

Safety aspects in primary high-rate lithium cells

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Abstract

A comprehensive presentation of the most important features influencing the safety of primary high-rate lithium cells is given. The design of such cells as well as the balance of cathode/electrolyte/anode are the most important features with respect to safety. The reliability of production, however, is of equal importance. The chemical reactions under electrical abuse conditions for the lithium/thionyl chloride system are given. Examples, how lithium/thionyl chloride spirally-wound 'C-size' cells behave under charging and forced overdischarge are presented. There are no indications that in the primary high-rate lithium systems, which are produced in a technical scale, dangerous chemical reactions influence the safety of the systems. Regarding the great number of primary high-rate lithium cells available in the market, the safety of these cells is excellent.

Introduction

Serious research on lithium batteries started already in 1962. Approximately ten years later, lithium primary cells and batteries were introduced into the consumer, commercial and military market.

In the meantime, the market for lithium cells has increased considerably. High-rate lithium primary cells have a considerable market share. Though most of the systems are already available for years, the safety of high-rate lithium cells is still of major concern. Therefore, it is worthwhile to summarize some of the relevant data regarding the safety of those systems.

Cell chemistry

Discharge reactions of several technically-important high-rate lithium cells are listed in Table 1.

The real discharge reactions may be more complicated. For Li/SOCl₂ discharge mechanisms, radicals have been suggested [1, 2]. The exact mechanism, however, is still not clear and radicals were not identified by, e.g., electron paramagnetic resonance (EPR). Most of the suggested mechanisms are thus based on speculation, and it is very likely that the real discharge reaction of SOCl₂ is complex.

In Li/SO₂ cells, more complex reactions are to be expected, than presented by the overall discharge equation. Independently from the exact mechanism, with respect to safety of lithium cells, it is important to stress that there are no indications that dangerous intermediate discharge products are formed in any of the lithium systems discussed here. Dangerous events that happened with high-rate lithium cells are

TABLE 1
Important high-rate lithium primary cell chemistries

Cell chemistry	Discharge reactions
Li/SO ₂	$2\text{Li} + 2\text{SO}_2 \longrightarrow \text{Li}_2\text{S}_2\text{O}_4$
Li/SOCl ₂	$4\text{Li} + 2\text{SOCl}_2 \longrightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$
Li/SO ₂ Cl ₂	$2\text{Li} + \text{SO}_2\text{Cl}_2 \longrightarrow 2\text{LiCl} + \text{SO}_2$
Li/MnO ₂	$\text{Li} + \text{Mn}^{\text{IV}}\text{O}_2 \longrightarrow (\text{Li}^+)\text{Mn}^{\text{III}}\text{O}_2$
Li/CF _n	$\text{Li} + (\text{CF})_n \longrightarrow \text{Li}(\text{CF})_n$

normally due to improper design and/or considerable abuse of the cells. There is no single case reported in the literature, proving that the cell chemistry was dangerous.

Design (internal safety features)

Cell core

The electrode areas have to be large to achieve a high-rate lithium cells. This can be achieved either by a stack or by a spirally-wound design. All commercial high-rate lithium cells have the spiral wound construction. Special precautions have to be taken to avoid the possibility of internal shorts, e.g., of the electrode current collectors and/or the current collector tabs for cathode and anode.

Vent

A built-in vent is necessary for a high-rate cell; it allows the release of the electrolyte, before the temperature inside the cell reaches critical values (melting point of lithium ~ 180 °C). The desired temperature range for the vent to operate is generally between 100 and 150 °C.

Overheating of the cell

To prevent overheating of the cell, an internal fuse can be used, e.g., the current collector tab can be very thin at a certain spot, so that it melts if the current becomes too high. However, this has to be tested very carefully, to avoid that the metallic tab which becomes very hot before it disconnects, leads to a thermal runaway reaction of the lithium cell.

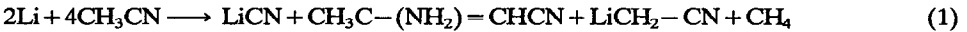
Another built-in safety feature may be a shut-down separator, which is a porous plastic material that closes most of the pores due to a shrinkage process at a temperature above 100 °C and well below the melting point of lithium. Thus, the maximum current which can be delivered from the cell under, e.g., short circuit will be drastically decreased and a critical overheating of the cell will be avoided.

