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Primary Li/$SOCl_2$ cells. XII. Performance and safety of super-high-rate cells

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Design and performance characteristics of a high-rate D-cell and a super-high-rate flat cell, three inches in diameter and less than an inch high, are discussed. The flat cell had a short-circuit current of 1500 A and delivered approximately 20 A h on a 20 A continuous or pulse mode. The cell delivered 14 A h on 100 A continuous drain. Both types of cells were found to be resistant to shorting and forced discharge abuses.

1. Introduction

The Li/$SOCl_2$ inorganic electrolyte system [1–5] is the highest energy density system known to date. It consists of a lithium anode, a carbon cathode and $SOCl_2$, which acts both as a solvent and a cathode active material. The most extensively used electrolyte salt has been $LiAlCl_4$, but salts such as $Li_2B_{10}Cl_{10}$ [6–8] and $Li_2O(AlCl_3)_2$ [9] have also been used successfully in this system for improving the shelf-life characteristics. Now, we have developed a super-high-rate Li/$SOCl_2$ cell which is capable of providing exceptionally high power in pulsed and continuous mode, without sacrificing the intrinsic energy density of the system to a substantial extent. We have established that the performance-limiting electrode of a spirally wound D-cell on high-rate discharge is the cathode. This is demonstrated in the longitudinal reaction profile of the cathode on discharge at 2.0 A, as shown in Fig. 1. Note that at the early stages of discharge the cell reaction occurs predominantly near the cathode tab. This indicates that the electronic impedance of the cathode grid is the limiting feature in so far as the high-rate discharge is concerned. Therefore, improvement of the current collection of the cathode is required to improve the current carrying capability of the cell. We have developed both a high-rate D-cell and a three-inch diameter flat cell for the super-high-rate application. The design details and the performance are described in this paper.

2. The spirally wound D-cell

The use of the spirally wound D-cell design for high-rate application is attractive since the technology is well developed. The cell incorporates proven packaging with a hermetic glass-to-metal seal and a low pressure vent which is hermetic until opening on short circuiting or other abusive use. Also, the spirally wound Li/$SOCl_2$ D-cell can be manufactured at our lithium battery manufacturing facility with a minimum of alterations and new tooling.

Earlier we developed two types of spirally wound cell, one for low rates, with electrodes 10–15 inch long and a 0.5 M $LiAlCl_4$–$SOCl_2$ electrolyte, and the other for medium rates with electrodes 20 inch long and a 1.0 M $LiAlCl_4$–$SOCl_2$ electrolyte. The design details are available elsewhere [10, 11]. The energy densities as a function of the discharge current for the two types of cells are shown in Fig. 2. Note that the low-rate cells are capable of delivering capacities of 18–19 A h corresponding to energy densities of 20 W h in^{-3} and 300 W h lb^{-1} and a $SOCl_2$ utilization of 95–98% based on the following cell reaction stoichiometry:

$$4Li + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S. \quad (1)$$

Therefore, this represents the upper limit of energy density available from this system. The medium-rate cells, on the other hand, deliver maximum energy densities of only 13 W h in^{-3} and

