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SAFETY TEST RESULTS OF LITHIUM–THIONYL CHLORIDE WOUND-TYPE CELLS

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Summary

Increase in the use of spirally-wound, lithium–thionyl chloride cells is currently limited because of unsafe incidents which have been reported during the early stages of development of this product. Today, we believe that these cells are safe over a wide range of operating conditions if properly designed.

This paper describes the external and internal SAFT design of Li–$SOCl_2$ LSH series cells, as well as the results of safety tests.

Introduction

The lithium–thionyl chloride (Li–$SOCl_2$) system involves a primary cell offering one of the highest energy densities, as well as a high operating voltage and a wide operating temperature range (−40 °C to +80 °C).

The rate capability for such an electrochemical system is related to the surface area of lithium. Low rate (bobbin type) and medium-to-high rate Li–$SOCl_2$ cells (spirally-wound type) have been developed to meet customers' specifications.

As the rate capability and capacity increase for a given specified volume (spirally wound "C" and "D" size Li–$SOCl_2$ cells, for example), however, the safety issue has to be addressed in depth through internal design improvements and knowledge of the safe operating range [1].

Long term SAFT experience with lithium–thionyl chloride spirally wound cells (early development in 1970 by Gabano [2] — 6 years experience in production) has resulted in improved knowledge of this product in terms of safety.

The aim of this paper is to present safety test results related to the internal design of "C" and "D" size Li–$SOCl_2$ wound-type cells.

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SAFT design of "C" and "D" size Li–$SOCl_2$ cells (LSH series)

The following features are involved in safety considerations of Li–$SOCl_2$ wound type cells:
(i) cell hardware;
(ii) internal cell design;
(iii) cell balance: electrolyte to lithium and lithium to carbon ratio.

(i) Cell hardware

Due to the corrosive nature of $SOCl_2$ the container must not leak under normal operating conditions. This is achieved by using a stainless steel can, with glass-to-metal seal and TIG welding of case to cover. This well-known design requires a mechanical safety vent which opens if internal over-pressurization occurs during high temperature excursions. To prevent such high internal temperatures, the cell hardware must include both internal and external fuses. The internal fuse protects against hazards resulting from either an external short or a too high discharge rate. The internal fuse acts as a safety feature during cell manufacture or in battery assembly, where a single fuse is used for several cells.

(ii) Internal cell design

The internal design must guard against internal shorts during production, storage, and discharge over a wide range of environmental conditions (vibration, shock; -40 °C to $+80$ °C, etc...). This can be achieved through suitable choice of separator material, geometric arrangement of both anode and carbon cathode, and location of internal tabs.

As we were using woven metallic grids as current collectors it was necessary to cut them during the process. Due to this operation, some metallic wires of the woven grid were projected beyond the carbon cathode resulting in possible internal short-circuit. During the development stage, internal shorts were observed at the end of discharge of "D" size cells using woven grids as current collectors. This problem was successfully overcome by using an edged grid for the carbon cathode and a nickel strip for the anode. This design avoids remaining metallic pin.

In order to avoid, as far as possible, excess lithium at the end of discharge, winding takes place in such a way that the lithium anode is completely surrounded by the carbon cathode.

(iii) Cell balance

(a) Lithium

Figure 1 shows the energy released, during an explosion of "C" size cells, as a function of the electric energy remaining in the cell after partial discharge. This energy is mainly a result of direct chemical reaction between lithium, $SOCl_2$ and sulphur. In order to reduce the energy remaining in the cell at the end of discharge, the quantity of lithium remaining must be reduced to a minimum. To this end, SAFT "C" and "D" size Li–$SOCl_2$ cells

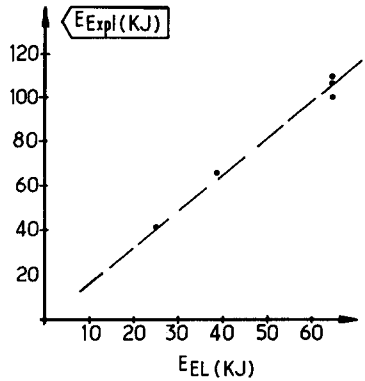


Fig. 1. Energy released during explosion of C cells (LSH 14) *vs.* the difference between the nominal capacity of the cell and the energy consumed during discharge (results obtained by the Norwegian Defense Research Establishment — NDRE).

were assembled with the following balance:

"D" size: nominal capacity 10 A h, stoichiometric lithium 10.8 A h;
"C" size: nominal capacity 5 A h, stoichiometric lithium 5.6 A h.

