FFI RAPPORT

Safety aspects of large lithium batteries

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8) **ABSTRACT**

A battery containing 294 cells in the form of 7 modules of 42 DD lithium / sulfuryl chloride cells in a 7S6P configuration exploded during in-line inspection pigging of a 30” gas pipeline in April 1999. The gas pressure in the pipeline was ca 160 atm. It is likely that the explosion was caused by a leak in the battery container. This report describes the behaviour of the 30 Ah lithium / sulfuryl chloride DD cell (CSC93) under hydrostatic compression (in water and in inert gas), the effect of state charge and the effect of potting. Potting was found to have a major effect on the behaviour. The explosion was reproduced when a battery module of 21 cells was exposed to a slow increase in pressure. The explosion occurred at ca 100 atm, as predicted from the compression experiments on single cells.

In addition, some experiments with respect to the behaviour of batteries with different battery chemistries under abuse conditions were made. This includes the effect of slow heating, the effect of fire on sealed battery containers, the effect of nail penetration, the effect of water intrusion and the effect of abusive charging.

Based on the experimental results, general recommendations on how to improve the safety of the use and storage of large lithium batteries have been made.

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Safety aspects of large lithium batteries

1 INTRODUCTION

Lithium batteries are used in ever increasing amounts because of their superior properties compared to more conventional batteries. Typically they exhibit good rate capability and low self discharge over a large range of temperature. Specific energy densities of more than 200 Wh/kg (or five time's lead acid batteries) are typical for the best rechargeable lithium batteries. Primary batteries may contain even more energy; specific energy density of 600 Wh/kg is reported for some systems. This is comparable in magnitude to traditional explosives and if the energy is not delivered to the user as electric energy, but transferred directly to heat in the battery over a short time period, the results might be devastating.

The history of lithium batteries is full of examples of explosive fires destroying plants and ware houses and of explosions in equipment using such batteries. As more and more knowledge has accumulated however, the frequency of accidents has decreased drastically in spite of an enormous increase in their use, but laptops and mobile phones catching fire is not totally uncommon – even today.

The Norwegian Army was one of the first to introduce lithium batteries (lithium sulphur dioxide (Li/SO_2) chemistry) in the late seventies because of their excellent properties, also at low temperature. Of cause we got our share of explosions and the Army Battery laboratory burned down in 1980. After these incidents, FFI has been more or less continuously involved with safety related work on lithium batteries (Vaaland and Eriksen1982, Hasvold et al 1984, Størkersen et al 1986) and has established an international network within NATO. In addition, FFI participates in The Lithium Battery Technical/Safety Group, a forum for US Government agencies. These networks give us access to unpublished results on safety incidents and valuable test results on battery abuse, fire fighting and damage reduction.

At present, FFI is actively working on lithium ion batteries (both polymer and hermetically sealed) for use in autonomous underwater vehicles (AUV) such as HUGIN 1 and HUGIN 1000, and as power sources for soldier systems (NORMANS project).

The major driving force for this specific project was an incident that happened in the Statpipe gas pipeline between Heimdal and Draupner. Lithium battery powered pipeline inspection tools ("Pigs") are used by the oil and gas industry for internal inspection of pipelines. Usually, the battery is confined within a sealed unit. If this seal develops a defect, an internal rise of pressure takes place until the external pressure is approached. A battery containing 294 cells in the form of 7 modules of 42 DD lithium/ sulphuryl chloride cells in a 7S6P configuration exploded during pigging of a 30" gas pipeline in April 1999. The gas pressure in the pipeline was 16 MPa (160 Bar). Even larger batteries, based on 567 cells, are used in 40" pigs. Similar batteries are used as emergency power in diver habitats.

FFI was asked to undertake a project for Statoil ASA and Gassco ASA with the objective of identifying the cause of the accident, and to look at ways to improve the safety of the system. Alternative power sources for this application were also of interest. The project started in the autumn of 2003 and was concluded in the spring of 2006. Ahead of this work, the SINTEF study "Risk analysis – use of lithium batteries in pipeline pigs" (Report no. STF38 F02403, January 2002) and Det Norske Veritas Report "Risk analysis of lithium Batteries in Pipeline Pigs" (DNV report no 2002-3217) as well as the Statoil governing document "Transportation, storage and pigging with internal pipeline tools containing Lithium batteries" WR1502, version 2.01 Valid from 01.06.2003 were made available to us.

The target for this project was to:

- Collect available literature on the safety aspects of lithium batteries
- Experimentally evaluate conditions that may induce fire or explosion in lithium batteries, specifically:
    - Determine the effect of hydrostatic pressure on cells
    - Determine the effect of penetration of water into cells and batteries
- Make recommendations on how to handle battery fires
- Make recommendations on how to build batteries

Because some of this work is of general interest to Kongsberg Maritime ASA (KM) and to the Norwegian Defence, part of this work was also financed by KM and by FFI.

2 SAFETY DEVICES IN LITHIUM CELLS AND BATTERIES

In addition to the selection of the best high quality chemicals and components in order to make the cells as safe as possible, responsible manufacturers of lithium cells and batteries invariably equipped them with a number of safety devices to protect the cells against abusive conditions such as short circuit, unintentional charge, overcharge and over-discharge and voltage reversal. One also tries to reduce the damage in case of exposure to external heating. However it should be understood that, as cells contain both fuel (lithium) and an oxidant (the cathode material) within a single container, a high energy cell that is "safe" under all conditions of abuse is not a possible option. Some cell chemistries also use an organic electrolyte. In presence of oxygen (air), burning electrolyte may contribute to the energy released by a battery fire.

Some of the more common safety devices will be described in the following:

2.1 Cells

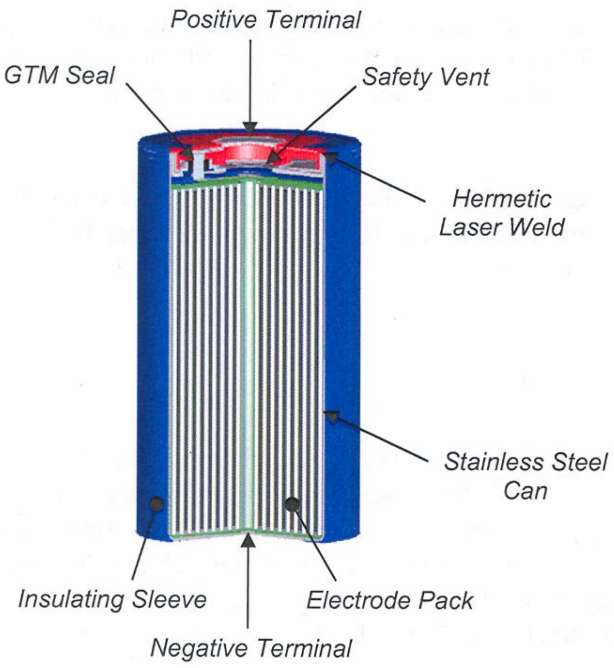
2.1.1 Hermetically sealed cells

The content of the cell can is contained within a metal container, commonly (but not always) connected to the negative electrode (anode). The contact to the positive electrode (the cathode) is via a glass to metal seal welded into the can. The can contains the anode or “fuel” (lithium, a lithium alloy or lithium intercalated into carbon or some other host lattice in lithium ion cells); an electrolyte (a liquid into which a lithium salt has been dissolved) and an oxidant. In addition, the cell contains a separator between the positive and negative electrode and current collectors to the electrodes. If the electrolyte liquid is also the oxidant, (e.g. sulphur dioxide, thionyl chloride or sulfuryl chloride), the term catholyte is often used. In solid cathode chemistries, (e.g. manganese dioxide and lithium ion cells) the electrolyte is made from a mixture of organic liquids with a flammability very similar to gasoline.

The cell also contains a void volume in order to tolerate expansion of the materials in the cell. When the cell is heated, an increase in the vapour pressure of the electrolyte takes place. Whether this heating is external, is caused by the current flowing in the cell or is caused by an exothermal reaction taking place in the cell, the result is an increase in pressure. At some temperature, the vapour pressure of the electrolyte will cause the cell can to burst open.

One consequence of this void volume is that if the cell is exposed to an external hydrostatic pressure exceeding a certain value it must collapse.

Figure 2.1 shows an example of a high rate, spirally wound cell design and figure 2.2 a low-rate design (bobbin cell). The spirally wound cell has very much lower internal resistance, resulting in very high current capability, but the larger amount of inert materials such as separators and current collectors also results in lower capacity at very low rate compared with the bobbin cell.



AGM cylindrical cell construction

Figure 2.1 High rate, spirally wound cell showing the design. The jelly roll in this D-cell is 1.8m long unwound, giving a large electrode surface area within a small cell. (Courtesy of AGM)

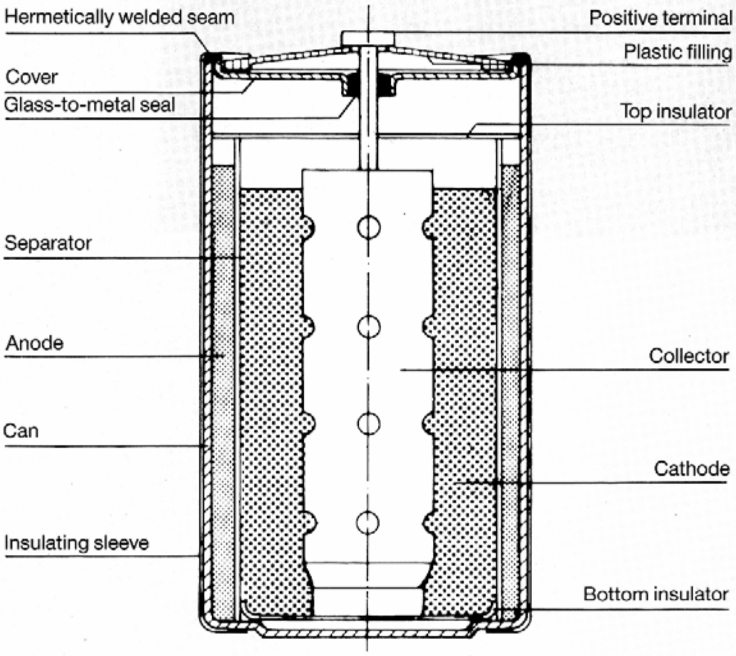


Figure 2.2 Lithium thionyl chloride low rate cell (bobbin design). The cathode is made from highly porous carbon powder and a binder. Courtesy of Sonnenschein GmbH.

Safety valve
Most manufacturers equip the cells with a weak spot, a safety valve, that allows the cell to burst open at a temperature well below the melting temperature of lithium (180ºC) and most also at a temperature well below the mechanical breakdown temperature of the separator between the electrodes. For cells with a liquid cathode, the composition of the electrolyte changes with state of charge (SOC), making the opening temperature of the safety valve a function of SOC. Note also that sulphur dioxide (boiling point -10ºC) is under a pressure of ca 3-4 atm at room temperature whereas the boiling point of most other electrolytes are in the 80 to 120ºC range.

Fuse
Some manufacturers equip their cells with a melting fuse. If the current exceeds a certain value, the fuse opens (and the cell stays open circuit). One producer (SAFT) has refined that so that if the cell pressure exceeds a certain level, the bulging of the cell top also breaks the circuit.

In rechargeable cells, it is more common to use a positive temperature coefficient resistor fuse (PTC). If the load is removed and the temperature allowed to fall sufficiently, the fuse reconnects.

Shut-down separator
This separator is a sandwich of different porous polymers. If the temperature exceeds a certain limit, the polymer with the lowest melting point melts and fills the pores of the high melting point polymer. The result is an increase in the internal resistance of the cell reducing the short circuit current. The cell is no longer operational as the change to the separator is permanent.

Shunt diode
If one cell in a cell string has lower capacity then the other cells, it will be driven into reversal at the end of discharge. The purpose of the diode is to limit the reverse voltage during conditions of over-discharge to a safe value. It may be built into the cell or added as part of the battery protection circuit.

2.1.2 Poach cells

Poach cells do not have a metal can, the cell contents are confined within a plastic poach, similar to vacuum packed coffee grains. If an internal pressure develops, the poach “balloons” and breaks, making the explosion hazard negligible. A fire may develop however. Because they do not contain a void volume, their operations is not affected by external pressure, making them the favourite candidate for deep-sea autonomous underwater vehicles (AUV) batteries.

With the exception of safety valves, poach cells and hermetic cells and batteries have similar protection devices. Poach cells typically get their mechanical rigidity from the solid electrolyte, typically a polymer into which a liquid electrolyte is absorbed, forming a gel. In addition, binders in the electrodes such as PVDF contribute to the stiffness of the cell.

Most polymer cells also depend on the external pressure for stiffness to some extent. During production, they are evacuated (very similar to vacuum bagged coffee). Poach cells are used commercially in lithium manganese dioxide primary batteries and in lithium ion polymer batteries. It is expected that more cell chemistries with solid cathodes will be available commercially as poach cells due to reduced weight and cost of production. Figure 4.2 shows a lithium ion polymer cell.

2.2 Primary Batteries

Good design practice for making primary lithium batteries is to connect the cells serially into strings and then connect the strings in parallel via serial diodes. Each string should also be protected by a fuse. An over-temperature device (thermo switch) is nearly always used in high rate batteries. Battery monitoring circuits are rare but their use is increasing, allowing the user full control over state of charge and state of health of the battery. In batteries with parallel strings, equal sharing of the current between the strings is essential and requires use of similar cells in the strings unless each string has the capability of taking the full load.

2.3 Rechargeable (secondary) batteries

Typically each cell is equipped with a fuse and the fused cells connected in parallel. These parallel assemblies are then serially connected. Because lithium ion batteries are very sensitive to over-charge and over-discharge, battery monitoring and control circuits are invariably used. As most batteries catch fire on overcharge, dual and independent protection circuits that work on the cell level are usually used.

2.4 Battery nomenclature

A battery composed of 4 serially connected cells is a **4S** battery and a battery composed of 3 parallel connected cells is a **3P** battery. Thus a **7S3P** battery is composed of. 3 parallel strings, each string consisting of 7 serially connected cells.

2.5 Battery containers

Battery containers shall either be vented or be equipped with a safety device that opens in a controlled manner before the container fragments.

3 PROJECT PLAN

A pre-project with the aim of defining the experimental approach and to develop equipment was undertaken in the Autumn of 2003, (Prosjektplan for oppdrag 328001, Sikkerhetsaspekter ved store litiumbatterier i undervannsystemer) the project was concluded in the Summer of 2006. Main focus of the project was the effect on external pressure on the behaviour of cells and batteries. The cell involved in this incident was the lithium sulfuryl chloride cell CSC93 (DD size) from Electrochem Industries, Wilson Greatbatch Inc and most work has been concentrated on this cell.

Increasing the external pressure has the following consequences on a lithium cell:

- The opening temperature of the safety valve increases
- At some pressure the cell-can may collapse resulting in an internal short
- The cell might develop a leak (equilibrating the pressure)

If the compressing medium is not inert (e.g. natural gas, nitrogen) but (sea-) water, other reactions may take place

- Traces of water inside the cell destroy the solid electrolyte interface, SEI, between lithium metal and the electrolyte.
- Hydrogen, chlorine and oxygen might be formed in the battery compartment due to electrolysis of water.
- If the battery compartment fills with water, the heat capacity and the heat conductivity of the system increases, reducing the maximum attainable temperature for the system.

Main safety concerns by users of these batteries are gas or water leaking into the battery container during operation, and exposure of the battery containers to fire during transport and storage. This was then reflected in the plan for the experiments.

The plan described 6 different test series. Detailed descriptions of the apparatus and the results have been published in a series of separate notes. In this report, only a few selected results and a summary will be given. The experiments were:

3.1 External short circuit

Test 1: The cell was either at room temperature or preheated to its maximum operation temperature. The short was made with the aid of an electronic circuit composed of 5 parallel MOSFETs with an internal resistance of ca 0.007 ohm. Cell current was measured with a 60 mV / 100A shunt and cell current and cell wall temperature logged. Cell current was also logged on a high-speed digital oscilloscope. Some experiments were also taped on video.

3.2 Internal short circuit (nail penetration test)

Test 2: A nail (ø= 3.6 mm and length 95 mm) was driven through the cell and into a wooden base by a falling weight. Cell voltage and temperature were logged and the experiment taped on video

3.3 External hydrostatic pressure

Test 3: The cells were compressed in a container with 50 mm internal diameter and a volume of 360 ml and a safe pressure rating of 120 MPa. Figure 5.8 shows the tank after a cell explosion. The pressure container was either connected to a Shimadzu High Pressure Liquid Chromatography (HPLC) pump using deionised water or to a bottle of compressed nitrogen (15 to 20 MPa). Stainless steel tubing of 0.3 mm internal diameter was used between the pump or the gas bottle and the pressure vessel. The HPLC pump switched off automatically at 40 MPa. Weak bolts were used so that a pressure in excess of 60 MPa stretched the bolts, allowing the Oring in the lid to open as a safety valve. Some cells were potted in silicone rubber (Elastosil RT607 (Wacker)) ahead of pressurization.

Pressure, temperature and cell voltage were logged at 5 Hz, in later experiments also at 96 kHz during rapid change of values. In some experiments, the cells were discharged during the test with 3ohm. At least 3 parallel experiments were made.

CSC93 cells at 50 % SOC (State of Charge) were produced from fresh cells discharged for 15 hours at 1.00A ahead of the experiments. Cells at 0 % SOC were discharged to 2.50 V at 1.00 A. (See FFI/NOTAT-2006/02782 for details)

3.4 Heating of single cells

Test 4: Cylindrical cells were inserted into an aluminium block and heated at 4ºC per minute until 250ºC or until a destructive event took place. FFI/NOTAT-2006/02358 describes the experiments and the results in details.

3.5 Abuse tests of large batteries and battery modules

Abusive experiments were performed on battery packs confined in strong battery containers simulating either transponders or pig batteries exposed to fire. Due to the large energy in the batteries, worst case scenarios required larger safety radius than possible at the facilities at FFI. They were therefore undertaken at the Hjerkinn shooting range. The results are described in FFI/NOTAT-2006/02356.

3.6 Exposure of battery packs to fire

Test 5: Battery packs composed of 48 D-cells (thionyl chloride) were put into a stainless steel tube, open in one end and closed in the other and heated by a propane torch. (See FFI/NOTAT-2006/02356 for details).

3.7 Exposure of batteries to seawater

Test 6: Battery packs were confined into two sealed containers with enough seawater to cover the battery. Pressure, cell voltage and temperature were monitored and recorded. (See FF/NOTAT-2006/02356 for details).

4 CELLS, CELL CHEMISTRY AND DESIGN

Based on the applications, a list of cell chemistries of interest for evaluation was made. Table 4.1 gives a summary.

Cell chemistry /designation	Cell voltage and capacity	Size	Weight /g	Producer
Li/SO_2Cl_2 CSC93	OCV 3.9 V/ 30 Ah	DD	213	Electrochem Industries Wilson Greatbatch
$Li/SOCl_2$ SL780	OCV 3.6V / 16.5 Ah	D	92	Sonnenschein
$Li/SOCl_2$ LS33600	OCV 3.6V / 16.5 Ah	D	90	SAFT
$Li/SOCl_2$ LSH20	OCV 3.6 V / 13.0 Ah	D	100	SAFT
Li/SO_2 LO26SX	OCV 3.0 V/ 7.5 Ah	D/	85	SAFT (Hawker)
Li/MnO_2 U3360H	OCV 3.0 V/ 11 Ah	D/	117	Ultralife
Li-ion ICR34600	nom 3.6 V / 5.2 Ah	D	138	AGM
Li-ion polymer	nom 3.8 V/ 36.4 Ah	“brick”	1623	Ultralife/FFI

Table 4.1 List of evaluated cells. Cell voltage is either OCV = open circuit voltage or nom = nominal voltage, average voltage during discharge .

Inorganic electrolytes (catholytes) consist of a lithium salt (typically ca 1M Lithium aluminium chloride or lithium bromide) dissolved in the oxidant. These liquids are reduced during the discharge of the cell.

Organic electrolytes, generally used in lithium ion and lithium solid cathode primaries (i.e. MnO_2) are considered inert and do not normally take part in the cell reaction. They may however react with lithium. Salts such as lithium carbonate play an important role in the development of the passivation layer on the anode in lithium primary cells as well as in lithium ion cells. Under abuse conditions (elevated temperatures), reduction of the organic electrolyte may take place at the anode or the electrolyte might be oxidized at the cathode. The salts most commonly used are lithium perchlorate ($LiClO_4$) for manganese dioxide cells and lithium hexa-flurophosphate ($LiPF_6$) in lithium ion cells. Lithium perchlorate might oxidize cell components under abuse conditions and decomposition of lithium hexa-flurophosphate might give hydrogen fluoride, a poisonous and corrosive gas.

The physical data for some of the pure solvents and oxidants are shown i table 4.2:
(FW = Formula weight, Mp= melting point, Bp = boiling point, Fp = Flash point, d = density)

Name	Formula	Mol weight g/mol	Melting point °C	Boiling point °C	Flash point °C	Density g/ml
Sulfuryl chloride	SO_2Cl_2	134.96	-54.1	69.1	--------	1.667
Chlorine	Cl_2	70.91	-101.6	-34.6	--------	1.41 (liq, 16 bar, 20°C)
Thionyl chloride	$SOCl_2$	118.07	-104.5	76	--------	1.638
Sulphur dioxide *)	SO_2	64.04	-72.7	-10	--------	1.434 (liq.)
Acetonitrile	CH_3CN	41.05	-48	80-82	5	0.786
Ethylene carbonate (EC)	$C_2H_4CO_3$	88.06	35-37	244-245	160	1.320
Propylene carbonate (PC)	$C_3H_6CO_3$	102.09	??	238-239	132	1.118
1,2-dimethoxyethane (DME)	$C_4H_{10}O_2$	90.12	-69	82-85	0	0.8683
Tetrahydrofuran (THF)	C_4H_8O	72.11	-108	66	-17	0.886

*) SO_2 is commonly used together with aceto-nitrile, CH_3CN, in which case the electrolyte will be flammable

Table 4.2 Catholytes and solvents used in lithium cells. Source: Alfa Aesar 2006-07 Research Chemicals Catalogue and Wikipedia

These organic compounds have in common a high dielectric constant, making them excellent solvents for ionic salts. For the same reason, they are all soluble in water and spills should be flushed away with water. The catholytes are very corrosive and forms acids with water. They are effectively destructed with sodium hydrogen carbonate powder. ($NaHCO_3$). The organic electrolytes are all flammable, but THF is special in having a low flashpoint and in its ability to form peroxides with oxygen.