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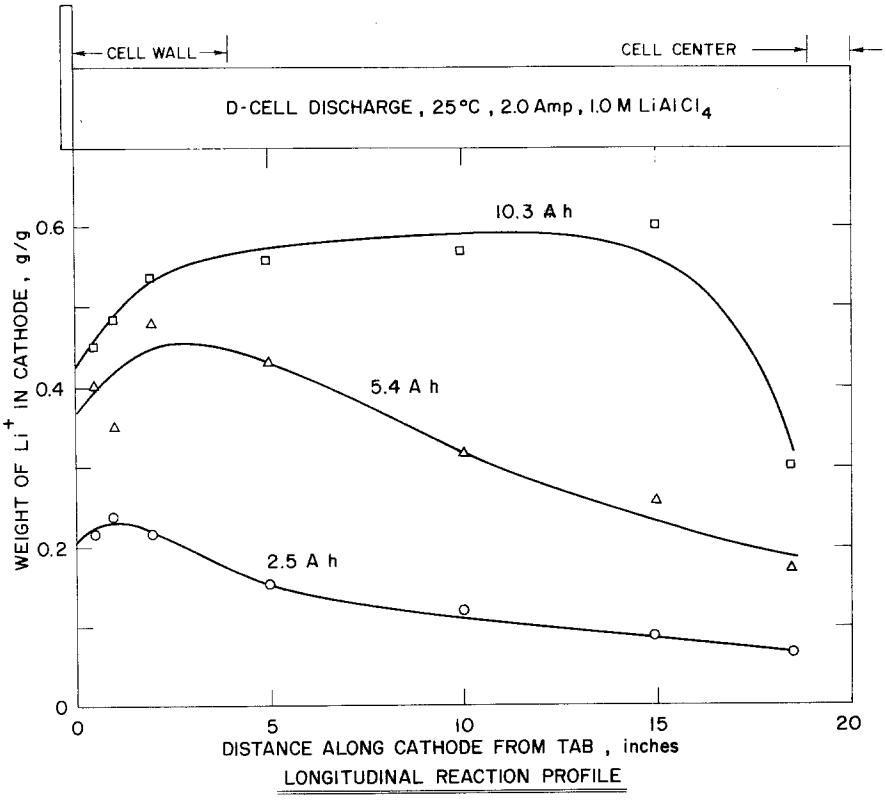

Fig. 1. Reaction profiles along length of carbon cathodes at three depths of discharge.

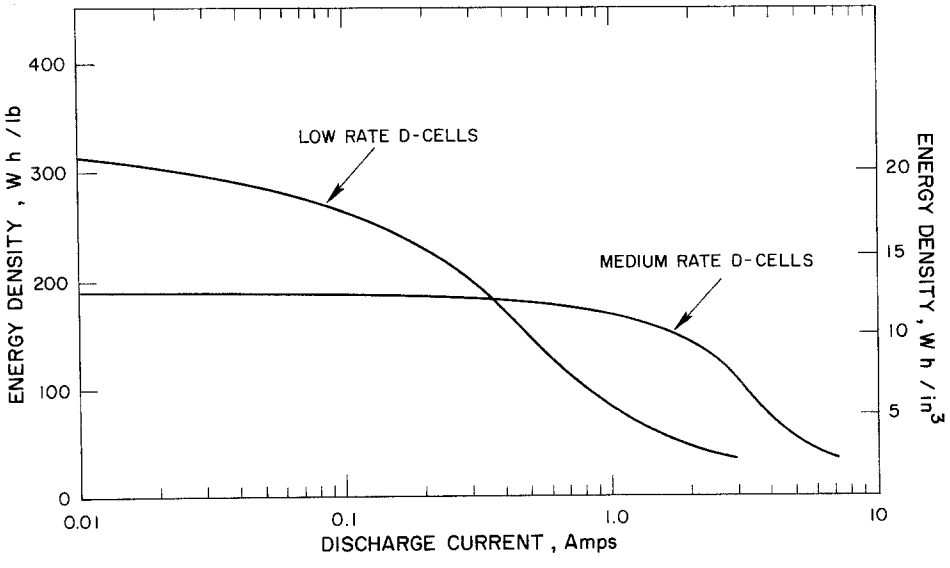

Fig. 2. Energy density–rate characteristics of low- and medium-rate D-cells.

190 W h lb^{-1}, although this energy density remains virtually constant up to 1.0 A drain. The energy densities drop sharply above 2.0 A. The rate capability of this medium-rate cell was found to be inadequate for meeting the 20 A pulse requirements of the super-high-rate application.

We have determined the longitudinal reaction profile of the carbon cathodes of this cell by monitoring the LiCl content of the discharged cathodes at the various parts along its length starting from the tab onwards. The results for 2A discharge, at three different stages of discharge, are shown in Fig. 1. Note that at the early stages of discharge (2.5 A h and 5.4 A h), most of the reaction occurs near the tab. This demonstrates that at currents of 2 A or higher, the electrical conductivity of the cathode grid controls the current distribution. The higher the current, the greater the non-uniformity of the current distribution. Therefore, our first task was to optimize the current collector design of the cathode of the spirally wound D-cell for the high-rate use.

