lithium ion batteries do not give off any gases, but cell failures may result in fire or explosion. Thus common practice is for the container to have a weak area or a valve so that the battery may vent with minimal damage to the surroundings.

For battery containers that must be sealed such as for under water applications, there are two options:

- Make the container so robust that it can take a battery explosion.
- Equip the container with a safety valve of sufficient cross section area to vent the gases at an acceptable pressure.

The first alternative is often a good alternative for containers where the free volume is of same order of magnitude as the battery volume or larger and where the container must be very strong anyhow in order to stand the pressure in deep water applications. The container must have a vent screw so that any internal pressure can be released before any attempt to open the container is made.

Battery explosions are very slow compared to other explosions, but the gases relieved may have a high temperature, affecting the solidity of aluminum or plastic containers.

The most powerful explosions FFI has been able to produce are made with lithium metal batteries with liquid cathodes such as (Li/SO_2, $Li/SOCl_2$ and Li/SO_2Cl_2). Batteries with solid cathodes (Li/MnO_2) give more fire. We have not been able to create explosions in lithium ion cells or in lithium polymer cells, only explosive fires. In discharged lithium ion batteries only the flammable electrolyte has been of concern. It is conceivable that other cathode chemistries such as lithium iron phosphate are safer as the cathodes are more stable. At present, these chemistries also give less energy however.

3.2.6 NATO battery designations – nomenclature

Example: BA-5590/U is a primary battery based on Li/ SO_2 chemistry whereas BB-2590 is a rechargeable battery based on lithium ion chemistry. The /U in BA-5590/U designates universal use. This battery is equipped with a complete discharge device ("CCD switch") that the user is supposed to activate before scrapping the battery. The BA 5590/N is made according to Norwegian specification. It differs from BA-5590/U in having shunt diodes across all cells and no CCD switch. Most equipment can use all three batteries as their discharge connector and geometry is similar.

First letter: B = Battery
Second letter: A = Primary battery
B = Rechargeable battery
Primary batteries:
First digit: Chemistry.
0001 – 0999 Leclanché (Zn/MnO_2)
1000 – 1999 Mercury batteries (no longer in use)
2000 – 2999 Zn based, low temperature batteries
3000 – 3999 Alkaline (Zn/MnO_2 e.g. BA3030/U a D-size cell)
4000 – 4999 Magnesium batteries
5000 – 5999 3.0 V lithium (i.e. SO_2 and MnO_2)
6000 – 6999 3.6V lithium (i.e. $SOCl_2$ and SO_2Cl_2)
Secondary batteries 0001 – 0999 NiCd and NiMH batteries
2000 – 2999 LiIon

There is not established a good standardization system on lithium ion at present and deviations from the above is common. Note also that many batteries have an internal fuse and the rating for that fuse may be different from different batteries with identical geometry but different labels. For some batteries the voltage difference may also be significant; the discharge voltage window for BA-5800/U is between 5 and 6V, for BB-2800 it is between 5.5 and 8V.

In some countries (e.g. Germany) a color system is in use for primary batteries:
Light green: $Li/SOCl_2$
Violet: Li/MnO_2
Orange: Li/SO_2

4 Battery selection

Battery selection should be based on good knowledge of the load, the environment and the acceptable minimum duration. Occasionally, battery size will be determined by the power consumption and the minimum temperature. The following are the minimum information that should be available to the battery developer:

Load voltage window (the input voltage range the load tolerates for optimal operation).
Type of load (variable or constant, constant resistance, power or current, capacitive, inductive component, reactive?)
Current versus time profile (may depend on input voltage - measure)
Minimum and maximum temperature
Time between battery exchanges
Shock and vibration
Encapsulation (water resistant, submersible)
State of charge information to user?
Other batteries for other applications (if your GPS operates from AA batteries, it is convenient if your radio transmitter could use AA batteries as well)
Transportability (Lithium batteries are UN class 9 and special provisions apply)

The importance of the reduction of the number of different types of batteries in a military organization should not be underestimated. At the end of the day, the ability to use an identical battery for rangefinder, GPS and radio may save your life. It also makes the logistics much easier and may give a significant reduction in cost if a high volume production battery can be used..

