

# *The technology of the Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> cell system*

## *IV. high temperature performance, storability, and safety characteristics*

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Received 17 August 1982

Tests were conducted to determine the performance, storability, and safety characteristics for specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> (Li/CSC) cells at temperatures as high as 150° C. Discharge tests at 150° C showed that practical Li/CSC D cells yield energy densities of 0.75 to 0.91 Wh cm<sup>-3</sup> for constant resistive loads of 3.0 to 75.0 ohms, respectively. Further, the performance results obtained for cells stored at 150° C and either discharged at 25° C or discharged at 150° C showed little loss in realized capacity but exhibited a noted loss in rate capability. These cells have been subjected to abusive conditions such as short circuit, forced overdischarge, incineration, puncture, and shock sensitivity testing following prolonged discharge at both ambient and elevated temperatures. Safety/hazard testing has also included specific combinations of the above abusive conditions. The results relative to the safe, efficient use of the cells at elevated as well as room temperatures will be discussed.

### 1. Introduction

The lithium/sulphur oxychloride inorganic battery systems possess the characteristics necessary for many applications requiring high energy densities, high current capabilities and effective operation over a wide range of temperature. Indeed, many investigations have been conducted to determine the performance characteristics for both the Li/SOCl<sub>2</sub> [1] and the Li/SO<sub>2</sub>Cl<sub>2</sub> system [2-5].

Studies were conducted in this laboratory to determine the effect of a halogen and interhalogen addition to the sulphur oxychlorides, SOCl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub>. Of especial interest in these investigations was the positive effects of these codepolarizers relative to the safety as well as to the performance and storability characteristics. Two novel batteries were developed as a result of these efforts: the Li/BrCl in SOCl<sub>2</sub> (Li/BCX) and the Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> (Li/CSC) systems [6-11]. During the course of performance evaluation for the two systems, it became apparent that cells of the Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> system were much less sensitive to performance degradation at temperatures of

72° C or higher than the Li/BCX system or the parent electrochemical systems, Li/SO<sub>2</sub>Cl<sub>2</sub> and Li/SOCl<sub>2</sub>, respectively. Therefore, a program was initiated to develop a Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> battery capable of operation at temperatures as high as 150° C. It was found that Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> cells which were filled with electrolyte could only operate effectively at temperatures of 93° C or less [10, 11]. At slightly higher temperatures of 110° C and under open circuit conditions the cells underwent venting through cracked glass to metal seals. These results indicated that the cells experienced high internal pressures due to both liquid and gas expansion. In addition, it was found that the high electrode geometric surface area, separator material and case construction contributed to the general deterioration in performance at temperatures above 93° C. In view of the above, special cells were designed and fabricated which incorporated optimized fill weights, limited electrode geometric surface areas, an alumina separator material and a stronger case construction. These spirally wound cells were used as the test vehicle in this study to investigate the

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performance, safety and storability characteristics at 150° C.

## 2. Experimental details

### 2.1. Electrode fabrication

The current collectors for both the anode and cathode were constructed from expanded nickel screen (Delker 3Ni20-189) and extended the entire length of the electrodes. Contact was effected through the use of previously spot welded nickel leads. The carbon electrodes contained 93 wt % Shawinigan acetylene black (50% compressed) and 7 wt % Teflon binder (TFE, dispersion No. 30, DuPont). The carbon electrode geometric surface area was 129 cm<sup>2</sup> (4.3 cm width × 15 mm length × 2 sides) for the D cells used in this study. The average thickness of the carbon electrodes was 0.25 cm.

The lithium anode (Foote Mineral Company) was fabricated from 0.055 cm thick foil. A second overlay of lithium foil was used to cover the area of the nickel screen exposed to the portion of the carbon electrode in the innermost windings of the spirally wound cell.

### 2.2. Depolarizer and electrolyte preparation

Details relative to the preparation and purification of the SO<sub>2</sub>Cl<sub>2</sub> (Alfa-Ventron), the collection of the Cl<sub>2</sub> (Matheson) and the preparation of LiAlCl<sub>4</sub> from LiCl (Fisher Scientific Company) and AlCl<sub>3</sub> (Fluka) have been given previously [10]. It was found that the optimum concentrations of Cl<sub>2</sub> and LiAlCl<sub>4</sub> in the Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> electrolyte were 0.45 and 1.45 mol dm<sup>-3</sup>, respectively.

### 2.3. Cell fabrication

Cells were fabricated by winding the lithium anode, the carbon cathode and a single layer of 0.051 cm thick alumina ceramic paper (Kaowool 3000, Babcock and Wilcox) into a cylindrical roll. The roll was then inserted into a 304L stainless steel can (Hudson Tool and Die) having an average wall thickness of 0.079 cm. A lid containing a hermetic glass to metal seal and an electrolyte fill port was fitted and subsequently welded to the cell can. The average thickness of the lid used in

these studies was 0.25 cm. The cell can served as the negative terminal for the cell.

Cell filling was accomplished by vacuum filling techniques. The maximum amount of electrolyte solution was limited to 35 g per cell in an effort to eliminate the effects of hydraulic pressure on the cell components, most notably the glass to metal seal.

