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Bromine chloride as a cathode component in lithium inorganic cells

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Investigations were conducted on a Li inorganic battery system using BrCl and $SOCl_2$ as co-depolarizers. The Li/BrCl, $SOCl_2$ cell exhibited an open-circuit voltage of 3.90 ± 0.02 V at room temperature. The discharge results of cells of various sizes showed that an energy density of 1 W h cm^{-3} is possible at low discharge rates at room temperature. The storage tests showed no significant capacity loss after a storage period of 15 months at ambient temperature or three months at 72° C. The cells were subjected to abuses such as short circuiting, forced overdischarge and charge. No hazard of any kind was encountered during these tests. In view of these results, we concluded that Li/BrCl, $SOCl_2$ is a practical system for high energy density batteries.

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1. Introduction

The Li/$SOCl_2$ inorganic cells have high energy densities, wide operating temperature ranges, reasonably high current delivering capabilities and low self-discharge rates. Despite these desirable characteristics, the use of Li/$SOCl_2$ inorganic cells has not been widespread due to problems related to safety. It has been reported [1, 2] that the Li/$SOCl_2$ inorganic cells have a tendency to explode under abuses such as short circuiting, forced overdischarge and charge. Although a great deal of progress has been made in cell designs [3, 4] which may alleviate most, if not all, safety problems, intrinsic safety characteristics and potential hazards of the system are still a concern for many users.

It has been postulated [2] that the explosion hazard of the Li/$SOCl_2$ cells may be related to discharge products such as elemental sulphur and/or intermediates. Assuming that the proposed mechanism for explosion is correct, the intrinsic safety characteristics may be improved if the discharge mechanism and/or discharge products can be altered by incorporating proper additives in the electrolyte/depolarizer. We have investigated the effect of BrCl as an additive and the discharge and safety characteristics of the Li/BrCl, $SOCl_2$ system are discussed in this article.

2. Experimental

2.1. *Depolarizer and electrolyte preparation*

Reagent-grade thionyl chloride (Hooker Chemical Company) was refluxed over lithium metal for a 24 hour period and subsequently distilled under an argon atmosphere. Bromine chloride (Dow Chemical Company) was passed through an activated-alumina drying column and added quantitatively to the thionyl chloride.

Lithium tetrachloroaluminate was prepared by fusing a mixture of dried reagent-grade lithium chloride (Fisher Scientific Company) and aluminium chloride (Fluka) (50:50 mol%) at 150° C. A 1 M solution of lithium tetrachloroaluminate was prepared by dissolving the requisite amount of $LiAlCl_4$ in the BrCl/$SOCl_2$ solution.

2.2. *Electrode preparation*

The carbon electrodes contained 93 wt% Shawinigan acetylene black (50% compressed) and 7wt% Teflon binder (TFE-fluorocarbon resin dispersion No. 30, Du Pont). A nickel screen (Delker 3Ni20-189), with a previously spot-welded nickel lead, was used as the current collector. The anodes were prepared by pressing lithium ribbon (Foote Mineral Company) on to a nickel screen (Delker

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3Ni20-189) with a previously spot-welded nickel lead. All electrodes were prepared in a dry room (typically less than 0.5% relative humidity, less than – 40° C dew point).

2.3. *Cell fabrication*

All test cells were made by winding the lithium anode, the carbon cathode and two layers of nonwoven glass separator into a cylindrical roll and packaging the roll in a 304L stainless steel can. A glass to metal seal with a tube feedthrough was TIG welded to the can. The tube feedthrough served as both the electrolyte/depolarizer fill port and a cell terminal. The cell can served as the other terminal. The quantity of electrolyte added to each cell was monitored by weighing the cell before and after filling. The tube feedthrough was welded shut after filling with the electrolyte/depolarizer.

2.4. *Discharge tests*

Test cells were discharged under various resistive loads at room temperature (24 ± 3° C), – 40 ± 2° C and 72 ± 2° C. For high- and low-temperature discharges, the test cells were stored in a Thelco oven at 72 ± 2° C or a Revco Ultra Low cold chamber at – 40 ± 2° C for at least three hours prior to discharge. The cell voltage during discharge was measured by a Keithley Model 610 electrometer and recorded on a single- or multiple-channel recorder.

2.5. *Safety tests*

Test cells of various sizes (AA, C and D) were subjected to short circuiting, forced overdischarge, charge and incineration tests. Test cells were short circuited across a copper wire (resistance = 0.015 Ω) at ambient temperature. The short-circuit current and skin temperature of the cells were monitored during the tests.