4.1 Lithium-liquid cathode batteries

Lithium-liquid cathode batteries comprise a versatile group of high energy density power sources with a variety of military and civilian application. The Li/SO_2Cl_2, Li/$SOCl_2$ and Li/SO_2 are such batteries. In these batteries, the electrolyte is composed of a lithium salt dissolved in a reducible solvent (e.g. SO_2, SO_2Cl_2, or $SOCl_2$). The electrolyte may also contain a halogen such as chlorine or bromine. Thus the electrolyte is also the oxidant and the cathode an inert material such as carbon. Because the cathode reaction is the reduction of the solvent, the term catholyte is often used for the electrolyte in the cell

The stability (K M Abraham, 1991) of the lithium-liquid cathode batteries is dependent on the formation of an insoluble, passivating film on the Li anode surface when the Li comes in direct contact with the catholyte. These films are described as solid-electrolyte-interphases, or SEI, since they are impermeable to electrolytes and other liquid reactants while transporting Li^+ across them. The film has a very low conductivity to electrons, thus the direct reaction between lithium metal and the catholyte slows down as soon as the film has been formed.

The SEI is responsible for the excellent storage properties of most lithium batteries and also for some of the less positive properties such as voltage delay. The properties of the film are affected positively by some proprietary additives in the electrolyte and negatively by impurities such as water or iron. Because the film is thin, it may crack if lithium melts allowing a direct reaction between the catholyte and lithium metal.

4.1.1 CSC93, Li/SO_2Cl_2

The Li/SO_2Cl_2 is spirally wounded, hermetically sealed and with a glass to metal penetrator for the positive electrode. The anode is lithium metal, welded to a metal strip which is welded to the can. The electrolyte consists of $LiAlCl_4$ dissolved in SO_2Cl_2 and saturated with Cl_2. The cathode is carbon with a binder pressed on to an expanded metal current collector.

During discharge, chlorine and sulfuryl chloride are reduced under formation of lithium chloride and sulphur dioxide. (Lazzar et al, 1981, Liang et al, 1981).

The overall cell reaction is

$$4\ Li + SO_2Cl_2 + Cl_2 \rightarrow 4\ LiCl + SO_2 \qquad (4.1)$$

or

$$2\ Li\ (s) + SO_2Cl_2 \rightarrow 2\ LiCl(s) + SO_2 \text{ ignoring chlorine} \qquad (4.2)$$

$LiAlCl_4$ forms a complex with SO_2 (Razzini et al, 1980), which as a consequence may lead to a reduced increase in the internal pressure during discharge as expected from equation 4.1. In addition Cl_2 and SO_2 will be consumed due to formation of SO_2Cl_2.

The dissociation reaction for SO_2Cl_2 is (Ciesla, 1986)

$$SO_2Cl_2 = Cl_2\ (g) + SO_2\ (g) \qquad (4.3)$$

When SO_2Cl_2 is consumed through equation (4.1) or (4.2), the equilibrium reaction (4.3) will be driven towards formation of SO_2Cl_2 reducing the available amount of free Cl_2 in the electrolyte.

The CSC93 cell and the 3PD0524 battery module were produced by Wilson Greatbatch / Electrochem Industries. The DD cell is 111 mm long and 33.6 mm in diameter. The cell is protected by an internal fuse and a shunt diode in the lid and a safety valve. Cell weight is ca 214 g. Each module contains 21 cells as 3 parallel strings of 7 serially connected cells (7S3P configuration). The module has a serial diode and a fuse in each string and a temperature breaker (104ºC) in the negative lead. The cells in the module are potted in an elastomer. Module weight was 6.141 kg.

4.1.2 Li/$SOCl_2$

Three types of Li/$SOCl_2$ cells were used, one with the designation LSH 20 which is a spirally wound high rate cell and two low rate bobbin cells (SL-780 and. LS33600). The cells LS33600 and LSH20 were equipped with safety vents, the SL-780 cell was not.

The anode (Besenhard, 1999) in the cell is lithium-metal foil and the cathode is made of porous carbon. Thionyl chloride serves as both the cathode active material and as solvent in the electrolyte, which is a 1M solution of lithium-tetra-chloro-aluminate ($LiAlCl_4$). The carbon cathode serves as a catalytic surface for the reduction of thionyl chloride.

The overall cell reaction is given by

$$4Li^+ + 2SOCl_2\,(l) \rightarrow 4LiCl(s) + S(s) + SO_2(g) \qquad (4.4)$$

Sulphur and SO_2 are soluble in the electrolyte, but sulphur may precipitates in the cathode pores at the end of discharge. LiCl is insoluble and precipitates at the surface of the carbon cathode, forming an insulating layer which terminates the operation of cathode-limited cells. (Fukuda et al, 1983). The distribution of LiCl within the cathode is rate dependent, partly explaining the low capacity of the bobbin cell at high discharge rate. Complex formation between SO_2 and $LiAlCl_4$ may reduce the pressure increase during discharge.
Transponders typically use batteries composed of 48 D cells and the duration of discharge may be up to some years.

4.1.3 Li/SO_2

The Li/SO_2 cell uses lithium as the anode and a porous carbon cathode electrode (Linden & MacDonald, 1980) with sulphur dioxide as the active cathode material. The electrolyte is a mixture of sulphur dioxide and an organic solvent, typically acetonitrile, containing dissolved lithium bromide. The discharge reaction is given below.

$$2Li^+ + 2SO_2\,(g) \rightarrow Li_2S_2O_4\,(s) \qquad (4.5)$$

As can be seen form equation (4.5), the SO_2 is consumed implying that the cell pressure is reduced during discharge. The discharge is generally terminated (Linden and MacDonald, 1980) by the full use of the available lithium or by the deactivation of carbon electrode due to blocking of the active area by the precipitation of the discharge product.

Li/SO_2 has been the preferred battery chemistry for the Norwegian Defence for the last 25 year and these batteries are used in large quantities in sizes from a few C-cells to large batteries of 10 D-cells or more. It has better low temperature properties than the chloro-halide cells, but its volumetric energy density is lower at moderate temperatures.

4.2 Lithium / solid cathodes

4.2.1 Li/MnO_2

The Li/MnO_2 cell has a lithium-metal anode and a MnO_2 cathode (Besenhard, 1999). The electrolyte is usually either lithium perchlorate ($LiClO_4$) or lithium trifluoromethanesulfonate ($LiCF_3SO_3$) dissolved in a mixture of tetrahydrofuran and 1,2-dimethoxyethane (DME) and propylene carbonate (PC). Different producers use different compositions and this affect both the safety characteristics and the low-temperature performance of the cell.

The MnO_2 used in the cell is anhydrous and have an optimized crystal structure allowing Li^+ to migrate into the crystal lattice. The overall battery reaction is

$$MnO_2 + Li \rightarrow MnO_2^-(Li^+) \qquad (4.6)$$

4.2.2 Lithium ion

In Li-ion cells the lithium metal anode is replaced with lithium intercalated in carbon. Carbon has the possibility to reversibly intercalate Li^+. The active material (AGM 2003 manual) of the cathode is also a compound that reversible intercalates lithium ions. $LiCoO_2$, which has a layered structure, is the most used material. During charging Li^+ is removed from the positive electrode and inserted in to the carbon electrode. The process is reversed on discharge. When lithium-ion cells are charged for the first time (or 'formed'), the lithium ions are transferred from the layers of the lithium cobaltite to the carbon material. Thereby the anode is formed.

$$LiCoO_2 + 6C \rightarrow Li_{1-x}CoO_2 + Li_xC_6 \qquad (4.7)$$

Subsequent discharge and charge reaction are then based on the migration of lithium ions between anode and cathode:

Discharging →

$$Li_{1-x}CoO_2 + Li_{x+y}C_6 = Li_{1-x+y}CoO_2 + Li_xC_6 \qquad (4.8)$$

← Charging

Figure 4.1 shows how the Li^+ ions and electrons migrate during discharge.

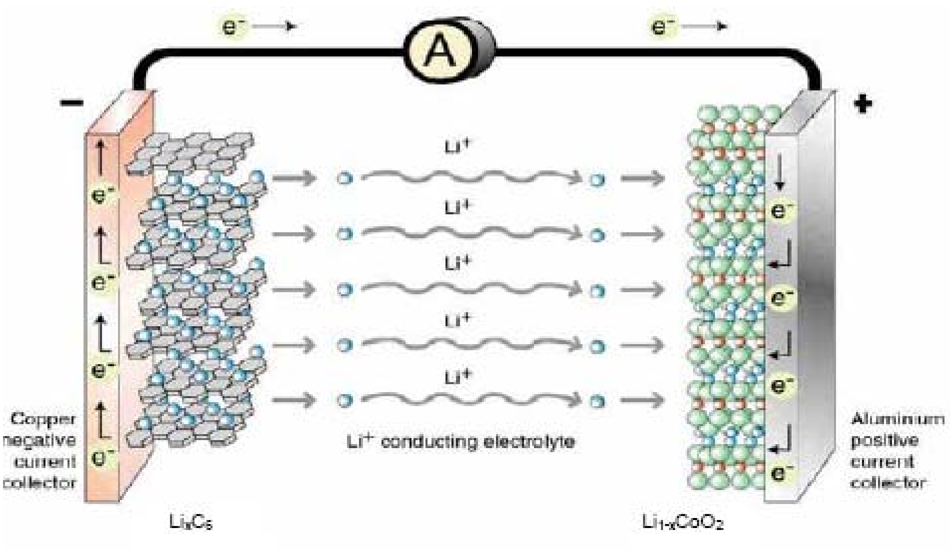


Figure 4.1 Lithium-ion discharge cycle (Courtesy AGM 2003).

A solution of a lithium salt in an organic solvent is used as electrolyte. In AGM cells, a mixture of ethylene carbonate and ethyl methyl carbonate with addition of lithium hexafluorophosphate (ca 1 M) is used for that purpose. This is a fairly typical composition, used by most producers.

4.3 Li-ion polymer

Lithium polymer batteries have the same common electrochemistry as conventional lithium ion batteries. The major difference (UBI) is that they contain a highly porous separator, which converts to a gel when a minimum amount of electrolyte is added to operate the cell. In addition, the lithium polymer technology commonly uses the flat, stacked plate cell architecture, see Figure 4.2. Typically the negative electrode is carbon pasted on a copper current collector sheet and the positive electrode a lithium metal oxide (e.g. $LiCoO_2$) pasted on an aluminium sheet. These electrodes are then stacked interlaced with separator membranes and contained in a plastic poach. The current collectors may be copper (-) and aluminium (+) foil strips protruding from the heat sealed pack. In a battery, the poach cells are typically moulded into a polymer in order to improve the mechanical strength of the assembly.

Figure 4.2 Lithium ion polymer cell with a stacked plate cell architecture (Courtesy of UBI).

4.4 Test matrix

In order to characterise the response of cells and battery packs to different malfunctions and abuse conditions, a set of tests were conducted. The type of cells/battery packs intended to use for each test as well as the tests are presented in Table 4.3

Test/cell type	DD-SO_2Cl_2	D-$SOCl_2$ LR	D-$SOCl_2$ HR	D-MnO_2	D-SO_2	D-LiIon	Liion polymer
1. External short	4 , 20, 70 °C	4, 55 °C	4, 55 °C	4, 20, 60 °C	RT	RT	RT
2. Internal short	20, 70 °C	RT	RT	20 ,60 °C	RT	RT	
3a. External press., H_2O	RT	RT	RT	RT	RT	RT	
3b. External press., N_2	RT						
4. Heating	250 °C	250 °C	250 °C	250 °C	250 °C	250 °C	250 °C
5. Fire in battery packs	3 packs	2 + 3 packs	1 pack				
6. Reaction with sea water		3 cells	3 cells				

Table 4.3 Cell types and tests that were performed.

The data sheets for the different cells are found in Appendix 1.

5 RESULTS

5.1 External short

For a full description of these tests and detailed results, please see FFI/NOTAT-2007/00705.

5.1.1 Lithium sulfuryl chloride, CSC93 cells

The cells were internally fused and the fuse opened after ca 16 msec. During that period, the current was between 25 and 30 A. No increase in temperature was observed.

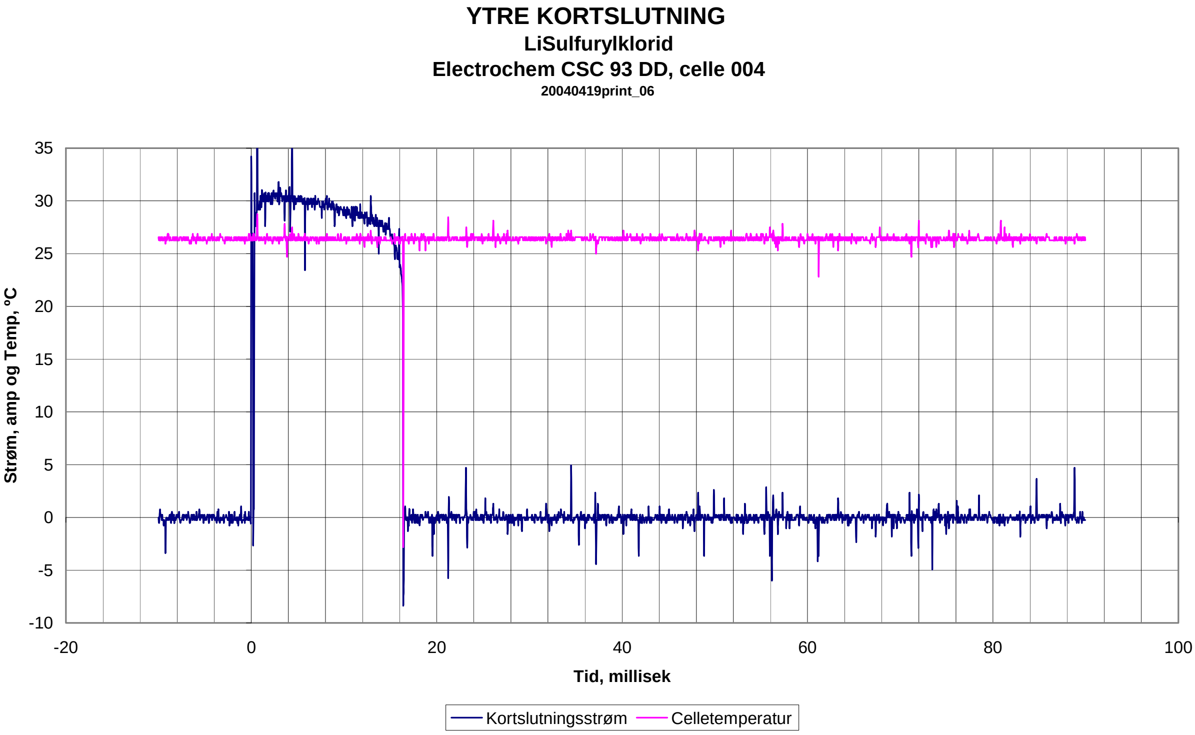


Figure 5.1 CSC93, cell current and cell temperature versus time. The fuse opened after 16 msec.

5.1.2 Thionyl chloride cells, LSH20

These cells are also internally fused. At room temperature, the short circuit current was initially 20A, falling to ca 10A. The fuse opened after 147 msec. No temperature increase was observed. Cells where the fuse was removed and by-passed self-heated until they vented as expected. Of the three fresh cells tested, none exploded or started to burn.

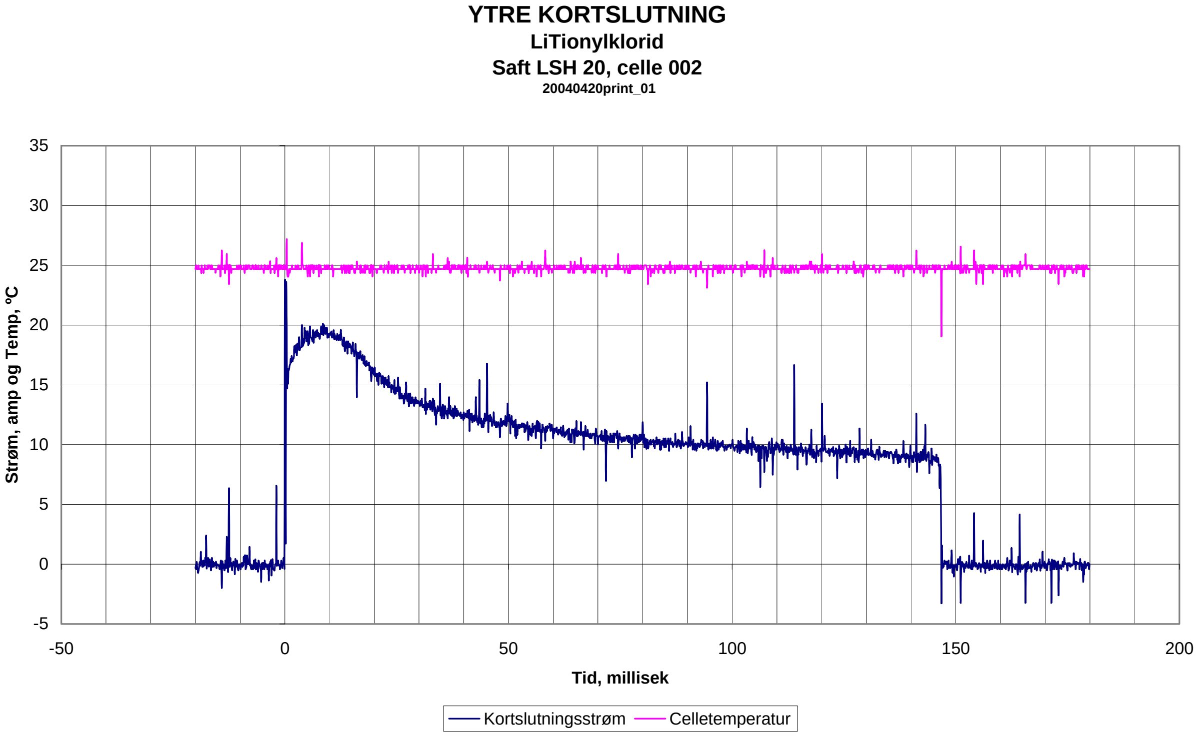


Figure 5.2 External short. LSH 20 cell current and cell temperature versus time. The fuse opened after 147 msec.

5.1.3 Thionyl chloride cells, low rate bobbin

The bobbin cells showed a minor short circuit current and a minor temperature increase above ambient.

5.1.4 Lithium manganese dioxide

6 cells were tested at room temperature, one cell vented. If preheated to 55°C, 2 cells out of 3 vented. The maximum currents observed were ca 50A. For cells shorted at room temperature the maximum cell temperature increase occurred after 13 - 18 hours and was ca 40°C above ambient.

5.1.5 Lithium sulphur dioxide cells, LO26SX

One cell was tested at 4^{o}C and 3 cells at room temperature. The maximum currents observed were ca 55 A. The cells vented at ca $50\text{-}60^{o}$C, before the maximum temperature was reached. Maximum measured surface temperature was 69^{o}C.

5.1.6 Lithium ion cells, ICR34600

Short circuit current >70A at 100% SOC and room temperature. Current collector tabs melted and burned off. In discharged cells, the current fell rapidly (20 sec) to below 10A.

Two later tests at 100% SOC and room temperature show maximum short circuit current values of 90A and 80 A. One cell reached a surface temperature of 95^{o}C and after the test a leak of electrolyte was observed under the cell. The other cell shows smoke and a small flame during test, and the current collector tab burned off after 179 seconds. Maximum measured surface temperature was 74°C. It was burned marks around the + end, but no leaks were observed.

5.1.7 Lithium polymer cell, Electrovaya 12Ah Super Polymer

The cells were without any cell protection devices. The maximum short circuit current was 94A and 116A for two different cells at 100% SOC. In the first test a white glowing tab (- tab) was observed which again ignited a small flame on the thin plastic cover on the tab surface. The flame burned out after few seconds. In the second test the distance between the contact points on the cell tabs and the cell were made as short as possible, resulting in the larger current. This time the glowing tab and small flame ignited the electrolyte as the cell vented, resulting in a violent fire.

Partly discharged cell, (as received) gave a maximum temperature increase of 38°C and a peak current of 61A.

5.1.8 Lithium polymer – HUGIN 1000 blocks

In these blocks, each parallel cell is connected via Polymer PTC fuses (SRP200 when Ultralife cells are used, STRP420 in blocks made from Electrovaya cells). The fuse opens after a few seconds and stays open as long as the load is connected and the heat evolved sufficient to keep the fuse above its trip temperature. If the load is removed, the fuse cools and closes again.

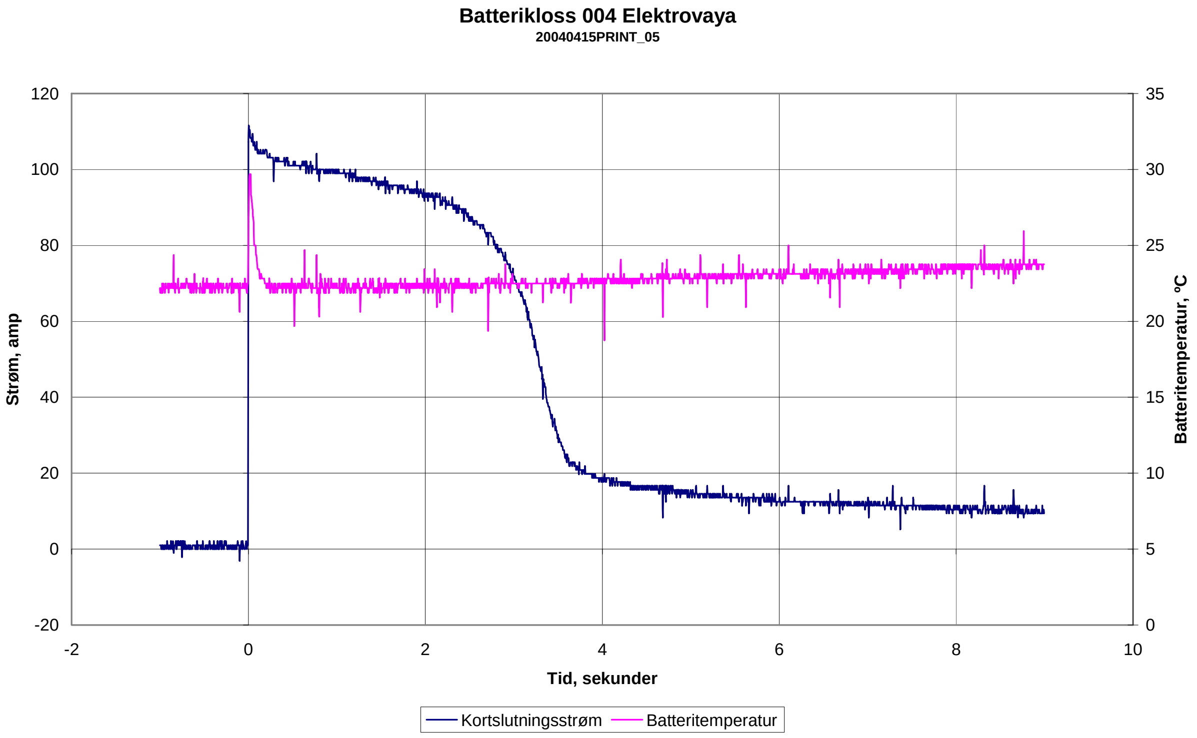


Figure 5.3 Block current and temperature versus time. 48Ah block made from 4 Electrovaya Super polymer cells. The cells are parallel connected via polymer fuses (SRP420). Initial 10 sec.

