

Short Communication

Failure process of Li/SOCl₂ cells at 200 °C

Tian Jian, Liu Shenzhong

Changchun College of Optics and Fine Mechanics, PO Box 1003, Changchun 130022, China

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Abstract

The failure process of Li/SOCl₂ cells at high temperature (200 °C) is investigated. The leakage of SOCl₂ vapour through microseams in the cell is found to be the main cause. Cells without microseams or vapour leakage have longer storage times and their decline in performance is ascribed to self-discharge processes.

Keywords Failure; Lithium; Thionyl chloride cells

1. Introduction

During the past two decades, lithium cells/batteries have become significant electrochemical power sources in the world. The military and commercial demand for high-performance, light-weight battery systems has resulted in the development of a series of lithium cells that meets the needs of armed forces, space probe programmes, and electronic devices that require power sources of small and long shelf life.

The aim of this study is two-fold: (i) to evaluate the tolerance of Li/SOCl₂ cells to temperatures above the melting point of lithium metal; (ii) to determine the failure mode of cells under such conditions. It should also be noted that many applications have very strict requirements with respect to the shelf life of lithium cells. Since the storage time of lithium cells is much greater than that of Zn/Mn cells, tests to determine this parameter will be time-consuming. Thus, it is necessary to develop a practical technique that will deliver results in a relatively short time, i.e., several weeks or months. Exposure to high temperature is one approach to achieving this goal.

The low solidifying point of SOCl₂ makes Li/SOCl₂ cells more competitive because they can be used at temperatures as low as -70 °C. In practice, the cells are normally operated below 70 °C. The temperature chosen for the studies reported here (namely, 200 °C) is not only higher than the boiling point of SOCl₂ (75 °C), but is also above the melting point of lithium metal (186 °C). At this test temperature, however, the vapour

pressure of SOCl₂ is quite significant. Moreover, the temperature also rises as the cell is discharged.

2. Experimental

The accelerated tests were performed at 200 °C in stainless-steel lined ovens. The test temperature was monitored by a standard glass mercury thermometer that was automatically controlled. The lithium cells were placed in glass containers that were fitted with lids. The storage time was measured from the introduction of the cells into the oven. For open-circuit potential (OCV) measurements, the cells were removed from the oven and cooled to room temperature for 1 h. An F-45/CH dual-display multimeter was used to measure the OCV. The cells were then returned to the oven for further storage at 200 °C. The 'failure' OCV was set at below 2.5 V.

Studies were conducted on three types of Li/SOCl₂ cells, designated A, B and C. Schematic diagrams of the different designs are given in Fig. 1.

All of the cell cans were made from stainless steel. The lithium was contacted to a nickel net. The cathode consisted of a mixture of carbon and plastic powders. The electrolyte was thionyl chloride (SOCl₂) mixed with LiAlCl₄. Experiments showed that the C-type of cell had the best sealing quality and the B-type cell the worst. The dimensions, capacities and other parameters of the cells are listed in Table 1.

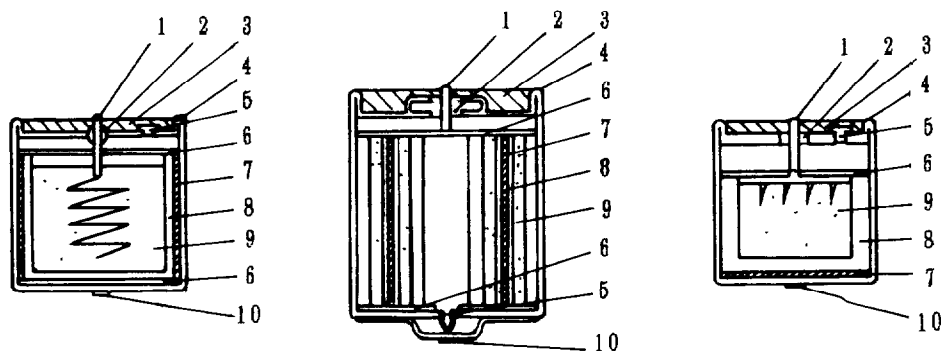


Fig. 1. Schematic diagrams of Li/SOCl₂ cells; (A-, B-, and C-type): (1) positive terminal; (2) glass-metal seal; (3) resin seal; (4) laser or TIG weld; (5) electrolyte feedthrough and metal weld; (6) insulator; (7) lithium anode; (8) separator; (9) cathode, and (10) cell can and negative terminal.