For this study, we kept the same cathode mix composition and fabrication process in order to keep the porosity of the carbon cathodes identical for all the cathode collector designs. The carbon cathode consists of an expanded nickel grid covered with Shawinigan Black + 10% Teflon mixtures on both sides of the grid. The selection of the above was made from the optimization of the carbon mixture and the carbon types carried out earlier [12, 13]. The Ni tabs were 0.002 inch thick and 0.25 inch wide and were folded over the expanded Ni grid, which was exposed by removing the carbon mix from the grid area where the tabs were welded. Thus each tab consists of a double layer of 0.002 inch Ni foil. The electrical resistance of the 2 inch wide Li anode was calculated to be 0.113 and 0.169 mΩ in^{-1} for 0.015 inch and 0.01 inch thick foils, respectively, using 8.6×10^{-6} Ω cm^{-1} as the resistivity of the Li metal. The electrical resistance of two layers of the 0.25 inch wide and 0.002 inch thick Ni foil was calculated to be 2.677 mΩ in^{-1} using 6.8×10^{-6} Ω cm^{-1} as the resistivity of Ni. The electrical resistance of the 1.75 inch wide expanded Ni was experimentally determined to be approximately 14.4 mΩ in^{-1}. Thus the cathode grid resistance was two orders of magnitude higher than the electrical resistance of the Li anode and as such the cathode current collector design becomes a controlling factor in the discharge of the cells at high rates.

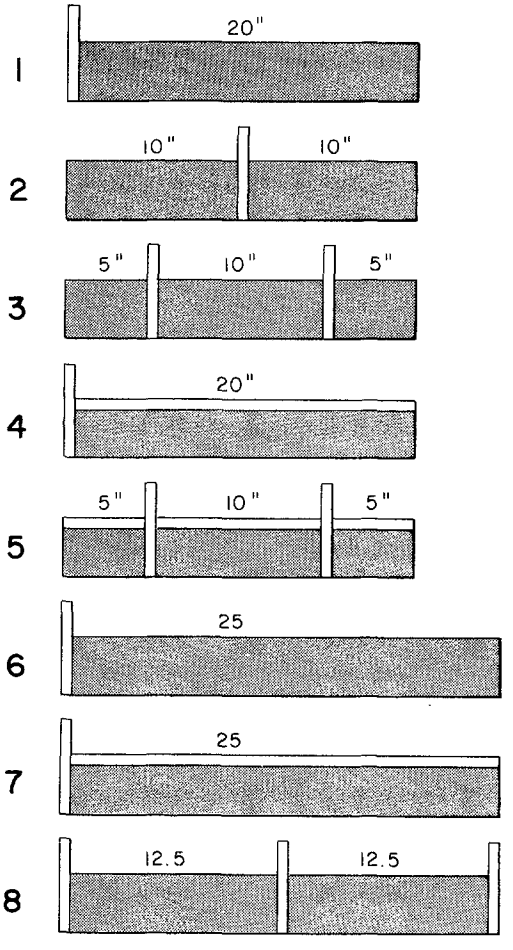

Fig. 3. Cathode current collector designs.

Based on the polarization characteristics of the D-cells with various cathode current collectors, we selected the cathode tab arrangement shown in design 3 of Fig. 3, but we increased the cathode length from 20 inch to 26 inch to increase the rate capability even further. We determined the performance characteristics of this cell under constant current discharges of 0.3–1.0 A. The cell delivered approximately 11 A h at 0.3 A and 9 A h at 3 A. At 10 A, the cell delivered 4.8 A h prior to venting. The cell was evaluated on a pulse duty cycle (Fig. 4) at 25° C by taking two D-cells in parallel. The voltage profiles of two D-cells in parallel are shown in Fig. 5. The cells delivered 220 pulses corresponding to a capacity of 14.2 A h for the two D-cells. The currently used Ni/Cd batteries