All manipulations relative to electrode fabrication, electrolyte solution preparation and cell construction were performed in a dry atmosphere of less than 0.5% relative humidity and - 50° C dew point.

### 2.4. Performance tests

Cells were discharged under various constant resistive loads at room temperature (25 ± 3° C) and at 150 ± 3° C. In order to ensure thermal equilibrium, test cells were stored for a minimum period of 20 h prior to discharge at the elevated temperature. The loads were positioned in the ambient environment, external to the Thelco oven high temperature chamber.

Load voltages were measured by a timed sequential electrometer and displayed on a multi-channel recorder. All realized capacities cited herein were obtained to a 2.0 V cutoff level.

### 2.5. Pressure tests

The internal pressure generated by the electrolyte was measured from ambient temperature to 150° C. A standard D case having a special lid fitted with a mating couple for a pressure transducer (Data Instruments Inc., Model AB-2000) was fabricated. Teflon (TFE, DuPont) pieces were used to simulate the volumes normally occupied by the lithium, carbon (accounting for approximately 85% porosity) and other cell components (11.8 cm<sup>3</sup>). An amount of electrolyte equal to that used in the D cell was added to the test "cell". The test was performed by placing the unit in a Thelco oven and allowing it to equilibrate for 4 h periods at various temperatures from 25 to 150° C. After a period of 8 h at 150° C, the oven temperature was lowered to 25° C in the same manner as described above. The test was repeated using the same test "cell" as well as newly fabricated "cells".

## 2.6. Safety tests

All safety/hazard testing was performed using D cells with all electrical protection devices such as fuses or fuse links removed. The tests included short circuit, forced overdischarge, puncture, incineration and shock sensitivity testing following high temperature discharge and storage. Cells were short circuited through a cable having a total resistance of less than 0.020 ohms. The short circuit current was monitored using a Current Gun (F. W. Bell Inc., Model CG-100A). The cell voltage and wall temperature were also recorded throughout the test period.

Cells were force-overdischarged through the use of a variable current, five volt power supply fabricated in-house. The cell voltage and cell wall temperature was measured throughout the testing period. High velocity puncture tests were effected through use of a .22 calibre rifle. Cells were also fitted with thermocouples to measure cell wall temperature and suspended approximately 10 cm above a naphtha fuel reservoir. The results of both the puncture and the incineration tests were videotaped.

Some of the specially designed cells were discharged at 150° C following prolonged storage at the elevated temperature. These cells as well as cells which were discharged at 25° C were subjected to shock sensitivity testing. This test was accomplished by discharging a 20 gauge shotgun (No. 7 shot) at the cells from a distance of 2 to 4 m. The results were photographed.

## 3. Results and discussion

The open circuit voltage (OCV) for cells of the Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> system was found to be  $3.95 \pm 0.02$  V at  $25 \pm 3^\circ$  C. When cells were stored at 150° C for periods as long as 382 h prior to discharge, the lowest OCV values were 3.92 V. Indeed, of the approximately 250 specially fabricated Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells which were employed in this study, only 20 exhibited OCV levels of less than 3.94 V at elevated temperatures.

The performance characteristics at 150° C for Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells were obtained after allowing a minimum period of 20 h for the cells to reach thermal equilibrium. The results given in Fig. 1 show that there is very little difference in

the realized capacity whether the cells were discharged under 10.0 or 40.0 ohm loads (12.5 Ah). There is, however, a noted decrease in realized capacity from 12.5 Ah to 10.5 and 11.1 Ah when cells were discharged under the heavier loads of 3.0 and 5.0 ohms, respectively. It is also interesting to note the effect of prolonged exposure at 150° C for the cells discharged under the lightest load of 75.0 ohms. The approximate time required to discharge these cells to the 2.0 V level was 240 h. It appears that the loss in realized capacity of 0.6 to 0.8 Ah is due mainly to simultaneous self-discharge associated with the low drain rate at the elevated temperature.

The energy densities for the results given in Fig. 1 vary between 0.75 and 0.91 Wh cm<sup>-3</sup> for cells discharged under loads of 3.0 to 75.0 ohms, respectively. These results are particularly noteworthy since the cells contain only 75 to 80% of the Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> electrolyte solution normally needed to fill the cell. In other words, the efficiencies associated with cells discharged under loads of 10.0 to 75.0 ohms are as high as 95 to 98% at the 2.0 V cutoff level.

For comparison purposes, specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells were discharged under identical loads at  $25 \pm 3^\circ$  C. These results are given in Fig. 2. The realized capacities for these cells comprise of a very narrow band at  $11.4 \pm 0.4$  Ah. None of the cells tested at 25° C yielded realized capacities greater than 12.0 Ah. Further, no loss in realized capacities was evident for cells discharged under the heavier loads of 3.0 and 5.0 ohms. However, examination of the results given in Fig. 2 shows that the cells which yield the lowest realized capacity were the cells discharged under the lightest load of 75.0 ohms, as was the case for cells discharged at 150° C (Fig. 1).

