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LOW TEMPERATURE TESTING OF Li–$SOCl_2$ CELLS

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Summary

The performance and safety characteristics of Li–$SOCl_2$ cells were evaluated at −40 °C. Tests were conducted on cells of several different designs to determine the influence of cell design on performance and safety. The cells exhibited low operating voltages, poor voltage regulation, and low capacity at −40 °C. The performance of the cells was found to be critically dependent on the cell design. No safety problems were observed during discharge to 2.0 V under constant current and constant load operating conditions. Cells subjected to prolonged periods of continuous drain at constant-load did not vent/rupture upon warm-up. Cells subjected to prolonged reversal were found to be potentially hazardous. Microcalorimetry and electrochemical impedance spectroscopy studies performed on the cells suggested that those containing a catalyst may exhibit poor shelf life.

Introduction

Jet Propulsion Laboratory is involved in a NASA sponsored program to investigate batteries required for the Search and Rescue Satellite (SARSAT) beacon and other space related applications. Some important requirements of the batteries for this application are: continuous and pulse load operations at −40 °C; long, unattended storage life and safety [1]. Li–$SOCl_2$ batteries are being considered for application to the 406 MHz beacon because of their high specificic energy. In the past, on occasion, Li–$SOCl_2$ batteries have vented or exploded during assembly of the beacons or during operation. Also, there have been several reports of venting or explosion of Li–$SOCl_2$ batteries following discharge at low temperature [2]. The hazardous operating conditions, and causes of the low temperature safety problems, are not fully understood. The work is aimed at determining the causes and operating limitations at low temperatures.

Tests were conducted with cells of different designs to determine the influence of cell design on performance and safety. Cells were discharged at −40 °C under constant current and constant load operating conditions. The

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safety of the cells was evaluated during normal discharge, prolonged periods of drain on constant load, reversal, and warm-up. Microcalorimetry and a.c. impedance methods were used for nondestructive diagnosis of the cells. This paper describes the results of performance and safety tests, and our hypothesis for the unsafe behavior at low temperature.

Experimental

Several different designs of 'D' size cells were used to determine the performance and safe operating limits at −40 °C. Cells of design X were custom-fabricated by a commercial vendor specifically for JPL. The rated capacity of these cells was 10 A h and each cell was equipped with a glass-to-metal seal-type vent. They contained 1 M $LiAlCl_4/SOCl_2$ electrolyte without any special additives. Cells from another vendor (design Y) were also evaluated to study the influence of alternative cell design. In addition, in-house fabricated 'D' cells (JPL design) were included in the study. The design details of the various cells tested are given in Table 1. The important differences between these three designs are: electrode area, electrolyte composition, catalysts, and type of vent. Design Y cells contain a catalyst to improve the rate performance of the cells. They were stored for 2 - 3 years under ambient conditions prior to testing. Cells of design X, and JPL, contain no special additives. Cells fabricated in-house contain electrodes of a higher surface area compared with the other two designs. In addition, electrolyte purification techniques were employed before use in the JPL cells.

TABLE 1

Details of cell designs

Design	X	Y	JPL
Cell configuration	Cyl. "D" size	Cyl. "D" size	Cyl. "D" size
Lithium (A h)	14.0	18.0	14.0
$SOCl_2$ (A h)	18.0	15.0	18.0
Carbon weight (g)	6.0	6.0	6.0
Carbon electrode area (cm^2)	203	271	429
Additives	NO	NO	NO
Catalysts	NO	YES	NO
Carbon type	Shw'n black	Shw'n black	Shw'n black

The performance and safety evaluation of the cells were carried out in a facility built specifically to handle 'D' size $Li-SOCl_2$ cells safely. The facility was equipped with remote manipulators, an air circulating environmental chamber, and an exhaust ventilation system. The performance of the cells was evaluated by discharging under constant current and constant load at −40 °C. The safety of the cells was evaluated during discharge, continuous drain under constant load, and reversal. At the end of each test, the cells were taken out of the environmental chamber and placed at ambient temperature. They were then allowed to warm-up under this condition. All tests were carried out in triplicate. The voltage and temperature of the cells was monitored during discharge, reversal, and warm-up. The time for voltage to recover to 2.0 V was also determined for the various test conditions.