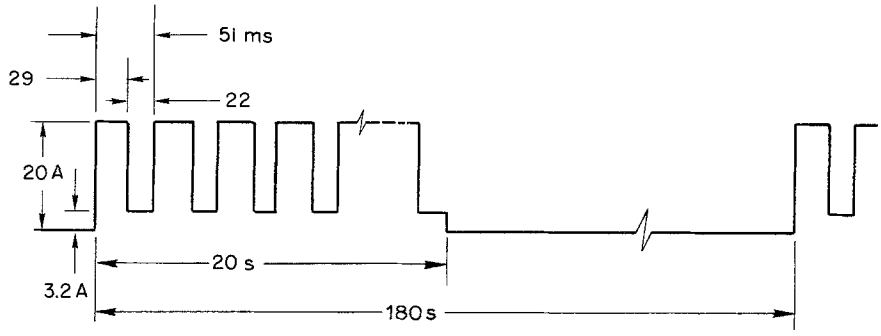

Fig. 4. High-rate pulse duty cycle.

deliver only 30 pulses corresponding to a capacity of 2 A h.

The abuse resistance of the D-cell was evaluated by shorting the cell while monitoring the current, voltage and wall temperature; profiles for which are shown in Fig. 6. The cell delivered a short-circuit current of 200 A and vented after approximately 0.65 s. The cell voltage remained constant at around 1.0 V during the shorting. The temperature of the cell wall could not be measured due to thermal lag. The D-cells were also force-discharged into reversal at various constant currents. Typical voltage and temperature profiles on 1.0 A reversal are shown in Fig. 7. Note that the cell voltage remained clamped at zero during the reversal. The cell temperature also remained constant at 25° C during this reversal. This demonstrates the 'voltage clamping' mechanism that is operational in these cells. Thus the abuse resistance of these spirally wound high-rate D-cells was found to be quite good.

3. The flat cylindrical cell

We have developed a flat cylindrical cell, 3 inch in diameter and 0.9 inch thick, for high-rate applications. The design of the cell case consists of two halves, one having a glass-to-metal seal and the other having a glass-to-metal seal vent, as shown in Fig. 8. The electrode assembly consists of 35 disc-

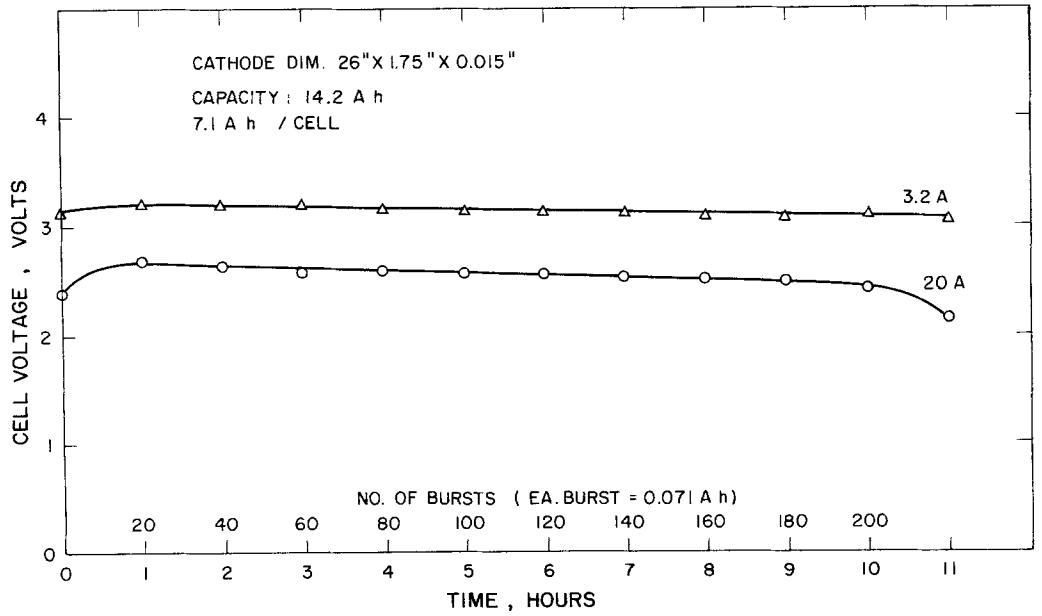

Fig. 5. Performance characteristics of two D-cells in parallel on high-rate pulse duty cycle (Fig. 1) at 25° C.