Single- and multi-cell batteries were discharged at a constant current and forced into voltage reversal, and the discharge continued for various periods of time. Following the forced discharge tests, some of the batteries were charged at a constant current. The voltage and skin temperature were monitored during these tests. Fresh cells and discharged cells with and without safety vents were incinerated above a naphtha flame. The skin temperature was monitored during the incineration.

3. Results and discussion

The open-circuit voltage of the Li/BrCl, $SOCl_2$ cell was found to be 3.90 ± 0.02 V at 24 ± 3° C, which is more than 0.2 V higher than that of the Li/$SOCl_2$ cell. One may speculate that the higher open-circuit voltage is due to the presence of Cl_2 in the solution resulting from a partial dissociation of BrCl [5]. We have observed [6] that the addition of Br_2 in $SOCl_2$ also results in an increase in open-circuit potential. The open-circuit voltage of the Li/Br_2, $SOCl_2$ cell was found to be 3.8 V at 24 ± 3° C, which is higher than that of either Li/$SOCl_2$ (3.67 V) or Li/Br_2 (3.5 V). We speculated that the higher open-circuit voltage of Li/Br_2, $SOCl_2$ may be due to the formation of a complex between Br_2 and $SOCl_2$ [6]. Accordingly, the formation of a complex between BrCl and $SOCl_2$ should not be ruled out in the case of the Li/BrCl, $SOCl_2$ cell.

The capacity and cell voltage during discharge of the Li/BrCl, $SOCl_2$ cell depends on the concentration of BrCl in the $SOCl_2$. At room temperature (24 ± 3° C) the optimal concentration was found to lie in the range 7 to 20 mol%. We selected 14 mol% BrCl in $SOCl_2$ as the depolarizer in the present investigation. Fig. 1 shows a comparison of the discharge behaviour of the Li/BrCl, $SOCl_2$ and the Li/$SOCl_2$ systems in AA-size cells with identical electrode structures. It is noted that the realized capacity as well as the cell voltage of the Li/BrCl, $SOCl_2$ are somewhat higher than that of the Li/$SOCl_2$ cell.

The discharge curves of Li/BrCl, $SOCl_2$ cells under various conditions are shown in Figs. 2–4. It was noted that the realized capacity at room temperature was higher than that at both elevated (72° C) and low (– 40° C) temperatures under the same discharge load. Based on these results, we rated AA-size cells at 2 A h at 20 mA, C-size cells at 7 A h at 150 mA, and D-size cells at 14 A h at 300 mA to a 2 V cut-off at room temperature. The practical volumetric energy density of these cells was approximately 1 W h cm^{-3}. Figs. 2–4 also show that the Li/BrCl, $SOCl_2$ cells are capable of delivering higher currents. For example,

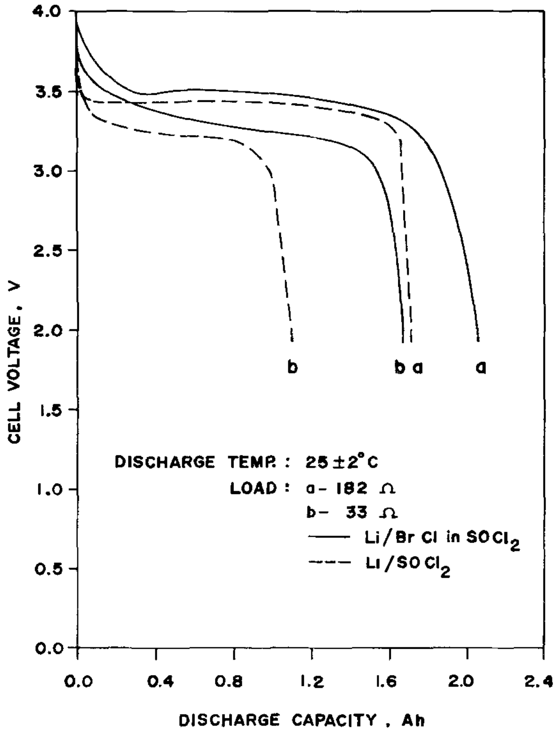

Fig. 1. Comparison of the room-temperature discharge characteristics of Li/$SOCl_2$ AA-cells and Li/BrCl, $SOCl_2$ AA-cells.