As an example, take the following requirement for a battery for a data logger. To make things simple, the equipment is unattended, thus a live SOC is not required (such as possible with a "smart battery"):

Voltage window / V_{min}, V_{max}	4.5V to 9.0V
Current / time	2.0 A for 10 sec, 0.2 A for 90 sec, periodic
Calculated average current	0.38 A
Temperature range T_{min}, T_{max}	-20 ºC to +50 ºC
Duration between change	1 day, i.e. 24 hours
=> Calculated required capacity	9.12 Ah

Table 4.1 Battery requirements for a hypothetical application.

4.1 Primary batteries

Given the voltage window and the cell chemistry, the serial connection must be **4S** with Li/FeS_2, **2S** or **3S** with Li/SO_2 or Li/MnO_2, and **2S** with $Li/SOCl_2$ and Li/SO_2Cl_2.

A battery that is able to deliver the required capacity at -20ºC and 2 A constant current discharge would be a conservative choice. As a start one might look at the technical data for LM33550, (a $LiMnO_2$ cell from SAFT, see Figures 4.1 and 4.2). Each cell string must have a serial diode and a voltage loss V_D of 0.3 V over the diode must be taken into consideration. Thus the relevant cut-off cell voltage V_C for this application is given by

$(2*V_C – V_D)/2 > 4.5V$, thus $V_C > 2.4V$

At room temperature the capacity is ca 10 Ah when discharged to 2.4V, but falls to ca 4 Ah at −20ºC at 2A discharge current and a cut-off voltage of 2.0V. Thus a parallel connection of cells is necessary. A guess is a 4 cell battery in a **2S2P** connection. The current is now reduced to 1A per cell and according to the figure the capacity per cell increased to ca 5.5Ah at 2.0 V cut-off. As the data for 2.4V cut-off are lacking, they need to be determined experimentally, but figure 4.2 gives an indication: at 1A and -20ºC the average voltage during discharge is 2.3V, less than the required 2.4V. At the average current 0.38A, the mid-discharge voltage is 2.4V according to figure 4.2. In any case, this battery design is marginal at -20ºC. The capacity at -20ºC and 2.0V cut-off is 11Ah which is greater than 9.12 Ah and the discharge is not constant 2A, but intermittent, so it might work, but this must be verified experimentally.

In a case like this when the average current is different from the peak current, experimental verification of the battery performance is essential, both in order to avoid excess battery size from being too conservative and in order to avoid performance loss at high current and low temperature. Note however that some over design should be made in order to compensate for aging. Manufacturer’s data are usually based on fresh cells.

Used at room temperature, the battery capacity will be ca 23 Ah, sufficient for more than 48 hours operation. Thus a SOC indicator may be a good investment as an alternative to a daily battery exchange.