One very striking effect noticeable in Figs. 1 and 2 is the increase in load voltage levels for cells discharged at 150° C compared to those for cells discharged at the lower temperature. Corresponding results for cells discharged under the heaviest load of 3.0 ohms show an increase in load voltage of approximately 0.6 V for the cell discharged at the higher temperature. The effect of the enhanced ionic conductivity at 150° C is less evident for cells discharged under the lightest load of 75.0 ohms, as expected. The difference in load voltage

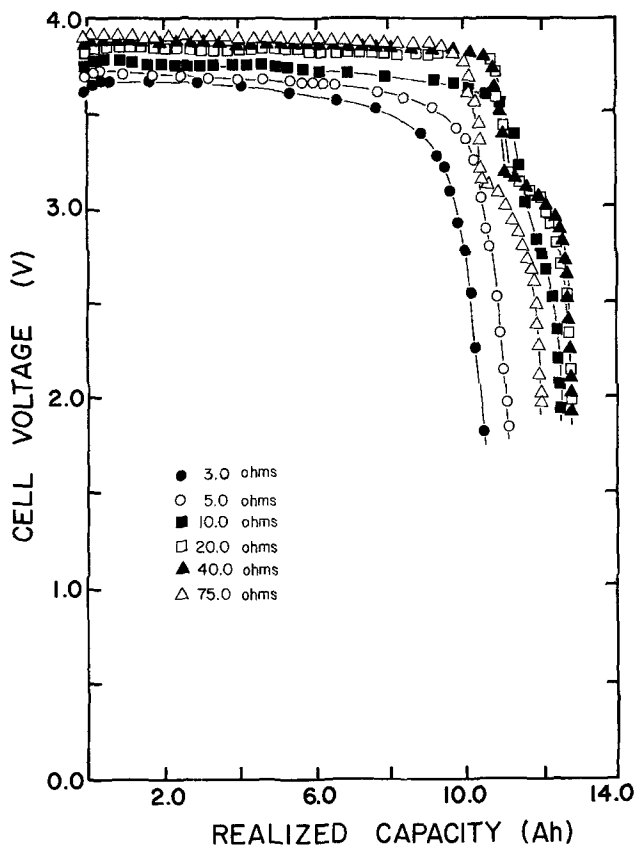


Fig. 1. Discharge performance characteristics for specially designed  $\text{Li}/\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$  D cells at  $150 \pm 3^\circ \text{C}$ .

levels for these cells at the two temperatures is approximately 0.13 V.

The storability characteristics for  $\text{Li}/\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$  cells having a maximum operational temperature of  $93^\circ \text{C}$  have been discussed previously [9–11]. The results obtained from high temperature storage at  $74^\circ \text{C}$  or from ambient temperature storage for extended periods of time for these cells showed that little or no capacity was lost when cells were discharged at medium to high rates. However, there was a noted capacity loss for these same cells discharged at particularly high rates (e.g. a  $\text{Li}/\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$  D cell discharged under loads of 0.50 ohms or less). In addition, a second effect of storage on performance was found to be a loss in rate capability.

A study was conducted to determine the self-discharge/storability characteristics for the specially designed  $\text{Li}/\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$  cells with emphasis on the effects of storage at  $150^\circ \text{C}$ . A series of D cells was stored for 382 h at  $150 \pm 3^\circ \text{C}$  prior to discharge. The results given in Fig. 3 show

significant realized capacity losses for all cells tested except for those cells discharged under 20.0 ohm loads. The maximum realized capacity losses of about 3.0 Ah were found for cells discharged under 10.0 and 40.0 ohm loads. It is apparent from Fig. 3 that the capacity losses of 2.0 Ah for cells discharged under the highest loads of 3.0 and 5.0 ohms was less than the losses experienced by cells discharged under lighter loads. No loss in realized capacity was noted for cells discharged under 20.0 ohm loads. All cells experienced a voltage delay upon application of the loads. The most severe delays were found for cells discharged under 3.0 and 5.0 ohm loads (approximately 5 and 1.5 min, respectively, for load voltages to reach equilibrium values at 3.30 and 3.45 V).

Comparison of the corresponding discharge curves given in Figs. 1 and 3 show that, in addition to the realized capacity losses and voltage delay characteristics for cells discharged under 3.0 and 5.0 ohm loads, there is a significant loss in load voltage levels as a result of long term high tempera-