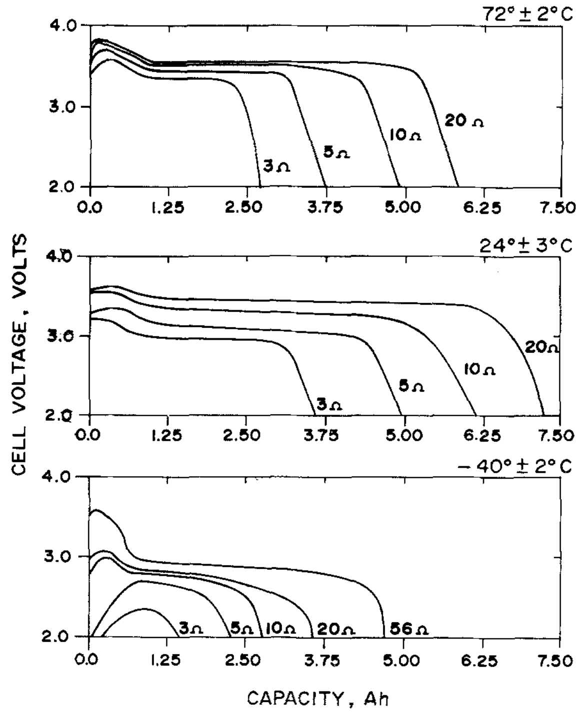

Fig. 3. Discharge characteristics of C-size Li/BrCl, $SOCl_2$ cells.

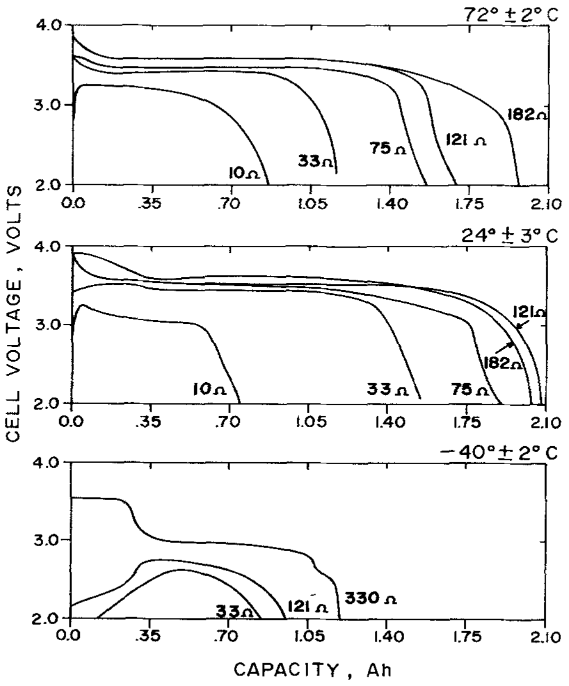

Fig. 2. Discharge characteristics of AA-size Li/BrCl, $SOCl_2$ cells.

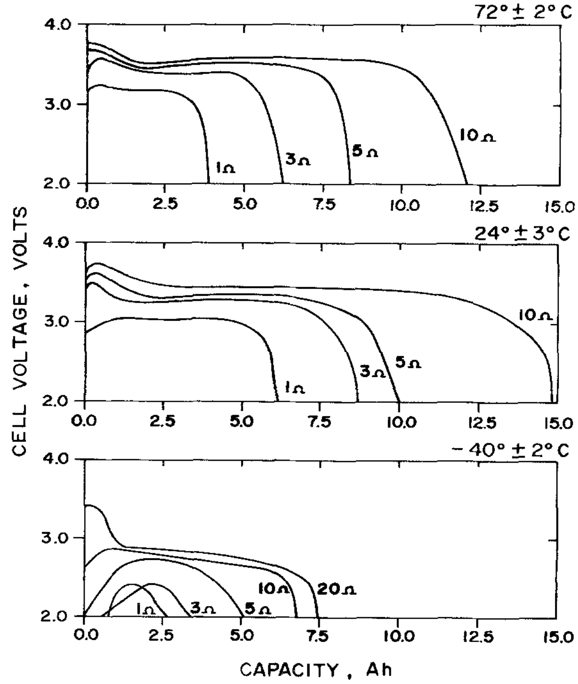

Fig. 4. Discharge characteristics of D-size Li/BrCl, $SOCl_2$ cells.