Microcalorimetric experiments were carried out on 'D' size Li–$SOCl_2$ cells of various designs as part of our investigation on predicting shelf life. The heat evolved from the cells was measured periodically in the open circuit condition at ambient temperature. A heat conduction, Hart Scientific microcalorimeter was used in these experiments.

Electrochemical impedance spectroscopy was used to study the characteristics of the surface film formed on the lithium electrode. The impedance spectra covered the frequency range 10 mHz - 64 kHz. A Solartron 1250 frequency analyzer and Solartron 1286 electrochemical interface were used in the study.

Results and discussion

Performance

The discharge characteristics of the cells at −40 °C under constant current (300 mA) and constant load (10 Ω) operating conditions are given in Fig. 1. From this Figure it can be observed that cells exhibit performance limitations at −40 °C. Some of the important observations are: low operating voltage, poor voltage regulation, low capacity, and considerable voltage delay. Performance characteristics of the cells of various designs are summarized in Table 2. From the results it can be seen that cell design has a significant influence on performance at −40 °C. Cells of design Y showed inferior performance compared with cells of other designs. They failed to deliver any measurable capacity during discharge under constant current and constant load operating conditions. This may be due to self discharge of the

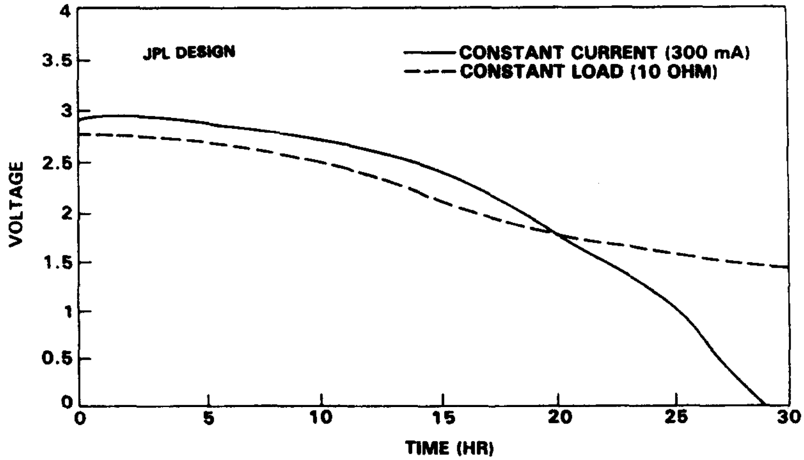

Fig. 1. Discharge characteristics of Li/$SOCl_2$ cells at −40 °C.

TABLE 2
Permanent characteristics of cells

Design	X		Y		JPL	
	C.L.	C.C.	C.L.	C.C.	C.L.	C.C.
Voltage delay (min to recovery)	18	9	N.R.	N.R.	18	9
Oper. voltage (V)	2.7	2.8	0.2	1.4	2.9	2.9
Capacity (A h) (to 2.0 V cutoff)	4.5	5.5	*	*	5.5	6.0
Specific energy (W h kg^{-1})	101	128	*	*	133	145
Specific energy (W h l^{-1})	233	290	*	*	300	328

C.L.: 10 Ω at −40 °C.
C.C.: 300 mA and −40 °C.
*No measurable capacity.

lithium electrode over a storage period of 2 - 3 years or failure of the lithium electrode at −40 °C operation due to the high passivation. Microcalorimetry and a.c. impedance methods were used to study these problems. Cells fabricated in-house showed the best performance in terms of capacity, operating voltage, and voltage delay. They contained no additives in the electrolyte and no catalyst in the carbon electrode, but these electrodes had a larger geometric area and this results in a lower operating current density. Cells of design X are similar to in-house-fabricated-cells except for differences in electrode size: they are of smaller geometric area and therefore exhibit lower capacity and operating voltage at −40 °C compared with the in-house fabricated cells. From the above it can be concluded that Li–$SOCl_2$ cells, in general, exhibit limited performance capability at −40 °C. Therefore, low temperature applications require development of cells of a special design.