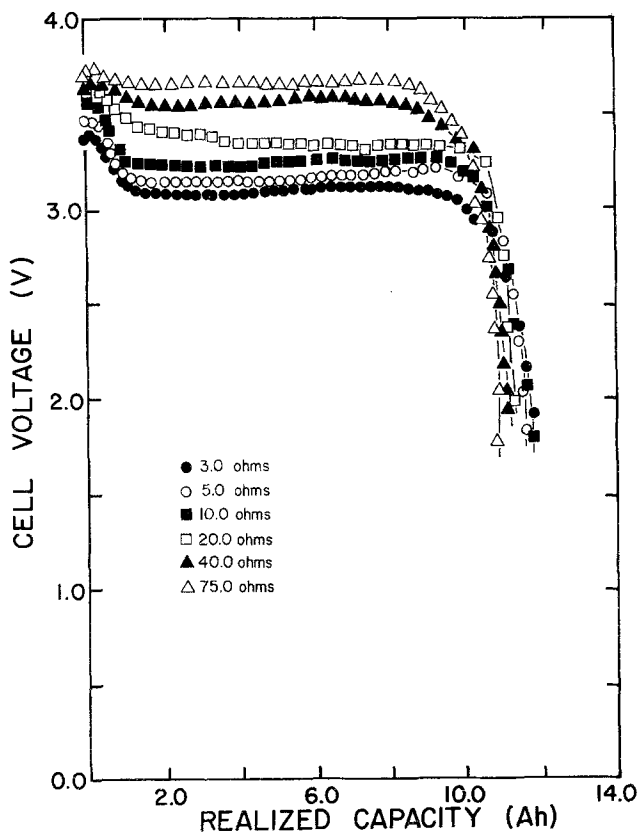


Fig. 2. Discharge performance characteristics for specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells at 25 ± 3°C.

ture exposure. For example, the average load voltage for the cells discharged under 3.0 ohm loads was 3.6 V (Fig. 1) and 3.0 V (Fig. 3) for cells discharged at 150°C after storage for 20 and 382 h, respectively.

High temperature storage testing was extended to include the determination of the high temperature effect relative to the performance characteristics at 25°C. Cells were stored at 150°C for a period of 170 h, subsequently removed and allowed to reach thermal equilibrium at 25°C prior to testing. The performance results in Fig. 4 indicate that the realized capacities obtained for cells discharged under 3.0 to 75.0 ohm loads comprise of a narrow band which ranges from 10.4 to 11.7 Ah. These results are not significantly different from those obtained for fresh cells discharged at 25°C (Fig. 2). There is exhibited a severe initial voltage delay for cells discharged under 3.0 and 5.0 ohm loads. Indeed, the time necessary for the load voltage to attain the 2.5 V level for cells tested under 3.0 ohm loads was almost 1 h. In contrast to those results presented

in Fig. 3, voltage delays were also evident for cells discharged under the lighter loads of 20.0 and 40.0 ohms. The loss in rate capability is evident for cells which were discharged under the heavier loads of 3.0 to 10.0 ohms. Comparison of the load voltage levels for Figs. 2 and 4 show that there is an almost 0.5 V difference for cells discharged under 3.0 and 5.0 ohm loads and a 0.3 V difference for cells discharged under 10.0 ohm loads. Except for the voltage delay characteristics, there are no noted differences among the results obtained for cells discharged under the 20.0, 40.0 and 75.0 ohm loads.

At the present time, no data exists which relates cell performance results at 150 or 25°C following such high temperature storage at 150°C to storage at ambient temperatures for extended periods of time. Nonetheless, from the results obtained from the discharge of cells following storage at 150°C and the results given previously [9, 11] for cells of the Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> system having a maximum operational temperature of 93°C, it can be said that very little loss in realized

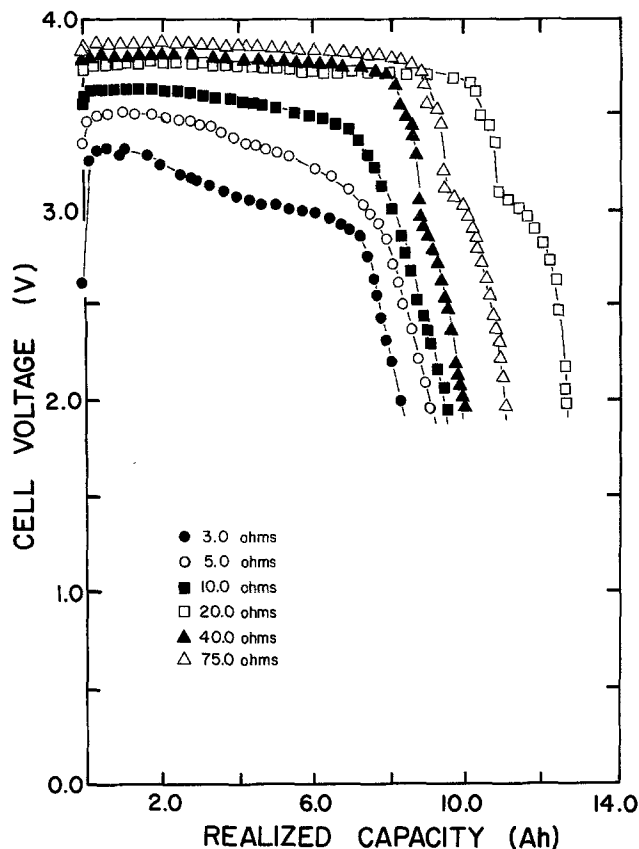


Fig. 3. Discharge performance characteristics at  $150 \pm 3^\circ \text{C}$  for specially designed  $\text{Li}/\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$  D cells following storage for 382 h at  $150 \pm 3^\circ \text{C}$ .

capacity would be expected as a result of long term storage at temperatures of  $25 \pm 5^\circ \text{C}$ . Two further effects of storage would be a loss of rate capability and voltage delay. These latter effects would be particularly dependent upon the discharge rate.