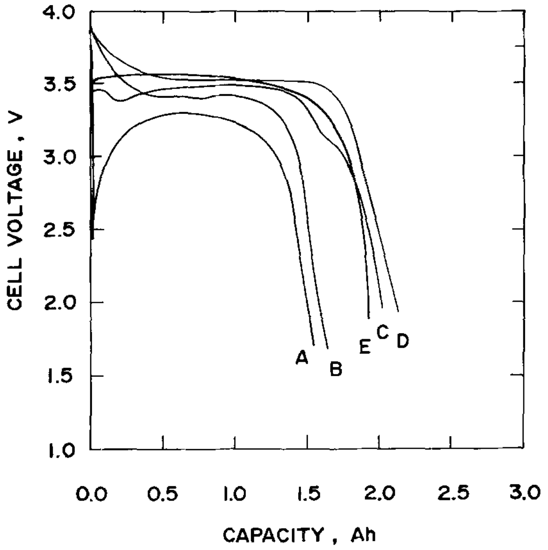

Fig. 5. Storage tests for the AA-size Li/BrCl, $SOCl_2$ cells. A, 30 Ω stored for three months at 72° C; B, 30 Ω fresh cell; C, 180 Ω stored for 3 months at 72° C; D, 180 Ω fresh cell; E, 180 Ω stored for 15 months at room temperature.

the D-size cells can deliver a current of approximately 1 A at room temperature, realizing about 8 A h to the 2 V cut-off.

It should be noted that although the test cells have a spirally wound electrode structure, the electrode surface area is relatively small. The electrode dimensions are 3.8 cm x 3 cm for AA-cells, 3.8 cm x 9.5 cm for C-cells, and 4.9 cm x 15 cm for D-cells. The current-delivering capability may be increased by using longer electrodes.

The storability of the Li/BrCl, $SOCl_2$ cells was investigated using AA-size cells. Fig. 5 shows the effect of storage at 72° C for three months and under uncontrolled room-temperature conditions for 15 months. It is noted that there was no significant loss in capacity as a result of storage, though the current-delivering capability was reduced somewhat after storage, as shown by the lower discharge voltage.

The incorporation of BrCl in the depolarizer was an attempt to modify the cell chemistry in the $Li/SOCl_2$ system. It has been reported in the

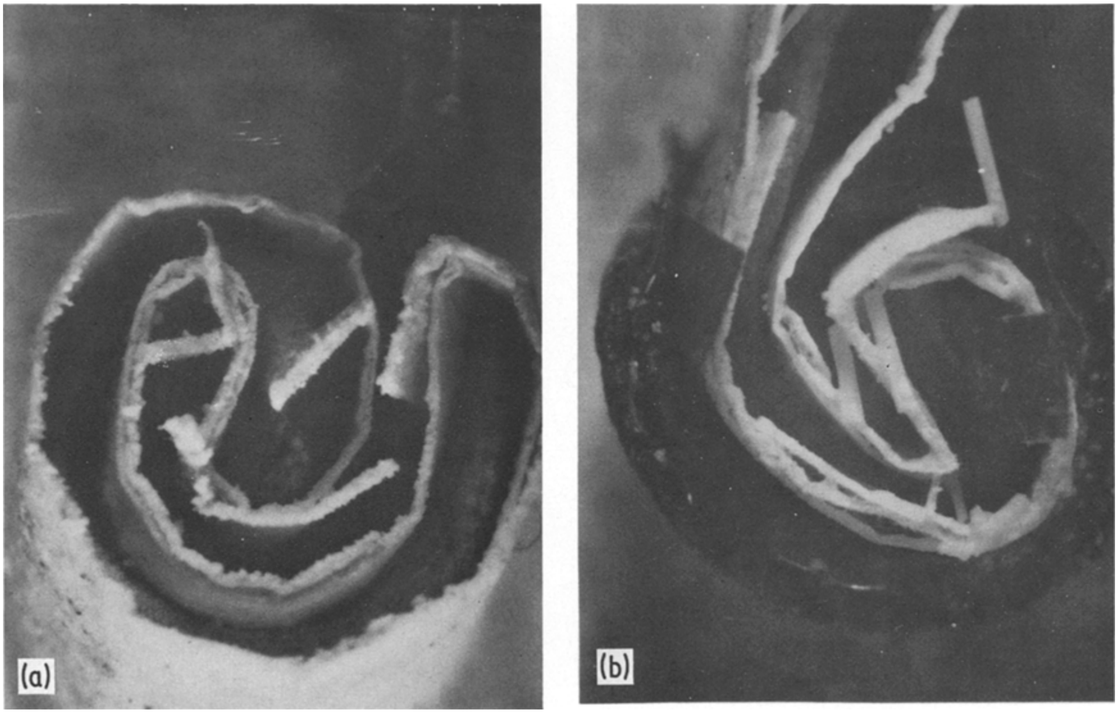

Fig. 6. Photographs of the discharged electrodes of (a) the Li/BrCl, $SOCl_2$ cell and (b) the $Li/SOCl_2$ cell. Note the needle-like crystals on the cathode of the discharged $Li/SOCl_2$ cell.