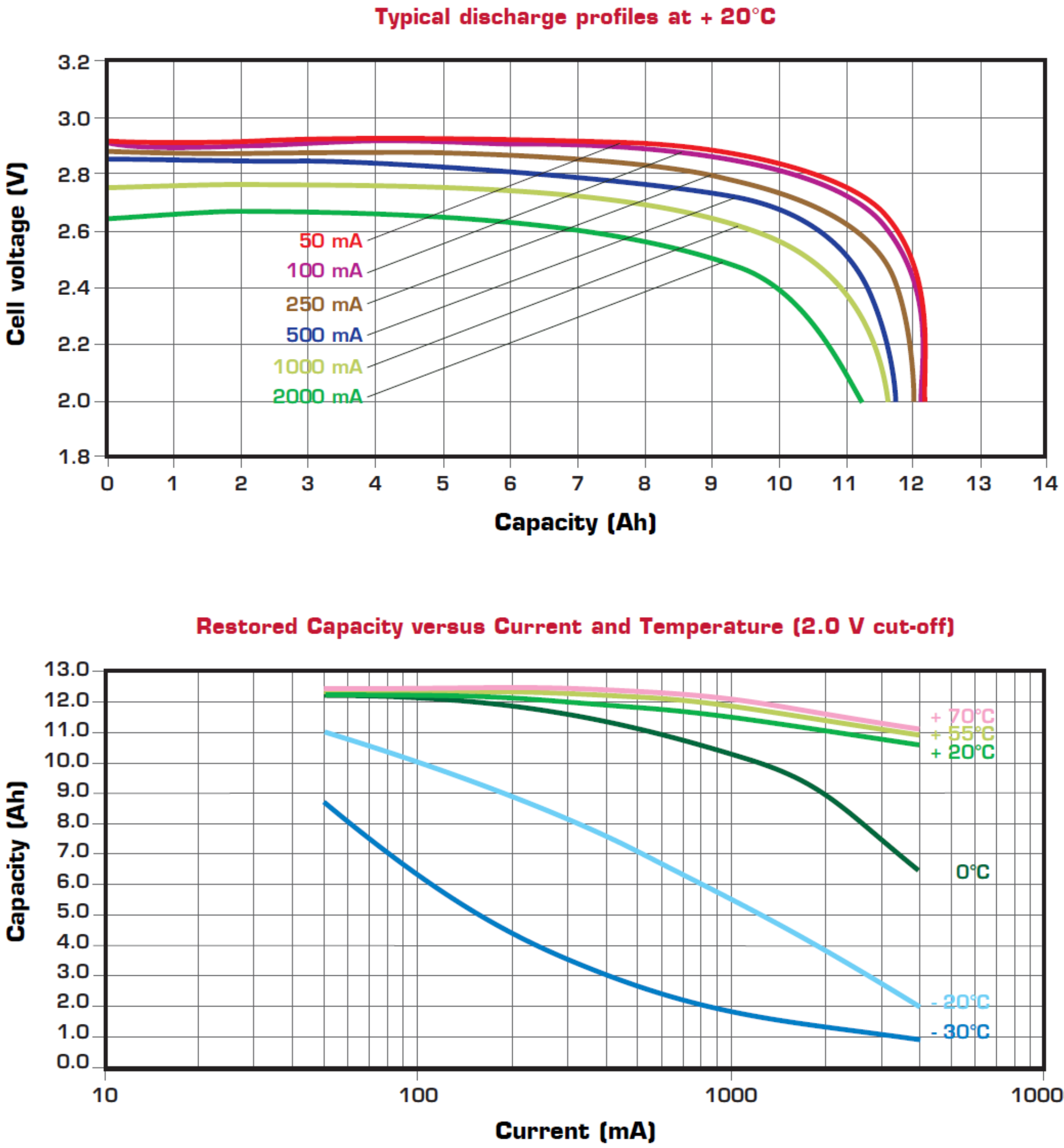


Figure 4.1 *Upper curve: Discharge voltage and capacity at room temperature as a function of load. Lower curve: Capacity to 2.0V discharge voltage as a function of load current and temperature. From SAFT LM33550 LiMnO$_2$ cell data sheet.*

A safe, but conservative solution would be to use a **3S2P** connection of cells. In this case exceeding the upper voltage limit at open circuit voltage is a consideration. As soon as the load is connected, the battery voltage will be within acceptable limits. Diodes with a large voltage drop may also be used.