(b) Electrolyte

There must be an excess of electrolyte to avoid drying of the cell at the end of discharge [3] (hazards reported).

"D" size: stoichiometric lithium = 10.8 A h, stoichiometric $SOCl_2$ = 17.2 A h, ratio $SOCl_2/Li$ = 1.6;
"C" size: stoichiometric lithium = 5.6 A h, stoichiometric $SOCl_2$ = 8.5 A h, ratio $SOCl_2/Li$ = 1.5

(c) Carbon cathode

From our experience, in the early stages of $SOCl_2$ development, the choices made by SAFT were:

*lithium limited design for low rate discharge;

*carbon limited design for moderate to high rate applications and/or low temperature (−40 °C). Due to our $SOCl_2/Li$ ratio, the cell is never $SOCl_2$ limited.

These choices determine the mechanisms and, consequently, the heat generation involved during discharge/overdischarge.

Safety test results

(i) External heating of cells

When externally heated, internal pressure in the cells increases due to electrolyte thermal expansion and the vapor pressure of $SOCl_2/SO_2$. To avoid an explosion resulting from over-pressurization of the container, the mechanical safety vent must open in the range 120 °C - 155 °C. Temperatures above 180 °C may result in the melting of lithium and an internal short.

(a) Slow external heating - sand bath

The temperature was increased step by step until venting occurred. These tests were performed on 0%, 50% and 75% discharged cells. As required, the vent opening between 120 °C and 150 °C allowed electrolyte and gas expulsion without explosion or fire.

(b) Rapid external heating — flame test

The cell was heated by a direct flame in such a way that the vent opened in 3 min maximum. The cell was not moved until the lithium fire occurred. Tests performed on 75% discharged cells showed that no metal fragments were formed or ejected from the cell.

(ii) High rate discharge

Our cells include an external fuse (5 A) to overcome hazards arising from external shorts and high rate discharge. Tests were performed with the current slightly higher than 5 A (without an external fuse). Figure 2 shows the results obtained under a 0.38 Ω load. The maximum temperature reached was 75 °C for a current in the range 6.4 - 6.8 A.

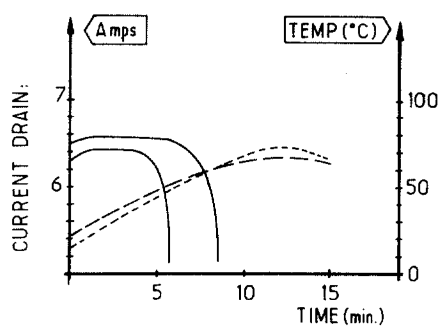


Fig. 2. High rate discharge of C cells (0.38 Ω load). Current and temperature *vs.* time.

(iii) Charge

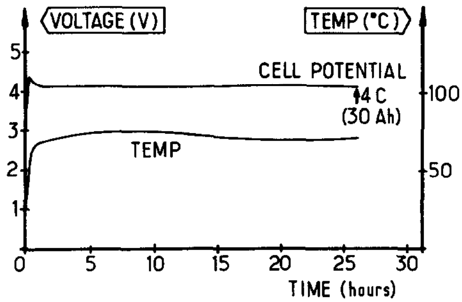
The tests were undertaken with a constant current power supply on "D" size cells.

(a) Undischarged cells

Typical behavior under 1.5 A is illustrated in Fig. 3. The cell voltage is constant (4.2 V) up to 26 h of charge (39 A h). The temperature reached was 75 °C after 5 h and no unsafe behavior was observed.

(b) 75% discharged cells

75% Discharged cells were charged under 1.5 A at 20 °C. Of the three cells tested, one cell exploded, and one cell exhibited container bulging. The



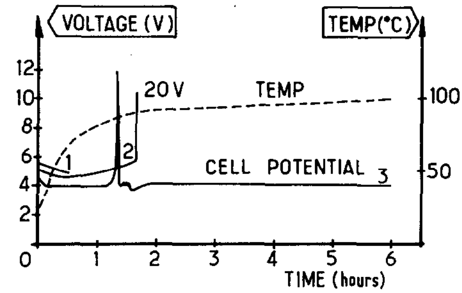


Fig. 3. Recharge at 20 °C and 1.5 A of undischarged D cell. Current and temperature *vs.* time.

Fig. 4. Recharge at 20 °C and 1.5 A of discharged D cells. Current and temperature *vs.* time. Cell 1: explosion; cell 2: rupture of internal tab; cell 3: safe behavior.

results obtained are shown in Fig. 4. From complementary tests carried out under 1 A and 0.75 A it would appear that a current equal to, or less than, 0.75 A may be acceptable.