One most notable physical effect on the specially designed  $\text{Li}/\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$  cells due to either storage or discharge at  $150^\circ \text{C}$  is the longitudinal bulging of the cell case, particularly at the case bottom. Dimensional measurements for D cells before and after exposure to a  $150^\circ \text{C}$  environment showed an average longitudinal expansion of 0.30 cm had occurred for cells which were discharged after long term storage (Fig. 3). No change in the dimensions of the cell diameter was found, however. In view of the above, studies were undertaken to measure the internal pressure of a D cell containing an appropriate amount of inert Teflon to account for the lithium, carbon, nickel screen, etc., in the cell. The cell was then filled with 35 g of the electrolyte solution and fitted to a pressure transducer. Vapour pressure

measurements were taken at various temperatures to approximately  $157^\circ \text{C}$ . The results showed that the internal pressures within a cell at 140, 150 and  $157^\circ \text{C}$  were 24.6, 31.6 and  $37.3 \text{ kg cm}^{-2}$ , respectively.

These results indicate that, although the effects of hydraulic expansion have been eliminated by reducing the electrolyte volume in the cell, the high vapour pressure at the operational temperature is sufficiently high to pose a problem relative to longitudinal expansion in multicell applications. It is important, therefore, that sufficient space be permitted between cells in a battery to allow for such an expansion.

A second study was undertaken to determine the combined effects of high internal cell pressure and long term exposure to the reactants and products of the  $\text{Li}/\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$  cells upon the glass to metal seal. Specially designed  $\text{Li}/\text{Cl}_2$  in  $\text{SO}_2\text{Cl}_2$  D cells were discharged at  $150^\circ \text{C}$  following storage for 382 h at  $150^\circ \text{C}$ . The performance results have been presented in Fig. 3. The cells were allowed to remain at  $150^\circ \text{C}$  until a total

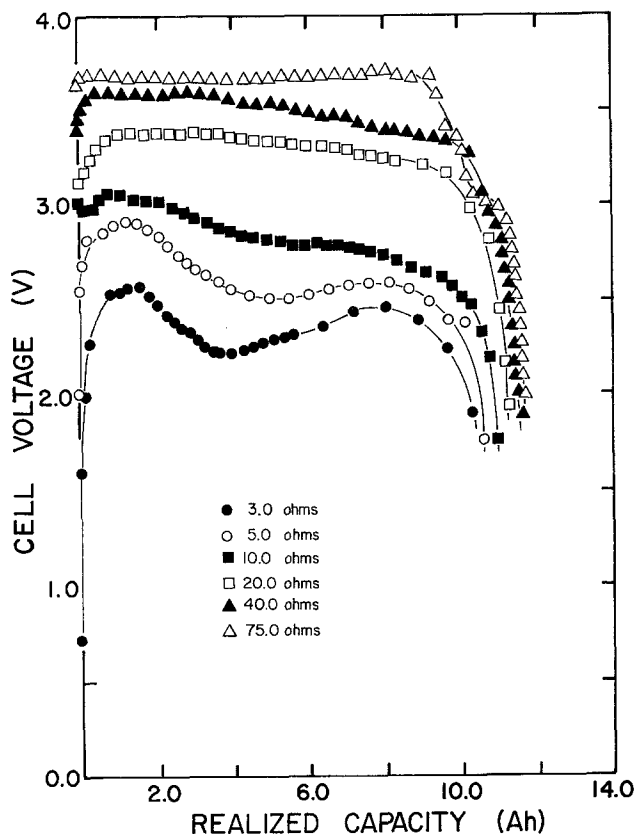


Fig. 4. Discharge performance characteristics at  $25 \pm 3^\circ \text{C}$  for specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells following storage for 170 h at  $150 \pm 3^\circ \text{C}$ .

accumulated duration of 650 h was reached. The cells were disassembled and the glass to metal seal was examined using a scanning electron microscopy (SEM). The glass comprising the seal used in these studies was Mansol MTL-05. Scanning electron micrographs of a typical seal from the cells which had undergone discharge and storage at  $150^\circ \text{C}$  are given in Fig. 5. These results may be compared to those obtained for a virgin glass to metal seal (Fig. 6). No detrimental effects due to either corrosion or cracking caused by long term exposure to high internal cell pressures or the electrolyte/reaction products can be found for the majority of the cells examined. In a few instances, however, spalling was found in the glass to metal seal. This was undoubtedly caused by the effect of lid expansion on the compression fit at the inner glass to metal seal surface. Further, no evidence of glass corrosion was found in these seals which showed spalling.