Voltage delay

Voltage delay characteristics of the cells under constant load (5 Ω) discharge at −40 °C are given in Fig. 2. From the Figure it can be seen that cells of design Y did not recover to 2.0 V, even after 20 min. In fact, the cells never recovered throughout the entire test. Cells fabricated in-house showed minimum voltage delay, and voltage recovery to 2.0 V after 18 min on load. Cells of design X also showed an 18 min voltage delay. The difference in the voltage delay times of the three types of cells is due to the varying degrees of passivation of the lithium electrodes.

A.C. Impedance

Electrochemical a.c. impedance spectroscopy was used to study the characteristics of the surface film formed on the lithium electrode. Electrochemical impedance spectra of the cells are shown in Fig. 3(a), (b) and (c). The cells studied were on storage for 2 - 3 years at ambient temperature.

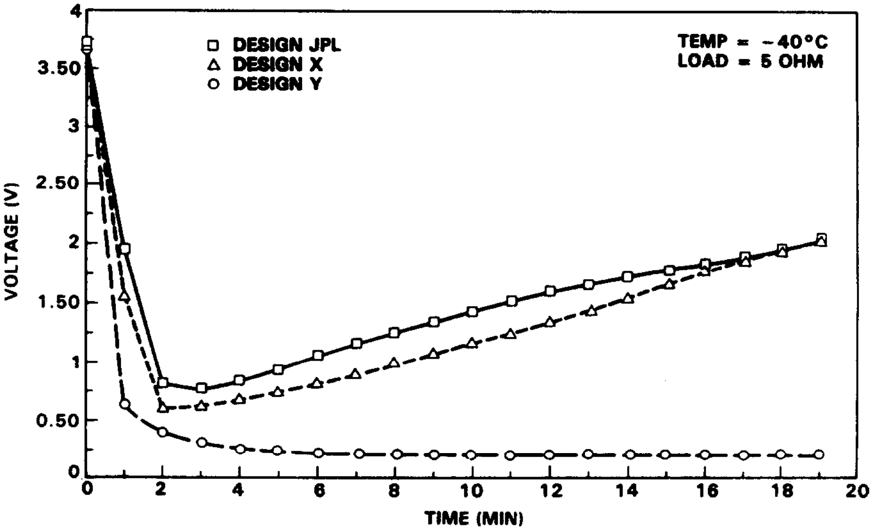

Fig. 2. Voltage delay characteristics of Li/SOCl$_2$ cells under constant load.

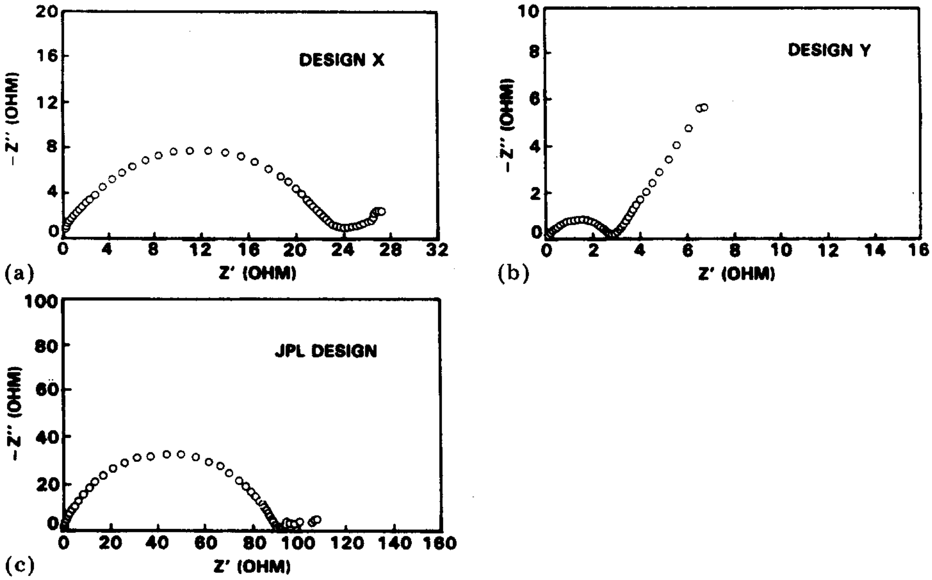

Fig. 3. A.C. impedance spectra of Li/SOCl$_2$ cells.