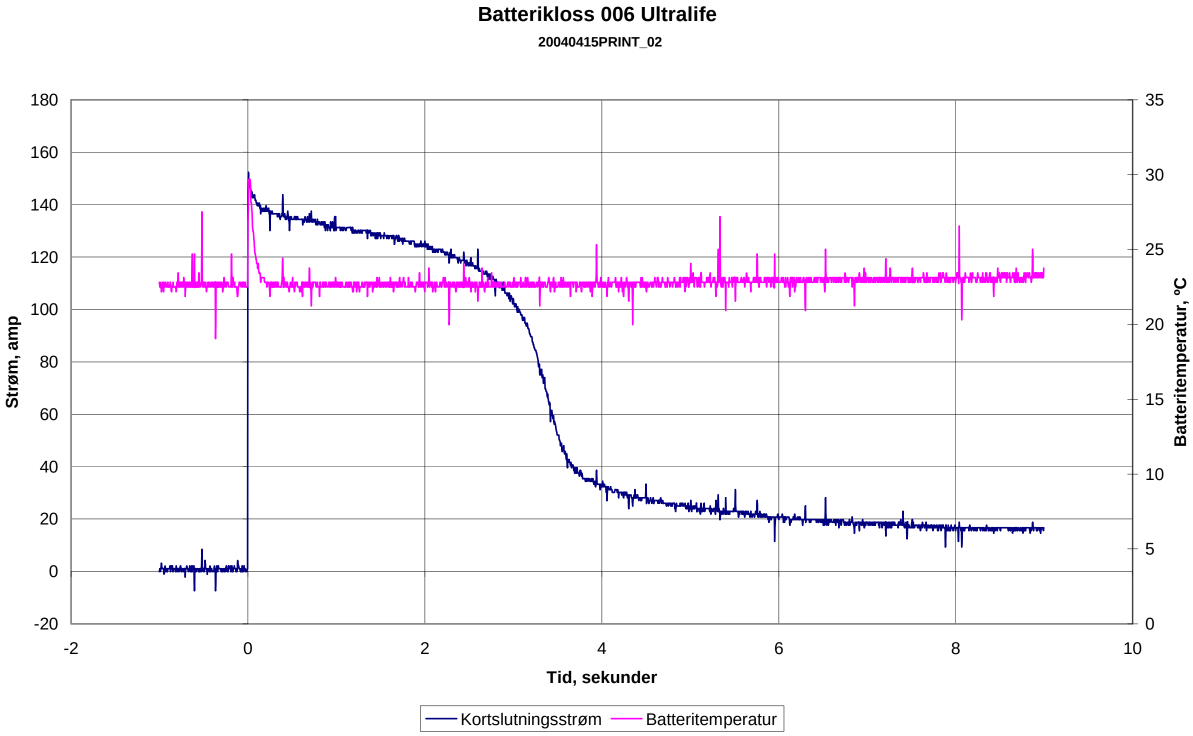


Figure 5.4 Block current and surface temperature during short circuit of HUGIN 1000 block based on 14 UBI cells. The cells are parallel connected via polymer fuses (SRP200).

5.2 Internal short

For a full description of the nail penetration tests, please see FFI/NOTAT-2007/00705. The temperature was measured with an external thermo-element, thus the core temperature of the cell must be significantly higher than measured externally.

5.2.1 Lithium sulfuryl chloride, CSC93 cells

Three discharged CSC93 cells, three at 50% SOC and three fresh cells were tested. All exploded instantaneously.

5.2.2 Thionyl chloride cells

Three fresh LSH20 cells were tested. They all exploded violently. Low-rate cells did not explode and the self-heating was minor (ΔT ca 20°C).

5.2.3 Lithium manganese dioxide

Fresh cells were tested. These cells heated to a maximum of 100°C, but no fire or explosions were observed.

5.2.4 Lithium sulphur dioxide cells

Fresh cells were tested. The cell temperature increased by ca 50°C, but no fire or explosions were observed.

5.2.5 Lithium ion cells, AGM ICR34600

3 cells were tested at 100% SOC, smoke was always observed and in one incident, the cell exploded 111 seconds after the impact. Figure shows the remains of the cell. Cells at 50% SOC also became very hot. Discharged cells were benign.

Figure 5.5 Lithium Ion D-cell after nail penetration at 100% SOC and room temperature. The cell exploded after 111seconds with flames.

5.3 External hydrostatic pressure, pressure media H_2O and N_2

A detailed description of these tests is given in FFI/NOTAT-2006/02782. The behaviour of the CSC93 cell has also been described in detail in a paper in the Proceedings of the 42nd Power Sources Conference, pp75-78, (2006).

5.3.1 CSC93, Li/SO_2Cl_2 DD-cells

Figure 5.6 shows the pressure versus time graph for a cell discharged to 2.50 V with 1.00 A (0% SOC). The flow rate of water is 2 ml/minute, gradually expanding the container and compressing the cell until something breaks at a pressure of ca 8 MPa. Initially the pressure rises non-linearly as the cell is compressed, then something breaks and the pressure increase stops. Subsequently the cell exploded. Note the difference in slope of the curve during the initial and the final phase of the compression. In the final phase only solid and liquid materials are present. At 40 MPa the pump is stopped. Figure 5.7 shows the delay between the collapse and the explosion. Initially the cell voltage falls gradually from 2.95V to 2.0V, and then the cell explodes.

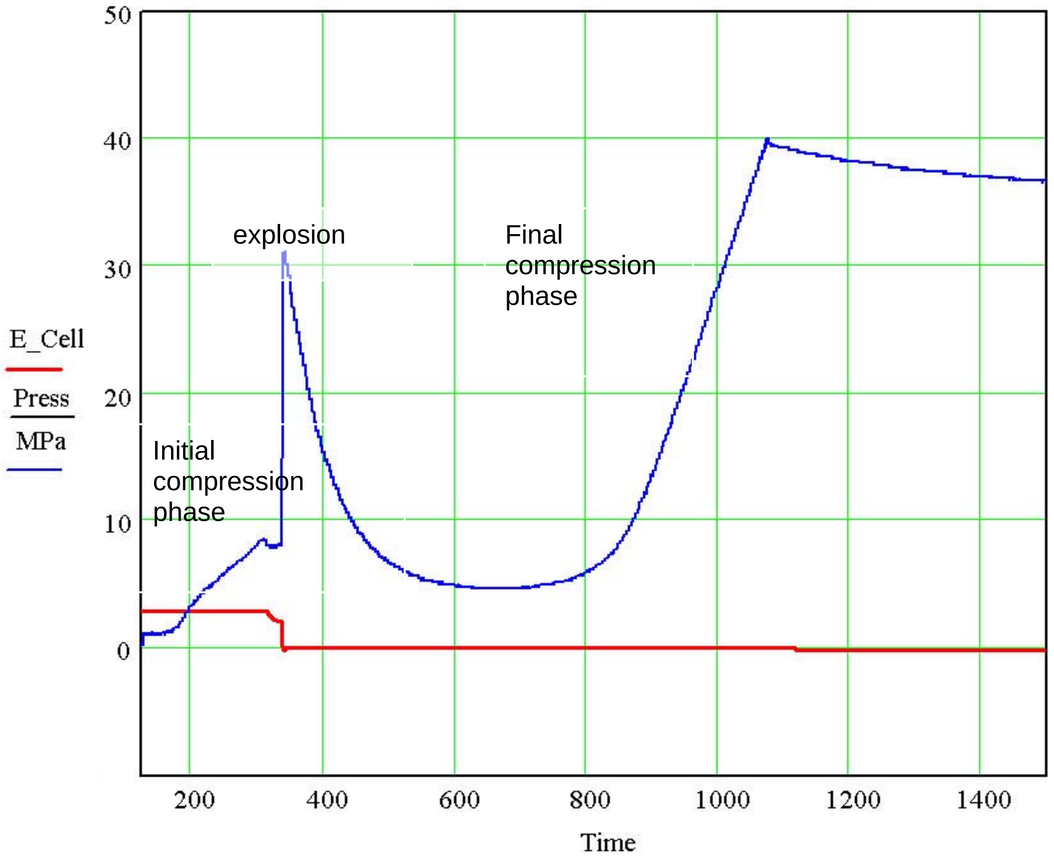


Figure 5.6 Discharged cell pressurized with water at a flow of 2 ml/min. Cell voltage/V and pressure/MPa versus time/s.

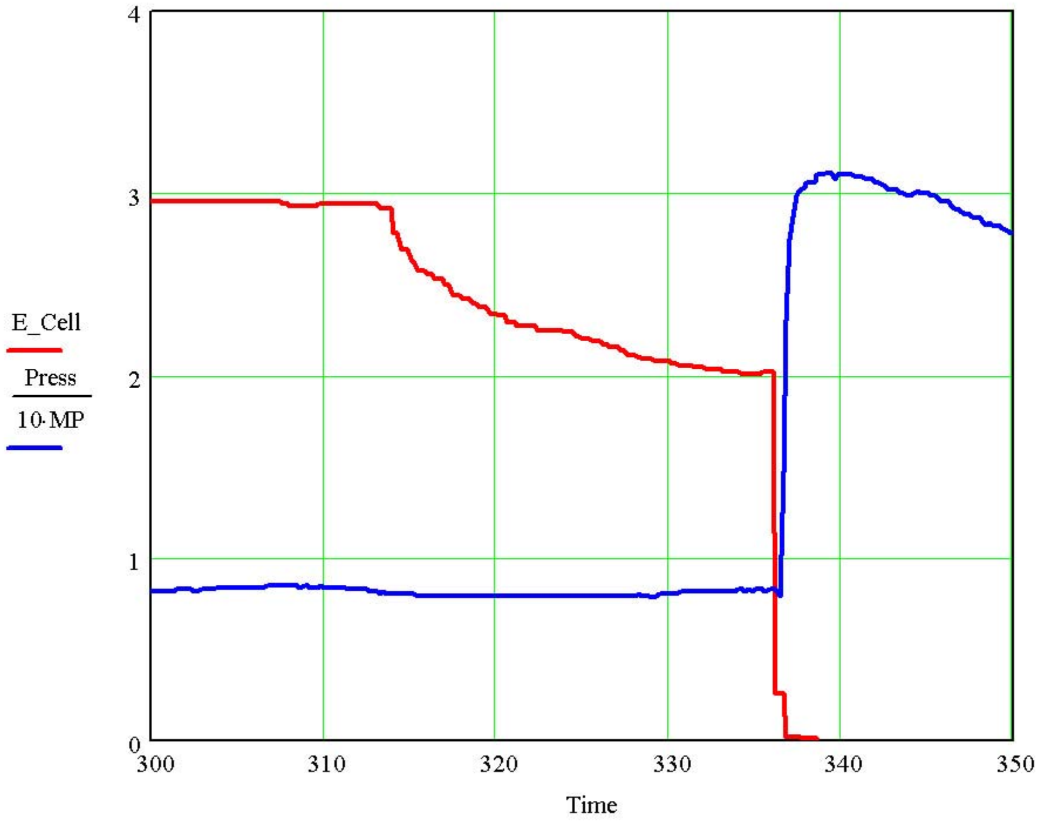


Figure 5.7 Enlarged part of cell voltage / V and pressure / 10 MPa versus time / seconds. Same experiment as in Figure 5.6.

Figure 5.8 shows the pressure vessel after pressurizing a cell at 50% SOC. In this case, the pressure increased above 60 MPa and the hot gases burned their way through the aluminium lid and body, creating a hole of ca 2 cm^2 and completely destroying the pressure vessel. Pressurization of fresh cells did not lead to explosions and the heat evolution was insignificant. After the test, the cells leaked electrolyte from the top (positive terminal) and showed a concave cell bottom. Figure 5.9 shows the pressure versus time curve for a fresh cell.

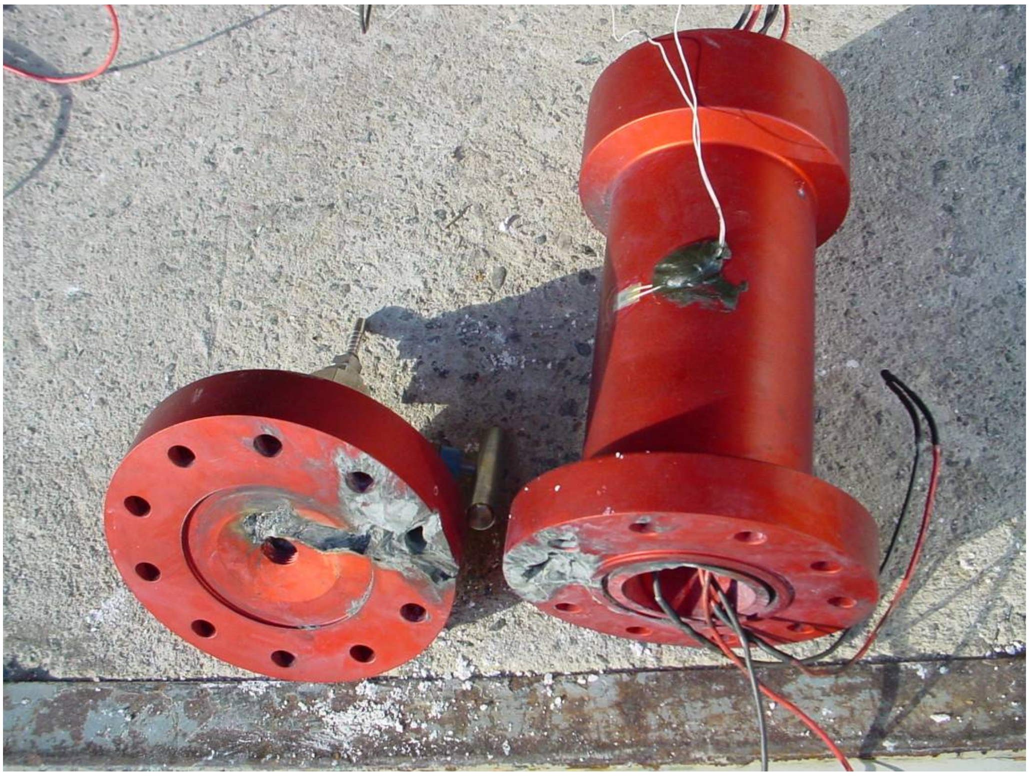


Figure 5.8 Pressure vessel after pressurizing a cell at 50% SOC with water at a flow of 2 ml/min.

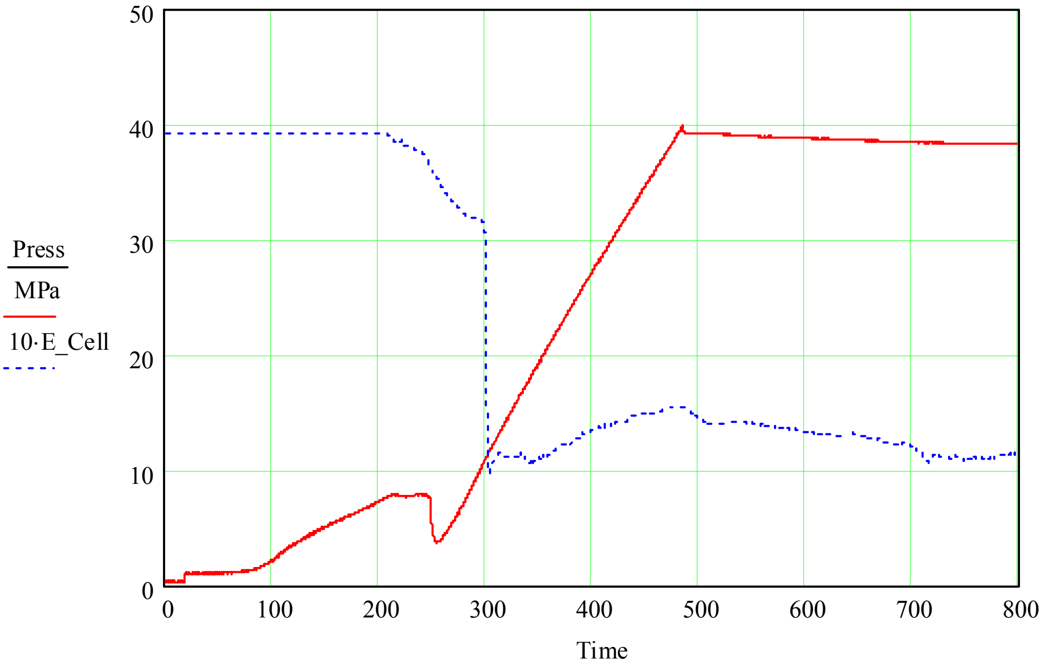


Figure 5.9 Pressure/MPa and open circuit cell voltage versus time/s. Fresh cell. Water flow 2 ml/min.

Discharged cells and cells at 50% SOC exploded, fresh cells did not. Collapse pressure was 7.28 MPa with a standard deviation of 0.24 MPa (n=8).

Subsequently cells at 0, 50 and 100 % SOC were pressurized with nitrogen gas. None of these cells exploded, but leaked electrolyte after the test. Collapse pressure in these experiments was difficult to determine and the cell voltage was unaffected.

Battery modules used in pigs are completely encapsulated in a rubber-like material. In the next experiment the cell was encapsulated in ca 5 mm thick silicone rubber. Figure 5.10 shows the pressure and cell voltage during the test and figure 5.11 the cell after the test.

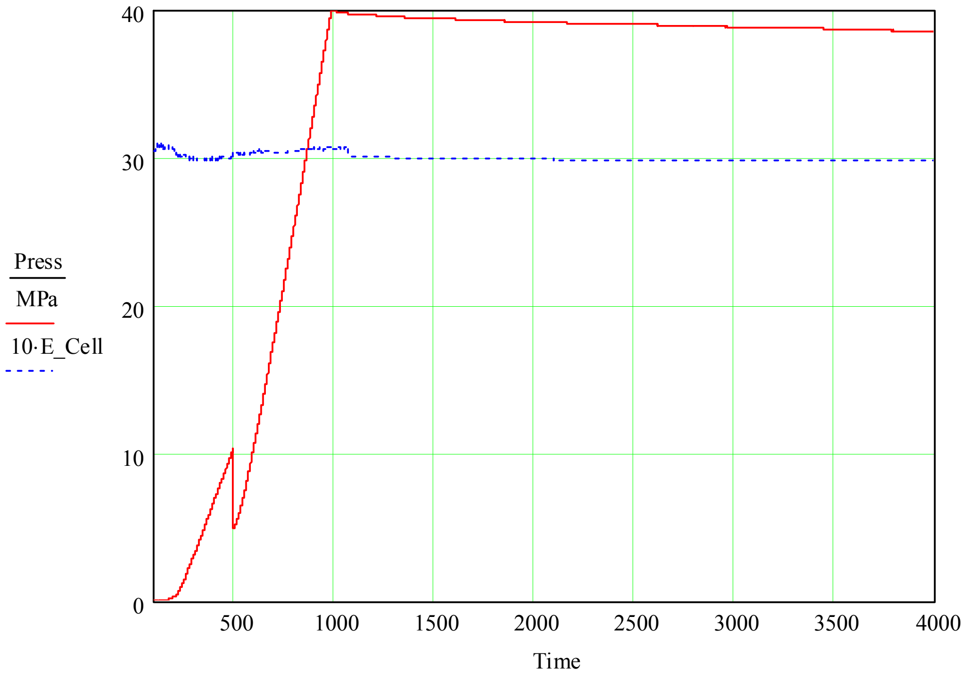


Figure 5.10 Pressure/MPa and cell voltage versus time/s. Potted cell at 100% SOC, load 3 ohm. Water flow 2 ml/min.

Figure 5.11 Cell after the experiment in fig 5.5. Left with potting, right after the removal of the potting.

Potting of the cell resulted in an increase in the collapse pressure from 7.28 MPa to 10.29 MPa with a standard deviation of 0.7 MPa (n=9). The damage to the cell was also changed. In addition to the indentation in the bottom of the cell, the cylinder wall collapsed. Of the three potted cells at 50% SOC, one exploded immediately at the collapse pressure, one exploded after 14.7 hours and one cell did not explode. Of three fresh cells and three completely discharged cells, none exploded.

Figure 5.12 shows the pressure and cell voltage versus time for one potted cell at 50% SOC pressurized in nitrogen.

From the high speed recording, the collapse pressure was 10.0 MPa and the peak pressure 59.7 MPa. The time between collapse and pressure increase was 46 msec.

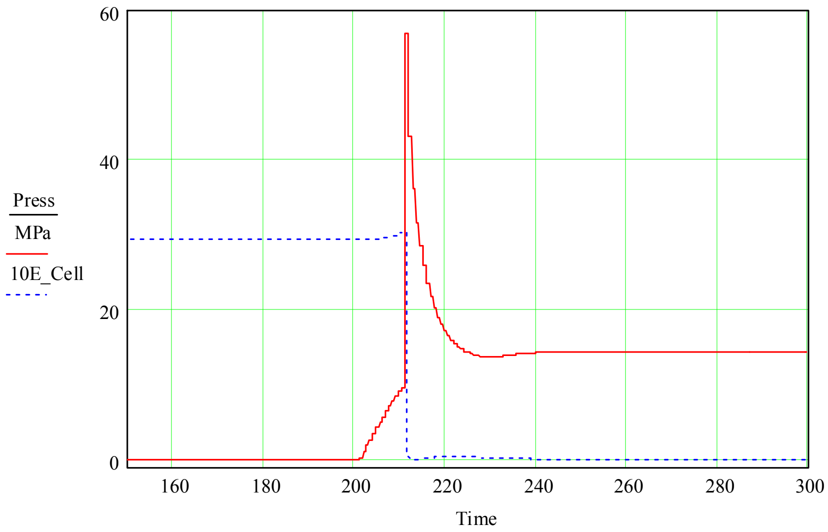


Figure 5.12 Pressure/MPa and cell voltage / 10V versus time/s. 50 % SOC, load 3 ohm. Nitrogen gas. This cell exploded during compression.