Tensile strength tests were performed on both the glass to metal seals from cells exposed to  $150^\circ \text{C}$  for 650 h and virgin glass to metal seals in

accordance with MIL STD 202, Method 211, Test Condition A. The average tensile strengths for virgin glass to metal seals was found to be 20.0 kg. The corresponding average results obtained from Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells exposed to a  $150^\circ \text{C}$  storage and discharge conditions for 650 h were 21.0 kg. The difference in tensile strengths between the virgin glass to metal seals and for all the cells exposed to the  $150^\circ \text{C}$  environment is due to the increase in the compression seal caused by a slight lid expansion. These results agree favourably with the glass to metal seal hermeticity requirements given in MIL H-28719. The ideal tensile strength required to maintain hermeticity is 15.89 kg for glass to metal seals having similar terminal pin and glass diameters.

Approximately 50 to 60% of the research and development effort in this laboratory is directed toward the safety and hazard characterization of the Li/BrCl in SOCl<sub>2</sub> [6] and Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> battery systems. Because of the required strengthening of the cell structure necessary for effective operation at the maximum elevated

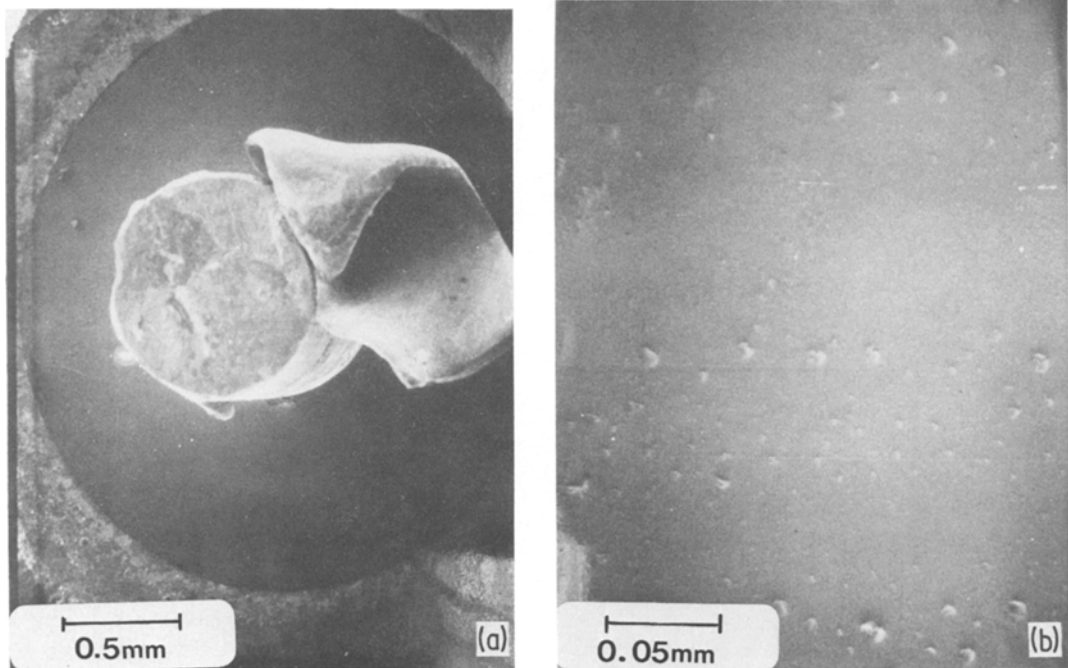


Fig. 5. Scanning electron micrograph of a typical glass to metal seal which had undergone discharge and storage at 150° C. (a): entire glass to metal seal; (b): glass surface. Dimensions are referenced to the glass to metal seal surface.