The semicircular component of the spectrum can be attributed to the passivating film present on the lithium electrode. The linear region in the lower frequency can be ascribed to the carbon electrode; this subject is not discussed in this paper. The ohmic component is represented by the high frequency intercept; this is the sum of the electrolyte resistance and the lead resistances. The difference between the low frequency and the high frequency intercepts represents the charge transfer resistance of the passi-

TABLE 3

A.C. impedance analysis results

Cell design	X	Y	JPL
Ohmic resistance (Ω)	0.01	0.20	0.01
SEI resistance (kΩ cm^2)	4.8	0.7	38.5
Capacitance (μF cm^{-2})	0.028	0.239	0.044
Apparent thickness (nm)	335	39	214
Conductivity (Ω^{-1} cm^{-1})(10^{-9})	6.93	5.53	0.556

vating film, referred to as the Solid Electrolyte Interface (SEI). From the impedance spectra the characteristic parameters describing the LiCl solid electrolyte interface were derived and summarized in Table 3. The apparent capacitance and thickness were calculated at 10 kHz using the equivalent circuit reported in the literature [3]. Cells of design Y showed higher ohmic resistance compared with those of the other two designs. The lithium electrode of the cells of this design has a much thinner SEI film (39 nm). This fact, together with the high conductivity of the SEI, predicts high lithium corrosion in these cells. This is probably due to the presence of the catalyst in the cells of design Y. Use of high purity materials in the fabrication of JPL cells probably resulted in an SEI of lower conductivity, which is desirable to reduce lithium electrode corrosion. The low conductivity and the thinness of the SEI observed in the JPL cells, suggest that they may have a longer shelf life.

Shelf life

Microcalorimetry measurements were performed on the cells to determine their shelf life characteristics. The results of the studies are summarized in Table 4. The capacity loss suffered by the lithium electrode was calculated

TABLE 4

Results of microcalorimetric studies

	X	Y	JPL
After 1.5 years			
Heat output (μW)	445	1570	150
Projected capacity loss (A h y^{-1})	1.08	3.82	0.37
After 3.0 years			
Heat output (μW)	340	2240	90
Projected capacity loss (A h y^{-1})	0.83	5.45	0.22

based on the heat output from the cells. From the Table it can be seen that cells fabricated in-house have the lowest lithium corrosion rate. This may be due to the high purity of the materials used in the cell construction and the absence of any additives or catalysts in the electrolyte/cathode. Cells of design Y showed significantly higher lithium corrosion rates compared with other cells. The high heat output observed in these cells can be attributed to the reaction of the catalysts with the electrolyte and/or accelerated corrosion of the lithium electrode in presence of the catalysts. From these results it can be inferred that cells containing no catalysts or additives may, at best, lose less than 20% of their rated capacity after storage for 5 years under ambient conditions.

Safety

The safety of the cells was studied during normal discharge (constant current and constant load), continuous drain under constant load (5 and 10 Ω), reversal at low temperature, and warm-up to ambient temperature after each test. Cells of design Y were not included in the study because of their poor performance. Cells fabricated in-house and cells of design X showed similar behavior during the tests. The findings of these safety tests are described below.

Normal discharge

No venting or violent rupture of the cells was observed during normal discharge to a 2.0 V cutoff under constant current and constant load operating conditions at −40 °C. The cells did not exhibit exothermic behavior during the warm-up period. No incidents were observed upon warm-up to ambient conditions. The voltage of the cells recovered to 3.6 V within 30 min (Fig. 4).