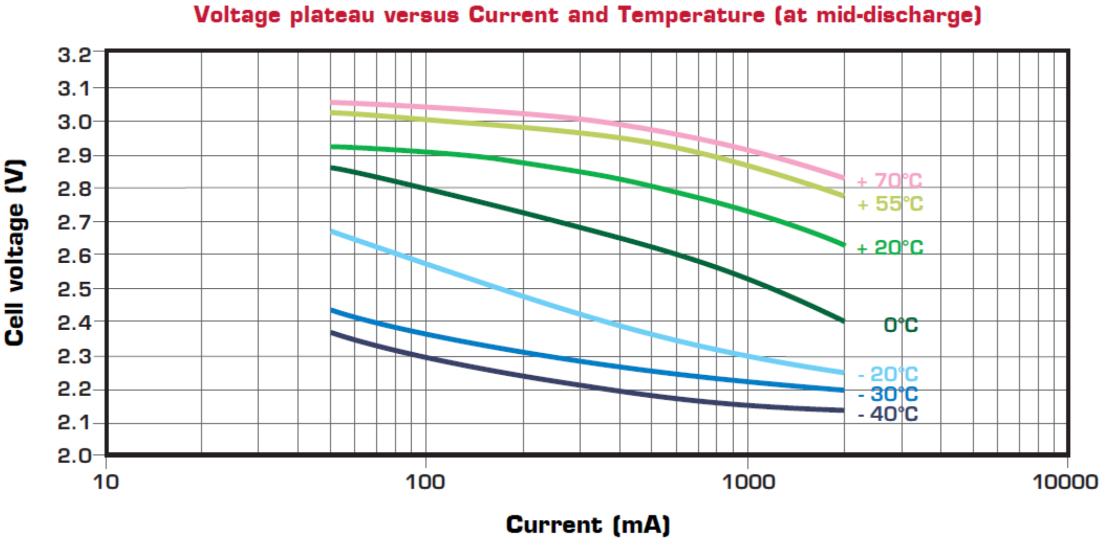


Figure 4.2 "Average" discharge voltage for SAFT LM33550 $LiMnO_2$ cell as a function of temperature and current.

A similar evaluation of other cell chemistries such as Li/SO_2 e.g. SAFT LO26SHX in a **3S2P** configuration, gives approximately identical performance at – 20ºC and lower weight, but also significantly less capacity at room temperature.

4.1.1 DC/DC converter

In the end, an evaluation of cost, logistics (availability), etc must be made. This consideration should also include the use of a standard battery with the required power and energy capability and the use a DC/DC converter to match the voltage window requirement. For this application the BA5598/U would be a good choice. This battery is produced in large numbers, is rugged and qualified for military use and transport according to UN rules and is easily available. The battery is made from 5 "fat D" Li/SO_2 cells in a **5S** configuration and contains ca 100 Wh. Similar batteries are available within the Bx y598 family. They share the same geometry, connector and voltage window and exist in both primary and secondary versions. Noise (EMI) from the DC/DC converter could be a concern.

4.1.2 AA and AAA primary cells

Most batteries in use today are based on one or more alkaline AA or AAA cells or cells with similar geometry and voltage. They exist as rechargeable cells (NiMH and NiCd) and as primary cells of different chemistries. Typical cell voltage is from 1.2 to 1.5V. Alkaline cells are cheap, available nearly anywhere and give a reasonable performance at room temperature. At low temperature or high current however, they perform poorly. Figure 4.3 shows the difference between alkaline AA-cells and lithium iron disulfide AA cells at room temperature and at 0ºC. For the user, the significantly lower weight of the iron disulfide cells comes as an added bonus

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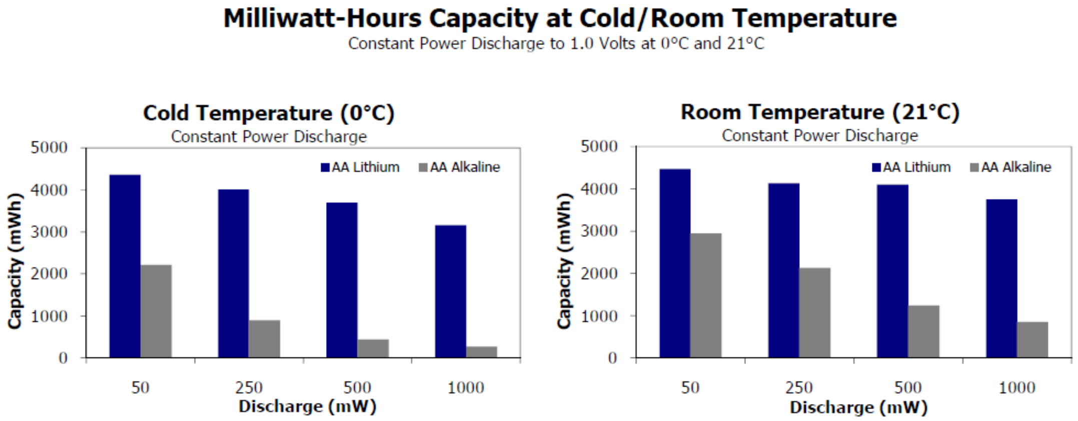

Figure 4.3 Comparison of Energizer L91Li/FeS$_2$ and Energizer alkaline (Zn/MnO$_2$) AA cells. (IEC designation LR6).

The weight of one L91 cell is 14.5 g versus 24.1 g for an alkaline cell. For a soldier carrying many cells, the reduced weight and increased capacity would be most welcome.