As an extra bonus, the void volume of cells that do not explode can be determined from the compression tests with water. The void volume of the CSC93 cell was ca 8.5 cm^3 compared with a total internal volume of the cell of ca 87 cm^3.

5.3.2 Full scale test of SO_2Cl_2 7S3P battery module in a battery container in a pig-trap

A battery container with one 7S3P module at 50% SOC and 2 dummy (Delrin) modules of similar volume was slowly filled with nitrogen until the container exploded. The battery container was placed within a 20 inch sealed tube section in order to simulate a pig trap. The tube section was 5.9 m long and had an internal diameter of 0.47 m. Ahead of the experiment; the pig trap was flushed with nitrogen at atmospheric pressure and subsequently sealed. The explosion occurred when the internal pressure reached 108.7 Bar. This is slightly higher than observed with the potted cells described in 5.3.1. Post mortem analysis showed that the battery container had been split at a maximum pressure of 192 Bar. The maximum recorded pressure in the pipe section was 3.0 Bar. Of the 21 cells in the battery, only 4 exploded, completely destroying the module.

The experiment is described in detail in [Johannessen, T C, Hasvold Ø, LianT, Forseth S: FFI/NOTAT-2006/02932 “Experimental study of the effect of external pressure on a pig-battery inside a closed 20” pipeline section”]

5.4 Heating:

Single cells were heated at 4ºC/min in an aluminium block with a central, cylindrical cavity Ø 37.6 mm and 133.5 mm deep. Usually, the temperature ramp was stopped at ca 260ºC. Block temperature and cell temperature as well as cell voltage were recorded. The cell temperature was measured on the underside of the cell with a thermocouple, type K, insulated from the aluminium block with mineral wool.

5.4.1 CSC93 DD cells

3 fresh cells vented at 119, 126 and 141ºC and a slow, calm lithium fire took place from ca 250 ºC. In contrast to this well-behaved manner, 2 cells previously discharged to ca 50 % SOC vented with flames at a cell temperature of 159 and 163ºC. The picture below is from the video and shows the cells. Time between frames is 40 msec. First, the cell vented, subsequently it burned. The noise was similar to a small rocket.

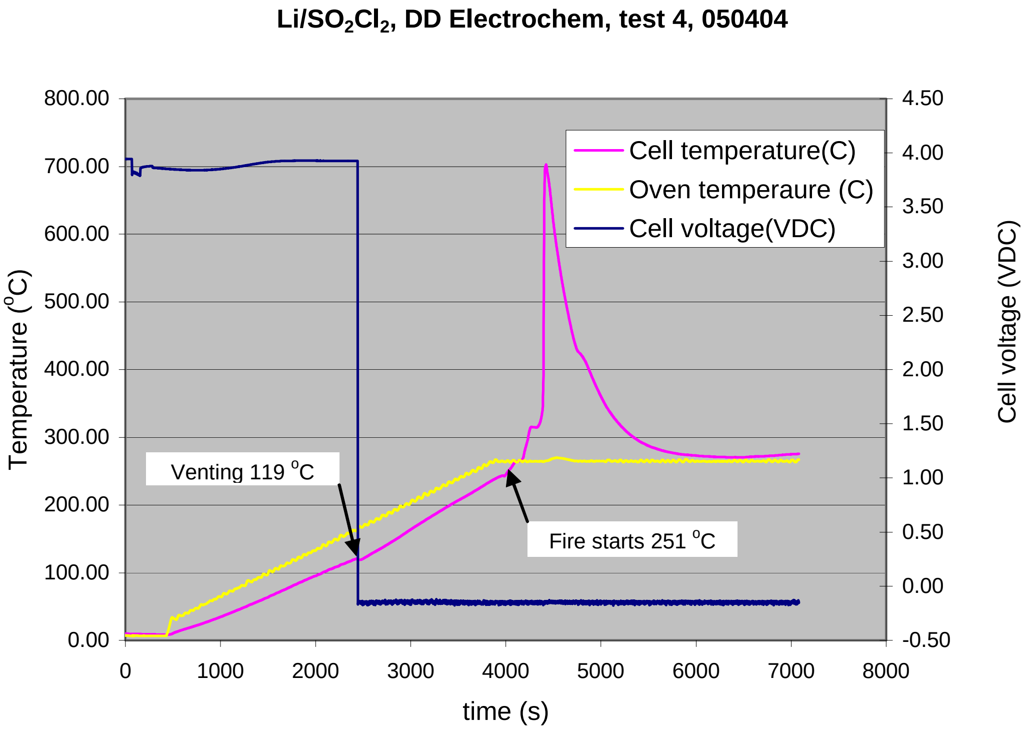


Figure 5.13 Heating of a fresh CSC cell. The event was peaceful and the fire barely visible

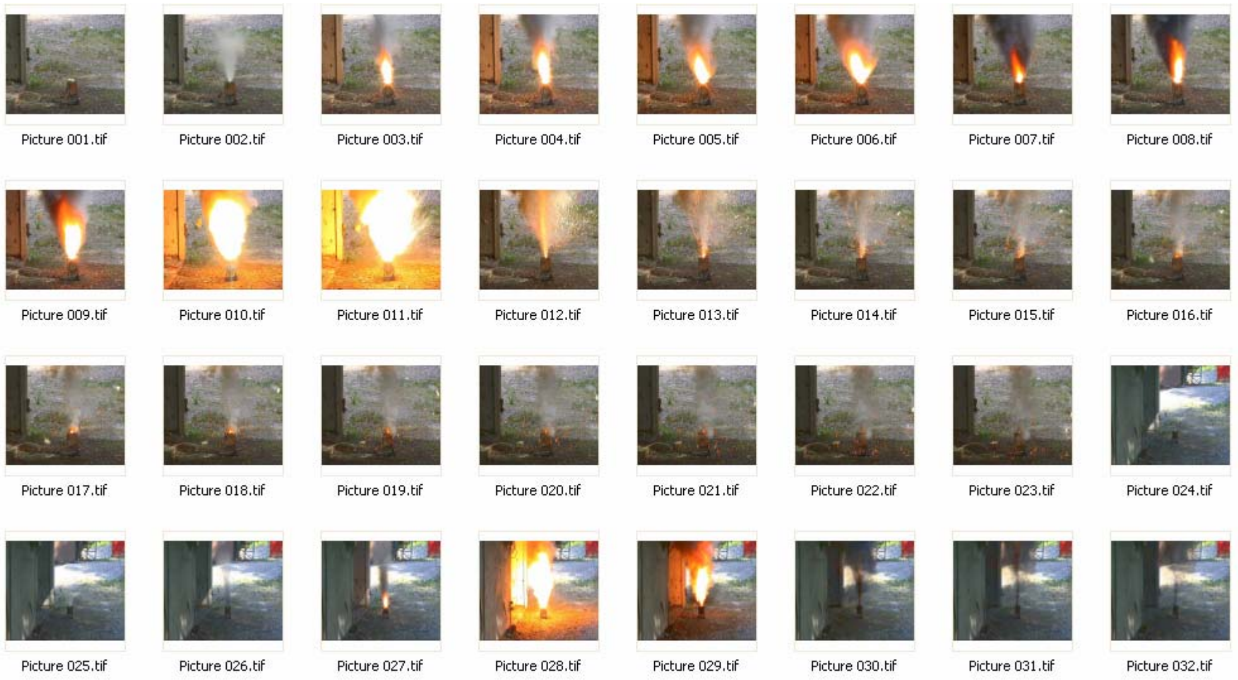


Figure 5.14 Heating of two partly discharged CSC 93 cells. Time between video-frames is 40 ms. Pictures 001 to 023 are from cell test 140504, pictures 24 to 32 cell are from test 100504

An enlarged frame, Picture 012.tif, is shown below:

Figure 5.15 Enlarged frame of Picture 012.tif showing violent venting of CSC cell at 50% SOC.

5.4.2 Heating of battery container with battery

A battery container with one fresh **7S3P** module based on CSC93 cells was heated with a propane torch. Figure 5.16 shows the resulting temperature and pressure in the container as well as the module voltage versus time.

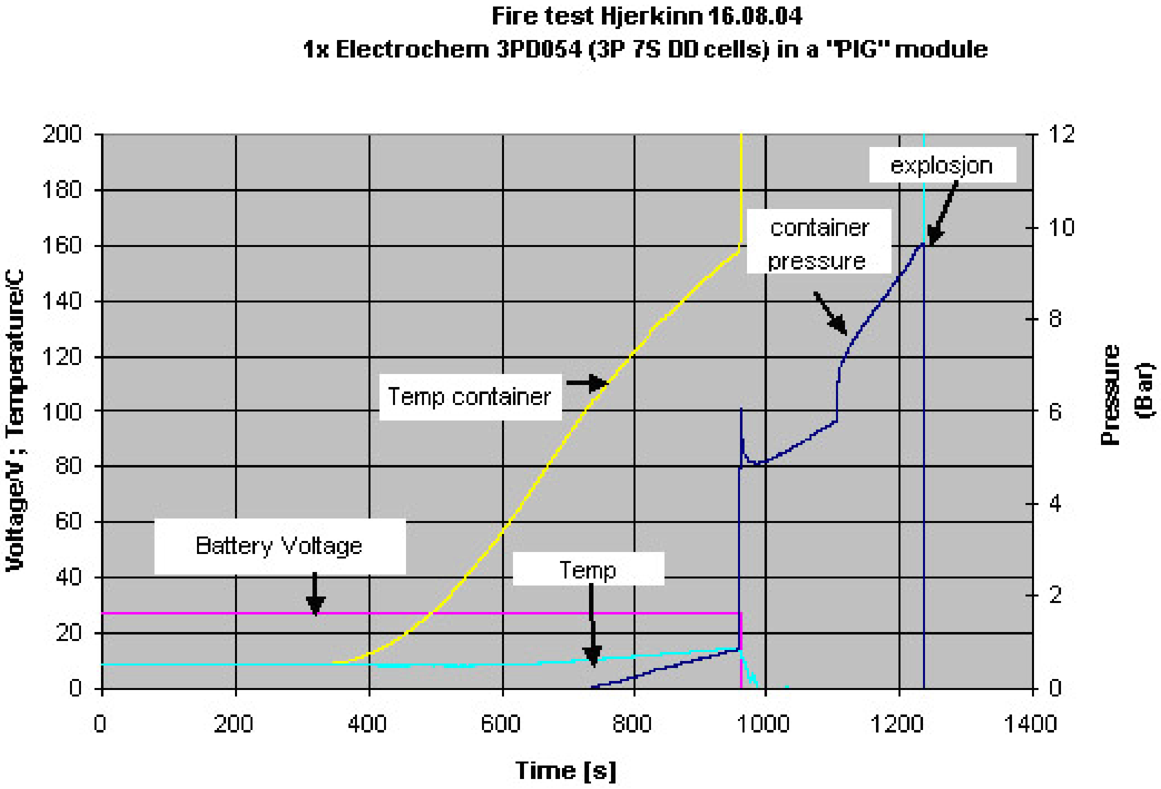


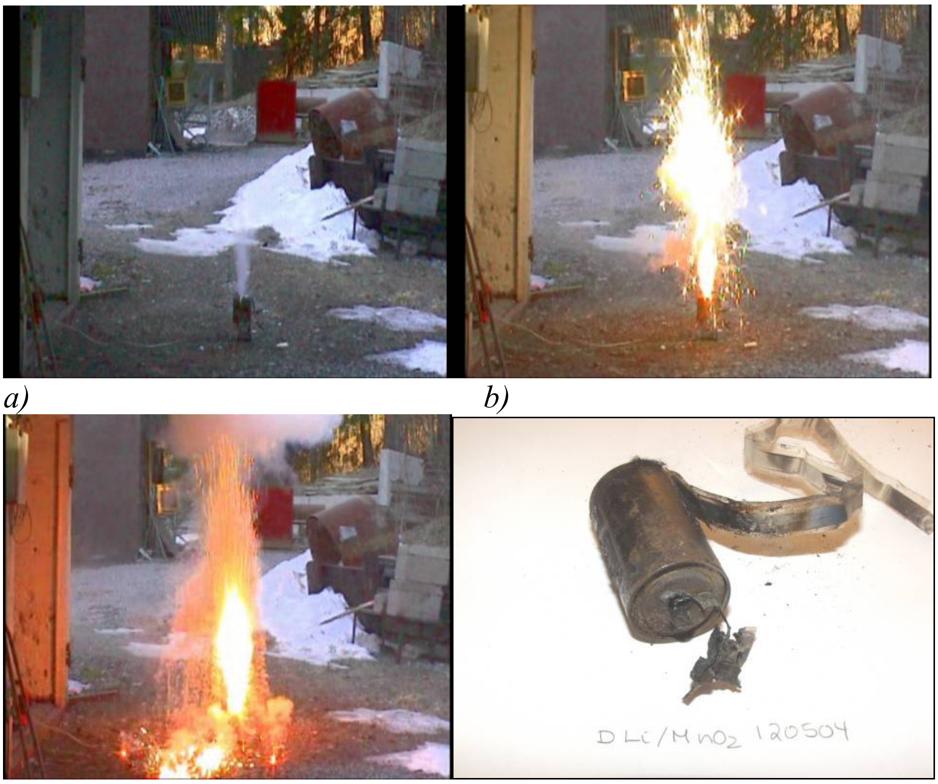
Figure 5.16 Fresh 21 cell battery module in battery container. The container is heated externally by a propane torch.

It is evident from the figure that at least two ventilations occurred (destroying the temperature sensor), then the container exploded. Rupture pressure was calculated from the strength and number of bolts to be at least ca 7 MPa. Post analysis showed that only 4 cells exploded, 5 cells had vented (developed a leak) and 12 cells were OK, but with compression damage in the bottom of the cell.

The explosion split the battery container and both the container lid and some of the cell cans were able to penetrate a 2 mm thick aluminium screen. FFI/NOTAT-2006/02356 gives a detailed description of the experiment.

5.4.3 Heating of Li/MnO_2 D-cells

The fresh cell vented at 158°C and caught fire at 201°C. The fire was fierce with sparks of burning lithium as shown in the picture below.



a) *b)*

c) *d)*

Figure5.17 Heating of Li/MnO_2 cell. a) Cell vents. Ca 9 min later flames are observed, (b and c). The remains are shown in (d).

5.4.4 Heating of Li/SO_2

The un-discharged cell vented at 121°C, after that the cell temperature followed the oven temperature. At 50% SOC, a more interesting curve is observed as in this case, the solid products of the cell reactions are still within the cell after the cell has vented. The cell vented at 121°C, resulting in a small decrease in cell temperature. After that, small exothermal and endothermal excursions are seen in the cell temperature until the cell voltage fell. After that, a small exotherm occurred after which the temperature followed the oven temperature closely, indicating no further reactions, even after 1 hour at 260°C. The exotherms are too small to have any impact on safety.

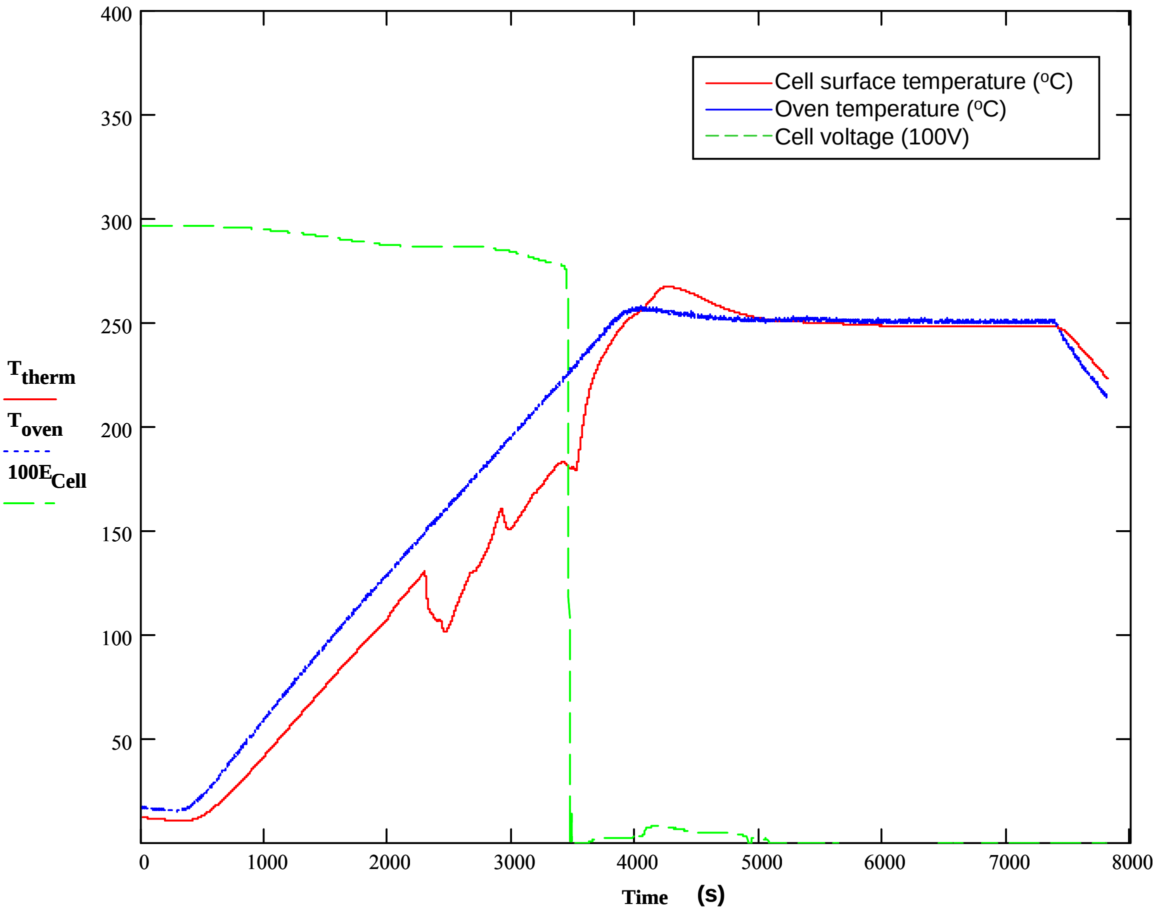
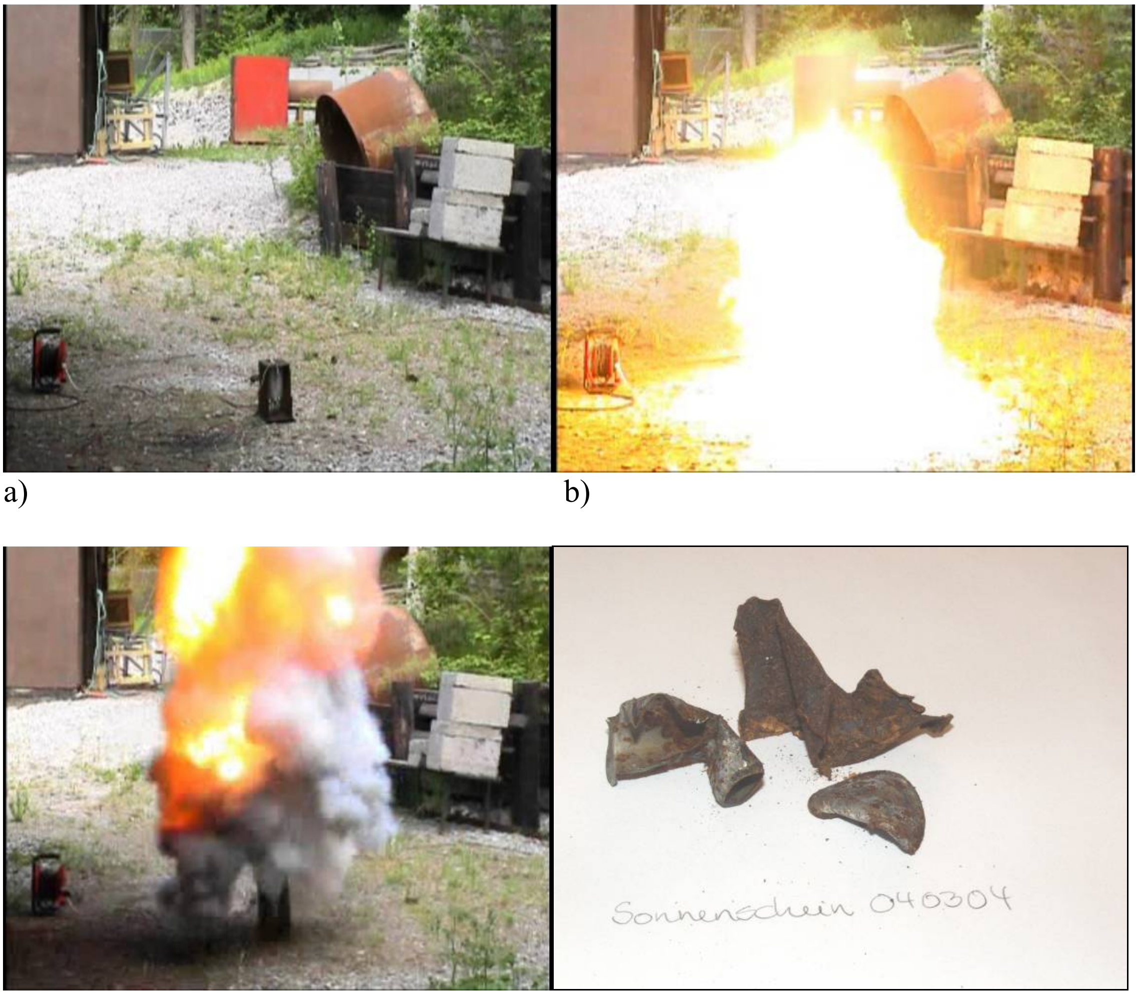


Figure 5.18 Heating of Li/SO₂ D-cell at 50% state of charge.

5.4.5 Heating of Li/SOCl₂

Thionyl chloride cells are used in a large number in transponders in both low-rate and medium rate applications. The low-rate cell SL-780 was not equipped with a safety valve and exploded very violently and reproducibly when heated above ca 220°C. Figure 5.19 shows the oven with the cell.



a)

b)

c)

d)

Figure 5.19 Heating of SL-780 Li/SOCl$_2$ *bobbin cell. a – c shows frames from the video, it is 40 ms between each frame. Picture d shows remains from the cell after the explosion.*

In contrast, the similar LS 33600 low rate cell vented at 174°C and the electrolyte distilled off. No evidence of exothermic reactions was observed. Figure 5.20 shows a typical result.