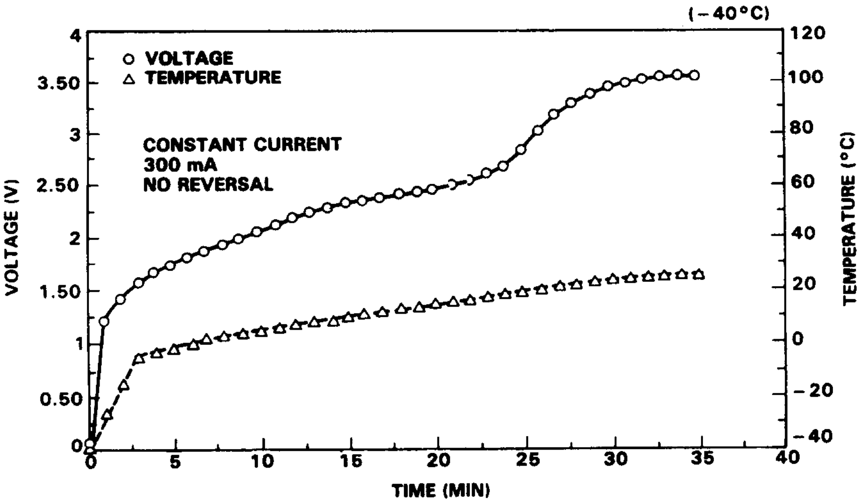

Fig. 4. V and T recovery for non-reversed cells

Continuous drain

Cells were discharged under 5 and 10 Ω contant load at −40 °C for different periods ranging from 50 h to 600 h. No venting or explosion was observed during the entire test period. After the completion of each test, cells were allowed to warm-up. Surprisingly they failed to exhibit any significant temperature increase during warm-up. The cells attained an open circuit voltage of 3.6 V after 40 min standing under ambient conditions (Fig. 5). Our observations on this subject are not in agreement with those reported in the literature. The reasons for these contradictory observations are not clearly understood. However, one may attribute them to the differences in the types of cells employed in the safety studies.

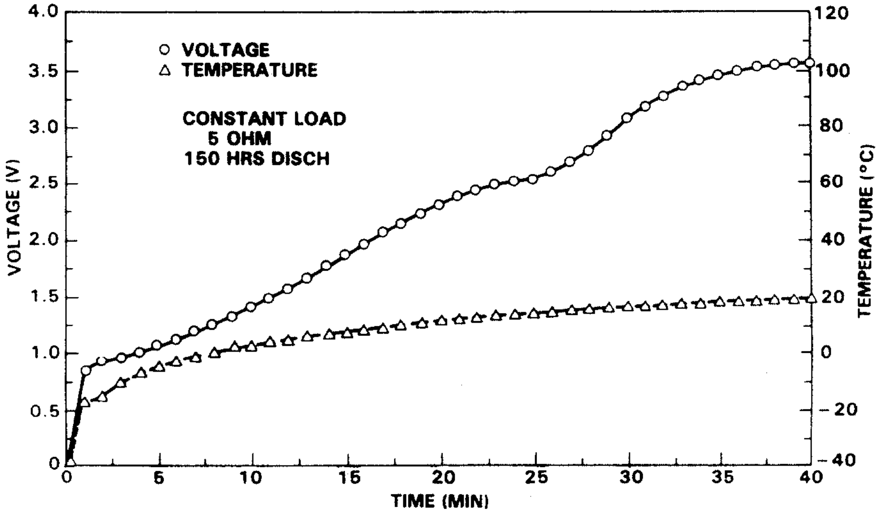

Fig. 5. V and T recovery of continuously drained cells.

Reversal

Cells were subjected to different periods of reversal (25%, 50%, 100%, and 150%) at 300 mA constant current and −40 °C. No venting or explosion of the cells was observed during reversal up to 150%. Upon warm-up to ambient temperature, cells subjected to reversal of 100% and above vented/ruptured violently. The venting/rupturing of the cells took place after 30 - 40 min of stand period under ambient conditions. Cells of design X and in-house fabricated cells, as well as others, exhibited similar behavior. This clearly suggests that the observed safety problems are intrinsic to the chemistry of the Li–$SOCl_2$ cells. Figure 6 gives the temperature and voltage characteristics of these cells during warm-up. It may be observed that the cell temperature rose to 60 °C within 30 min and thereafter the cell skin temperature rose at a fast rate. These results clearly suggest that exothermic reactions are taking place within the cell. These exothermic reactions could lead to thermal runaway.