Table 1
Specifications of Li/SOCl₂ cells

Cell type	Dimensions (mm)		Nominal voltage (V)	Nominal capacity (mAh)	Nominal discharge current (mA)
	Diameter	Height			
A	13	15	3.6	300	0.3
B	14.2	25	3.6	800	0.6
C	11.5	12	3.6	100	

Table 2
Failure time (h) of test cells at 200 °C

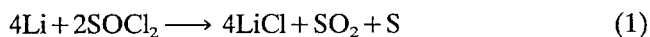
Cell type	Sample number						Average
	1	2	3	4	5	6	
A	143	160	161	200	241	378	214
B	23	41	53	63	67	69	53
C	136	205	276	317	525		292

3. Results and discussion

The failure times (in h) of batches of the three types of cell are listed in Table 2. It can be seen that the C-type cell with perfect sealing exhibited the longest average storage time (292 h). The B-type cell was inferior to either C or A in terms of sealing stability. On average, B-type cells failed after about 50 h. The failure was easily attributed to the escape of SOCl₂ vapour (and, of course, some other gases). At 200 °C, the vapour pressure of SOCl₂ can reach several MPa. The SOCl₂ vapour can leak through microseams in the glass-metal seal region. These seams became wider and wider and, finally, the seal is crushed. This was confirmed by the fact that the leakage of a small amount of vapour caused a noticeable smell and that corroded spots appeared around the positive terminal pin on the top lid. From then on, the cell failed rapidly. Stereomicroscopic examination of the crushed glass-metal seal in failed examples of types A and B revealed both

leakages of electrolyte and the formation of salt crystals in the corroded regions around the pin sealing position.

In Li/SOCl₂ cells, the pressure generally originates from two sources. One is due to a physical cause that involves increased vaporization of SOCl₂ at 200 °C together with accelerated escape of SO₂ dissolved in SOCl₂. The other cause of pressure is from a chemical reaction in which SO₂ is generated from the cell reaction between lithium and SOCl₂ [1,2], i.e.:



This electrochemical reaction proceeds only slowly at room temperature, but increases markedly at 200 °C until either the lithium or the SOCl₂ is totally consumed. The capacity of the C-type cell was 100 mAh. If it is assumed that SO₂ is generated wholly from Eq. (1), the volume of gas produced under standard conditions is:

$$\frac{0.1 \times 3600}{96500 \times 2} \times 22400 = 41.8 \approx 40 \text{ cm}^3 \quad (2)$$

The thickness of the can wall is about 0.4 mm, the diameter 11.5 mm and the height 12 mm. Thus, the volume of the cell is:

$$\left(\frac{11-0.8}{2}\right)^2 \pi (12-0.4) = 947.8 \text{ mm}^3 \approx 1 \text{ cm}^3 \quad (3)$$

Under the standard conditions, assuming the gas occupied the whole space of the cell, the pressure can reach 4 MPa. If the temperature is taken into account, then:

$$\frac{4.0 \times (273 + 200)}{273} = 6.93 \text{ MPa} \approx 7 \text{ MPa} \quad (4)$$

Because the volume of SOCl₂ in the stainless-steel can is smaller than 1 cm³, the internal pressure of the cell would be larger than 7 MPa.

Since there was not any leakage of vapour and gases in the C-type cell, the observed deformation of the cell can was caused by a build-up of the internal pressure.

Each cell exhibited a bulge in the bottom of the can at 200 °C. Let it be assumed that the raised cell bottom approximates to a sphere when the internal pressure is q and the stress on the internal bottom is σ_T . As permanent deformation has taken place at this time, then $\sigma_T = \sigma_S$. For stainless steel, $\sigma_S = 420 \text{ MN m}^{-2}$ [3]. The elastic equation of a hollow sphere that suffers an even pressure is [4]:

$$\sigma_T = \frac{E}{(1+\mu)(1-2\mu)} \left(\mu \frac{dU_R}{dR} + \frac{U_R}{R} \right) \quad (5)$$

where σ_T is the direct tangent upon radial surface, E the modulus of elasticity, μ the Poisson ratio, R the radius of sphere, and U_R the radial displacement. If only an internal pressure exists in the hollow sphere, the stress component would be:

$$\sigma_T = \frac{1/2R^3 + 1/b^3}{1/a^3 - 1/b^3} q \quad (6)$$

where a is the internal radius of sphere, b the outside radius of sphere, and q the internal pressure.

For $R=a=22 \text{ mm}$, and $b=20.37 \text{ mm}$:

$$q = \frac{\sigma_T}{28.76} = \frac{\sigma_S}{28.76} = \frac{420}{28.76} = 14.6 \frac{\text{MN}}{\text{m}} = 14 \text{ MPa} \quad (7)$$

The result (14 MPa) from the calculation of permanent deformation is approximately double that (7 MPa) obtained from the calculation of the chemical reaction. Thus, the internal pressure would be about 10 MPa.

Finally, a rough calculation can be made of the cell failure rate. Suppose that self-discharge is the only

failure mode of the C-type cell, that vapour leakage can be neglected, and that the average value of the failure rate due to self-discharge is 1/(292 h) or approximately 1/(290 h). If the leakage rate of the A-type cell is $1/X_A$, then:

$$\frac{1}{290} + \frac{1}{X_A} = \frac{1}{214} \approx \frac{1}{210} \quad (8)$$

that is, $X_A = 760 \text{ h}$.

If the leakage rate of the B-type cell is $1/X_B$, then:

$$\frac{1}{290} + \frac{1}{X_B} = \frac{1}{53} \quad (9)$$

that is, $X_B = 63 \text{ h}$.

Note, X_A, X_B are average values for the total leakage time.

4. Conclusions

The failure of Li/SOCl₂ cells at 200 °C is due to the escape of SOCl₂ vapour through microseams in the glass-metal seal, and to self-discharge reactions.

References

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