DESIGN OF A SAFE CYLINDRICAL LITHIUM/THIONYL CHLORIDE CELL

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Summary

Cell design criteria have been established which can result in a safe lithium/thionyl chloride cell. A cell vent, a low area internal anode design, cell balance and composition of the cathode–electrolyte solution have been found to be important factors in the design of a safe cell. In addition to routine testing, both undischarged and discharged cells have been subjected to electrical abuse, environmental abuse and mechanical abuse without disassembly.

Introduction

The design of a safe battery must take into account the chemistry of the system being used and must deal with the peculiarity of the individual system. During the evolution of both the alkaline manganese dioxide and nickel cadmium battery systems, special design and safety features were developed to render them safe for consumer use. To achieve substantially higher energy density from batteries, more aggressive chemicals have been employed and greater care in the battery design is required. Extensive testing must be conducted during the design of these batteries to insure their safety.

The lithium/thionyl chloride cell system is one of the highest energy density systems available today [1 - 5]. The anode, lithium, is a low melting metal which is oxidized during discharge. The cathode, thionyl chloride ($SOCl_2$), is a liquid which is reduced on a conductive carbon current collector during cell discharge. The thionyl chloride also serves as a solvent for the electrolyte salt and is in 'direct' contact with the anode. The high energy density and the 'direct' contact of the anode and cathode provide a potentially unstable condition which must be taken into account when designing lithium/thionyl chloride cells. A protective LiCl film forms on the anode and prevents the direct reaction of the anode and cathode. The lithium/thionyl chloride cell must be designed so that the passivating anode film is preserved whenever the cathode or other reactive material is in contact with

the anode. The film may be disrupted and the cell rendered unstable if the anode is melted especially if conditions for spontaneous repair of the film are not present.

Experimental

Small cylindrical cells constructed, as shown in Fig. 1, and incorporating design features discussed below were subjected to a series of abuse tests. There were three types of abuse tests:

(1) Electrical abuse — including charging, short circuit and overdischarge.

(2) Environmental abuse — including incineration, hotplate and sand bath tests and water immersion.

(3) Mechanical abuse — including cutting, crushing, smashing, puncturing, dropping and shock and vibration tests.

Rated capacity of the cells was 1.1 A h when discharged on a 250 Ω load. In total, more than 8000 cells were safety tested to arrive at the current design which gives the results shown in Tables 1 - 4. Cells were subjected
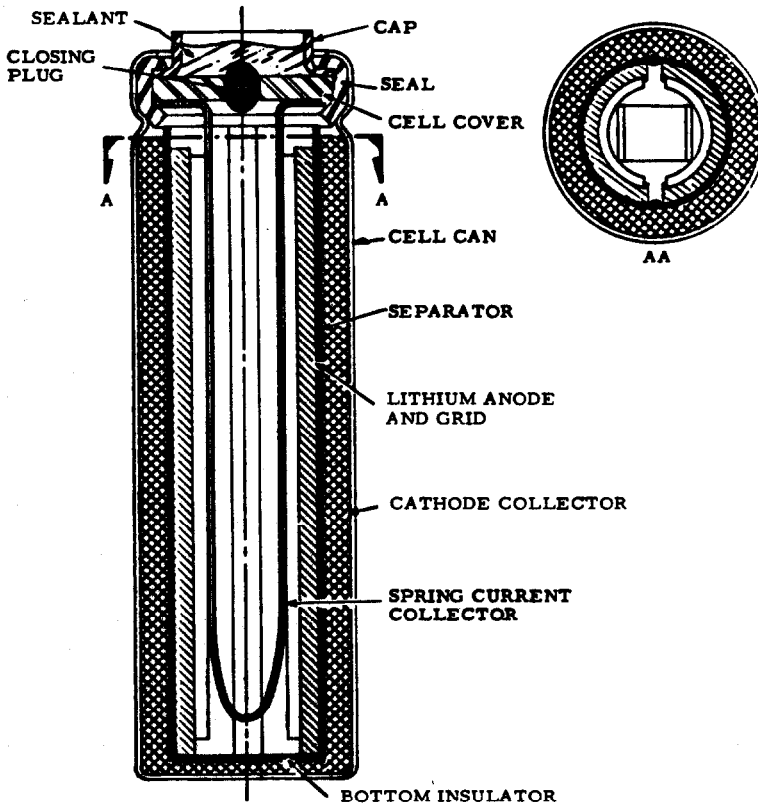

Fig. 1. Li–SOCl$_2$ cell, internal anode.