4.2 Secondary batteries

In many applications, the use of rechargeable batteries is both better and cheaper than the use of primary batteries. Nickel cadmium batteries (NiCd) cells have excellent low temperature performance, long life, but low energy density. Cadmium has recently been banned in consumer batteries and the market for small NiCd batteries have been taken by the NiMH systems or by lithium ion. For larger, vented or valve regulated batteries, both lead acid and NiCd are in use.

NiMH cells are in use in large numbers as AA and AAA cells for consumer and military applications. Be aware of the large difference in low temperature performance and self discharge rate between the different producers of NiMH batteries. Good power capability and low cost has made NiMH batteries market leaders in power tools, but this position is now challenged by lithium ion batteries which have higher specific energy and power.

Some lithium ion and lithium ion polymer batteries are very good with respect to energy density, power capability and performance at low temperature. A typical example is the capacity of the Saft MP 176065 cell where the capacity at C/5 is reduced only from 6.8Ah at +20ºC to ca 6.0Ah at −20ºC. The reduction in energy content is of course larger as the voltage during discharge at low temperature is reduced, but still the performance is impressive. The datasheet for MP176065 is shown in Appendix A.

Similar good performance is available from other producers such as KOKAM and AGM. Other products may have a large reduction in capacity at low temperature.

Going back to the requirements in Table 4.1 it looks as if a good solution might be a lithium ion battery in **2P2S** configuration. Even after aging to 80% of nominal capacity, a battery made from e.g. 4 MP176065 cells would exceed the requirements with a good margin. Batteries based on this cell are used in Norwegian military equipment such as the multirole radio MRR and the light multirole radio LFR.

The cell that is produced in the highest volume at present is the cylindrical 18650 cell. (The designation describes the geometry: 18 mm in diameter and 65 mm tall). The cell (see figure 3.4) is used in nearly everything from laptops to electric vehicles (EV) because of its relatively low cost. An EV battery may be composed of modules, each module made from 240 cells in a **20P12S** configuration (48V / 50Ah). A 20 kWh EV battery may be composed of 10 such modules. Appendix B shows the datasheet for an 18650 cell.

5 Transport

Lithium and lithium ion batteries are dangerous goods and classified in UN group 9. They are classified as UN3090 (lithium primary battery), UN3091 (lithium primary battery in equipment), UN3480 (lithium ion battery) and UN3481 (lithium primary battery in equipment). The batteries must pass specified tests in order to be legally transported and special restrictions apply to their transport by land (ADR), air (IATA and ICAO) and sea (IMO) including requirement to their packaging. The foundations for the rules are given in UN rules and recommendations for transport of dangerous goods. http://www.unece.org/trans/danger/publi/manual/manual_e.html. Most restrictions are on transport in airplanes and the rules at the time of writing can be found in http://safetravel.dot.gov/PHMSA_battery_guide.pdf. Note that the individual airlines may have more restrictive policies.

Cells and batteries below a certain energy content and that have passed the tests are exempt from the restrictions mentioned above. As the rules change, it is the user's responsibility to be informed of the newest set.

6 Storage

Batteries are best fresh, but if they need to be stored, they should be stored dry and not too warm. For batteries with an aqueous electrolyte, fridge storage has proved very effective in extending the storage time. Lithium ion and lithium polymer should be stored at ca 30% SOC, and as most BMUs are powered by the battery, the BMU should be disconnected or they need frequent maintenance charging. They should not be stored fully charged however, as the rate of deteriorating is largest when fully charged, nor should they be stored in a discharged condition as discharge below the end of discharge voltage (by self discharge or load from the BMU) destroys the battery. The deterioration (non recoverable capacity loss) rises significantly when stored at elevated temperature.

Larger amounts of lithium batteries should be stored in a separate building. Both the risk of fire and the corrosive nature of the gas from venting or burning lithium and lithium ion batteries make separate storage sensible. The storage facility should be equipped with a sprinkler system for firefighting that can be connected and activated from outside the building. In order to avoid unintentional water damage, water should not be permanently connected. Remote activation is important as experiments in our lab show that the penetration power of cell fragments is sufficient to penetrate 2 mm Al sheet. Flame tongues from the door opening in a burning German battery storage facility left burn marks on trees 40 m from the door. (Largely Li/MnO_2 batteries).