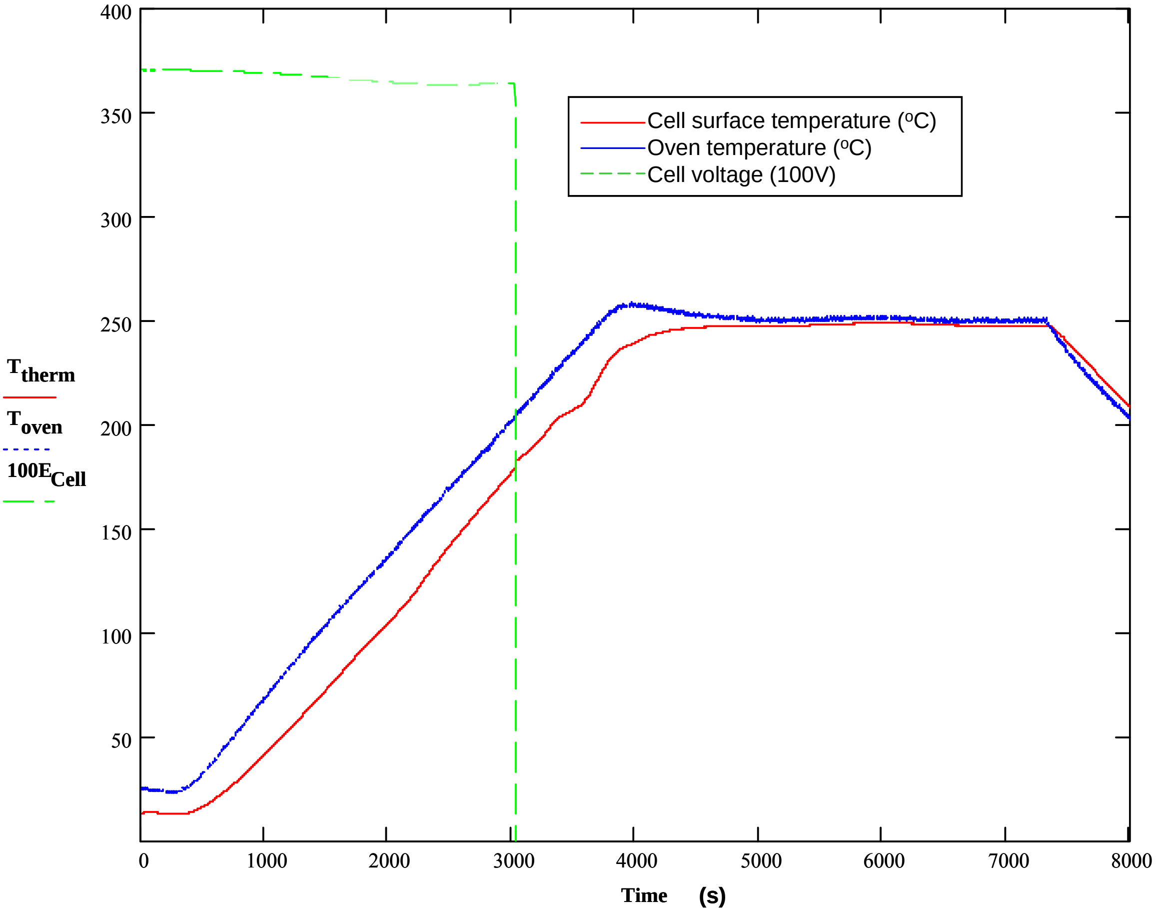


Figure 5.20 *Heating of fully charged LS 33600 Li/SOCl$_2$ bobbin cell. Cell temperature (red, solid), oven temperature (blue, dotted) and cell voltage X100 (green, dashed) versus time in seconds. The cell vented at 174°C.*

5.4.5.1 Spirally wound with safety valve

The LSH 20 cell behaved similar to the LS33600 during the initial phase, but caught fire at 265°C. The fire was hot, but peaceful. The figure below shows the behaviour of a cell that was discharged to 50% SOC. No significant differences between 50% and 100% SOC was observed.

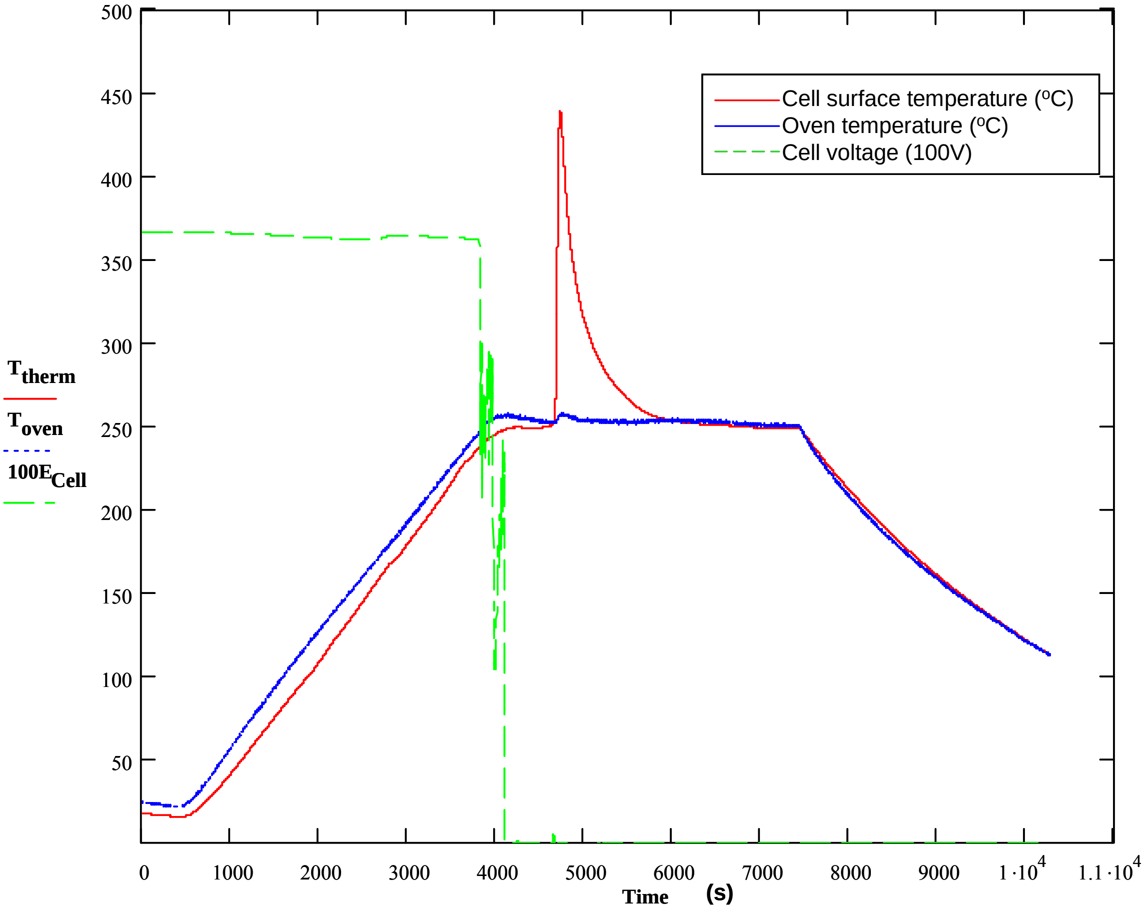
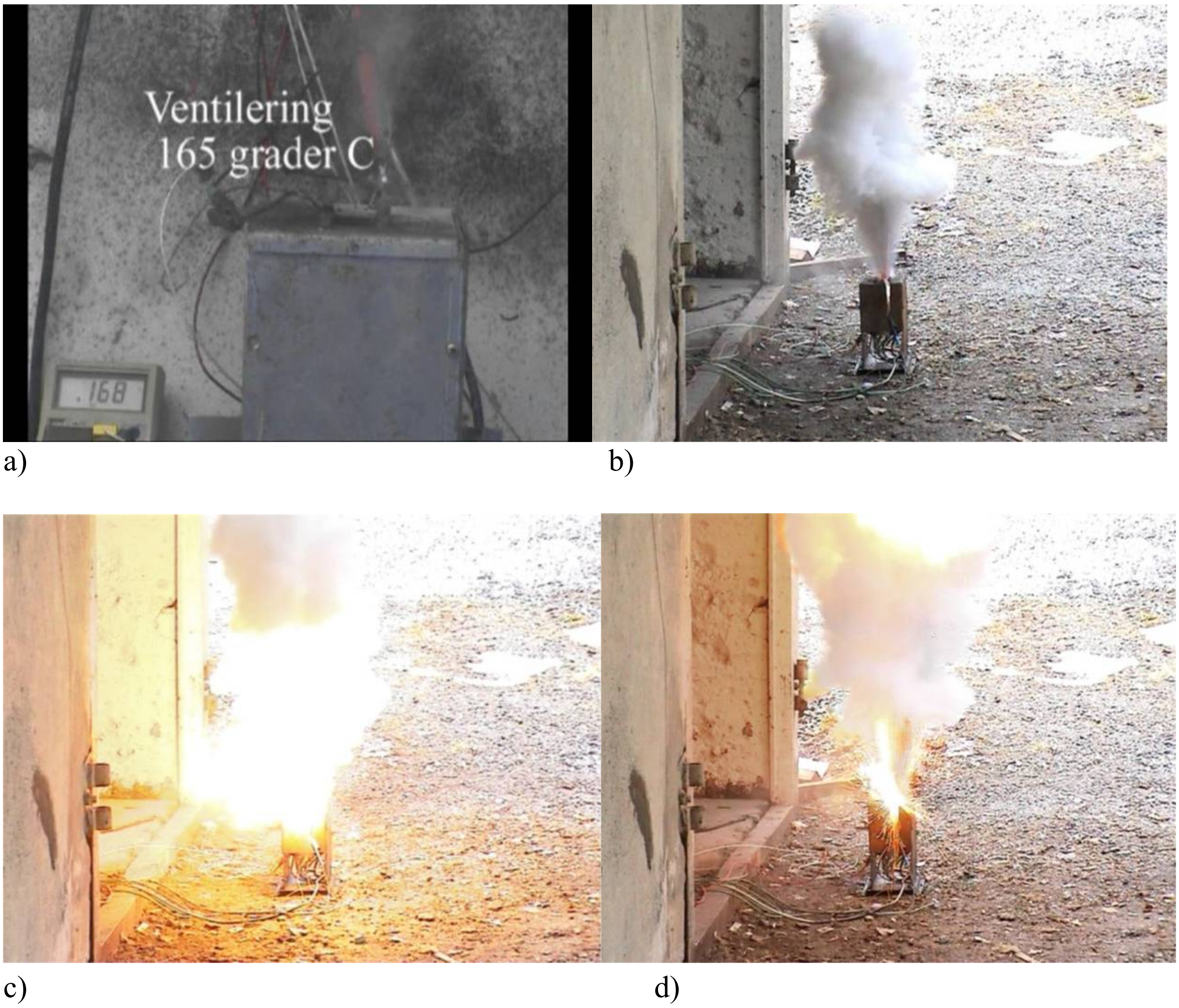


Figure 5.21 Heating of spirally wound Li/SOCl$_2$ LSH20 at 50% SOC.

5.4.6 Lithium ion (AGM ICR 34600)

The behaviour of this cell at 100% SOC was very similar to the Li/MnO$_2$ cell. The fire was fierce. Figure 5.22 shows frames from the video:



a) b)

c) d)

Figure 5.22 Heating of AGM ICR 34600 lithium ion cell. a) Cell venting at 165°C, b), c) and d) fume, then fire at ca 198°C.

The cell in figure 5.22 vented at 165 and started to burn at 198°C. Data from a different cell is shown below in figure 5.23. This cell vented at 147°C and the fire started at a cell temperature of 176°C.

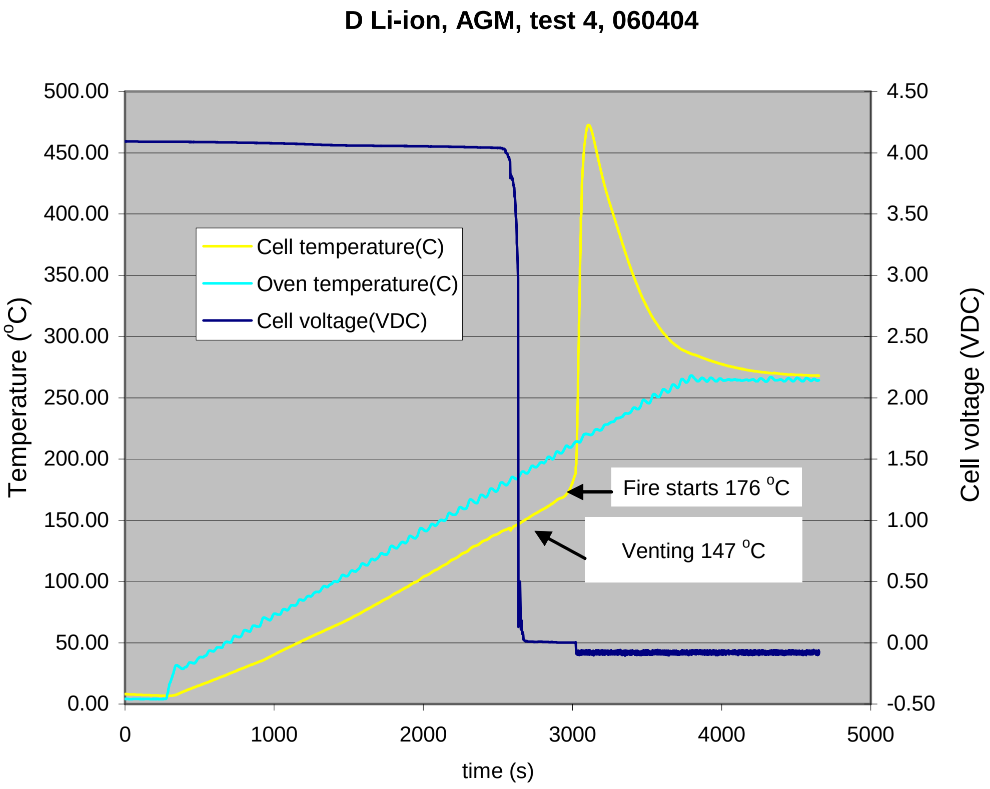


Figure 5.23   Heating of fully charged AGM ICR 34600 Lithium ion cell.

In contrast, an AGM cell that was discharged to 3.0 V (fully discharged), showed no dangerous behaviour at all. A small exothermal reaction inside the cell is observed between 150 and 250°C however. The figure 5.24 below shows the results.

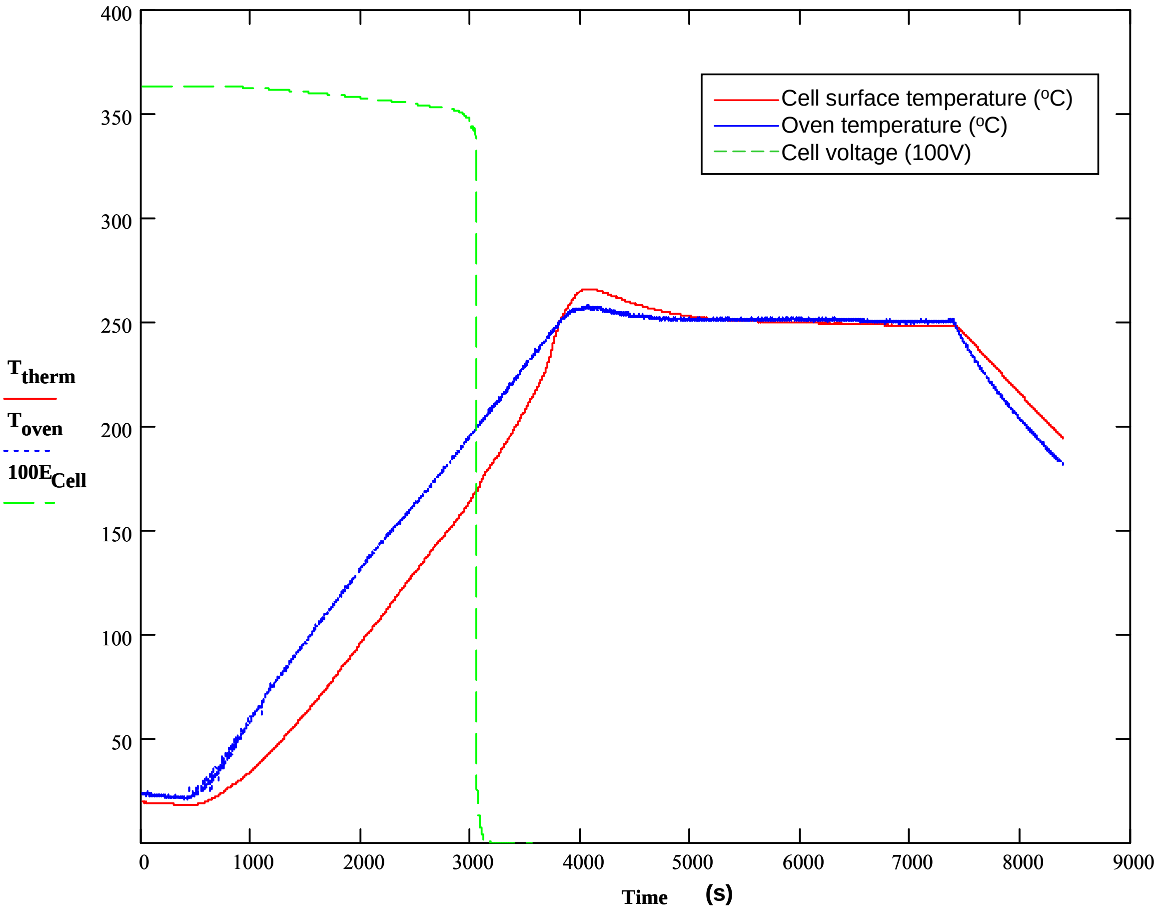


Figure 5.24 Heating of AGM 33400 Lithium Ion D-cell discharged to 3.0V (≈ 0% SOC).

5.4.7 Lithium polymer

A fully charged, pressure tolerant lithium ion polymer battery composed of 14 polymer cells moulded into a bloc with polyurethane was heated in a large cavity in an aluminium block. Figure 5.25 shows the experimental set-up. The cavity was filled with silicone oil to ensure good heat transfer between the block and the battery. This battery is a sub-module used in HUGIN 1000 AUV.

a) b)

Figure 5.25 a) Oven with white insulation and polymer battery.

b) 5 minutes after the venting.

Figure 5.26 shows the results.

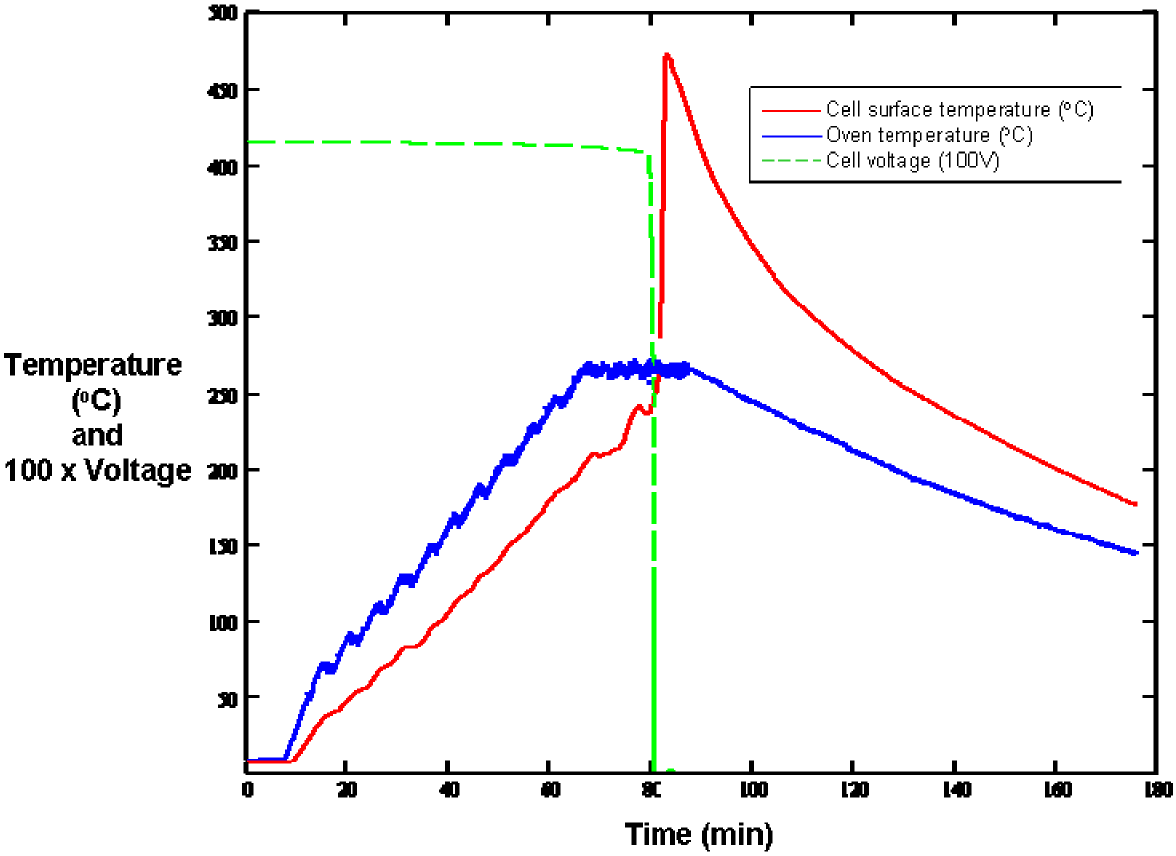


Figure 5.26 Heating of lithium ion polymer battery. Red curve = temperature below the battery (thermocouple), Blue curve = oven temperature (thermocouple), Green curve = 100 x cell voltage.

The figure showed that exothermic reactions took place within the battery as soon as the battery temperature exceeded 240°C. The battery vented visibly and the cell voltage fell to zero at ca 240°C followed by a rapid evolution of heat. Flames were not observed, but this may be because of the thick smoke, partly from decomposing silicone oil and partly from the battery. The silicone oil is stable to 200°C and has a flash point of more than 315°C [Dow Corning 200 Fluid].

5.5 Summary of the heating experiments

Table 5.1 shows a summary of the results.

