

Lithium thionyl chloride cells and batteries Technical predictions versus 1994 realities

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Abstract

Lithium thionyl chloride D-cells, when discharged at moderate rates of 50 W/kg, provide an impressive energy density of > 350 Wh/kg; however, multiple cell batteries present serious challenges for thermal management when subjected to discharge to 0 V and overdischarge into voltage reversal at the 50 W/kg rate. This paper describes the important influence electrochemical cell balance and design has upon decreasing the heat generation within batteries.

Keywords: Lithium batteries; Thionyl chloride

1. Introduction

Over the past twenty years the lithium thionyl chloride electrochemistry has been a widely researched primary battery technology, partly because of great commercial expectations arising from demonstrated practical cell energy densities as high as 520 Wh/kg and 1000 Wh/l. The first scientific papers describing the general behavior of metallic lithium in oxyhalide electrolytes appeared in 1972-1974 and the initial results were quite encouraging [1-3]. In the ensuing years, thousands of papers have been published, aimed at better understanding the science and technology related to the use of this high voltage couple. Despite increased understanding of this chemistry, initial predictions have not been fully realized regarding wide-scale use of the chemistry for a variety of moderate to high rate military and industrial applications. The estimated worldwide total commercial sales in 1991 were US\$ 89 million, with cells of A-size or smaller accounting for 68% of the total. This means that low-rate or bobbin designs represent the majority of cell designs. Moderate- and high-rate cells using thin electrodes of less than 1 mm thick have gained less acceptance due to technology challenges arising from safety, thermal management, and voltage-delay considerations. The purpose of this paper is to focus on some of the recent advances and understanding that have been applied to the design of moderate to high-rate cells.

2. Li/SOCl₂ energy and power capability

The comparison in Fig. 1 shows that Li/SOCl₂ cells and batteries have been tested over a five-decade power domain representing energy densities from 100 to 520 Wh/kg. Low-rate bobbin cells characterize the energy region between 400 and 520 Wh/kg, spiral-wound cells or cells having greater electrode area represent moderate rate, and cells near and below 200 Wh/kg are high-power, reserve, or pulse-power applications. The upper limit of 520 Wh/kg represents approximately 35% of the theoretical energy density for the Li/SOCl₂ couple. A curve representing the volumetric power and energy densities is also shown in Fig. 1, low-rate bobbin cells are near 1000 Wh/l, moderate rate near 700 Wh/l and

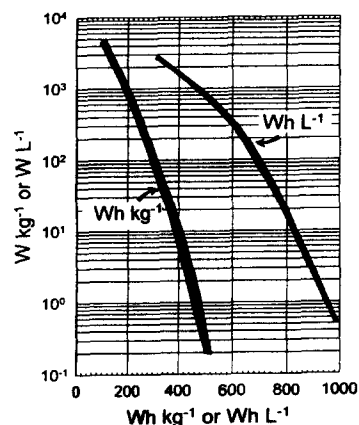


Fig. 1. Energy and power capabilities of Li/SOCl₂ cells.

Table 1
Evolution of battery design for an eight-cell BA-6590 battery discharged at 2 A and voltage reversal at 1 A

Design 1	Design 2	Design 3
Cell design Lithium limited 40% excess electrolyte	Cell design 'Combination' design Lithium limited in discharge Excess lithium for forced overdischarge 35% excess electrolyte	Cell design 'Combination' design Excess lithium 2.5 Ah 35% excess electrolyte
Vent pressure 10-12 bar 38 mm diameter can	Vent pressure 19 bar 38 mm diameter can	Vent pressure 22 bar 36.5 diameter can
Heat management Half-battery void space Filled with heat conductive epoxy	Heat management Thermally conductive grease at cell base	Heat management None required
Maximum battery temperature No epoxy: 90 °C Epoxy: 85 °C	Maximum battery temperature 75 to 80 °C	Maximum battery temperature 70 °C

high-rate below 500 Wh/l. The 1000 Wh/l equates to 50% of the theoretical volumetric energy density.

Continuous high-power discharge (>100 W/kg or >200 W/l) of cells is generally acknowledged to depend upon the generation of thermal power within the cell rather than intrinsic electrochemical limitations. In other words, the temperature rise of a cell during high-power discharge is the limiting factor rather than the intrinsic ability of the cell to generate the electrical power. This limitation was discovered early on in development of spiral-wound Li/SOCl₂ cells and was manifested by testing cells at high rate wherein the internal cell temperature increase was large, exceeding the melting point of lithium and consequent direct reaction between the molten lithium and SOCl₂.