7 Disposal

After discharge or when the end of life for a rechargeable battery has been reached, the battery must be disposed of. In contrast to silver zinc or lead acid batteries, the scrap value of lithium primaries is negative. At the same time, they are not very harmful to nature, locally however they may inflict harm to the environment caused by poisonous or corrosive components. (Sulfur dioxide, thionyl chloride and sulfuryl chloride batteries and lithium ion batteries containing hexafluoro phosphate). Both residual electric energy and their content of organic electrolyte (lithium ion, lithium manganese oxide and lithium polymer) may also make disposed batteries a fire risk.

The scrap values of cobalt and of nickel based batteries are positive and collection of used batteries is taking place in most countries. Cells with cobalt containing cathodes (such as most PC-batteries) are considered environmentally harmful which makes regulated disposal mandatory. Lithium ion batteries with manganese oxide or iron phosphate cathodes have a negative scrap value. An increase in the cost of lithium is expected from the increased use of EV and this will affect the interest for recycling.

Collection of spent batteries in Norway is organized by AS Batteriretur. See www.batteriretur.no

8 If an accident takes place...

One should have seen the video ”Lithium Batteries – A matter of safety”. The video can be down loaded from www.ffi.no and from www.mil.no/multimedia/archive/00110/Lithium_Battery_Saf_110961a.wmv

8.1 Fire

Experience has shown that water or water based foam are the best extinguishing agents. This is totally independent of battery type or chemistry. The point is to cool the cells in the battery as rapidly as possible. The smoke is probably poisonous, so use self contained breathing apparatus or at least a gas mask. If the battery is large or within a pressure resistant container it is recommended to evacuate to safe distance.

After the fire is it important to wash all equipment with water in order to remove adsorbed acids and salts. If this is not done, the risk is that it continues to corrode.

8.2 Venting / electrolyte leak

Remove the battery and dispose of it according to local rules and regulations. Wash exposed equipment with water. Avoid skin contact, use gloves. The esters used in lithium ion and polymer cells smell good, but avoid getting it on the skin as hydro fluoric acid may be formed from hydrolysis of the salts. Wash with large amounts of water if contact is suspected.

Equipment that has been exposed to electrolyte or electrolyte vapor must be cleaned quickly to avoid corrosion. Switch it off, disconnect and remove any batteries.
Sodium hydrogen carbonate ($NaHCO_3$) is a universal agent when neutralizing electrolyte from nearly all battery chemistries. It is cheap and non-toxic and can be used as a powder or as a solution for washing equipment.

9 Acknowledgements

I would like to thank Captain Steinar Mathiesen at the Forsvarets laboratorietjeneste (FOLAT) EMC / Kraftforsyningslaboratorium for help with chapter 3.2.6 and for his proof reading and comments.

10 List of acronyms

AC	Alternating current
ADR	The European Agreement concerning the International Carriage of Dangerous Goods by Road
BMU	Battery management unit (“battery control electronics”)
CCD	Complete discharge device, connects a resistor to the battery (suspect of occasional arson)
CID	Current interrupt device.
C-rate	See chapter 3.2.1
DC	Direct current
IATA	International Air Transport Association
ICAO	International Civil Aviation Organization
IMO	International Maritime Organization
GTM	Glas to metal seal, a penetrator used in hermetic cells
LEL	Lower Explosive Limit (4% for H_2 in air)
NiCd	Nickel cadmium
NiMH	Nickel metal hydride
PTC	Resistor with very Positive Temperature Coefficient (“polymer fuse”)
SOC	State of Charge, capacity relative to fully charged capacity (%)
TCO	Temperature cut-off device, a CID that reacts on temperature

Further reading

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Hasvold Ø, Forseth S, Johannessen T C, Lian T (2007): ”Safety aspects of large lithium batteries”. FFI-rapport 2007/01666 (Kan lastes ned fra www.ffi.no)

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IEEE Standard for Rechargable Batteries for Multi-Cell Mobile Computing Devices. **IEEE Std 1625 – 2008.**

S9310-AQ-SAF-010 Technical manual for batteries, navy lithium safety program responsibilities and procedures. NAVSEA 2004.