TABLE 1

Direct flame abuse: Comparison of external anode to internal anode constructions in undischarged cells

Direct flame test	Internal anode (Fig. 1)	External anode (Fig. 2)
Heating cell in open flame 600 °C	100% Normal vent	33% Normal vent 66% Cell disassembly

TABLE 2

Electrical abuse

Test	Observed effect	Comments
1. Direct short at 21 °C		
(a) Undischarged	None	3 A maximum
(b) Discharged (80%)	None	
2. Direct short at 71 °C		
(a) Undischarged	None	5 A maximum
(b) Discharged (80%)	None	
3. Charge test		
(a) Undischarged		If cell vents, some release of $SOCl_2$ will occur
1.5 A/24 h	Cell venting ~30 min	
1.0 A/24 h	Some venting	
500 mA/24 h	None	
250 mA/24 h	None	
100 mA/24 h	None	
(b) Discharged (80% 250 ohms)		Same as above
1.5 A/24 h	Cell venting ⎫	
1.0 A/24 h	Cell venting ⎬ 5 min	
500 mA/24 h	Cell venting ⎭	
250 mA/24 h	None	
100 mA/24 h	None	
4. Forced discharge		
Undischarged and discharged		
100 mA/24 h	None	Cell heats to ~40 °C
250 mA/24 h	None	Cell heats to ~40 °C
500 mA/24 h	None	Cell heats to ~40 °C

to these tests in the undischarged, 50% discharged and 80% discharged conditions. Test results indicated that the fresh and 80% discharged cells represented the worst test condition and testing was concentrated on these cells. Cells were discharged at 71 °C, 21 °C, and —40 °C. Normally a five cell sample was replicated on three separate occasions. On the more severe tests such as flame tests and high rate electrical abuse, larger samples were replicated a greater number of times.

TABLE 3

Environmental abuse

Test	Observed effect	Comments
1. Water bath		
(a) Discharged		Some evolution of gas
Fresh water	None	and corrosion of cell
Salt water	None	container
Direct short in salt water	None	
(b) Undischarged		Some evolution of gas
Fresh water	None	
Salt water	None	
Direct short in salt water	None	
2. Propane torch* (localized)		
(a) Seal area		When cell vents, some
Undischarged	Cell venting 20 s	release of $SOCl_2$.
Discharged (50%)	Cell venting 20 s	Fumes occurred along
Discharged (80%)	Cell venting 20 s	with melting of the seal
(b) Bottom of can		Same as above
Undischarged	Cell venting 30 s	
Discharged (50%)	Cell venting 30 s	
Discharged (80%)	Cell venting 30 s	
(c) Side of can		Same as above
Undischarged	Cell venting 45 s	
Discharged (50%)	Cell venting 45 s	
Discharged (80%)	Cell venting 45 s	
3. Open flame test (600 °C)*		Same as above
Undischarged	Cell venting	
Discharged (50%)	Cell venting	
Discharged (80%)	Cell venting	
4. Sand bath (slow heating to 250 °C)*		Same as above
Undischarged	Cell venting 15 min	
Discharged (50%)	Cell venting 15 min	1 hour heating to 250 °C
Discharged (80%)	Cell venting 15 min	
5. Hot plate 210 °C (cell on side)*		
Undischarged	Cell venting	Cell temp. 160 °C
Discharged (50%)	Cell venting	Plate temp. 210 °C
Discharged (80%)	Cell venting	
6. Opened cell (dropped in water)		Some reaction and
Undischarged	None	evolution of gas in water
Discharged (50%)	None	
Discharged (80%)	None	
7. Opened cell (exposed to fire)		
Undischarged	None	
Discharged (50%)	None	
Discharged (80%)	None	

*On any heating test, finishing a cell into a battery construction may extend the time to venting.