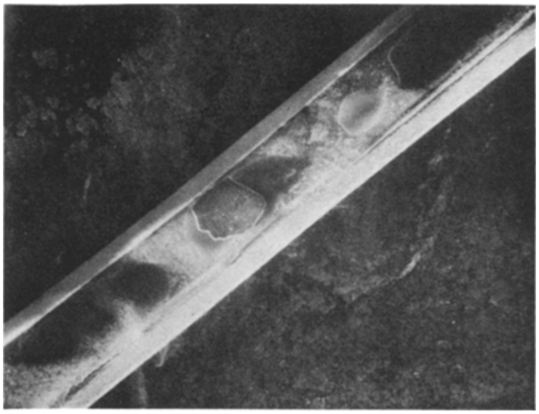

Fig. 7. Scanning electron micrograph of the needle-like crystal on the cathode of the discharged Li/$SOCl_2$ cell.

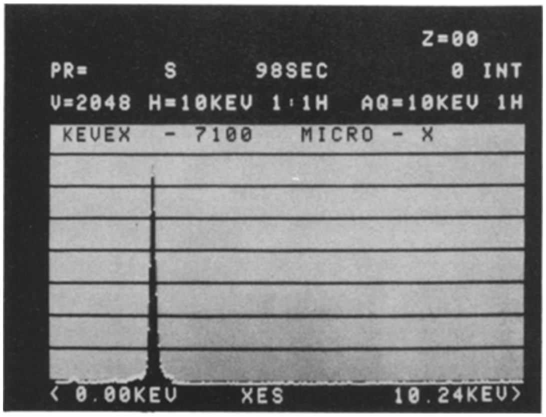

Fig. 8. EDAX of the needle-like crystal on the cathode of the discharged Li/$SOCl_2$ cell.

literature that the hazard resulting from abuses of the Li/$SOCl_2$ system may be attributable to sulphur or discharge intermediates [2]. We have observed that BrCl reacts with elemental sulphur forming a volatile product or products. Consequently, we reason that it is possible that the presence of BrCl in $SOCl_2$ may prevent the formation of sulphur as a discharge product, at least in the early stage of discharge. Indeed, an examination of the discharged electrodes under a microscope revealed that there is a difference in appearance between the discharged Li/$SOCl_2$ and discharged Li/BrCl, $SOCl_2$ cells. Fig. 6 shows that a number of needle-like crystals (yellow) are evident on the cathode of the discharged Li/$SOCl_2$ cell whereas no yellow crystals are present on the cathode of the discharged Li/BrCl, $SOCl_2$ cell. The scanning electron micrograph of the crystal is shown in Fig. 7 and the result of energy dispersion X-ray analysis (EDAX) (Fig. 8) clearly showed that the yellow crystal was sulphur. However, in as much as sulphur can be present in forms other than crystalline (e.g. amorphous or dissolved in residual $SOCl_2$), the absence of sulphur crystals is not sufficient evidence to conclude that sulphur is not a product. In fact, preliminary analyses of discharged cells have shown that some elemental sulphur is present on the discharged cathode. Nonetheless, in view of the difference in physical appearance, we speculate that the presence of BrCl may have changed the crystal structure, the morphology or the amount of the elemental sulphur during discharge.

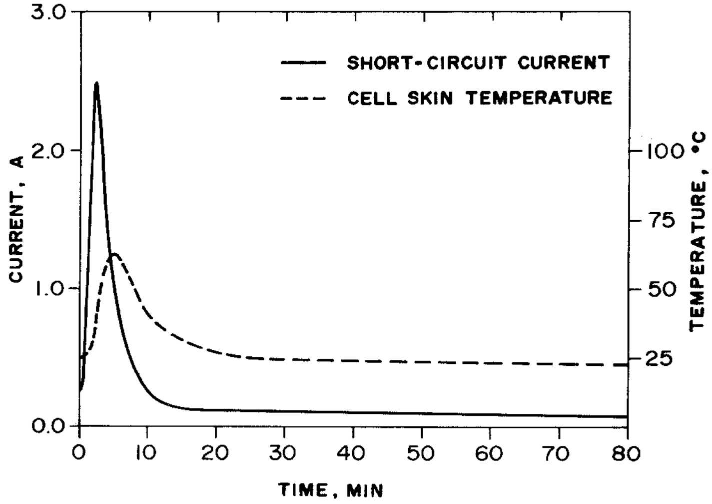

Fig. 9. Short-circuit current and skin temperature of an AA-size Li/BrCl, $SOCl_2$ cell during short-circuit test.