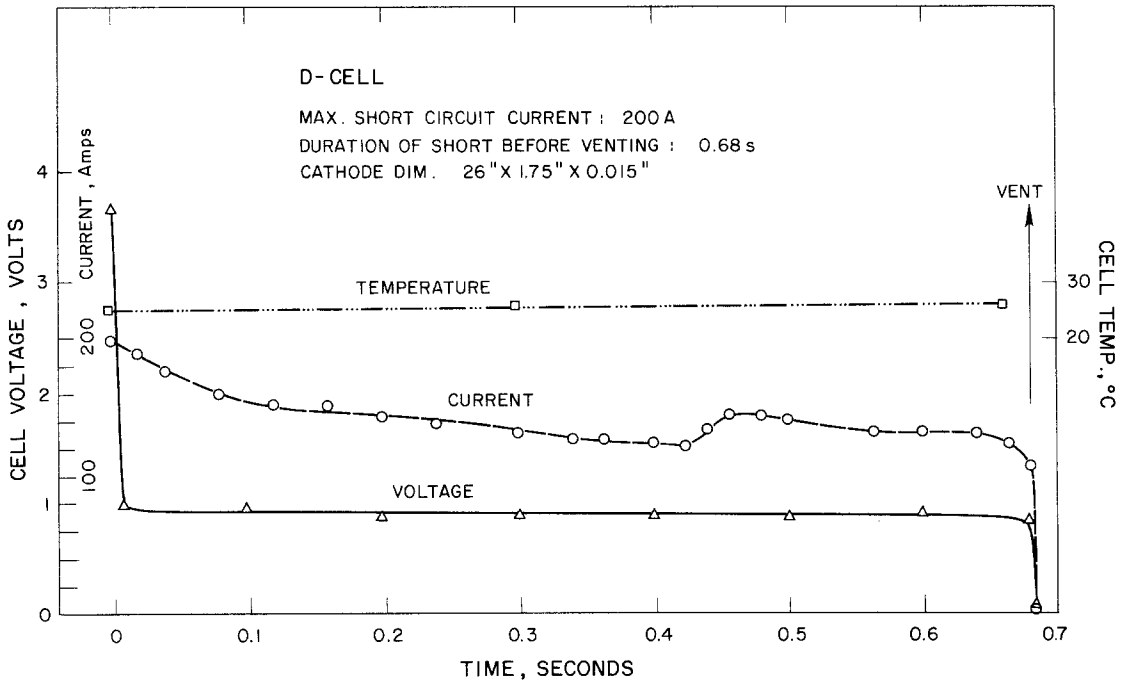

Fig. 6. Voltage, current and wall temperature profiles of high-rate D-cell on shorting.

shaped anodes and cathodes with glass separators stacked in parallel. The Li anodes are welded to the centre post of the seal and the carbon cathodes are connected to the can. The cells were filled with 1.8 M $LiAlCl_4$–$SOCl_2$ electrolyte through the fill port which was welded shut. The cell weighs 225 g.

The voltage profiles of a flat cell on the pulse cycle (Fig. 1) at 25° C are shown in Fig. 9. Note