TABLE 4

Mechanical abuse

Test	Observed effect	Comments
1. Abuse and curiosity		
(a) Cut with saw		When the cell container is
Undischarged	None	broken, some release of
Discharged (50%)	None	$SOCl_2$. Possible sparks if
Discharged (80%)	None	cut quickly
(b) Crush with vise		Same as above
Undischarged	None	
Discharged (50%)	None	
Discharged (80%)	None	
(c) Crush with hammer		Same as above
Undischarged	None	
Discharged (50%)	None	
Discharged (80%)	None	
(d) Puncture with nail		Same as above
Undischarged	None	
Discharged (50%)	None	
Discharged (80%	None	
2. Drop test		
(a) Undischarged		
6 feet	None	Some cell denting occurred
20 feet	None	Some cell denting occurred
60 feet	None	Some cell denting occurred
(b) Discharged (50%)		
6 feet	None	Some cell denting occurred
20 feet	None	Some cell denting occurred
60 feet	None	Some cell denting occurred
(c) Discharged (80%)		
6 feet	None	Some cell denting occurred
20 feet	None	Some cell denting occurred
60 feet	None	Some cell denting occurred
3. Shock and vibration*		
(a) Undischarged	None	
(b) Discharged (50%)	None	
(c) Discharged (80%)	None	

*Military Spec. MIL-B-180, 4.7.11.1, 4.7.12.1.

1. Vent release pressure

    The vent must be designed so that it will not open during normal operating conditions which the cell may encounter, but opens upon increasing internal pressure. This pressure can be caused from external sources such as fire or internal sources such as heat generated during charging. The vent must release before the lithium anode melts and reacts directly with the liquid cathode. Upon venting, most of the liquid cathode material is removed and is thus unavailable for reaction with the anode.

The major sources of internal cell pressure as a result of increasing temperature are the vapor pressures of the liquid cathode, the sulfur dioxide produced as a discharge product and the air or other gas trapped in the cell during construction. In addition, the liquid expansions resulting from heat increase the internal pressure.

In order to determine the normal operating pressure range for a given construction, four items need to be quantified:

(1) Internal void volume (without electrolyte).

(2) Electrolyte volume.

(3) Production variations of internal void volume and electrolyte fill volume.

(4) Changes in volume due to the discharge reaction.

The internal cell pressure can be calculated as a function of temperature and depth of discharge for the range of anode and cathode inputs expected during manufacture. In these calculations, the electrolyte volume (and hence the internal void volume) and variations expected during construction should be quantified. Any calculation of internal pressure should take into account the changes in density and vapor pressure of the $SOCl_2$ and SO_2 as a function of temperature so that hydraulic pressure conditions are recognized. Although behavior of the system at the critical point of SO_2 is uncertain, the pressure derived from these calculations will give a degree of confidence that an accidental vent would not occur on standard high temperature discharge but that the cell should vent if the temperature approaches the lithium melting point.

For the cell shown in Fig. 1, a vent release pressure of 2.76 - 4.14 MPa (400 - 600 psig) insures that the cell will safely vent for cathode and anode inputs expected in production. If the design features discussed below are followed, the vent will not operate during any normal use of the cell. The vent is intended only to provide protection during abuse conditions such as incineration or high rate charging. This cell, at any state of discharge, should not vent upon heating to 100 °C. Helium leak rates of less than 10^{-9} ml s^{-1} have been found for this seal and vent.

2. Electrode configuration

The electrode configuration and location will have an impact upon the safety of the lithium/thionyl chloride cell. A cell which has a 1.64 cm^2 interface area per ml of internal cell volume has been found to be a cell construction which is safe and does not vent on direct shorting or overdischarge at rates up to 500 mA. A high area electrode construction (spiral wound cells), unless rate limited by the separator or cathode collector, can generate a large amount of heat on electrical abuse which is not easily dissipated and may result in the localized melting of lithium on electrical abuse tests. The low area cells have a greater heat capacity and external surface area per square centimeter of electrode area and are better able to dissipate any heat generated during electrical abuse conditions.