The results of the safety test are summarized in Table 5. Some of the important findings are:

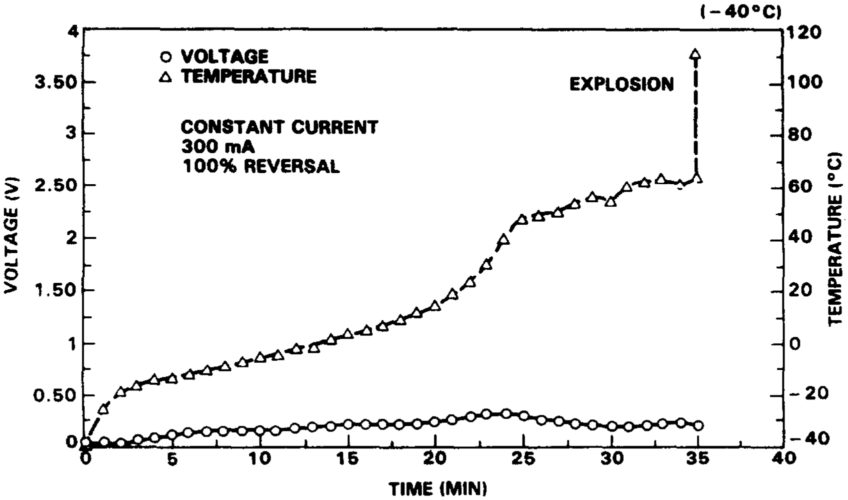

Fig. 6. V and T recovery of 100% reversed cells.

TABLE 5

Summary of safety test results
JPL and design X.

Temperature (°C)	Method	Rate	Length	Result
—40	Constant current	300 mA	0, 20, 50% rev	No explosion
—40	Constant current	300 mA	100% rev	Explosion
—20	Constant current	300 mA	0, 25, 50, 100% reversal	No explosion
0	Constant current	300 mA	0, 25, 50, 100% reversal	No explosion
—40	Constant load	10 Ω	100 - 600 h	No explosion
—40	Constant load	5 Ω	100 - 600 h	No explosion

(i) cells operate safely during normal discharge under constant current and constant load operating conditions;

(ii) no safety problems were observed upon warm-up of the cell subjected to prolonged periods of drain of 5 and 10 Ω at —40 °C;

(iii) cells subjected to prolonged reversal became potentially hazardous, and may vent/rupture violently upon warm-up. This safety problem appears to be intrinsic to the chemistry of Li–$SOCl_2$ cells.

Causes

The observed hazardous behavior of the cells at low temperature can be explained in two possible ways. The first theory is based on the accumulation of lithium during reversal at low temperature, followed by a rapid reaction during warm-up. The second theory assumes the formation of internal short circuits.

The accumulation of lithium at low temperature is explained by relative rates of lithium formation and depletion. Our earlier studies [4] on this subject have revealed that finely-divided lithium deposits at the carbon cathode during reversal of the cells at constant current and −40 °C. This lithium was found to be extremely reactive and pyrophoric in nature. The morphology of the lithium deposits appeared to be dendritic. The finely-divided lithium was found to react with the electrolyte at room temperature [4]. As this reaction is exothermic in nature, it can lead to cell thermal runaway if large quantities of material are involved. The rate of lithium/electrolyte reaction at −40 °C, even though quantitatively unknown, is probably much lower than that at room temperature. The amount of heat produced upon warm-up of a cell depends on the net amount of lithium present at the carbon cathode prior to warm-up. During reversal at −40 °C the rate of deposition of lithium may exceed the rate of lithium corrosion, resulting in the accumulation of lithium at the carbon cathode. Hence, the cells subjected to prolonged reversal at −40 °C may become potentially hazardous upon warm-up.