Cell / date and orientation in the cavity	**Event**	**Cell temperature at event, °C**
$LiSOCl_2$, SL 780, Sonnenschein, 021203, positive UP	explosion	234
041203, positive UP	explosion	228
040303, positive UP	explosion	222
310304, positive UP	explosion	227
$LiSOCl_2$, LSH 20 SAFT 160304, positive UP	venting fire	161 265
170304, positive UP	venting	173
200304, positive UP	venting fire	172 265
090207, positive UP (SOC 50%)	venting fire	152/159 250
230307, positive UP (SOC 50%)	venting fire	164.4 250
$LiSOCl_2$, LS 33600 SAFT 131106, positive UP	venting	174
141106, positive UP	venting	160
151106, positive UP	venting	168
260207, positive UP	venting	180
$LiSO_2Cl_2$, CSC93, Electrochem 160204, positive UP	venting fire	126 253
170204, positive UP	venting fire	141 253
050404, positive UP	venting fire	119 251
100504, positive UP (SOC 50%)	venting with fire	159
140504, positive UP (SOC 50%)	venting with fire	163
$LiMnO_2$, U3360H, Ultralife 180204, positive UP	venting, jumped out	158
200204, positive DOWN	venting fire	165 200
050304, positive DOWN	venting fire	153 200
020404, positive DOWN	venting fire	158 201
$LiSO_2$, LO26SX, SAFT 290304, positive DOWN	venting, jumped out	121
190304, positive DOWN	venting	121
180304, positive UP	venting	133
070207, positive UP (SOC 50%)	venting	not readable
210207, positive UP (SOC 50%)	venting	130.7

Liion, ICR34600, AGM 091203, positive UP	venting fire	165 198
111203, positive UP	venting fire	165 200
060404, positive UP	venting fire	150 176
080207, positive UP (SOC 0%)	venting	199
220207, positive UP (SOC 0%)	venting	170.3
Li ion polymer block, HUGIN 061006	venting	239

Table 5.1 Summary of the heating experiments with cells.

5.6 Charging of a single string of CSC93 cells in a module

One crucial question when evaluating the safety of a battery pack is this: If one cell within a battery explodes, does that lead to an explosion of the other cells in the battery? In order to generate a cell explosion, we needed a reproducible way of making the cells explode.

In strong contrast to the findings by Liang et al [Liang 1981], charging was found to be a reproducible way of bringing the CSC93 cells to explosion. Typically the cell exploded after 2 hours at 2 A and room temperature. If the external temperature was lower, the time to explosion was longer. Charging heated the cell to ca 90ºC measured at the side of the cell at the time of explosion.

We used this method to evaluate the effect of cell explosions on a large battery. In one **7S3P** module, the thermal switch was shorted and the diode protecting the string against overcharge bypassed. Three modules, two original and one modified were placed in a standard battery container. In total, the battery contained 63 cells. The instrumented battery container was subsequently placed in a 40 inch diameter 6.7 m long steel tube that was equipped with endplates and filled with dry nitrogen. Figure 5.27 shows the battery with the modified module in the centre.

The 7 cell string was then charged with 2 A until the battery container exploded.

From the pressure/time data, it was evident that initially one cell exploded, followed by a second explosion of two cells. The third explosion destroyed the pressure measuring sensor. Figure 5.28 shows the remains after the explosion and figure 5.29 the distribution of the cell weights after the explosion. It is clear that 6 cells exploded, one cell was not found. Thus it seems reasonable to assume that only the 7 charged cells exploded and that **no evidence of sympathetic explosions was observed.**

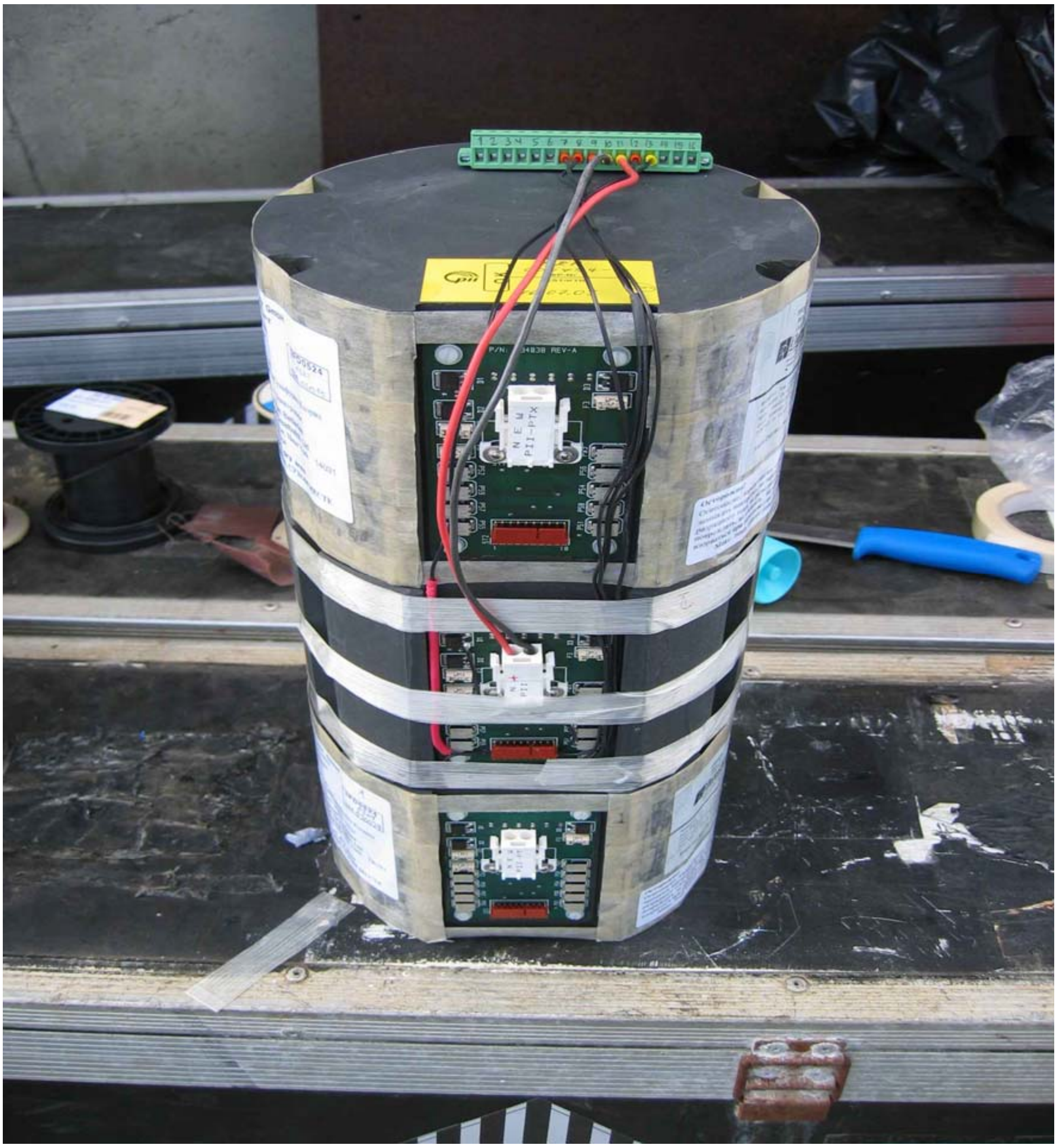


Figure 5.27 Three 7S3P modules. Centre module has the safety electronics disabled and one 7S string is prepared for charging.

Figure 5.28 The cell modules after the explosion. Note concave bulge in the cell bottom. Note also the yellow powder on the cells (sulphur?)

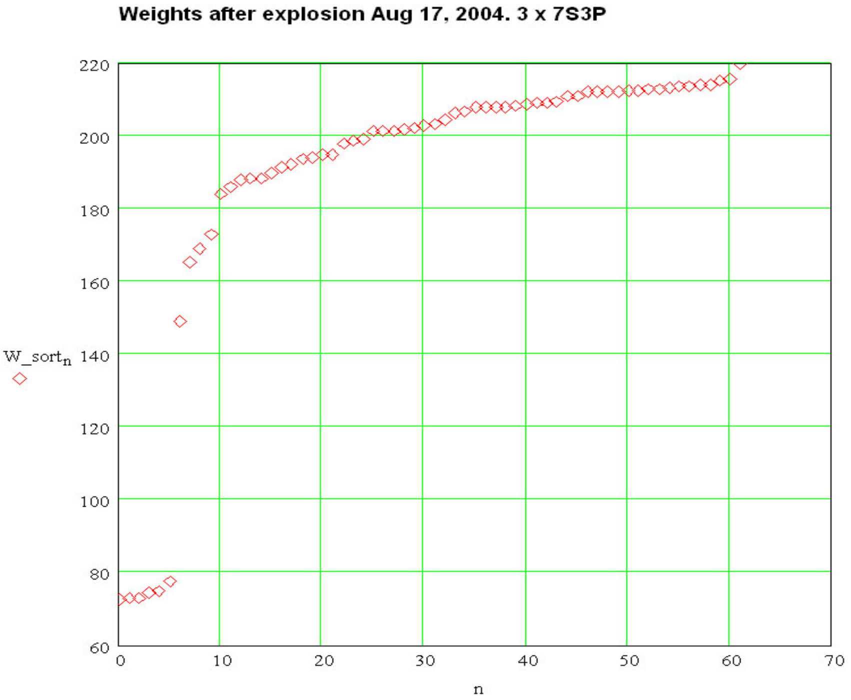


Figure 5.29 Distribution of the cell weight/g after the explosion. 6 cells exploded, 30 vented or leaked, 26 looked OK and one cell was not found. In total 63 cells from three modules.

6 EFFECT OF SEAWATER INGRESSION IN BATTERY CONTAINERS

6.1 Single cells

When a lithium cell is immersed in seawater, electrolysis reactions that are independent of the battery chemistry occur immediately. These reactions are:

At the negative electrode, evolution of hydrogen takes place and the maximum amount can be calculated from the capacity of the cell and Faradays law.

$2\ H_2O + 2e^- = H_2 + 2\ OH^-$

Thus the negative electrode becomes alkaline. One Faraday corresponds to one mole of electrons and a charge of 26.8 Ah. One Faraday generates one half mole of hydrogen gas. At standard temperature and pressure (STP) one mole of ideal gas has a volume of 24.790 litre. Thus the maximum volume of hydrogen that can be generated is 0.4625 litre per Ah cell capacity.

At the positive electrode, gas evolution (chlorine or oxygen) and corrosion may take place, depending on the material in the positive electrode. With nickel, the main reaction will be dissolution of nickel

$Ni = Ni^{++} + 2e^-$

The amount of nickel on a single cell is low and will be fairly rapidly removed. Subsequently, after the nickel strip has corroded away, the metal (typically molybdenum) in the glass to metal seal corrodes until a hole in the cell is formed. Water may then enter the cell, increasing the rate of self discharge and also lead to other chemical reactions within the cell.

The rate of these reactions is determined by the conductivity of the electrolyte path and by the voltage between the electrodes. As the metal in glass to metal seal has a very small cross-section, this rate may be low, but increases with the voltage.

Experiments with thionyl chloride bobbin cells (Sonnenschein SL-780, nominal capacity 16.5 Ah) confirmed this behaviour. The amount of gas observed was much less than predicted from the cell capacity. The amount corresponded to ca two times the available amount of nickel strip on the positive electrode (observed ca 0.1 L versus 6.24 L from capacity estimates). Initially a smell of SO_2 was observed, but after a month in salt water the smell had changed to H_2S indicating that a further reduction had taken place within the cell. Only the positive electrode was corroded away.

6.2 Serially connected cells

Depending on the insulation of the string and the electrolyte path, the reactions taking place may be different. The simplest case is when the string is completely insulated by a shrink tube and only the positive and negative ends exposed. Initially, this will be similar to a single cell, but the rate of reaction will be much faster as the voltage is higher. In addition, the negative electrode of the most positive cell may or may not be at a positive potential sufficient for anodic dissolution to occur, eventually forming a large hole in the cell wall allowing rapid water ingression into the cell. As soon as the positive electrode of the most positive cell is corroded away, the can of the most positive cell will definitely be at a positive potential relative to the negative electrode in the battery and corrode.

6.3 Effect of water under pressure

At ambient pressure, the rate of water ingression into the cell will be low if only the thin glass to metal seal has been holed. At increased pressure (or in a closed container where the production of gas increases the pressure) water may rapidly enter the cell, resulting in a rapid reaction with the cell contents. If this reaction rate is sufficiently large, the heat of reaction will warm the cell, further increasing the reaction rate etc until the cell explodes.

This was the case for partially and fully discharged CSC cells exposed to water under high pressure whereas nothing seems to happen to fresh CSC cells exposed to water. For the other chemistries, only fresh cells have been tested and only with fresh water. At more thorough study on this subject will be undertaken during 2007.

7 OVER-CHARGING OF LITHIUM ION CELLS

Only polymer cells were charged and given that the current was not too high, it invariably resulted in the development of a fierce fire at ca 80% overcharge and a cell voltage of about 5 V. At very high current (C/2 and more), the cell went open circuit. See FFI/NOTAT- 2006/02464 for more details.

8 DISCUSSION

8.1 CSC cells and batteries

One immediate result is that bare cells exposed to external pressure above a certain value develop a leak in the top of the cell. This leak is via the glass to metal seal or the safety valve and allows gas or liquid to enter the cell removing the mechanical forces on the cell. With water, partly and fully discharged cells explode a short time after the collapse. With nitrogen nothing happens after the leak has developed. Why water penetration into fresh cells did not result in a significant rate of heat production is not understood. Even the reaction of sulfuryl chloride with water is exothermic [National Bureau of Standards 1952], resulting in a production of sulphuric and hydrochloric acid. One significant difference between fresh and partly discharged cells is the presences of free chlorine in fresh cells. This may be sufficient to stabilize the SEI against destruction by water, slowing the rate of the reaction.
When the cell is potted, potting seals off the top and the cylinder wall collapses. This takes place at a significantly higher pressure, but is still below the operating pressure of a gas pipeline. Whether this results in an internal short or not may be completely accidental. If internally

shorted, the cell explodes immediately as shown. This is also consistent with the nail penetration tests where the CSC93 cells always exploded, irrespective of their state of charge.
There is an indication that partly and fully discharged cells are more dangerous than fresh cells if compressed hydrostatically. This is also the case when the cells are exposed to external heating. Fresh cells vented in a benign way at ca 120ºC, cells at 50% SOC vented violently with flames at ca 160°C. A fresh cell that vents, distils off the oxidant completely. Assuming that sulphur or $Li_2S_2O_4$ have been formed during discharge [Razzini et al 1980], this stays in the cell and can react violently with lithium.

Thus the common practice of discharging modules sequentially has a safety advantage as well as an economic advantage as only fully discharged modules are scrapped.

In a sealed battery container exposed to fire, the pressure build-up from the initial cell venting increases the venting temperature for the next cell etc until finally an explosion of sufficient strength to destroy the container takes place. This is irrespective of the state of charge of the battery and also of the battery chemistry. The positive finding is that usually there are sufficiently large temperature gradients within the battery container so that only a small number of cells explode. Thus a safety assessment based on the total battery energy is probably unnecessarily conservative.

8.2 Batteries and water

We have observed that partly and fully discharged CSC cells explode if water penetrates the cells. In our experiment, a mechanical failure (caused by pressure above ca 7 MPa) caused the penetration of water. But also galvanic corrosion may hole a cell and allow water to penetrate the cell. At present, CSC cells are used in diver emergency power supplies. If penetration of water into a cell makes it explode, also at moderate pressure, different batteries should be used for this application. Ongoing work will clarify this question.

We would also like to emphasize that cells of other chemistries have not yet been tested in a partly or fully discharged state. Further work in 2007 will clarify these questions.

8.3 Batteries and fire

There has been a tendency in the past to use the recommendations for the fire-fighting of lithium metal for lithium batteries. This is equivalent to using recommendations for extinguishing a fire of sulphur and charcoal for the extinguishing of gunpowder. Lithium, when heated sufficiently reacts explosively with the cathode material in the cell and no air is necessary for the fire. For cells with organic electrolytes however, combustion of the electrolyte gives a very significant contribution to the fire.
Because of the focus on lithium metal, graphite powder ("Litex") and class D extinguishers have been recommended and the use of water strongly discouraged due to the hydrogen producing reaction between water and lithium. In contrast, experimental evidence shows that water and water based heavy foam are by far the most effective agents and that the ABC, BC and Metatroxin (Class D) extinguishers had only a minor impact on the fire. (Matiszik 2001).
Similar observations were made by Attewell (Attewell 1989) in a series of test with lithium batteries of different chemistries. His conclusions are (quote):

1. Under warehouse conditions, the major contributor to a lithium battery fire is, when present, the flammable electrolyte. Lithium metal itself makes only a minor contribution.
2. Copious application of water, as a spray, is an effective extinguisher for burning batteries or individual cells, irrespective of their type.
3. In a fire fed by wood and card, it will take several minutes for the individual cells in a bulk stock of packaged batteries to react to the fire
4. The objective should be to extinguish the fire by the quickest method available. The residue will contain cells in a variety of conditions.
5. Several cell systems react violently in a fire. The explosive rupturing of the cases of oxyhalide* cells and the projection of fragments will be a hazard to fire-fighters. Effective, lowpressure vents in all such cells is advocated. The nature of the vent in the SO_2 system affects its behaviour.
6. Of the solid cathode system, the CuO type with dioxolane electrolyte behaves spectacularly, projecting empty cell cases tens of meters from the fire
7. The other solid cathode types, MnO_2 and $(CF)_n$, behaves benignly. Little is expelled from the fire site and, although the solvent fires are fierce, they would present no special problems to the fire-fighters.
8. Wet batteries may present a minor hazard for several hours after the fire has been extinguished.

End quote.

*) oxyhalide cells are BCX (bromine thionyl chloride), thionyl chloride and sulfuryl chloride cells.

To this can be added that the flames in a German warehouse (mainly Li/MnO_2 batteries) burned the trees 40 m from the garage door opening in the warehouse. A fully charged lithium ion battery is expected to behave fairly similarly to the other solid cathode lithium cells.

A recent report on the flammability assessment of lithium primaries by the US Department of Transportation, Federal Aviation Administration concludes similarly. (Webster, US DOT 2004). In addition they studied the effect of Halon 1301 and found that it had no impact at all on the fire, but changed the colour of the flames from white to deep red.

Batteries contain a mixture of fuel (lithium) and oxidant (the reducible cathode material). If heated to a sufficiently high temperature, they react. Thus the combustion of lithium is air independent and restriction of the access of air to the burning batteries will have a negligible impact on the fire. One exception is batteries where the electrolyte is combustible (i.e. lithium ion and lithium solid cathode cells). However, even in these batteries, the most important factor will be to cool the cells as quick as possible in order to stop the direct chemical reactions within the cells.

We, (Hjerkinn 2005), as well as others have observed parts from exploding cells that has sufficient velocity to severely harm humans. This must be taken into account when deciding whether to fight the fire or to pull back to a safe distance, letting the fire burn out. For fires involving batteries in strong battery containers, this may be the safest option unless armoured protection is available.

The second concern should be the toxic and corrosive fumes that may develop. Leaking oxyhalide and SO_2 cells give off very irritating, toxic and corrosive gases and require an immediate evacuation from the exposed area. Most lithium ion and lithium polymer cells contain ca 1M $LiPF_6$ in the electrolyte and during a battery fire or if spilled on the skin, this will be converted partly into hydrogen fluoride and phosphoric acid according to

$LiPF_6 + H_2O = LiF + 5HF + H_3PO_4$

Hydrogen fluoride is highly toxic and corrosive.

Lithium ion batteries with lithiated cobalt oxide cathodes (all cells in this report) behave very differently to abuse depending on their state of charge. Cobalt oxide in a fully charged cell decomposes at ca 150°C with the release of oxygen. This may result in a spectacular fire. In contrast, the fully discharged cell is nearly inert. New cathode materials such as lithium iron phosphate and lithium manganese spinels may be safer, but they have lower energy density at present.

Historically a number of incidents with spontaneous fires in lithium ion batteries have taken place. Compared to the number of cells in PCs and mobile phones, the frequency is very low, but it shows that incidents do happen and that no laboratory testing will be able to guarantee against this. Internal hot spots, caused by local shorts, have been shown via computer simulation to result in thermal runaway in cells. Whether the short is caused by separator failure, contamination with conducting particles, vibration or aging is irrelevant. In USA last year, 110 safety incidents were reported and resulted in 12 recalls involving 4.5 million batteries (Source: Battery and Energy Storage Technology, Spring 2007). As the batteries get larger, the severity of the incident may increase.

9 RECOMMENDATIONS

For many applications, there are no good alternatives to the use of high energy density lithium cells and batteries. However, a few steps can be taken to increase system safety:

- Irrespective of the battery chemistry, electrolysis will always increase the pressure in a sealed battery container that contains water. Thus any battery container for marine use should at least be equipped with a vent screw that allows relief of the pressure ahead of the opening of the battery container.

- A safety device with adequate pressure and flow capability to ensure the integrity of the battery container under all abusive conditions is highly recommended.

- For rechargeable batteries at least two protection circuits/devices should be present during charging. Both devices being able to independently terminate the charging if any cell voltage or cell temperature is outside the allowable window.

- Protection circuits do not protect against internal cell failures, thus only high quality lithium and lithium ion cells should be used for batteries.

- Discharged lithium ion cells have been shown to behave benignly under all abusive conditions. Thus they should preferably be transported and stored in a discharged condition.

- During transport and storage, high pressure battery containers should not have their lids bolted. Alternatively, an open vent of sufficient cross section may be used. In case of external heating (fire), this will significantly reduce the risk of an explosion.

- Battery modules should not be potted in a way that interferes with the operation of the cell safety valve. This is a standard procedure, but for systems that may be exposed to external pressure, a two-way operation shall be allowed in order to allow a leak in stead of a cell crunch and shorting.

- Partially and fully discharged primary CSC cells are more likely to explode than fresh cells under abusive conditions. The amount of energy in fully discharged cells is however small. Thus the present practice of discharging modules sequentially is not only economically sensible, but also increases safety.

- The fear of using water to extinguish fires were lithium batteries are involved is in our opinion not justified. On the contrary: Cooling of the batteries below the melting point of lithium is an efficient way to avoid cell explosions and to extinguish an explosion makes no sense.