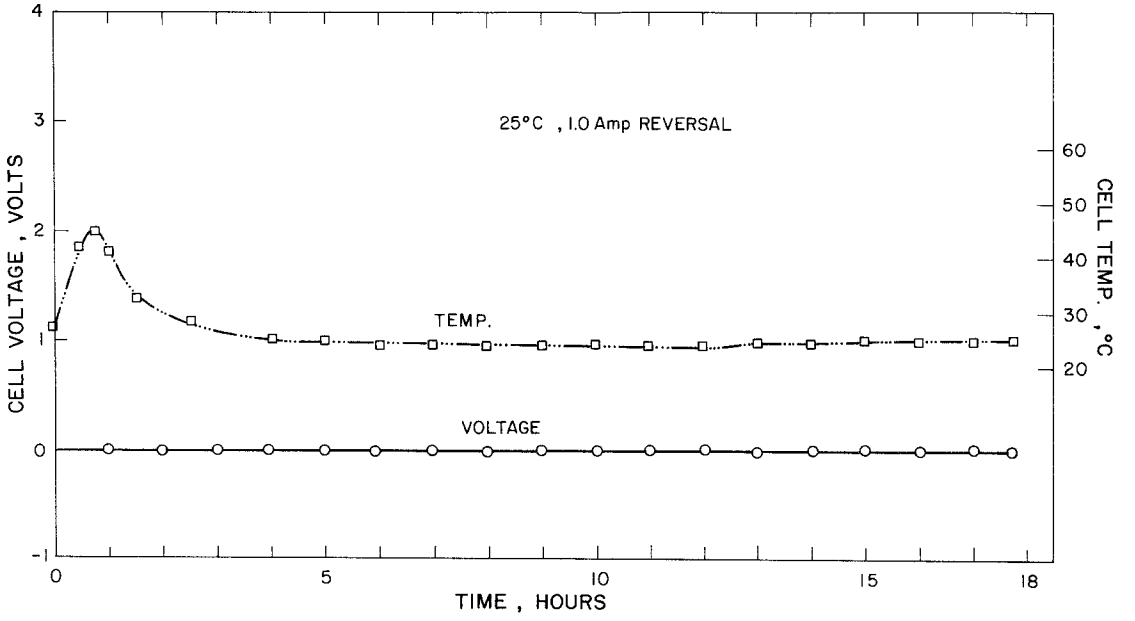

Fig. 7. Voltage and wall temperature profiles of a D-cell on force-discharge and reversal at 1.0 A.

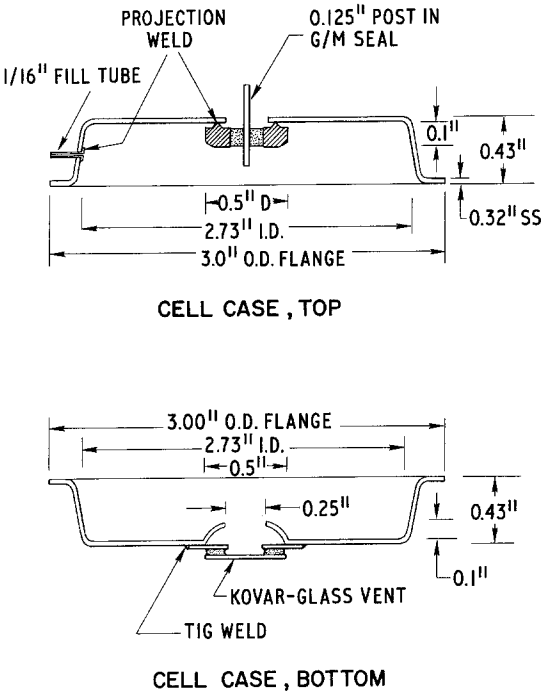

Fig. 8. Flat cell case design.

that the cell exhibits very little polarization on the 20 A load. The operating voltage of the cell remained substantially above 3.0 V during most of its life. The cell delivered in excess of 300 bursts, corresponding to a capacity of 21 A h. The cell temperature remained below 30° C throughout the test. This represents a tenfold improvement in performance over the presently used Ni/Cd batteries for the same application.

We discharged the flat cell on a continuous load of 20 A, and realized 19.8 A h to a 2 V cut-off. We evaluated the exceptional rate capability of the cell by discharging on a resistive load corresponding to a constant current of 100 A. We monitored voltage, current, wall temperature and the internal pressure of this cell during the test. The results are shown in Fig. 10. Note that the cell delivered 13.6 A h prior to venting. The cell voltage remained near 3.0 V during most of the test. The internal pressure of the cell rose to 250 psi and the wall temperature to 70° C, prior to venting. The cell did not exhibit any hazardous behaviour.