Whereas a vent in a high-rate lithium cell is a standard feature, shut-down separators, until now, exist only in materials that can be used in cells with organic electrolytes.

For safety purposes of a cell it is important that only materials are used which are compatible with the other cell ingredients, like lithium and the electrolyte, especially for separator and insulating washers, and for the sealants, e.g., plastic feed-throughs and glass-to-metal seals. The chemical balance of materials (e.g. cathode/anode ratio) is certainly one of the most important points influencing inherent safety of a high-

rate lithium cell. If this balance is improper, critical situations may evolve, due to chemical corrosion reactions in the cell or due to resistive overheating of the cell at the end of discharge.

The criticality of a not suitably balanced cell may be explained best by using the example of the Li/SO₂ cells. The electrolyte of Li/SO₂ cells consists of sulfur dioxide, dissolved in acetonitrile and a conductivity salt (mostly LiBr). The lithium surface is protected by a lithium dithionite film (due to a reaction between lithium and sulfur dioxide). However, if the cell chemistry is unbalanced and excess lithium is present, at the end of discharge no sulfur dioxide is available to form the protection layer on the lithium surface. Dey and Holmes have shown in a differential thermal analysis (DTA) measurement that lithium metal reacts exothermic with acetonitrile, even at room temperature [3]. The decomposition reaction between Li and acetonitrile is [4]:



These reaction products can cause disastrous events in the cell. This situation can be avoided if an excess of sulfur dioxide is used or even a better balanced design (stoichiometric cathode/anode ratio, approximately 1:1).

An example in which resistive overheating of the cell at the end of discharge may occur if the cell does not contain a suitable electrolyte/anode ratio, is the lithium/thionyl chloride high-rate cell. In this system, the electrolyte is reduced during the discharge reaction and forms lithium chloride, sulfur dioxide and sulfur. Sufficiently large excess of electrolyte has to be used [5, 6] in order to avoid a very high internal cell resistance at the end of discharge due to a drying out of the cell.

External safety devices

In addition to the internal safety features, external safety devices should be added. If a high-rate lithium cell is applied as a single cell, it is advisable to equip it with a suitable electric fuse, or preferably with a reversible thermofuse (PTC, widely known under the tradename Polyswitch). This thermofuse has to be selected properly in order to shut down the maximum current, at an external short circuit, to uncritical values.

External contacts and insulators (at the top of the can) have to be applied in a way that prevents incidental short circuits. The vent should be protected against incidental damage.

In a multicell battery, in which a chance of charging of cells or strings of cells exists, protective diodes should be used, as well as a suitable fuse for the battery pack.

All intercell connectors in a battery pack should be properly insulated to avoid incidental shorts, even under severe mechanical shock or vibration.

Reliability

The reliability of production is another topic which is of utmost importance regarding the safety of lithium cells. Suitable quality control measures, e.g. statistical process control and other quality control methods, are necessary to achieve at the end a total quality management.

The failure mode and effect analysis is a good tool, which can be applied for the development and for the production.

Abuse tests

As until now there are no international standards regarding the testing of lithium cells and batteries, several military standards may be applied, as well as the tests required by Underwriter Laboratories for industrial applications.

Though the requirements differ slightly from country to country, common qualification tests for lithium batteries include environmental tests, such as shock, vibration (flight and transport), drop test, low pressure, extreme temperature storage, as well as electrical abuse tests, such as short-circuit tests and forced overdischarge. Besides these tests, charging of the cells is another important electrical abuse test.

Forced overdischarge

The chemical reactions which may occur in a primary high-rate lithium cell during forced overdischarge depend on the actual situation of the cell. Lithium/thionyl chloride is an example giving the cell reactions under abuse conditions in detail.