RECOMMENDATIONS ON THE TRANSPORT OG DANGEROUS GOODS, Manual of Tests and Criteria, ST/SG/AC.10/11/Rev.4 United Nations, New York and Geneva, 2003 (always look up the last revision)

www.batteriretur.no (for Norwegian rules and regulations regarding disposal)

Appendix A

Rechargeable lithium-ion battery
MP 176065 Integration™

High performance
Medium Prismatic cell

Saft always supplies MP cells in assemblies or as customized battery system constructions

Benefits

- A broad operating temperature range
- Extended autonomy and life for mobile systems
- Recommended for ruggedized designs
- Easy integration into compact and light systems
- Used in potentially explosible atmospheres
- Reliability and peace of mind
- Aluminium casing
- Very high energy density *(375 Wh/l and 178 Wh/kg)*
- Unrivalled low temperature performance

Key features

- Excellent charge recovery after long storage, even at high temperature
- Maintenance-free
- Long cycle life *(over 70 % initial capacity after 600 cycles, C charge rate, C/2 rate 100 % DoD at 20°C)*
- Restricted for transport *(Class 9)*
- Compliant with IEC 61960 standard
- Underwriters Laboratories *(UL)* Component Recognition *(File Number MH 12609)*

Main applications

- Mobile asset tracking
- Rack-mount telecom batteries
- Small UPS
- Future soldier equipment
- Portable radios
- Portable defibrillators
- Professional portable lighting
- Electric bikes and personal mobility

Electrical characteristics

Nominal voltage (1.4 A rate at 20°C)	3.75 V
Typical capacity 20°C (at 1.4 A 20°C 2.5 V cut-off)	6.8 Ah
Nominal energy	26 Wh

Mechanical characteristics (sleeved 100 % charged cell)

Thickness *(Thickness tends to increase with cycling, typically obtained after 600 cycles. Consult Saft)* *(At beginning of life 18.6 mm)*	20.3 mm
Width max	60.5 mm
Height max (including protection circuit)	70 mm
Typical weight (including protection circuit)	143 g
Lithium equivalent content	2.04 g
Volume	68 cm^3

Operating conditions

Charge method	Constant Current/Constant Voltage
End charge voltage	4.20 +/– 0.05 V
Maximum recommended charge current**	7.0 A (~C rate)
Charge temperature range*	– 20°C to + 60°C
Charge time at 20°C	To be set as a function of the charge current: C rate → 2 to 3 h C/2 rate → 3 to 4 h C/5 rate → 6 to 7 h
Maximum continuous discharge current**	14 A (~2C rate)
Pulse discharge current at 20°C	up to 30 A (~4C rate)
Discharge cut-off voltage	2.5 V
Discharge temperature range*	– 50°C to + 60°C

* *For optimized charging below 0°C, 60°C and discharging at – 50°C, consult Saft.*
** *Electronic protection circuits within battery packs may limit the maximum charge/discharge current allowable. Consult Saft.*

September 2009

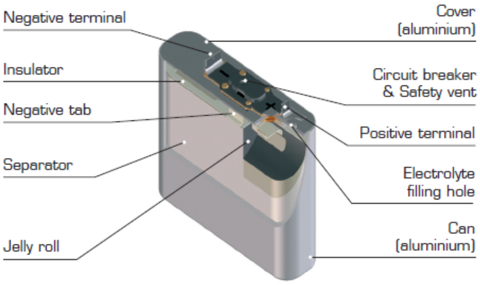
MP 176065 Integration™

Battery assembly

In order to operate properly, individual Li-ion cells are mechanically and electrically integrated in battery assemblies specific to each application. The battery assembly incorporates electronics for performance, thermal and safety management.