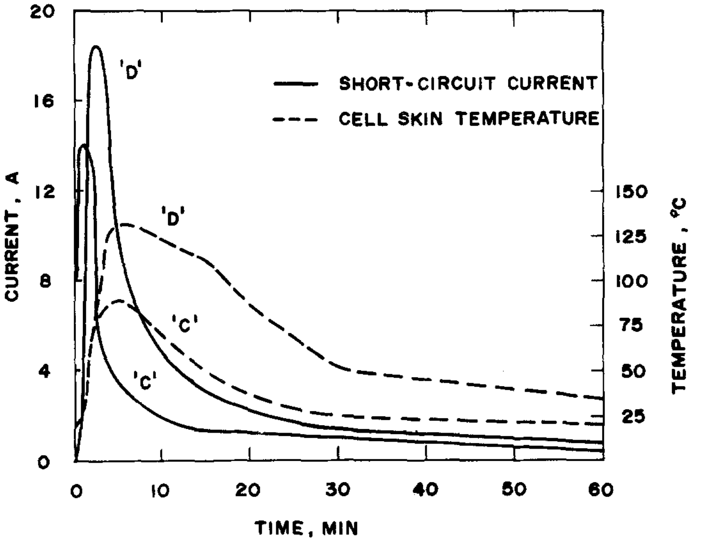

Fig. 10. Short-circuit current and skin temperature of C- and D-size Li/BrCl, $SOCl_2$ cells during short-circuit tests.

In any event, we have investigated the safety of the Li/BrCl, $SOCl_2$ cells under abusive conditions such as short circuiting, forced overdischarge and charge. The rusults of these tests are discussed below. Fresh AA-, C- and D-cells were short circuited across a copper wire (resistance = 0.015 Ω) at ambient temperature. The maximum short-circuit currents were about 2 A, 14 A and 20 A, respectively. The maximum skin temperature ranged between 65 and 140° C. No explosion hazard or venting problem was encountered during the short-circuit tests. The short-circuit current and temperature profiles are shown in Figs. 9 and 10.

Forced overdischarge tests were conducted on C-size cells under a variety of conditions. The C-size cells were discharged at room temperature under a constant current of 0.5 A and forced into voltage reversal. The discharge was continued for 60 hours or longer (Fig. 11). No venting, explosion or any other hazard was observed during these tests. Indeed, the 0.5 A forced overdischarge tests were conducted on numerous C-size cells and results were reproducible. In order to increase the severity of the overdischarge test, we constructed 27.4 V batteries by connecting seven C-size cells in series and subjected these batteries to a 3 A forced discharge at room temperature. The

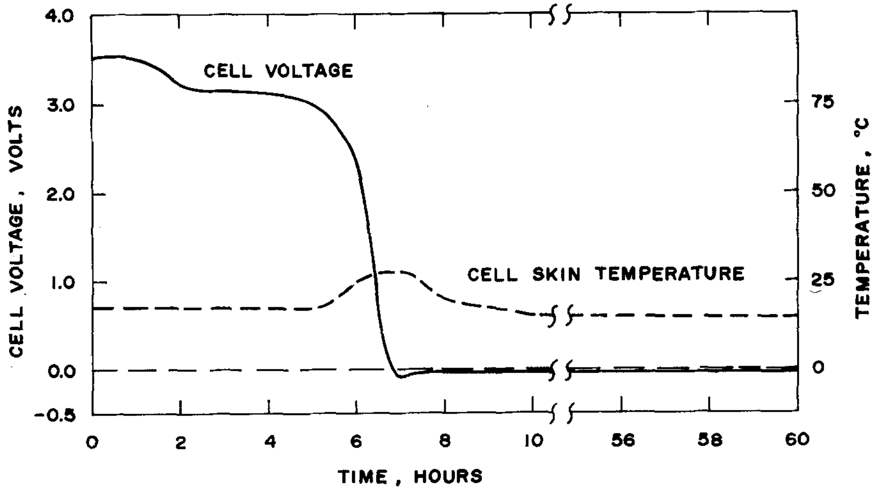

Fig. 11. Voltage and skin temperature of a C-size Li/BrCl, $SOCl_2$ cell during forced discharge at 0.5 A.