Thermal analysis was performed to investigate the safety issues during warm-up of the cells subjected to reversal [5]. Some of the parameters considered in the analysis are cell size and shape, ambient temperature and heat transfer environment. Conductive heat transfer was not considered. A summary of the results is given in Fig. 7, where two safety regions are indicated: the low hazard region and the high hazard region. All results are applicable to the constant current reversal of cells at −40 °C. They indicate that cells subjected to reversal at −40 °C for long periods at low reversal current (10 mA) may not exhibit safety problems upon warm-up. Cells may become potentially hazardous if they are subjected to high reversal current (300 mA) at −40 °C for 20 h or more. The experimental observations are in agreement with this prediction.

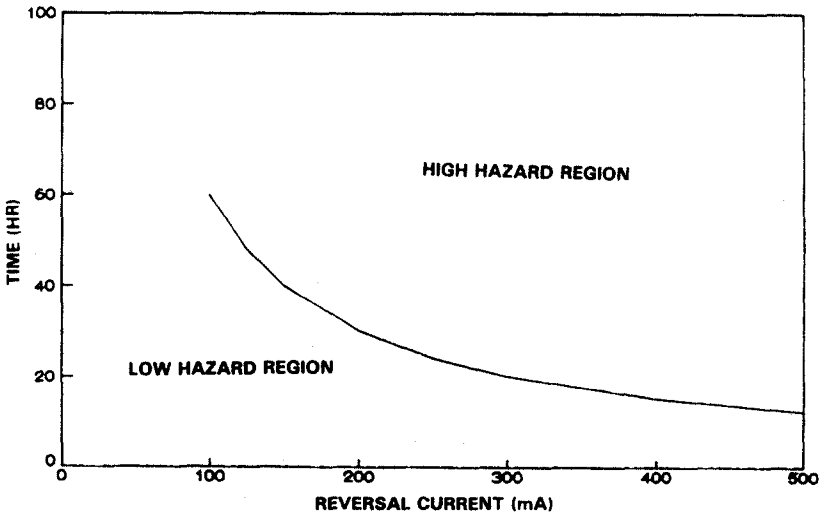

Fig. 7. Low temperature safety envelope.

In the case of cells on continuous drain at constant low load (5 and 10 Ω) for prolonged periods (after normal discharge to 1.0 V), accumulation of lithium may not be taking place at the carbon electrode. In view of this, cells subjected to prolonged periods of drain on constant load may not be hazardous upon warm-up.

Another possible explanation for the unsafe behavior of cells subjected to prolonged reversal is formation of internal short-circuits. The dendritic lithium being formed at the carbon cathode during reversal at −40 °C may ultimately lead to the formation of internal short circuits. Upon warm-up such a cell can then exhibit hazardous behavior from the rapid heat generation by the shorting currents.

The first theory is clearly in agreement with all the experimental evidence, and the results of *post mortem* analysis of the experimental cells [4]. Although the short circuit theory cannot be ruled out at present, it cannot account for all the observed facts. It is possible that each of these mechanisms ('Lithium Accumulation/Reaction' and 'Development of Short Circuits') may occur simultaneously and be responsible for the unsafe behavior. Thermal measurements on the cells are planned to gain a better understanding of this subject.

Conclusions

$Li-SOCl_2$ cells of various designs were evaluated for their performance and safety at −40 °C under constant current and constant load operating conditions. Some of the important findings of the study are:

(i) Cells exhibited low operating voltage, poor voltage regulation, and low capacity at −40 °C. The performance of the cells was found to be critically dependent on the cell design.

(ii) Cells of design Y containing the proprietary catalyst showed considerable voltage delay and poor shelf life characteristics, and failed to deliver any meaningful capacity at −40 °C.

(iii) No hazardous behavior was observed during discharge under constant current and constant load operating conditions to 2.0 V cutoff.

(iv) Cells subjected to prolonged periods of continuous drain at constant-load, did not vent/rupture upon warm-up.

(v) Cells subjected to prolonged reversal ($>100\%$) at −40 °C were found to become potentially hazardous. Two mechanisms were proposed ('Lithium Accumulation/Reaction' and 'Development of Short Circuits') to explain this unsafe behavior. Experimental observations so far favor the 'Lithium Accumulation/Reaction' theory.

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