Technology

- Graphite-based anode
- Lithium Cobalt oxide-based cathode
- Electrolyte: organic solvents
- Built-in redundant safety protections
  (shutdown separator, circuit breaker, safety vent)
- Batteries assembled from MP cells feature an electronic protection circuit



Built-in protection devices ensure safety in case of:

- Exposure to heat
- Exposure to direct sunlight for extended periods of time
- Short circuit
- Overcharge
- Overdischarge

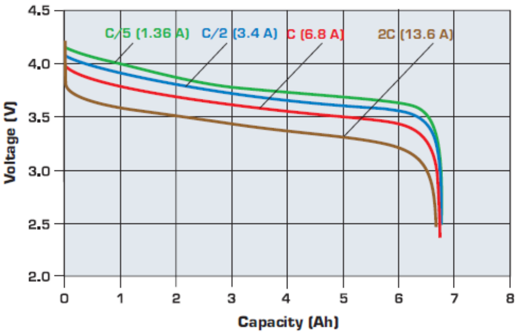
When handling Saft MP batteries:

- Do not disassemble
- Do not remove the protection circuit
- Do not incinerate

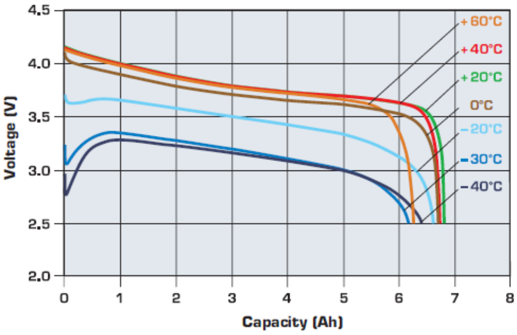
Transportation and storage:

- Store in a dry place at a temperature preferably not exceeding 30°C
- For long-term storage, keep the battery within a 30 ± 15 % state of charge

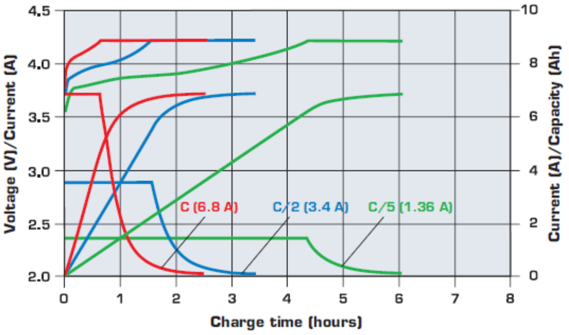
Capacity versus current at +20°C



Typical discharge profiles (1.36 A - C/5 rate)



Charge characteristics to 4.2 V at +20°C



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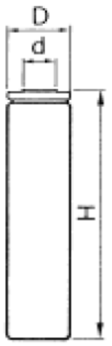
Appendix B

SANYO
Lithium ion

May. 2007

Cell Type UR18650F

Specifications



Dimensions(Typ.) of Bare Cell	H	64.7 mm
	D	18.05 mm
	d	9.0 mm

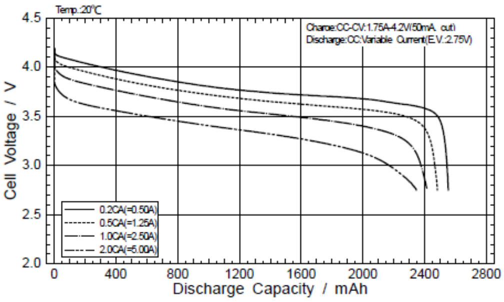
Nominal Capacity		Min.2500mAh
Nominal Voltage		3.7V
Charging Method		Constant Current -Constant Voltage
Charging Voltage		4.2V
Charging Current		Std.1750mA
Charging Time		3hrs.
Ambient Temperature	Charge	0～+40℃
	Discharge	-20～+60℃
	Storage	-20～+50℃
Weight (Max.)		47.0g
Dimensions (Max.)	(D)	18.10mm
	(H)	64.80mm
Volumetric Energy Density		554Wh/l
Gravimetric Energy Density		196Wh/kg

Maximum size without tube

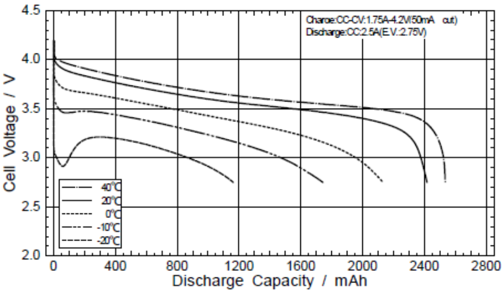
*When designing a battery pack, get the precise information on a cell battery drawing

Typical Characteristics

Discharge rate characteristics



Discharge temperature characteristics



Charge characteristics