The results show that charging Li–$SOCl_2$ cells at low currents may not incur safety problems, especially with undischarged cells. However, batteries (or cells in a battery) must be equipped with blocking diodes to prevent any unsafe behavior when cell charging appears to be possible.

(iv) Overdischarge

As previously stated, the SAFT internal cell design results in anode limited or carbon cathode limited cells, depending on the rate of discharge.

(a) Anode limited overdischarge

The typical behavior during discharge/overdischarge of a "D" size cell (220 mA, 25 °C) is shown in Fig. 5. Due to the oxidation potential of the electrolyte on the anodic current collector, the cell potential reverses. The electrochemical reactions involved during overdischarge of lithium-limited cells give rise, mainly, to chlorine and aluminium chloride resulting from the oxidation of $SOCl_2/LiAlCl_4$ [4, 5].

A regenerative process occurs as Cl_2 is reduced on the carbon cathode to form LiCl. Aluminium chloride reacts with LiCl leading to $LiAlCl_4$. Excess electrolyte at the end of discharge facilitates the regenerative process, and heat transfer, possibly explaining the results obtained.

(b) Carbon cathode limited overdischarge (CCL)

During overdischarge of "D" size cells at 25 °C or at −40 °C, the main occurrence is lithium dendrite growth from the carbon cathode through an electrodeposition process. A study performed at SAFT demonstrates that these lithium dendrites produce electronically conductive bridges between anode and carbon cathode (internally shorted cell) as suggested by Abraham *et al.* [4].

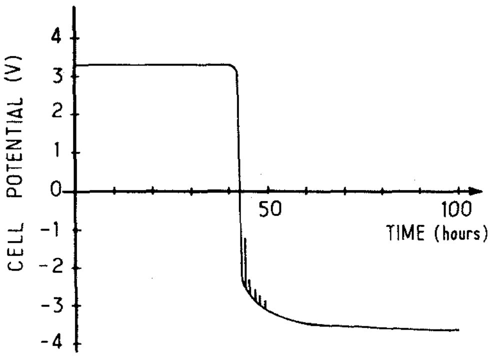


Fig. 5. Discharge/overdischarge at 25 °C and 220 mA of a D cell (anode-limited cell).

CCL overdischarge at 25 °C. Typical behavior is shown in Fig. 6.

The small exothermic peak is a result of polarization processes at the end of discharge. Below 0 V, lithium dendrites cause internal short circuits which effectively reduce the probability of thermal runaway by internal resistive heating.

Being electronically conductive, the current goes via lithium bridges and does not lead to any chemical or electrochemical reaction. The cell potential is equal to −0.2 V, even after complete theoretical consumption of stoichiometric lithium.

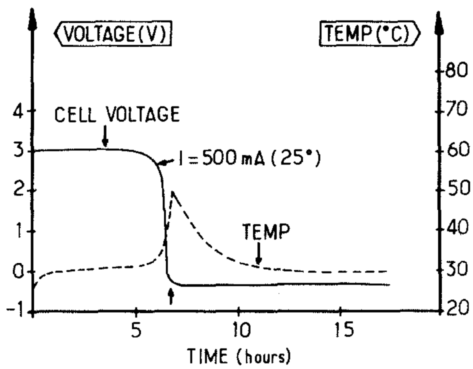


Fig. 6. Discharge/overdischarge at 25 °C and 500 mA of a C cell (carbon cathode-limited cell).

CCL overdischarge at −40 °C. Some hazardous behavior was reported in the literature after discharge at low temperature. These problems were probably related to improper internal cell design causing shorting of the cell at the end of low temperature discharge.

As this cell is allowed to warm up, exothermic effects may occur, due to recovering of the electrochemical reduction of $SOCl_2$ on the carbon cathode. No unsafe behavior, involving a large number of single Li–$SOCl_2$ cells of various sizes discharged at low temperature, was observed in SAFT's laboratories.

The problem of overdischarge at −40 °C is related to shorting of the cell by lithium dendrites.

The discharge/overdischarge curve and cell temperature response of a "C" size cell at −40 °C is shown in Fig, 7. Due to dendrites, the cell is internally shorted during overdischarge, and exhibits safe behavior. Warming this cell immediately after overdischarge results in a slight exothermic effect (Fig. 8). If the cell is kept at −40 °C for a few hours after overdischarge, however, no exothermic effect is observed, probably due to dendrite dissolution by chemical reaction with $SOCl_2$.