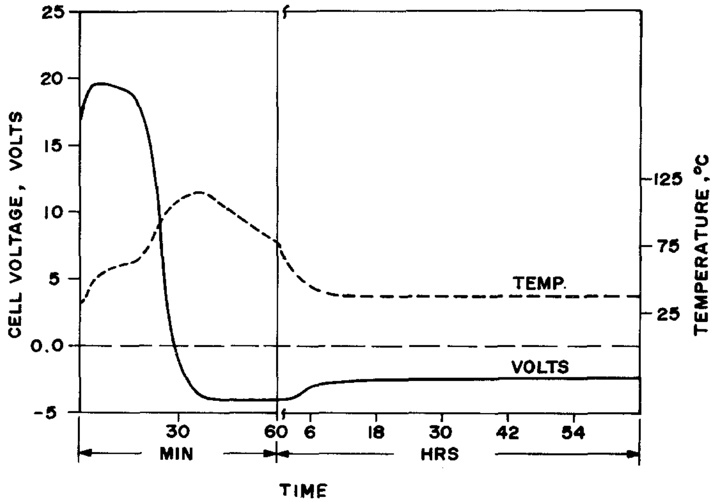

Fig. 12. Voltage and skin temperature of a 27.4 V, seven C-cell battery during forced discharge at 3 A.

discharge current was maintained at 3 A for 50 hours or longer after the batteries had been forced into voltage reversal. No hazard of any kind was encountered. In addition, we constructed multicell batteries by connecting in series six undischarged C-cells and one discharged C-cell and subjected these batteries to the 3 A forced discharge tests. The discharge was continued for 18 hours or longer. No venting or explosion was ever observed during these tests. The voltage and temperature profiles during these tests are shown in Figs. 12 and 13.

The forced overdischarge tests were also conducted on D-size cells at 1 A and 5 A. No hazard of any kind was encountered. Fig. 14 shows the voltage and temperature profile during these tests. It was reported [3] that at the end of such a prolonged forced overdischarge (reversal), Li/$SOCl_2$ cells tend to become percussion sensitive. In order to test whether the Li/BrCl, $SOCl_2$ had similar sensitivity to percussion, we subjected several overdischarged cells (5 A, at least 120 hours) to shotgun tests. A Springfield Model 410 shotgun was used for these tests. The cells were hit by shotgun pellets from a distance of about 3 m, four times each. No explosion hazard was encountered. Accordingly, we concluded that the Li/BrCl, $SOCl_2$ cells are not percussion sensitive even after the cell voltage has been driven into reversal for a long time during forced overdischarge.

After the D-size cells were forced into voltage reversal at 1 A, they were charged at the same current for over 100 hours (Fig. 15). It was observed that after the cells had been charged for

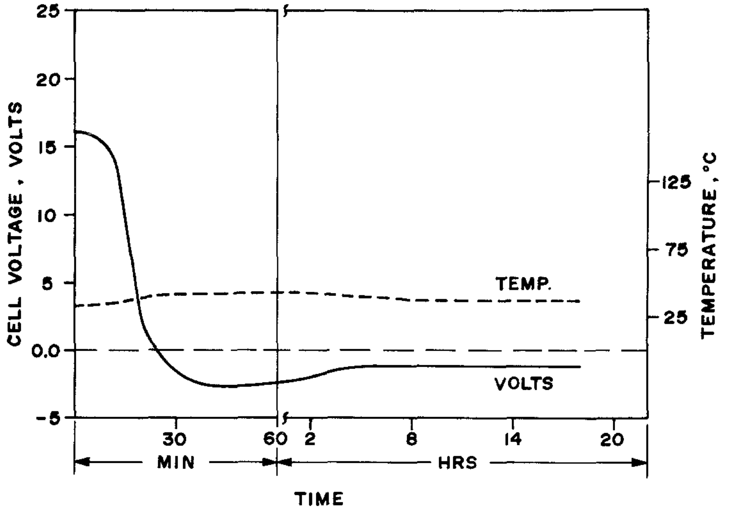

Fig. 13. Voltage and skin temperature of a Li/BrCl, $SOCl_2$ battery (6 fresh C-size cells and 1 discharged C-size cell connected in series) during forced discharge at 3 A. The temperature of the discharged cell was monitored.