Anode-limited cell

In this case (no lithium left after discharge of the cell down to 0 V) the cell potential reverses to -3.5 to -4 V. The chemical reaction is mainly the formation of chlorine at the anode current collector, resulting from the oxidation of $\text{SOCl}_2/\text{LiAlCl}_4$. This chlorine may be reduced at the carbon cathode, leading to the formation of LiCl . LiCl can recombine with AlCl_3 to LiAlCl_4 (as long as enough electrolyte is left):



Carbon-(‘cathode’) limited cell

This situation occurs even in normally anode-limited cells at high discharge currents and at low discharge temperatures. The main reaction during forced overdischarge is the formation of lithium dendrites on the carbon cathode:



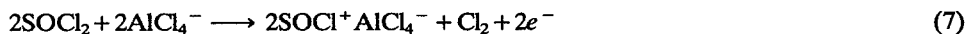
These dendrites lead to small internal shorts, which obviously are not critical with respect to safety. In contrast, these shorts offer electronically-conductive bridges where the current can pass through, without causing excessive heat or excessive gas formation [7].

The overdischarge behaviour of $\text{Li}/\text{SO}_2\text{Cl}_2$ or Li/CSC ($\text{Li}/\text{SO}_2\text{Cl}_2 + \text{Cl}_2$) cells is comparable with the behaviour of Li/SOCl_2 cells, if the ratio of initial lithium to cathode is the same [3].

The above reactions are just an example, demonstrating what happens during forced overdischarge in lithium high-rate cells of a certain chemistry. In other chemical systems, like Li/SO_2 , Li/MnO_2 and Li/CF_x , the reactions are different, however, in all cases the cells can safely withstand extended discharge below 0 V into voltage reversal if the currents are not too high.

Charging of cells

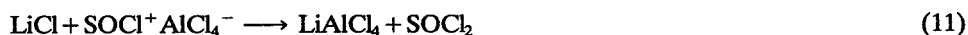
The processes occurring during charging of lithium high-rate cells shall be demonstrated by using again the example of lithium/thionyl chloride. The data obtained suggest that regenerative processes occur [7]. The predominant reactions on the carbon electrode at the measured potentials are:



and,



On the lithium electrode reduction processes can take place:



Test results with practical cells

Spiral-wound 'C-size' cells in lithium/thionyl chloride technology were subjected to a number of performance and abuse tests.

The cells were lithium limited with excess of electrolyte, to prevent excessive overheating at the end of a high-rate discharge. The can had a stamped vent that operated reliably at temperatures between 120 and 140 °C.

Typical discharge data of these cells are given in Table 2. The results demonstrate, that even at high currents (1 A), the cells show a good performance. After the cells are being tested under regular discharge conditions at different currents and no critical heating of the cells at the end of a constant current discharge determined, several tests under electrical abuse conditions were done.

Cells were subjected to a charging current of 500 mA for 15 h, after being discharged to 50% of their nominal capacity. An other set of cells was subjected to the same charging conditions, after being fully discharged at 500 mA (down to 0 V cutoff). The results of this test are presented in Table 3.

Charging with 500 mA of the completely discharged cells at room temperature lead to a venting of two out of three test cells; in all other cases neither a venting nor any other safety relevant effect occurred. The cell voltage during this charging test levelled at a plateau of ~3.8–4 V due to the chemical reactions which occur at the anode and at the cathode, which have been explained in the preceding chapter.

The electrical behaviour of a cell under charging conditions is shown in Fig. 1.

Table 3 shows also the results of a forced overdischarge test at three different currents and at three different temperatures. No critical event was observed, which is due to the mechanism explained earlier for carbon ('cathode') limited cells. This mechanism, however, can only work as long as lithium is left, before the cell goes to voltage reversal. This condition is normally fulfilled, unless the cell is discharged at very low currents. In this case, the cell is really anode limited, since all lithium is consumed before the voltage reversal occurs.