A key factor in the design of the cell is the placement of the anode. If the cathode collector and liquid cathode are located next to the container wall and the lithium anode is placed at the center of the cell, then heat from an external source must be transmitted through the liquid cathode to reach the anode. This means that the internal pressure will substantially increase prior to melting the lithium. In cells where the lithium is next to the container wall, the lithium may melt and react with the liquid cathode before the internal pressure is high enough to open a vent system and evaporate the thionyl chloride. The results of open flame testing are shown in Table 1 for the cell construction shown in Figs. 1 and 2.

If the external anode cell is thermally insulated, it should be able to withstand greater thermal abuse. The better the insulation the greater the abuse that the cell can withstand.

3. Active material balance

Active material balance of a lithium/thionyl chloride cell is the ratio of the ampere hour capacity of thionyl chloride to that of the lithium anode. Initially, it would appear that an active material balance of 1.0 would be the
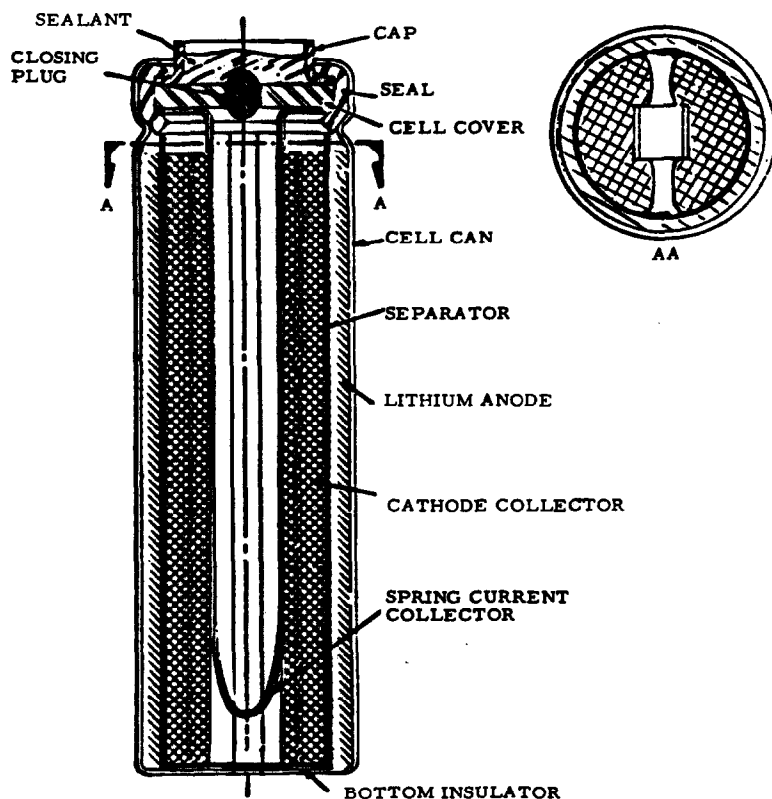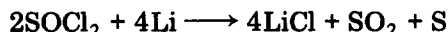

Fig. 2. Li–SOCl$_2$ cell, external anode.

best for maximum cell capacity. However, the liquid cathode is continually consumed throughout the discharge of the cell via the following reaction:

$$2SOCl_2 + 4Li \longrightarrow 4LiCl + SO_2 + S$$

Although a portion of the liquid volume is replaced with sulfur dioxide, the cell dries out on discharge. As a result, only a portion of the original area retains ionic conductivity. This problem is more severe for a deeply discharged cell such as those at low rates of discharge. If the cell is charged or force discharged, the current density on those locally conductive areas is significantly increased to a point where local melting of the lithium could occur and produce rapid heating and thermal runaway. A cell vent is not effective in preventing this process. Local deficiencies in ionic conductivity may lead also to hot spots under abuse. However, if the cell is balanced so that there is excess liquid cathode, and if a means is provided to maintain pressure on a uniformly absorbent separator, then these local deficiencies in ionic conductivity can be avoided. A second result of excess cathode balance and uniform electrode contact is that lithium usage is more complete and more uniform after complete discharge and reaction products are uniformly distributed. The anode grid also insures complete and uniform lithium usage.