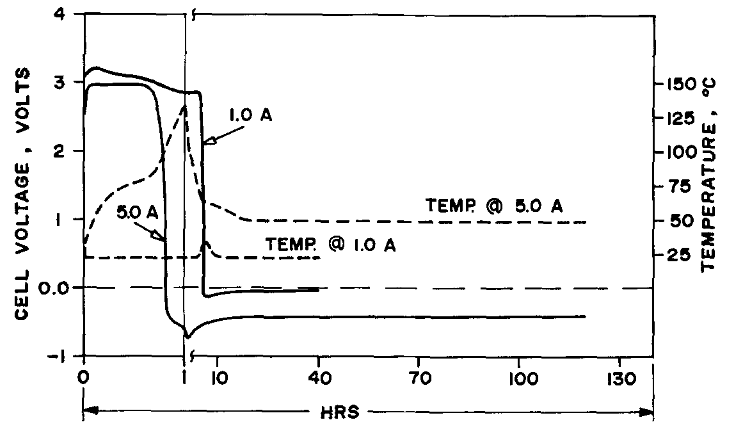

Fig. 14. Voltage and skin temperature of D-size Li/BrCl, $SOCl_2$ cells during forced discharge at 1 A and 5 A.

about six hours, the cell voltage began to increase. Shortly after the increase, the cell voltage began to fluctuate. Nonetheless, no explosion or venting was observed at any time during these tests. The voltage fluctuation was a reproducible behaviour upon charging. More than 12 cells were tested and the voltage fluctuation was noted in every test, though it may occur sooner or later than the time shown in Fig. 15. Our experience with Li/$SOCl_2$ cells has been that the voltage fluctuation almost always precedes the explosion hazard during forced discharging or charging. However, in the case of the Li/BrCl, $SOCl_2$ cell, no explosion occurred.

The Li/BrCl, $SOCl_2$ cells with no safety vents were incinerated above a naphtha flame. They exploded as the skin temperature of the cell reached about 420° C. However, the explosion upon incineration could be prevented by the incorporation of a safety vent which opened at an internal pressure less than 400 psi.

The results of the present investigation have shown that Li/BrCl, $SOCl_2$ is a practical system which has a high energy density, low self-discharge rate and wide operating temperature range. Moreover, the Li/BrCl, $SOCl_2$ cells appear to be abuse resistant.

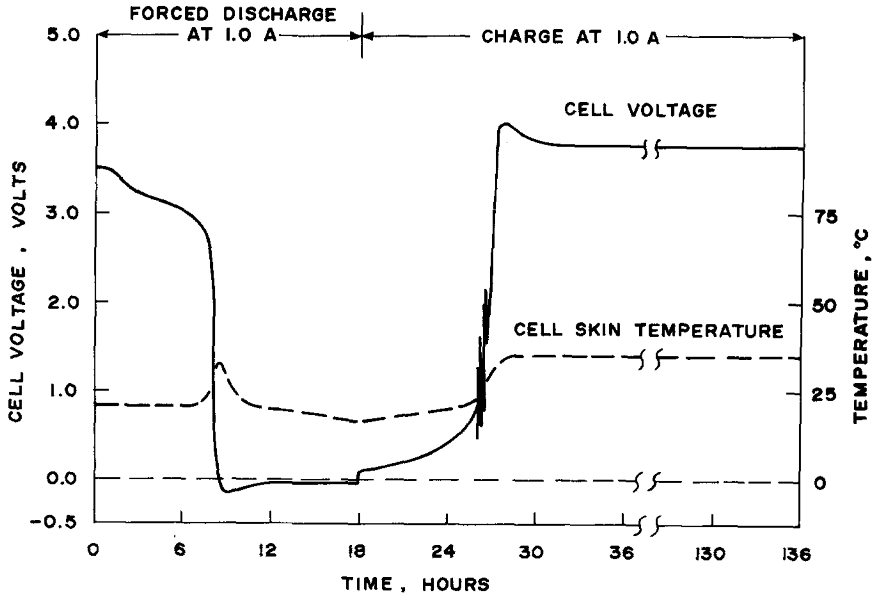

Fig. 15. Voltage and skin temperature of a D-size Li/BrCl, $SOCl_2$ cell during forced discharge and charge at 1 A.

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