The reactions which may occur in this situation are described in ref. 7. Reaction products found in such cells by applying infrared and partly also cyclic voltammetric techniques, include Cl_2 , SCl_2 , SO_2Cl_2 and $\text{SOCl}^+ \text{AlCl}_4^-$ [7–9]. SO_2Cl_2 seems to be a

TABLE 2

Spiral wound 'C-size' cells: typical discharge results

Discharge current	Temperature (°C)	Capacity (A h) (cutoff 2.5 V)
20	63	5.9
	room temperature	6.0
	-30	4.1
100	63	6.6
	room temperature	4.6
	-30	2.5
200	63	6.2
	room temperature	4.3
	-30	2.0
500	63	5.4
	room temperature	3.4
	-30	2.1
1000	63	4.2
	room temperature	2.4
	-30	1.8

TABLE 3

Abuse tests of spiral-wound 'C-size' cells

Test conditions	Temperature (°C)	Current	Status of cell	Effect
Charging	60	500 mA	Discharge to 50% of capacity	None
	room temperature	at 10 V		None
	-30	for 15 h		None
Charging	60	500 mA	Completely discharged (to 0 V)	None
	room temperature	at 10 V		Vent open
	-30	for 15 h		None
Forced overdischarge	65	1000 mA	After complete discharge	None
	room temperature	>7 h		None
	-40			None
	65	500 mA	After complete discharge	None
	room temperature	>15 h		None
	-40			None
	65	200 mA	After complete discharge	None
	room temperature	>37.5 h		None

reaction product from SO₂ (regular discharge product) and Cl₂ (formed during overdischarge).

Regarding safety of the system, it is very important to notice that the formation of ClO₂ and Cl₂O which was proposed earlier [10], was not verified in later work [11, 12].

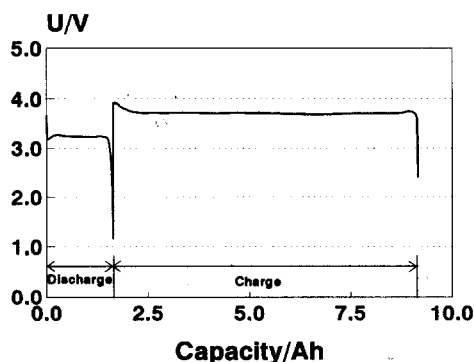


Fig. 1. Discharge and charging curve of a spiral-wound lithium/thionyl chloride 'C-size' cell at a constant current of 500 mA.

Conclusions

Summarizing the results from the literature and our own test results with high-rate lithium/thionyl chloride cells, we conclude that the high-rate lithium cells show considerable stability, even under electric abuse [6].

Regarding the chemistry in Li/SO₂ high-rate cells under electric abuse conditions, reference is made to earlier publications [3, 13, 14].

For the solid-state cathode systems, much less information on electrical abuse tests is available, especially on the chemistry occurring in the cells under abusive conditions. The test results of a high-rate Li/MnO₂ 'D-size' cell under forced over-discharge conditions, applying 5 A at -30 °C, however, show that even though the maximum temperature of the cell reached approximately 120 °C, the cell resisted this test [15].

According to reported data, primary lithium high-rate cells can be considered to be safe, even under forced overdischarge and charging conditions in the specified range of currents for regular discharge.

Nevertheless nearly all manufacturers are demanded to avoid such abusive conditions. This can be achieved by using blocking diodes. Excellent safety for primary lithium high rate cells was achieved by using state-of-the-art design for the cells and by applying additional external safety devices, such as suitable thermofuses and diodes. This may be demonstrated by the history of the Li/SO₂ batteries [16]. In the early days of development of the system, in 1974, several incidents with Li/SO₂ battery packs were reported. It should be kept in mind, however, that at that time the cells did not have a 'balanced' design, that they were not hermetically sealed and that they had no or only an ineffective venting mechanism.

Other safety related failures in battery packs were caused by peripheral components, not by the lithium cells. After having improved the cell construction and the periphery, the safety of the cells improved considerably [17].

In early days a safety related failure rate of 0.011% is reported (295 000 batteries delivered to the field in the US Army); after application of the above-mentioned improvements, the safety-related failure rate of more than 1.4 million batteries in the field decreased to 0.0006% [18]. This is an impressive value. Furthermore, this example demonstrates, that battery chemistry is not dangerous, but that the design and the peripheral safety measures as well as the reliability of a production make a primary lithium high-rate cell more or less safe.

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