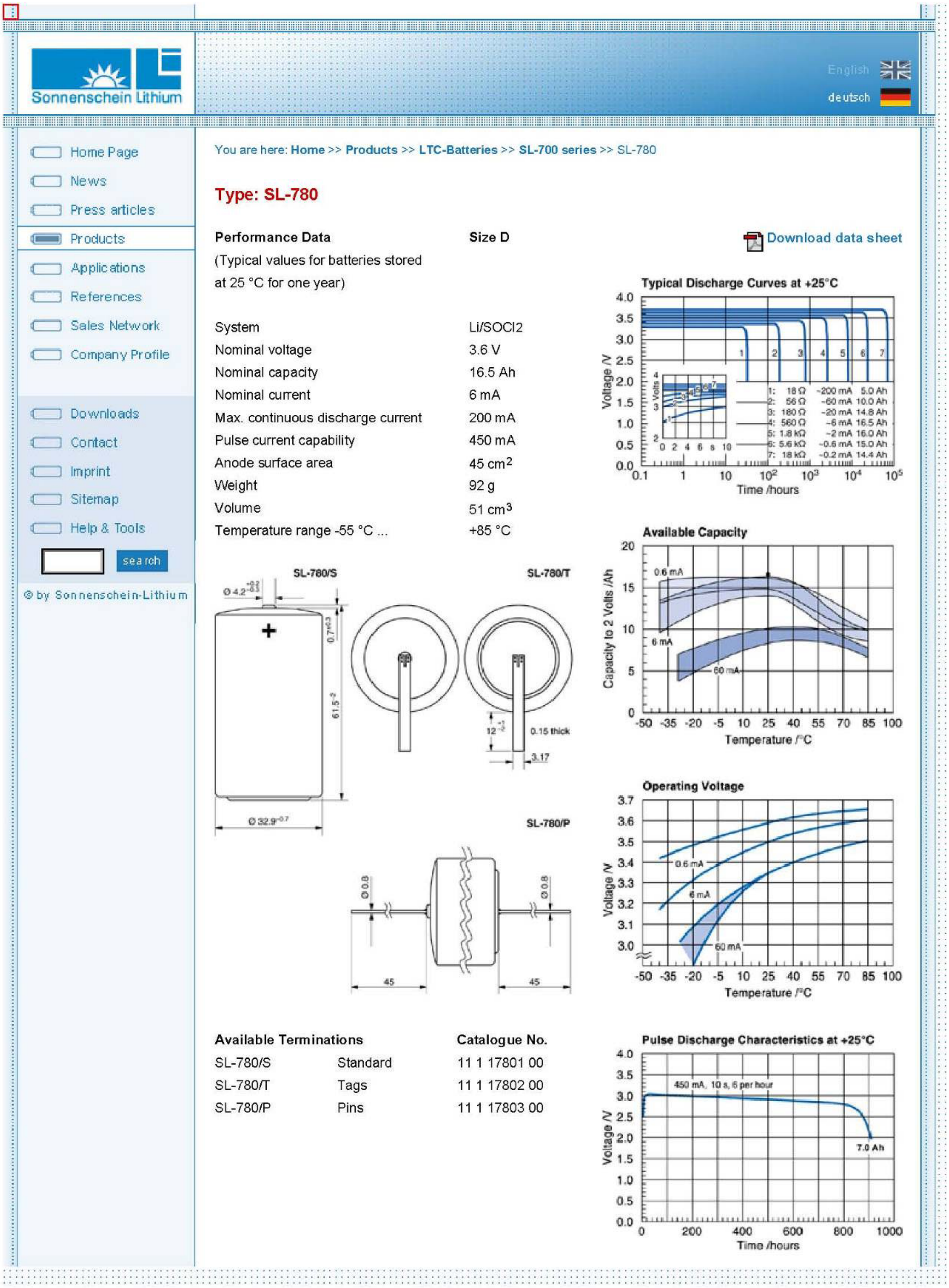
- Leakage of electrolyte from cells may result in extensive corrosion damage on equipment in the vicinity. Store batteries dry, in a well ventilated area and away from expensive equipment.

10 CONCLUSION

Lithium batteries of existing and new chemistries are in continuous development and will be used in an increasing amount. It is imperative that the user understands the differences between the different battery chemistries both with respect to performance and safety.

A TECHNICAL INFORMATION

Sonnenschein Lithium GmbH - Products - LTC-Batteries - SL-700 series - SL-780



You are here: Home >> Products >> LTC-Batteries >> SL-700 series >> SL-780

Type: SL-780

Performance Data (Typical values for batteries stored at 25 °C for one year)	**Size D**
System	Li/SOCl2
Nominal voltage	3.6 V
Nominal capacity	16.5 Ah
Nominal current	6 mA
Max. continuous discharge current	200 mA
Pulse current capability	450 mA
Anode surface area	45 cm^2
Weight	92 g
Volume	51 cm^3
Temperature range -55 °C ...	+85 °C

Available Terminations		**Catalogue No.**
SL-780/S	Standard	11 1 17801 00
SL-780/T	Tags	11 1 17802 00
SL-780/P	Pins	11 1 17803 00

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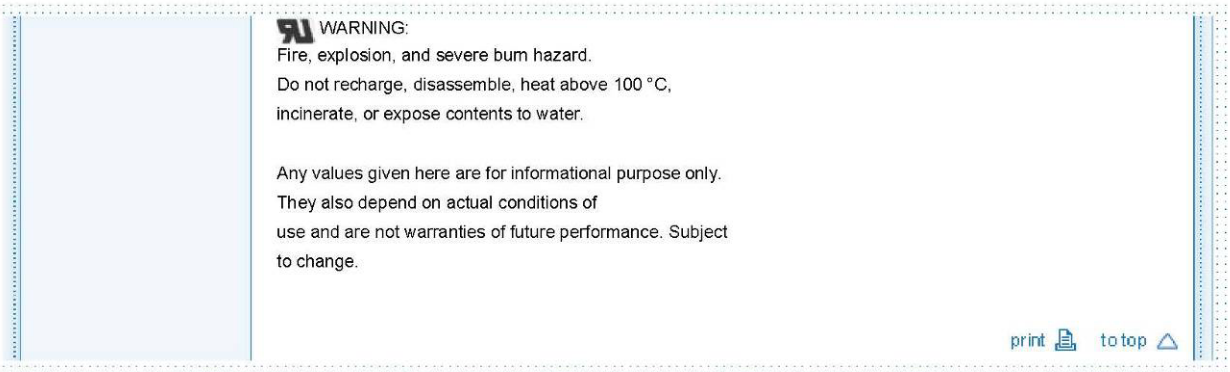


WARNING:
Fire, explosion, and severe burn hazard.
Do not recharge, disassemble, heat above 100 °C,
incinerate, or expose contents to water.

Any values given here are for informational purpose only.
They also depend on actual conditions of
use and are not warranties of future performance. Subject
to change.

Primary lithium batteries
LSH 20

3.6V Primary lithium-thionyl chloride ($Li-SOCl_2$)
High power
D-size spiral cell

For high drain/high pulses applications requesting superior voltage response in - 60°C/+ 85°C environments.

Key features

- High and stable operating voltage
- Superior drain capability
- Low self-discharge rate *(less than 3% after 1 year of storage at + 20°C)*
- Stainless steel container
- Hermetic glass-to-metal sealing
- Built-in safety vent
- Finish with 5 A fuse
- Non-flammable electrolyte
- Underwriters Laboratories (UL) Component Recognition (File Number MH 12609)
- Restricted for transport (Class 9)

Main applications

- Radiocommunication and other military applications
- Alarms and security systems
- Beacons and emergency location transmitters
- GPS
- Metering systems
- Sonobuoys
- Tracking systems
- GSM communication

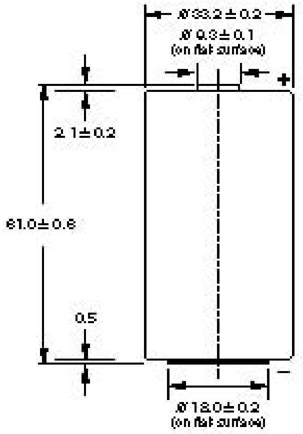
etc...

NATO stock number
6135 14 440 1213

Cell size references	**UM1 – R20 – D**
Electrical characteristics	
(typical values relative to cells stored for one year or less at + 20°C max.)	
Nominal capacity *(at 15 mA + 20°C 2.0V cut off. The capacity restored by the cell varies according to current drain, temperature and cut off)*	13.0 Ah
Open circuit voltage (at + 20°C)	3.67V
Nominal voltage (at 2 mA + 20°C)	3.6V
Pulse capability: Typically up to 4000 mA *(4000 mA/0.1 second pulses, drained every 2 mn at + 20°C from undischarged cells with 10 µA base current, yield voltage readings above 3.0V. The readings may vary according to the pulse characteristics, the temperature, and the cell's previous history. Fitting the cell with a capacitor may be recommended in severe conditions. Consult Saft)*	
Maximum recommended continuous current *(to maintain cell heating within safe limits)*	1800 mA
Storage *(recommended)* *(for more severe conditions, consult Saft)*	+ 30°C (+ 86°F) max
Operating temperature range *(Operation above ambient T may lead to reduced capacity and lower voltage readings at the beginning of pulses. Operation with current continuously above 1 A may restrict upper T range. Consult Saft)*	- 60°C/+85°C (- 76°F/+ 185°F)
Physical characteristics	
Diameter *(max)*	33.4 mm (1.32 in)
Height *(max)*	61.5 mm (2.42 in)
Typical weight	100 g (3.5 oz)
Li metal content	approx. 4.0 g
Available termination suffix CN , CNR — radial tabs CNA (AX) — axial leads FL — flying leads ...etc.	

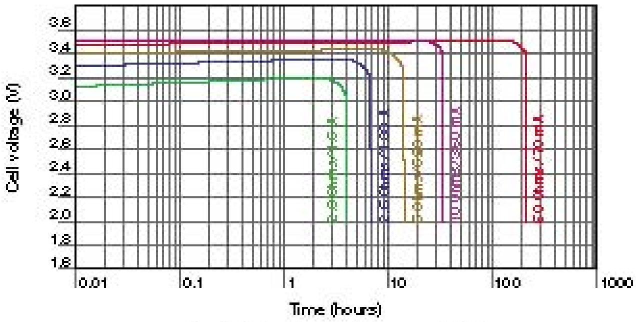
November 2004

LSH 20

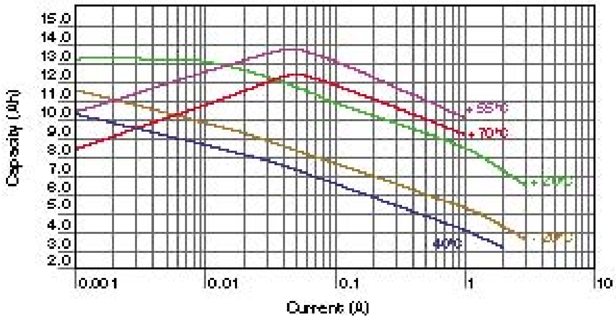


Dimensions in mm.

Voltage plateau versus Current and Temperature (at mid-discharge)



Typical discharge profiles at + 20°C



Restored Capacity versus Current and Temperature (2.0V cut off)

Storage

- The storage area should be clean, cool (not exceeding +30°C), dry and ventilated.

Warning

- Fire, explosion and severe burn hazard.
- Do not recharge, short circuit, crush, disassemble, heat above 100°C (212°F), incinerate, or expose contents to water.
- Do not solder directly to the cell.

Saft
12, rue Sadi Carnot
93170 Bagnolet - France
Tel +33 1 49 93 19 18
Fax +33 1 49 93 19 69

www.saftbatteries.com

Doc. N° 31015-2-0904
Published by the Communications Department

For more details on primary lithium technologies please refer to Primary Lithium Batteries Selector Guide Doc N° 31048-2-0604.
Photo credit: Saft
Produced by Arthur Associates

Société anonyme au capital de 31 944 000 €
RCS Bobigny B 383 703 873

P/N: 3B36 CSC93 DD

ELECTROCHEM COMMERCIAL POWER
a division of Greatbatch Ltd.
9645 Wehrle Drive Clarence, NY 14031
Tel: (716) 759-5800 Fax: (716) 759-2562
www.electrochempower.com

- **Lithium / Sulfuryl Chloride Chemistry**
- **Custom cell terminations and battery packs available**

CSC93 - High Performance Lithium Cell Size DD

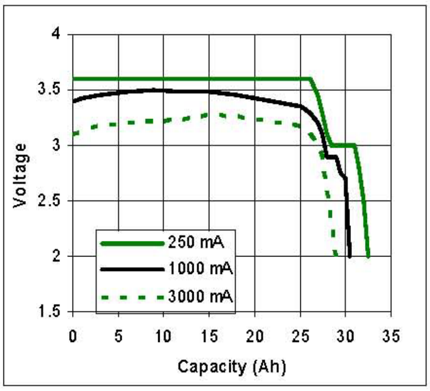
CELL SPECIFICATIONS:

Open Circuit Voltage (25°C)	3.9 V
Rated Capacity	30 Ah
Rated Discharge Current	1.0 A
Maximum continuous current	4.0 A
Cell Diameter	33.5 mm (1.32 in.)
Cell Length	111.4 mm (4.39 in.)
Cell Weight	213 g
Lithium weight	10.2 g
Safety Fuse	7.0 A
Self Discharge	3% per year at 25°C
Operating temperature	-20°C to +93°C (-4°F to +200°F)

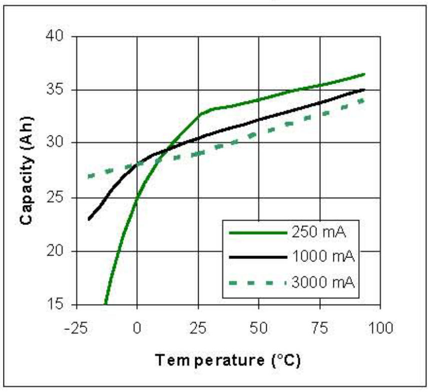
Temperature Range

°C	°F
200	392
190	374
180	356
170	338
160	320
150	302
140	284
130	266
120	248
110	230
100	212
90	194
80	176
70	158
60	140
50	122
40	104
30	86
20	68
10	50
0	32
-10	14
-20	-4
-30	-22
-40	-40
-50	-58
-60	-76

25°C discharge



Capacity as a function of current and temperature

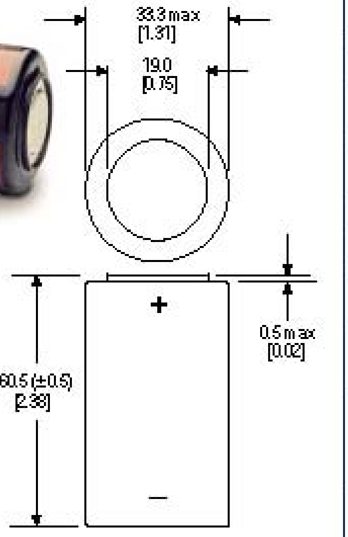


Rev: July 2005

ULTRALIFE
BATTERIES INC

TECHNICAL DATA

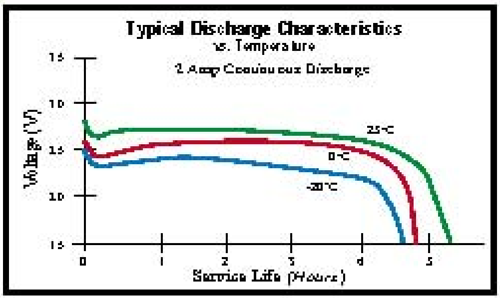
U3360H 3V Size Cell

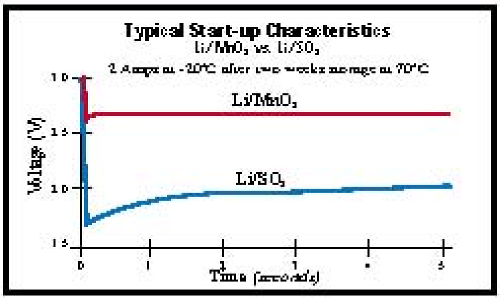


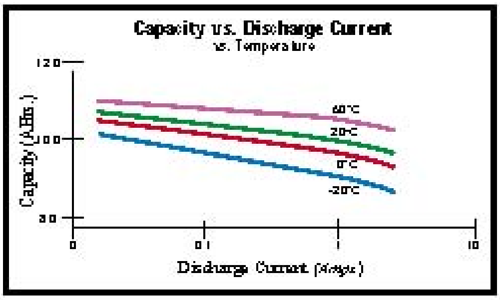
Dimensions in mm (inches)

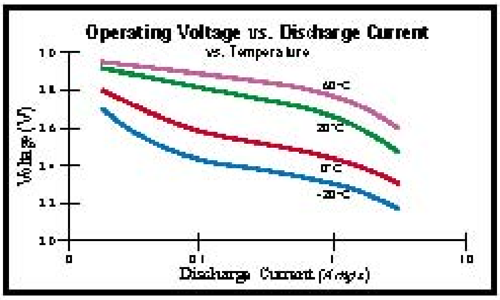
System:	Non-Rechargeable Lithium/Manganese Dioxide
Designation:	D size Primary Cell, High Rate
Nominal Voltage:	3.0 Volts
Capacity (C):	11 AHrs @ 200 mA to 2V @ 23°C
Max. Discharge:	3.0 Amps Continuous
Weight:	117 grams max.
Oper. Temp. Range:	-40° to 72°C
Storage Temp. Range:	-55° to 80°C
Volume:	52 cm³
Terminals:	Flat End Caps; Tabs Available
Housing:	Stainless Steel with Laser Welded Hermetic Seal and Insulating Label
Notes:	High pulse currents and higher continuous currents can be achieved. Contact Ultralife Batteries, Inc. for details.
Transportation:	Class 9

For a complete description of transportation regulations and definitions of the transportation classifications "Excepted" and Class 9," refer to Ultralife's web site at: http://www.ulbi.com/whitepapers/Ultralife_Batteries_Lithium_Battery_Transportation_Regulations.pdf









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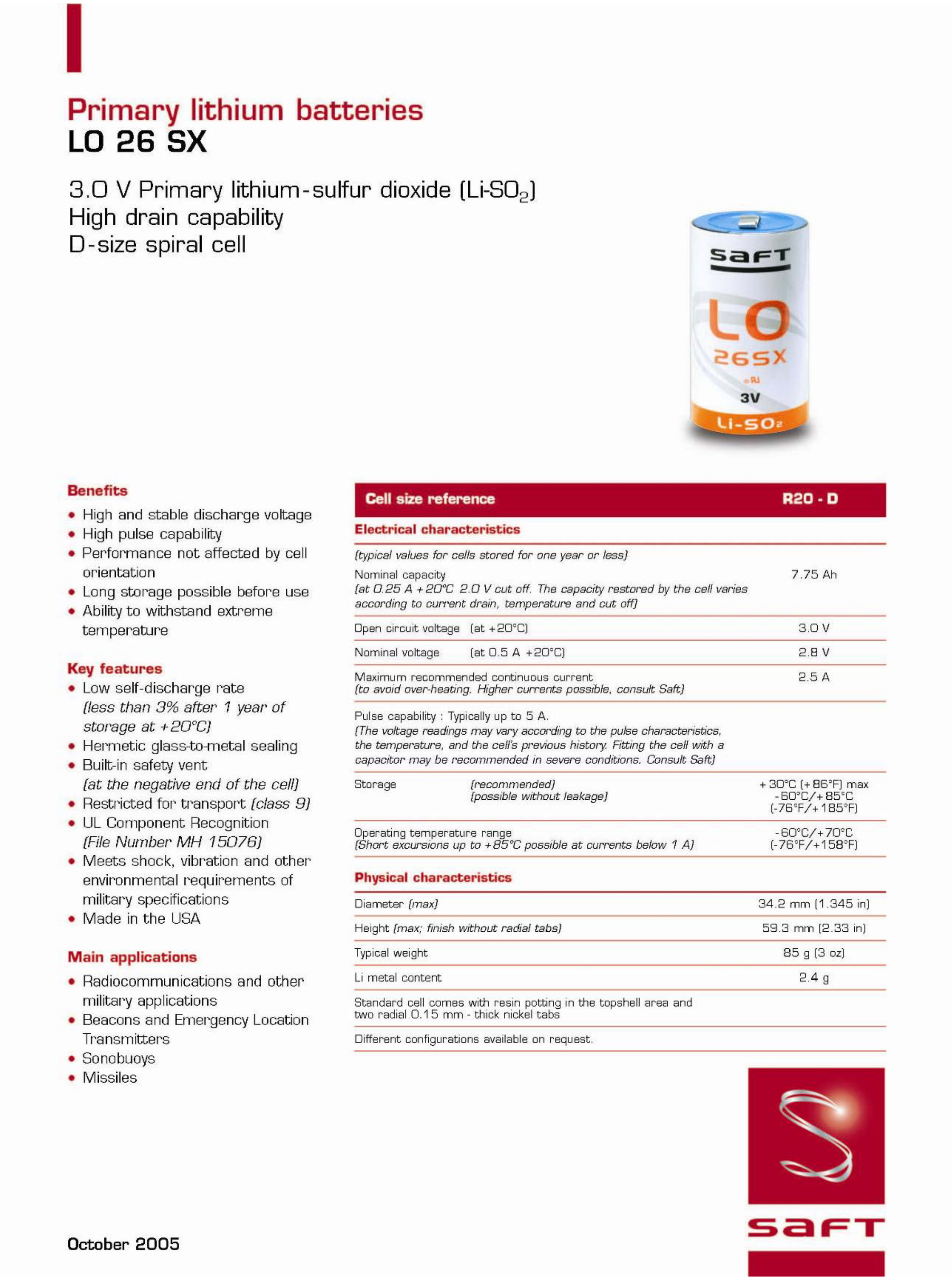

Primary lithium batteries
LO 26 SX

3.0 V Primary lithium-sulfur dioxide (Li-SO_2)
High drain capability
D-size spiral cell

Benefits

- High and stable discharge voltage
- High pulse capability
- Performance not affected by cell orientation
- Long storage possible before use
- Ability to withstand extreme temperature

Key features

- Low self-discharge rate *(less than 3% after 1 year of storage at +20°C)*
- Hermetic glass-to-metal sealing
- Built-in safety vent *(at the negative end of the cell)*
- Restricted for transport *(class 9)*
- UL Component Recognition *(File Number MH 15076)*
- Meets shock, vibration and other environmental requirements of military specifications
- Made in the USA

Main applications

- Radiocommunications and other military applications
- Beacons and Emergency Location Transmitters
- Sonobuoys
- Missiles

Cell size reference		**R20 - D**
Electrical characteristics		
(typical values for cells stored for one year or less)		
Nominal capacity *(at 0.25 A +20°C 2.0 V cut off. The capacity restored by the cell varies according to current drain, temperature and cut off)*		7.75 Ah
Open circuit voltage	(at +20°C)	3.0 V
Nominal voltage	(at 0.5 A +20°C)	2.8 V
Maximum recommended continuous current *(to avoid over-heating. Higher currents possible, consult Saft)*		2.5 A
Pulse capability : Typically up to 5 A. *(The voltage readings may vary according to the pulse characteristics, the temperature, and the cell's previous history. Fitting the cell with a capacitor may be recommended in severe conditions. Consult Saft)*		
Storage	*(recommended)*	+30°C (+86°F) max
	(possible without leakage)	-60°C/+85°C (-76°F/+185°F)
Operating temperature range *(Short excursions up to +85°C possible at currents below 1 A)*		-60°C/+70°C (-76°F/+158°F)
Physical characteristics		
Diameter *(max)*		34.2 mm (1.345 in)
Height *(max; finish without radial tabs)*		59.3 mm (2.33 in)
Typical weight		85 g (3 oz)
Li metal content		2.4 g
Standard cell comes with resin potting in the topshell area and two radial 0.15 mm - thick nickel tabs		
Different configurations available on request.		