3. Thermal management

The intrinsic heat generation of Li/SOCl₂ cells has been extensively studied by many groups because of the afore-mentioned limitation that the heat presents. Some of the studies have focused on fundamental scientific or thermodynamic parameters, e.g., Δ*S*, thermoneutral potential, etc., while other studies have concentrated in a more general fashion on understanding heat evolution or heat flux of a cell during discharge [4-7]. From a practical technological sense, the goal is to minimize the thermal power *W_T* compared with the useful electrical power a cell generates (*P_E* = *I**E₁*). The thermal output is the sum of three factors:

$$W_T = W_p + W_s + W_A \tag{1}$$

or,

$$W_T = I(E_h - E_1) \tag{2}$$

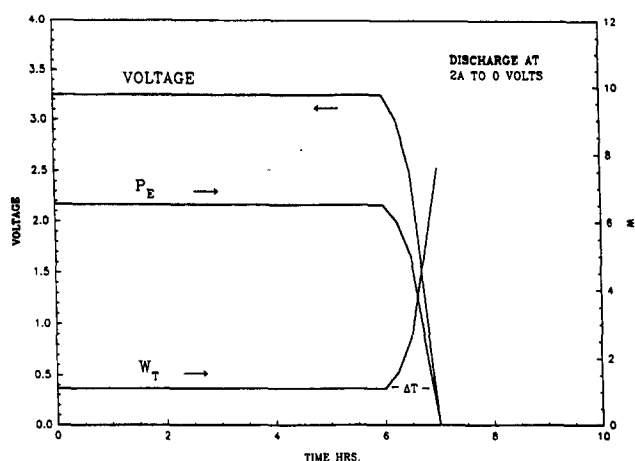


Fig. 2. Thermal and electrical power vs. discharge in an Li/SOCl₂ D-cell.

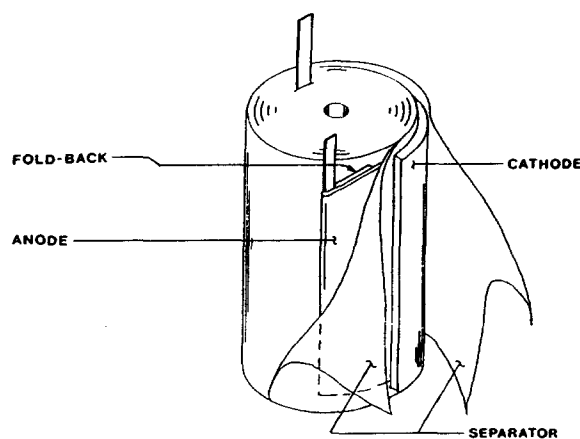


Fig. 3. Li/SOCl₂ cell with fold-back anode design.

where *I* is the discharge current, *E_h* the thermoneutral potential, and *E₁* the loaded cell potential.

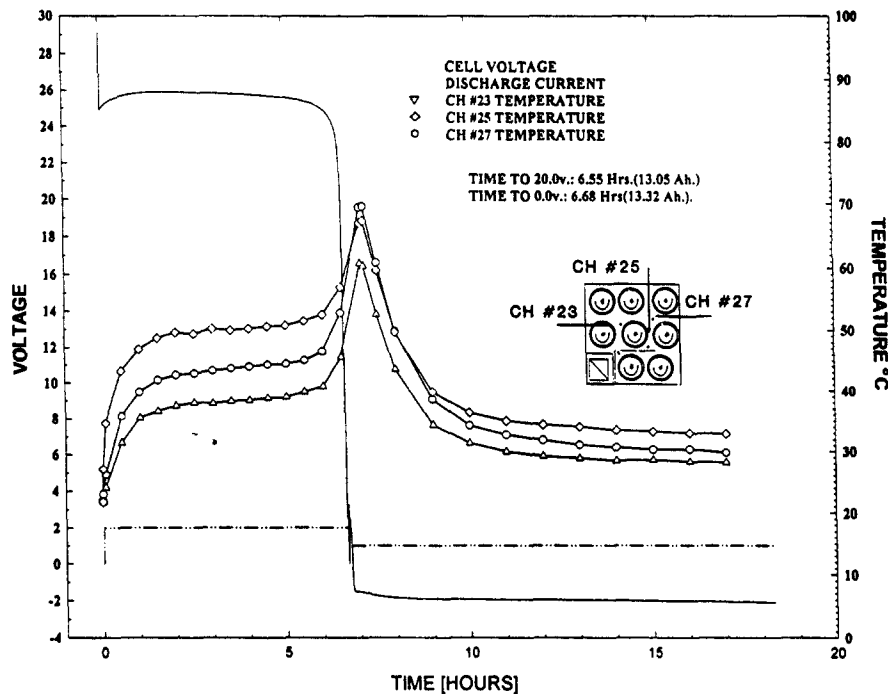


Fig. 4. Discharge of an eight-cell battery within a plastic battery case (BA-6590), at 2 A discharge/1 A reversal, and at room temperature.