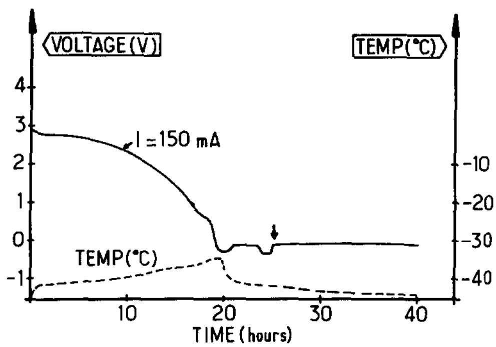


Fig. 7. Discharge/overdischarge at −40 °C and 150 mA of a C cell (carbon cathode-limited cell).

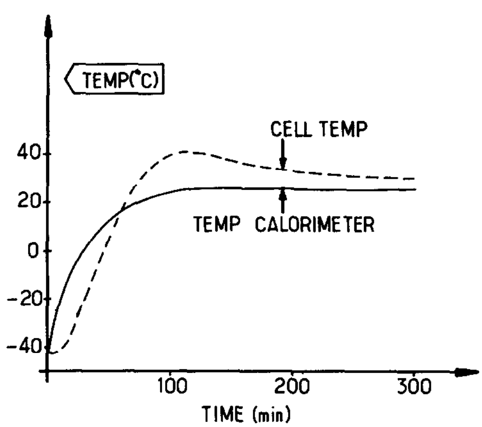


Fig. 8. Typical heating profile for a C cell after overdischarge at −40 °C for 22 h. The cell is kept at open circuit during warming up (results obtained by N.D.R.E.).

This thermal effect is attributed to the resumption of electrochemical reactions as the internally shorted cell warms up. Of many tests performed at −40 °C on "C" and "D" size cells (current density ranging from 1.5 to 5 mA cm^{-2}) no hazardous situations were observed, contrary to reported incidents involving Li–$SOCl_2$ cells [6]. The tests were carried out on unit cells, with a constant current power supply. Additional tests have been

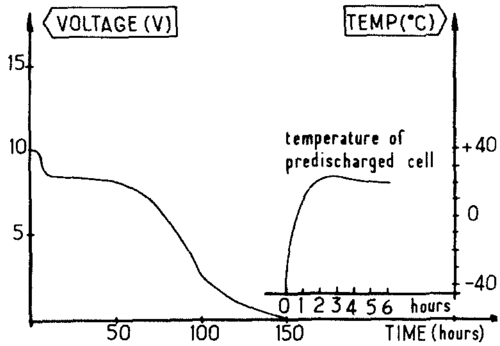


Fig. 9. Discharge of 4 "D" size cell batteries containing one predischarged cell (—40 °C, 35 Ω, open-circuit voltage: 2 V).
Discharge load: —40 °C; 1 A/0.55 - 50 mA/590 s; average curve for three batteries.

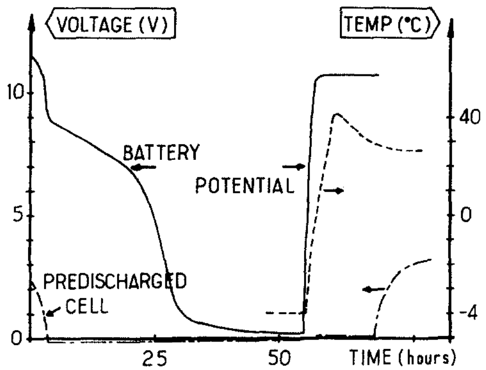


Fig. 10. Discharge of 4 "D" size cell batteries containing one predischarged cell (—40 °C, 0.28 A, 60%).
Discharge load: —40 °C; 30 Ω.

conducted in a multicell configuration to determine the safety level of low temperature overdischarge performed under realistic conditions. Batteries of 4 "D" size cells in series, with one predischarged cell, were assembled. To reproduce the worst possible conditions, the cells were not fitted with protecting diodes against overdischarge, and were allowed to warm up immediately after overdischarge. Typical results are shown in Figs. 9 and 10.

No hazardous behavior was observed during discharge/overdischarge. Only a slight exothermic peak occurred on the predischarged cell during warming up.

Conclusion

A properly designed, spirally-wound, lithium–thionyl chloride cell is safe under normal operating conditions, assuming strict quality control and good engineering design practice during the manufacturing process.

Based on our experience and knowledge of this system, we believe that hypothetically hazardous chemical intermediates (metastable compounds) are not involved in the operation of Li–$SOCl_2$ cells.

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