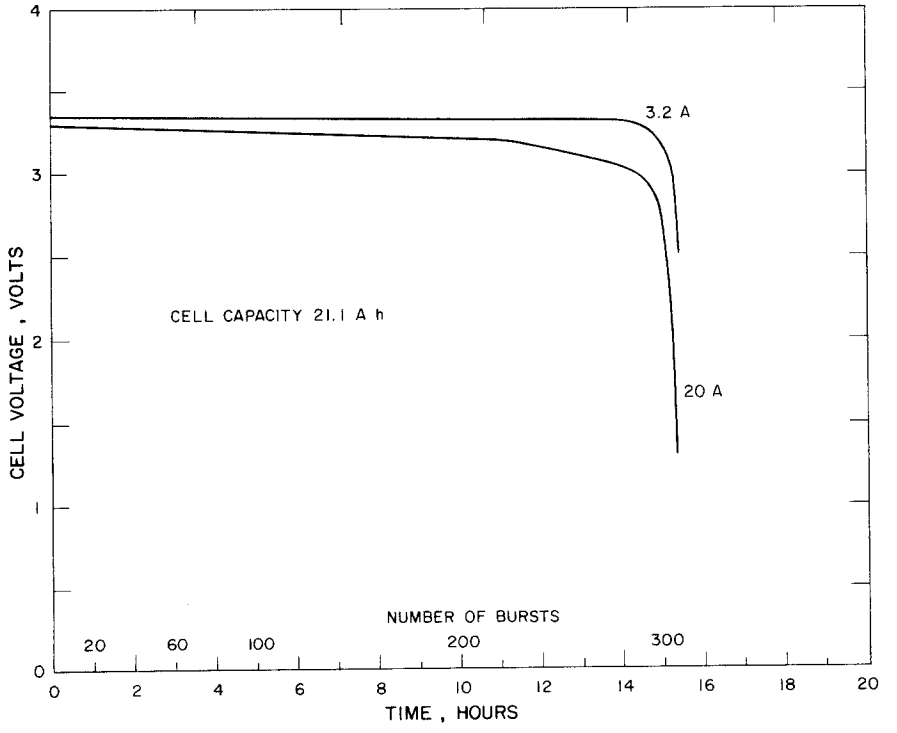

Fig. 9. Performance characteristics of the flat cell on high-rate pulse duty cycle (Fig. 1) at 25° C.