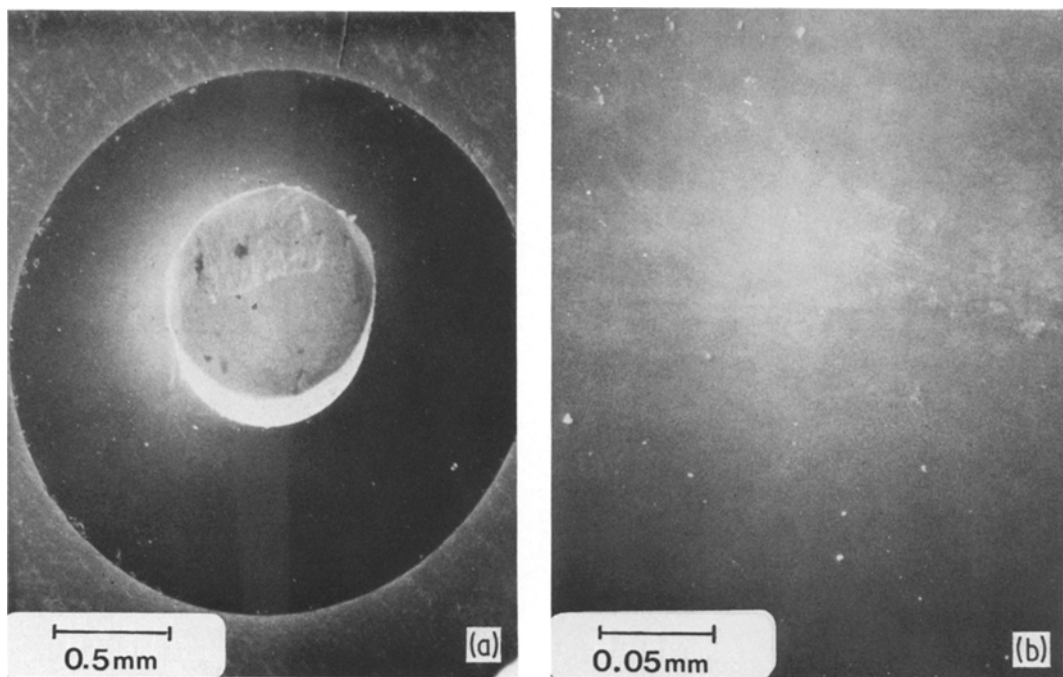


Fig. 6. Scanning electron micrograph of a virgin glass to metal seal. (a): entire glass to metal seal; (b): glass surface. Dimensions are referenced to the glass to metal seal surface.



temperature of 150° C, specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> cells should be considered potentially more hazardous than cells containing the same electrolyte material having an upper operational limit of 93° C [8, 10, 11]. In view of this fact, each cell is protected from short circuit, high current discharge or high current charge conditions by the inclusion of a fuse or fusible link within the cell structure. All safety and hazard characterization studies, however, were performed with cells containing no protective devices in the effort to simulate worst case conditions.

Short circuit tests were performed at 25, 150, 162 and 172° C using the specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cell as the test vehicle. The cells were short circuited through a cable having a total resistance of less than 0.020 ohms. The short circuit current, cell voltage and cell wall temperature were monitored throughout the test period. The post mortem results showed that the internal lead from the carbon electrode to the terminal pin was incinerated within five minutes for cells tested at 150 and 162° C. The cell wall temperature for these cells increased 8 to 10° C above the test temperature before the internal lead was incinerated. No ventings or explosions occurred for any of the cells tested at 150 or 162° C. The values of the short circuit current for these cells were typically 18 to 25 A. Cells were also short circuited at 172° C. Although the results relative to the short circuit current and lead incineration were nearly identical to those described for cells short circuited at 150 and 162° C, the temperature rise of approximately 10 to 12° C was sufficient to increase the cell temperature above the melting point of lithium. All cells tested at 172° C exploded violently.

The combined effects of decreased conductivity at lower temperatures and reduced electrode geometric surface areas were demonstrated by the results of the short circuit tests performed at 25° C. The average initial short circuit current measured for the cells was 14 A. The results showed that the cells were able to sustain current levels of 8 to 12 A throughout the duration of the test. However, after a period of 10 to 20 min, the cell temperature had risen to 180° C or higher with resultant cell explosions. These results are in sharp contrast to those obtained for cells having an operational temperature limit of 93° C [10, 11].

When the latter cells were short circuited at 25° C, the internal leads were incinerated within 10 s. The current delivering capabilities of these cells were enhanced by the greatly increased carbon electrode geometric surface area (239 cm<sup>2</sup>) as compared to the area for D cells of the high temperature design (129 cm<sup>2</sup>).

Specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells were force overdischarged at various rates at 150° C. Fig. 7 shows the typical results for the forced overdischarge of cells at the maximum suggested discharge rate of 1.0 A. The average realized capacities at the 2.0 V cutoff level were approximately 10.0 to 10.5 Ah. The cell voltage dropped precipitously from the 2.0 V level to approximately -0.2 V. During the next 5 h period, the cell voltage further decreased to the -2.0 V level. The cell voltage then recovered and remained at the -0.2 to -0.4 V level throughout the remainder of the test period. The total time that this cell (Fig. 7) remained in voltage reversal was approximately 125 h. This reversal period was equivalent to ten times the nominal capacity of the cell. The maximum cell wall temperature increase of 8 to 10° C occurred at the voltage reversal point. The temperature then decreased to 150° C during the next 6 to 8 h period and remained at 150° C throughout the duration of the test. No cell ventings or explosions occurred during any of these tests.

Cells were also subjected to both high velocity puncture and incineration tests. Specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells were punctured at 25° C by firing a .22 calibre bullet at the cell. In the majority of cases, only slight smouldering at the puncture site was noted. However, in some instances, a lithium fire occurred approximately two minutes following the initial cell puncture. It is believed that the combination of reduced electrolyte volume and small carbon electrode geometric surface area contributed to the comparatively benign behaviour of these cells. When D cells of the Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> system having an operational temperature limit of 93° C were exposed to identical puncture tests, explosions or cell ruptures occurred in every instance [11].