October 2005

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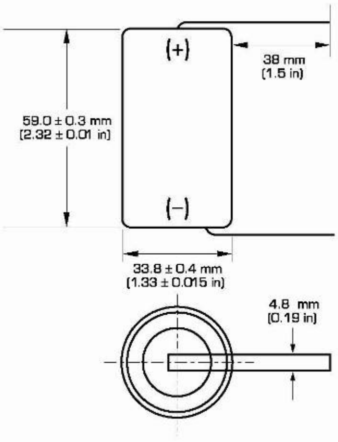

Overall dimensions

Handling precautions

- Cell is pressurised.
- Do not puncture, open or mutilate.
- Do not obstruct the safety vent mechanism.
- Do not short circuit or charge.
- Do not expose to fire or temperatures above +70°C (+158°F).

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313, Crescent Street,
Valdese NC 28690 - USA
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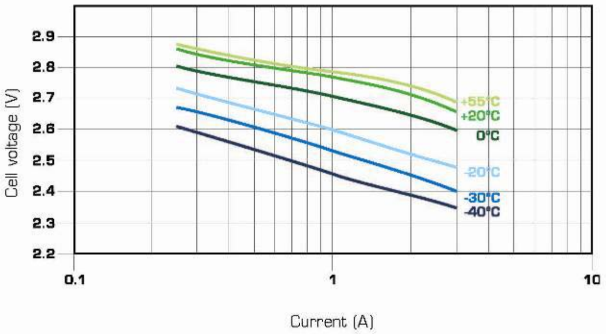
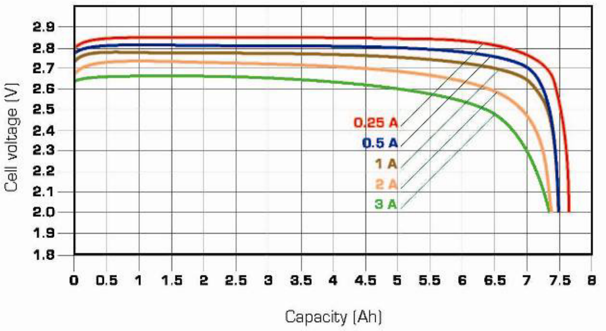
Fax +1 (828) 879 39 81

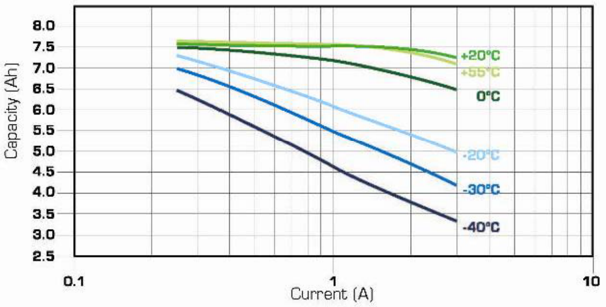
www.saftbatteries.com



Voltage at mid-discharge versus Current and Temperature (2.0 V cut off)



Typical discharge profiles at +20°C



Capacity versus Current and Temperature (continuous discharges - 2.0 V cut off)

Doc. N° 31033-2-1005

For more details on primary lithium technologies please refer to Primary Lithium Batteries Selector Guide Doc N° 31048-2.

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AGM
AGM Batteries Ltd

Product data

ICR34600 Li-ion Cell

Electrical Characteristics

Nominal Voltage	**3.6V**
Rated Capacity	**5.2Ah**

Physical Characteristics

Height	**60.3 ±0.2mm**
Diameter	**33.9 ±0.1mm**
Weight (nominal)	**138g**

Operating Conditions

Discharge Temperature Range	**-40°C to +70°C**
Max. Continuous Discharge Current	**10 Amps**
End (of discharge) Voltage	**2.5V**
Charging Method	**Constant current followed by constant voltage**
Charge Temperature Range	**0°C to +50°C**
End (of charge) Voltage	**4.2V ±0.05V**

Consult AGM for operation outside the above parameters

Safety Testing

The ICR34600 has undergone extensive safety testing in hostile environments to ensure it meets stringent requirements set by the IEC specification (IEC 61960 Pt1).

Continuous Charge	✔
Shock	✔
Vibration	✔
High Temperature Storage	✔
Thermal Shock	✔
Altitude Simulation	✔

Abuse Testing

AGM products have been tested in accordance with severe abuse conditions, laid out in the IEC specification (IEC 61960 Pt1), to ensure rigorous standards of safety and security for the user.

Short-circuit	✔
Forced Discharge	✔
Overcharge*	✔
Internal Short-circuit	✔
High Rate Charge	✔
Free Fall	✔

**Tested with integral protection*

Transportation Testing

The ICR34600 has been tested and conforms to the requirements of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria (ST/SG/AC.10/11/Rev.3 Amendment 1) as applicable from 1st January 2003. The cell may therefore be shipped by any commercial method of transport.

Refer to AGM for guidance on battery pack regulations

At our state-of-the-art factory in Thurso we design, develop and manufacture specialist lithium-ion cells. Our expertise in this field ensures that our products provide the ultimate in performance, reliability and operational efficiency in the harshest of operating environments.

Call +44 (0)1847 808060 for further information on the complete range of products and services from AGM Batteries Ltd

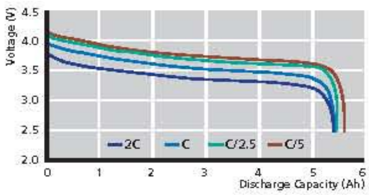
AGM Batteries Limited
reserve the right to modify
data in this publication
without prior notice

ICR34600 Li-ion Cell
Cell Performance Characteristics

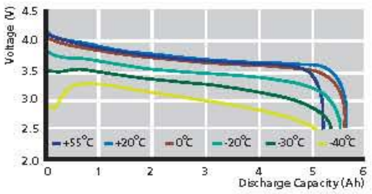
Product Benefits:

- **High energy density** *up to three times that of NiCd cells*
- **High running voltage** *replaces three NiCd or NiMH cells*
- **Excellent low temperature performance** *will operate down to -40°C and below*
- **Simple charging methods** *combination of constant current and constant voltage*
- **No memory effect** *unlike NiCd cells no need for conditioning cycles after shallow discharge*
- **Proven cycle life** *extended cycle life throughout operational environment*
- **Environmentally friendly** *contains no cadmium or lead*

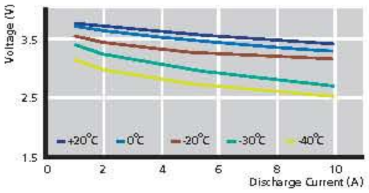
Discharge capacity vs current drain *Discharge at + 20°C*



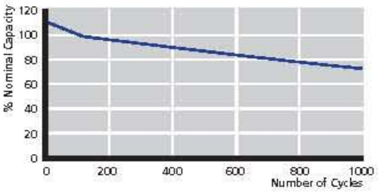
Discharge capacity vs temperature *Discharge at C/2.5 rate*



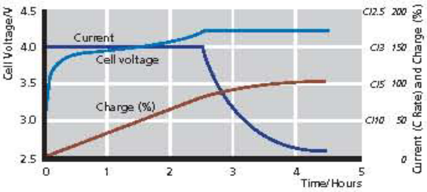
Voltage vs current and temperature *Average discharge voltage*



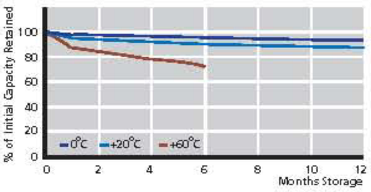
Cycle life* *Discharge at C/2.5 rate at +20°C charge at C/3 rate*



Charging method *CCCV Charging*



Charge retention *Discharge at C/2.5 rate*



**Cycle life will vary with charge rate, discharge rate, depth of discharge and operating temperature, consult AGM for details.*

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Issue: 0702/1

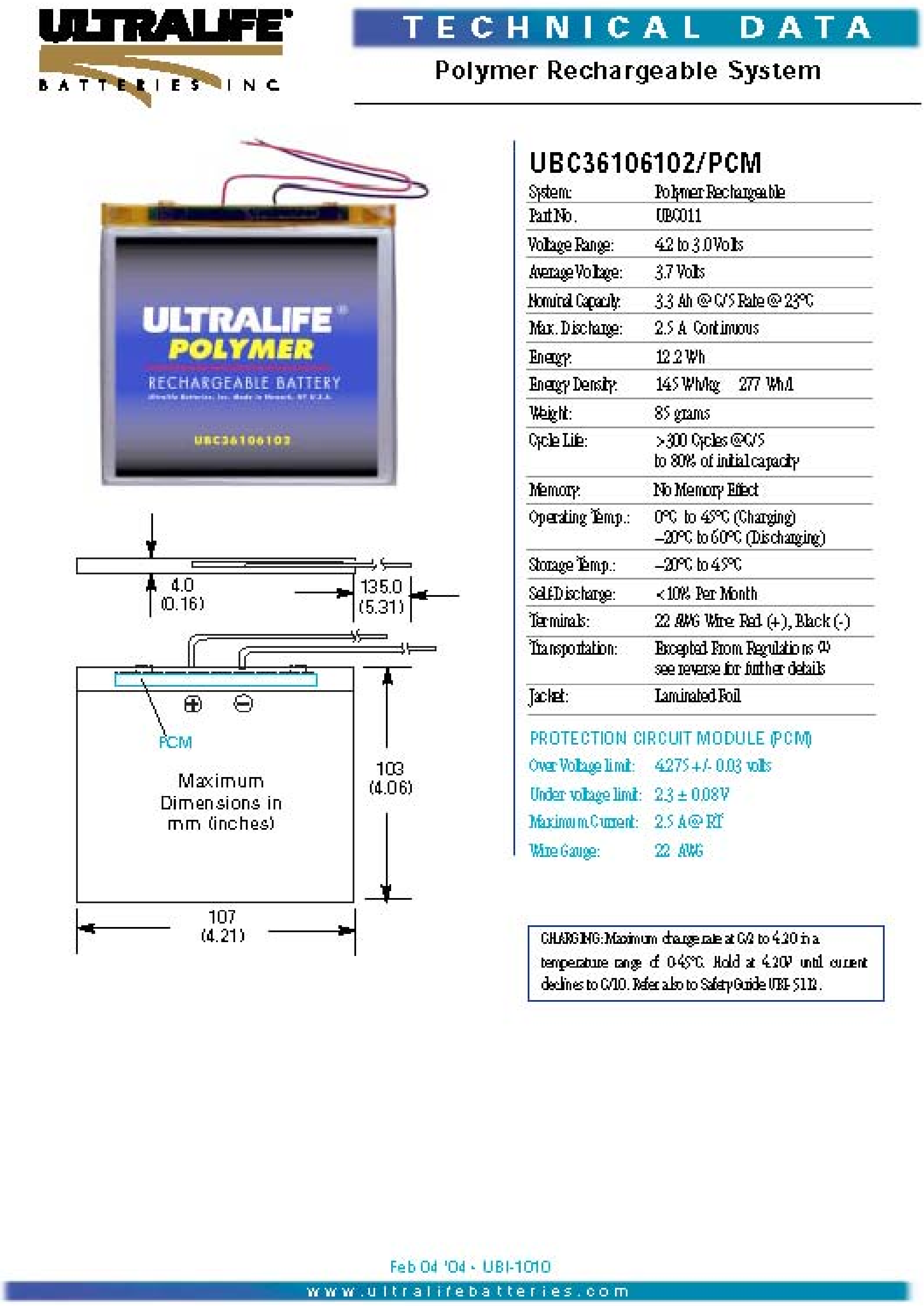
AGM Batteries Ltd

AEA TECHNOLOGY THE INNOVATION BUSINESS

GS JAPAN STORAGE BATTERY CO., LTD.

MITSUBISHI MATERIALS CORPORATION

AGM Batteries Limited is a joint venture company between AEA Technology plc, Japan Storage Battery Co., Limited and Mitsubishi Materials Corporation



ULTRALIFE BATTERIES INC

TECHNICAL DATA

Polymer Rechargeable System

UBC36106102/PCM

System:	Polymer Rechargeable
Part No.	UBC011
Voltage Range:	4.2 to 3.0 Volts
Average Voltage:	3.7 Volts
Nominal Capacity:	3.3 Ah @ C/5 Rate @ 23°C
Max. Discharge:	2.5 A Continuous
Energy:	12.2 Wh
Energy Density:	145 Wh/kg 277 Wh/l
Weight:	85 grams
Cycle Life:	>300 Cycles @C/5 to 80% of initial capacity
Memory:	No Memory Effect
Operating Temp.:	0°C to 45°C (Charging) –20°C to 60°C (Discharging)
Storage Temp.:	–20°C to 45°C
Self-Discharge:	<10% Per Month
Terminals:	22 AWG Wire Red (+), Black (-)
Transportation:	Excepted From Regulations (1) see reverse for further details
Jacket:	Laminated Foil

PROTECTION CIRCUIT MODULE (PCM)

Over Voltage limit:	4.275 +/- 0.03 volts
Under voltage limit:	2.3 ± 0.08V
Maximum Current:	2.5 A @ RT
Wire Gauge:	22 AWG

CHARGING: Maximum charge rate at C/2 to 4.20 in a temperature range of 0-45°C. Hold at 4.20V until current declines to C/10. Refer also to Safety Guide UBI-5118.

Feb 04 '04 - UBI-1010

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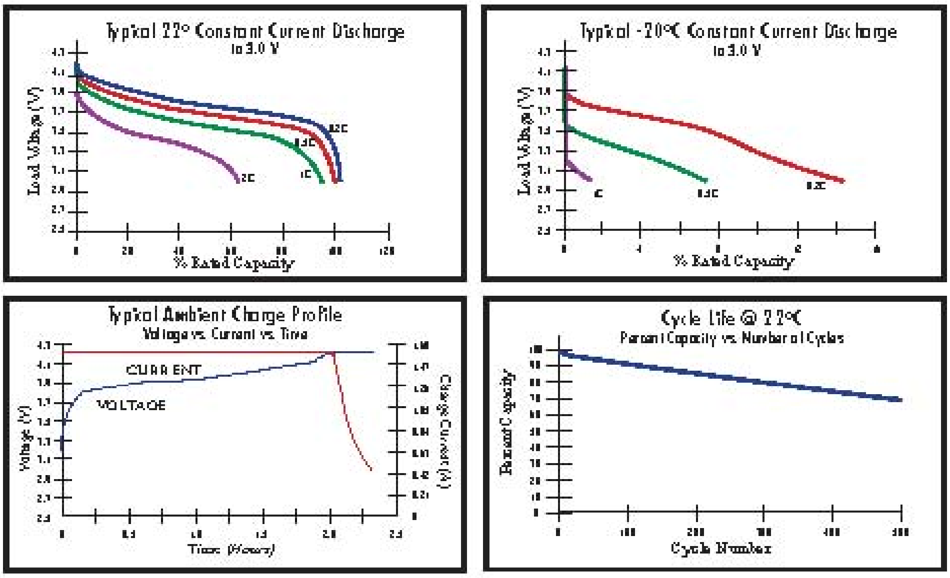
UBC36106102 Performance Characteristics



- Lithium polymer's thin, flat form factor accommodates tomorrow's thin application design requirements
- High energy density reduces weight without sacrificing performance
- Non-liquid electrolyte construction
- Discharge load characteristics, low-temperature and cycle performance similar to conventional Lithium Ion batteries based on liquid electrolytes

(1) For a complete description of transportation regulations and definitions of the transportation classifications "Excepted" and "Class 9," refer to Ultralife's web site at:

http://www.ulbi.com/whitepapers/Ultralife_Batteries_Lithium_Battery_Transportation_Regulations.pdf

Primary lithium battery
LS 33600

3.6 V Primary lithium-thionyl chloride (Li-$SOCl_2$)
High energy
D-size bobbin cell

Benefits

- High voltage response, stable during most of the lifetime of the application
- Wide operating temperature range *(-60°C/85°C)*
- Easy integration in compact system
- Low self-discharge rate *(less than 3% after 1 year of storage at +20°C)*

Key features

- Stainless steel container
- Hermetic glass-to-metal sealing
- Built-in safety vent
- Finish with or without flat positive end
- Non-flammable electrolyte
- Compliant with IEC 86-4 safety standard and EN 50020 intrinsic safety standard
- Underwriters Laboratories *(UL)* Component Recognition *(File Number MH 12609)*
- Restricted for transport *(Class 9)*

Main applications

- Utility metering
- Automatic meter readers
- Buoys
- Measuring equipment
- Industrial applications
- Professional electronics
- Marine equipment

Optional upon request

- Low magnetic version

Cell size references — **UM1 – R20 – D**

Electrical characteristics

(typical values relative to cells stored for one year or less at + 30°C max.)

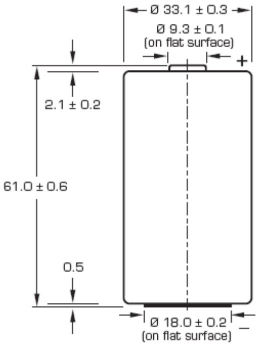
Nominal capacity *(at 5 mA + 20°C 2.0 V cut off. The capacity restored by the cell varies according to current drain, temperature and cut off)*		17.0 Ah
Open circuit voltage	(at + 20°C)	3.67 V
Nominal voltage	(at 0.7 mA + 20°C)	3.6 V
Pulse capability: Typically up to 400 mA *(400 mA/0.1 second pulses, drained every 2 mn at + 20°C from undischarged cells with 10 µA base current, yield voltage readings above 3.0 V. The readings may vary according to the pulse characteristics, the temperature, and the cell's previous history. Fitting the cell with a capacitor may be recommended in severe conditions. Consult Saft)*		
Continuous current permitting 50% of the nominal capacity to be achieved at + 20°C with 2.0 V cut off. *(to maintain cell heating within safe limits. Battery packs may imply lower level of maximum current and may request specific thermal protection. Consult Saft)*		250 mA
Storage	*(recommended)* *(for more severe conditions, consult Saft)*	+ 30°C (+ 86°F) max
Operating temperature range *(Operation above ambient T may lead to reduced capacity and lower voltage readings at the beginning of pulses. Consult Saft)*		- 60°C/+ 85°C (- 76°F/+ 185°F)

Physical characteristics

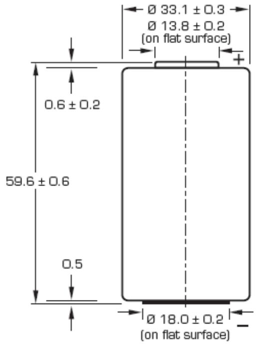
Diameter *(max)*		33.4 mm (1.32 in)
Height *(max)*		60.2 or 61.6 mm (2.37 in or 2.42 in) depending on finish type
Typical weight		90 g (3.2 oz)
Li metal content		approx. 4.5 g
Available termination suffix		
	CN, CNR	radial tabs
	CNA (AX)	axial leads
	FL	flying leads... etc.

November 2006

LS 33600



Finished version with protruding positive end cap



Finished version with flat positive end cap

Dimensions in mm.

Storage

- The storage area should be clean, cool (preferably not exceeding + 30°C), dry and ventilated.

Warning

- Fire, explosion and burn hazard.
- Do not recharge, short circuit, crush, disassemble, heat above 100°C (212°F), incinerate, or expose contents to water.
- Do not solder directly to the cell (use tabbed cell versions instead).

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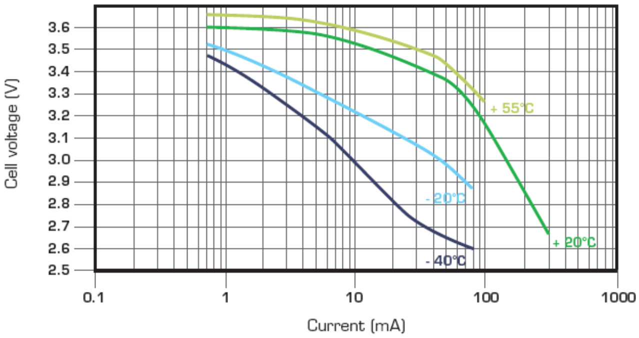
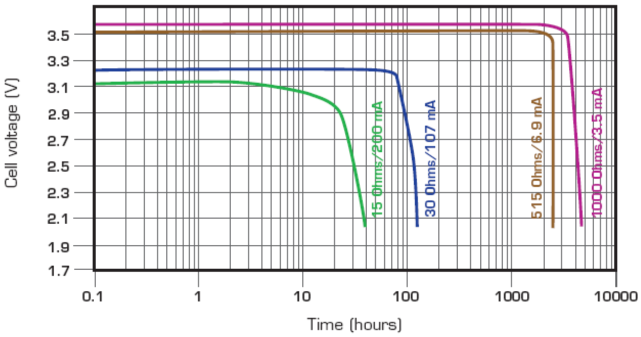
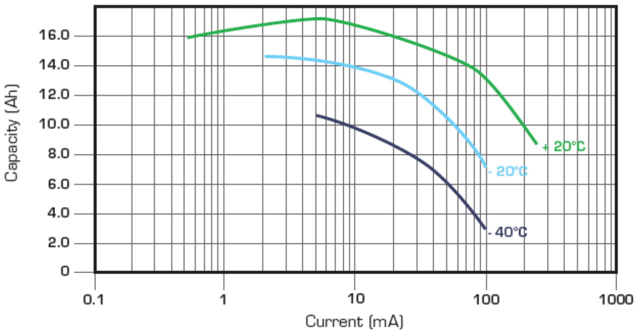


Voltage plateau versus Current and Temperature (at mid-discharge)



Typical discharge profiles at +20°C



Restored Capacity versus Current and Temperature (2.0 V cut off)

Doc. Nº 31007-2-1106

For more details on primary lithium technologies please refer to Primary Lithium Batteries Selector Guide Doc N° 31048-2.

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