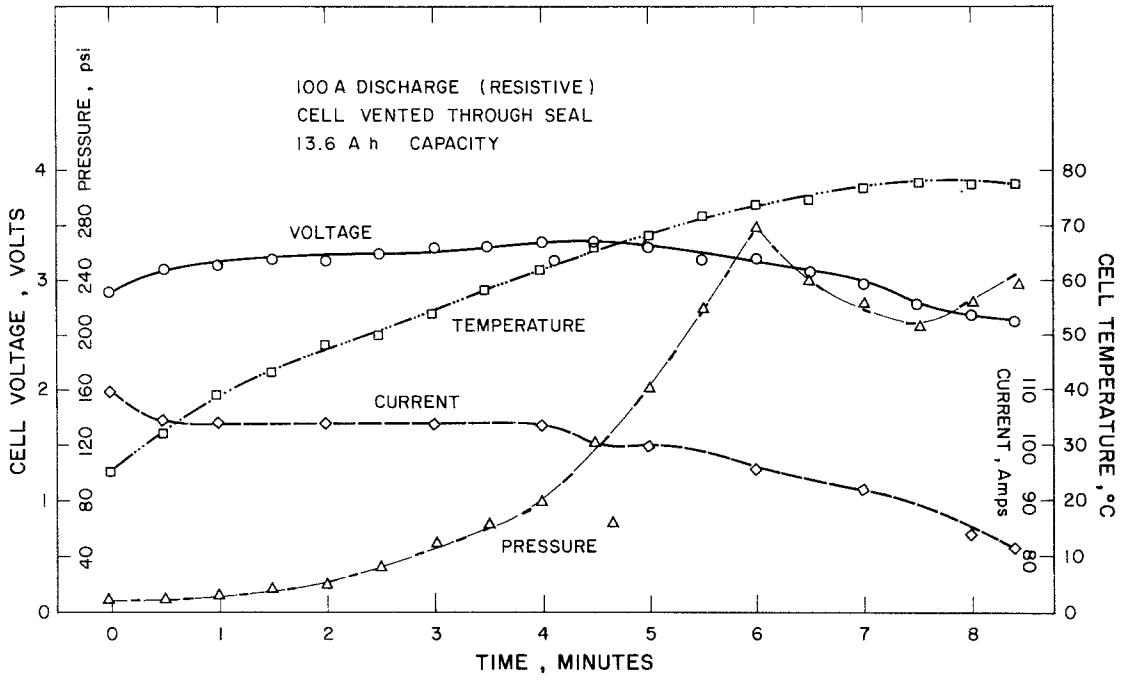

Fig. 10. Voltage, current, wall temperature and internal pressure profiles of a flat cell on 100 A discharge.

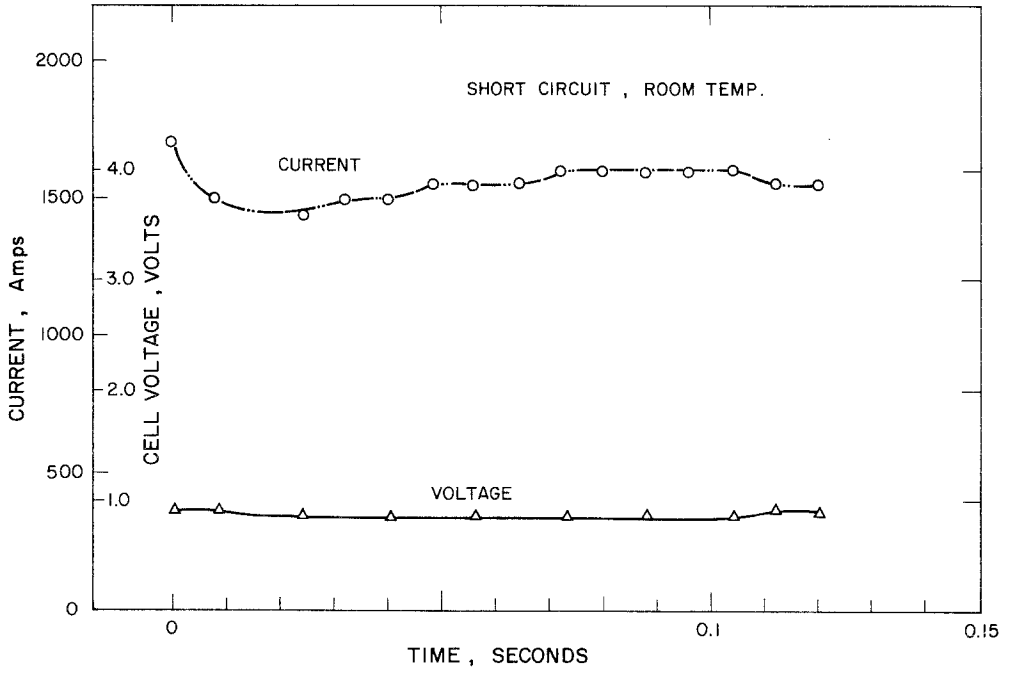

Fig. 11. Voltage and current profiles of a flat cell on short circuiting.

One flat cell was short circuited and both the current and the voltage of this cell monitored: the results are shown in Fig. 11. The cell delivered a short-circuit current of 1500 A at a voltage of 1.0 V. Both the current and the voltage remained constant in excess of 0.1 s prior to venting. There was no rupture of the cell, although the venting process is accompanied by sparks very similar to a Roman Candle. The internal impedance of the cell was 1.7 mΩ which is the lowest ever achieved in lithium batteries to date.

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