By looking at the individual contributions we see that W_p is the polarization heat. This heat arises from overpotentials at the anode and cathode and ohmic drop arising from the electrolyte resistivity. The overpotential at the cathode increases throughout discharge because of LiCl formation within the porous carbon and, similarly, the electrolyte composition changes give rise to changes in the solution contribution. From a practical sense, the polarization heat is the major contribution that we can decrease by making wise electrochemical design choices for the cell. Further, most applications require multi-cell batteries typically operating at >20 V, thus the battery components (connectors, wiring, fuses, diodes, etc.) and battery-design factors (geometrical packing, material selection, sensible heat, etc.) are also quite important to study from a heat-generation/heat-transfer viewpoint.

The second heat contribution, W_s , is due to entropic changes while the third component, W_A , is due to chemical heat, not resulting from the discharge reaction. The most significant W_A factor is metallic lithium corrosion, though other factors arising from impurities and chemical side reactions may also be important.

By inspection of Eq. (2) and using $E_h = 3.8$ V [7], the heat-power generation becomes the dominant term over useful electrical power when the cell or battery is discharged to 0 V. For example, a typical Li/SOCl₂ D-cell discharged at 2 A delivers 6 W of electrical power and 1.6 W of thermal power when the loaded cell voltage is 3.0 V but the inverse at 0.8 V, 6 W of heat and 1.6 W of electrical power. A high-power discharge of an Li/SOCl₂ D-cell at 5 A and 3.0 V would

represent approximately 125 W/kg of useful electrical power but would generate 158 W/kg of heat at 0 V. Fig. 2 shows the relationship between thermal and electrical power as a function of discharge at 2 A to 0 V. One approach, then, to cells for moderate or high rates is to design a cell such that ΔT , the time between the plateau discharge voltage and 0 V, is minimized. This results in decreased heat output.

4. Influence of cell design on thermal management

It should be noted that our experience with the Li/SOCl₂ chemistry has shown that cell designs which deliver excellent capacities and safety testings as single cells will not necessarily perform well for a battery design. A cell design has to be fine-tuned, specifically for the battery environment where the heat transfer is reduced, consequently, resulting in higher cell temperatures. The higher cell temperature, in turn, gives rise to increased corrosion of the lithium during discharge and forced overdischarge and to increased internal cell pressure because of the PVT response of the liquid/vapor within the cell. A classic design case is an oversize D-cell used in an eight-cell BA-6590 military battery operating at 2 A that has been reported previously [8,9]. Table 1 shows the evolution of cell and battery design. There were two approaches taken to meet both the needed capacity and withstand discharge to 0 V into voltage reversal: heat-conductive materials for the battery and optimization of cell design and electrode design for reduced heating.

By concentrating on the electrochemical design, it was possible to remove all special heat-transfer materials and still meet capacity and the forced overdischarge test. Our approach for moderate rate batteries such as the BA-6590 was:

(1) excess electrolyte (35%) for heat transfer and for minimum cell polarization in reversal test;

(2) an anode design ('combination') which incorporated a full nickel current collector to prevent 'isolated' lithium domains, an excess of lithium outside the end of the wind which could not be electroxidized in the normal galvanic reaction but could form an electrical shunt during forced overdischarge, and

(3) overdesign of carbon capacity so that the overpotential on the carbon was not controlling the discharge duration.

The concept drawing of Fig. 3 shows the lithium fold back or 'combination' anode design that maintains a known localized excess of metallic lithium. A 'combination' design allows a lithium-limited situation for discharge and a reserved of lithium outside the wind for forced overdischarge. The 'combination' design runs cooler and maintains a stable potential during the 12 h at 1 A. The discharge of an eight-cell battery within a plastic battery case (BA-6590) is shown in Fig. 4. The key influence of the cell design show:

(i) a lithium-limited design enables a rapid decline in potential from cutoff of 20 V to 0 V minimizing W_T , resulting in a maximum temperature of 70 °C within the battery for a short period, and

(ii) the excess lithium outside the wind maintains a stable battery voltage of -2 V and temperatures of 28 to 33 °C for most of the forced overdischarged duration.

5. Conclusions

Our conclusion is that the use of basic heat-generation principles can aid in cell and battery design. These principles also help explain why a particular design delivers power safety to 0 V and into voltage reversal.

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