Incineration testing was accomplished by suspending the high temperature D cells approximately 10 cm above the surface of a naphtha fuel reservoir. Each cell was equipped with a chromel/

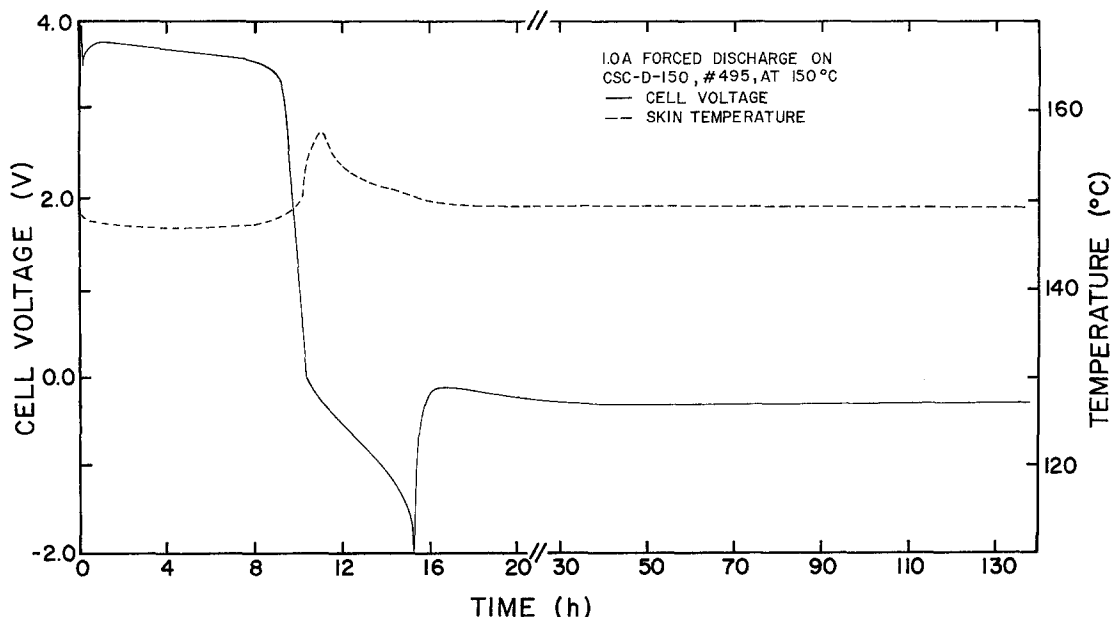


Fig. 7. Forced overdischarge test at 1.0 A of a specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cell at 150° C. Solid line, cell voltage; broken line, cell wall temperature.

alumel thermocouple to measure skin temperatures during testing. Every cell tested in the above manner exploded violently within 1.6 and 2.5 min of test initiation. Cell wall temperatures rapidly rose to the 400 to 600° C level just prior to the cell explosion. Incineration testing performed upon Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells having an operational temperature limit of 93° C results in only mild ventings and is independent of the cell discharge state. The case and lid construction for cells of the lower temperature design allow the lid to deflect easily, thereby effecting a cracked glass to metal seal. This is not the case for cells of the high temperature design. The case and lid construction does not allow enough lid deflection to cause the glass to metal seal to rupture. Instead, the cells remain intact until the melting point of lithium is reached. The cells explode violently through the spontaneous reaction of fused lithium with the electrolyte material.

Specially designed cells were discharged to 0.0 V at 150° C following long term storage at the elevated temperature. These cells, as well as cells which were discharged to 0.0 V at 25° C, were subjected to shock sensitivity testing. This test was accomplished by repeatedly firing a 20 gauge shotgun (no. 7 shot) at the cells from a distance of 2 to 4 m. In no instance was there an explosion

or lithium fire. However, because of the mechanical force of the shock, glass to metal seals often ruptured, with cells emitting SO<sub>2</sub> gas.

It is believed that many incidents involving lithium batteries (venting, cell rupture or explosion) which present physical hazards to both equipment and personnel are often the result of cell or battery exposure to a combination of hazardous conditions rather than to one single hazardous condition. Therefore, much of the hazard/safety testing performed in this laboratory is concerned with the determination of the safety characteristics for cells or batteries which have been subjected to two or more abusive conditions. One example of this testing is given below. Specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> D cells were short circuited after being heated at a rate of 2° C per minute for a 30 min period. The intent of these tests was to determine the effects of short circuit conditions upon cells which were not thermally equilibrated and to simulate massive internal short circuit conditions for cells exposed to high temperatures for only short time periods. In contrast to the results described previously for cells short circuited at 25° C, these cells exploded violently within 8 to 10 min after initiation of the short circuit condition.

In summary, the results of the present investi-

gation have shown that specially designed cells of the Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> system are efficient power sources for applications requiring operating temperatures of up to 150° C. The cells have high energy densities and low self discharge characteristics at the maximum operating temperature. Even though each cell is protected from short circuit, high rate forced discharge and high rate charge conditions by the inclusion of a fuse or fusible link, special care must be taken to insure that the cell temperature under any conditions does not reach 180° C, the melting point of lithium. In all tests which have resulted in cell temperatures of 180° C or higher, the specially designed Li/Cl<sub>2</sub> in SO<sub>2</sub>Cl<sub>2</sub> cells ruptured or exploded violently.

#### Acknowledgement

The authors express their appreciation to Ms M. E. Bolster and Mr D. P. Sieminski for their assistance relative to cell fabrication and internal pressure measurements, respectively. Further, the authors

express their thanks to Dr R. Frank Bis of the US Naval Surface Weapons Centre for many helpful discussions relative to lithium battery safety.

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