4. Composition and purity of the cathode–electrolyte

There are other factors which can affect the safety of a thionyl chloride cell. They are:

(1) Salt concentration in the cathode–electrolyte.
(2) Raw material purity.

An investigation was conducted to evaluate the effect of salt concentration ($LiAlCl_4$) between 0.75 M and 2.5 M on the distribution of reaction products
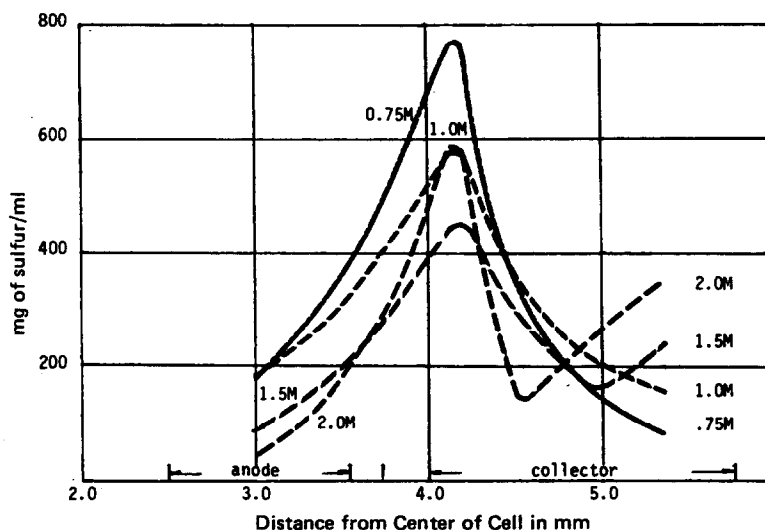

Fig. 3. Deposition of sulfur as a function of salt concentration.

after low rate discharge. The solid reaction product distribution was then determined as a function of distance from the anode following discharge to 0 volts on a 2 kΩ load. These data are shown in Fig. 3. Low salt concentrations resulted in a build-up of elemental sulfur in the separator region and in the reservoir regions of the cell. The deposition of sulfur at the separator/anode interface decreases with increasing salt concentration. It has been found that a salt concentration of 1.5 to 1.6 M $LiAlCl_4$ in thionyl chloride is preferable based on both analytical data and safety testing of cells.

Corrosion of the lithium anode is via the following reaction:

$$4Li + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$$
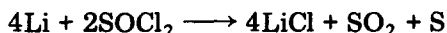
The solid products in this case are deposited on or very near the anode. The presence of water, acids and organics in the electrolyte causes corrosions thus increasing the likelihood that the cell will be unsafe if abused electrically or by heating. Control of the purity of the cathode–electrolyte is necessary.

Conclusions

Extensive abuse testing of thousands of cells made to these design criteria has been completed. As discussed above, these tests include electrical abuse, environmental abuse and mechanical abuse of undischarged and discharged cells. Cells were discharged at 71 °C, 21 °C and −40 °C. No cell disassemblies were observed on any of the tests.

Based on the safety and performance testing, the following factors have been found to be important in the design of small cylindrical cells that will be safe both in normal use and when abused:

(1) A cell should vent to prevent the occurrence of an energy releasing reaction between lithium and thionyl chloride.

(2) A cell constructed with low area electrodes should have the cathode collector in contact with the wall of the cell container (internal anode).

(3) A cell should be anode limited and contain design features so that complete anode utilization and uniform reaction product distribution are obtained.

(4) Control of the composition and purity of the cathode-electrolyte solution should be maintained.

Further tests are still being conducted. The results of tests conducted to date indicate that a safe cylindrical lithium/thionyl chloride cell can be made if properly designed.

References

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