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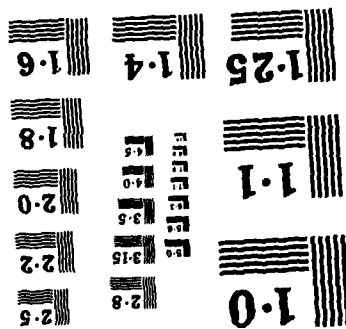
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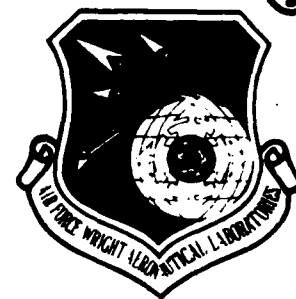
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LITHIUM-THIONYL CHLORIDE CELL SYSTEM SAFETY HAZARD ANALYSIS

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MARCH 1985

FINAL REPORT FOR PERIOD DECEMBER 1981 - DECEMBER 1984

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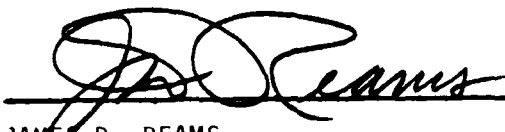
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--This system safety analysis for the lithium thionyl chloride cell is a critical review of the technical literature pertaining to cell safety and draws conclusions and makes recommendations based on this data. The thermodynamics and kinetics of the electrochemical reactions occurring during discharge are discussed with particular attention given to unstable SOCl_2 reduction intermediates. Potentially hazardous reactions between the various cell components and discharge products or impurities that could occur during electrical or thermal abuse are described and the most hazardous conditions and reactions identified. Design factors influencing the safety of Li/SOCl_2 cells, shipping and disposal methods and the toxicity of Li/SOCl_2 battery components are additional safety issues that are also addressed. It was concluded that long lived SOCl_2 reduction intermediates are not formed and that properly designed low rate Li/SOCl_2 cells with thick cathodes have a				
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negligible safety hazard under even the most severe abuse conditions such as short circuit or crushing. However, high rate Li/SOCl_2 cells with thin electrodes, capable of power densities over approximately 45 watts/liter, can undergo thermal runaway and explode if subjected to electrical abuse such as short circuits.

Ten specific recommendations are made for future research to improve the safety of Li/SOCl_2 cells. In particular, the chemical reactions occurring in electrolyte limited cells and the shock sensitivity of overdischarged carbon limited cells merit further investigation. New technology is required to eliminate the thermal runaway hazard in high rate cells and several promising approaches are identified such as microencapsulated electrode poisons and thermally sensitive separators.

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1. INTRODUCTION

The following Systems Safety Hazard Analysis Report was prepared as a separate document from the final and interim reports as specified in the contract. This report is limited to primary cells and only a few comments are made pertaining to primary batteries and reserve lithium-thionyl chloride cells and batteries.

The objective of this report is to summarize and critically assess current published information pertaining to the safety hazards of the lithium-thionyl chloride cell and to recommend preferred designs and procedures. In addition, critical gaps in current knowledge about the system and areas that should be given priority in further research will be identified.

The technical literature dealing with the lithium-thionyl chloride cell is vast* thus achieving the above objectives within a restricted time frame means that certain compromises have to be made. Thus in many cases only references will be given dealing with a particular subject and it will not be possible to summarize and analyze the results of the various investigators.

It is intended that this safety analysis will be expanded and revised at a later date so that a second edition can be prepared within a few years. The rapid pace of research and development dealing with the safety of lithium-thionyl chloride cells will certainly make such a revision necessary before too long.

There are really two types of safety situations with Li/SOCl_2 cells. Those possible in low rate cells with thick cathodes and good heat transfer characteristics and those in high rate cells that have a thermal management problem. Low rate cells have acceptable safety characteristics under a range of abuse conditions and are suitable for a wide range of military applications and some civilian applications. High rate cells larger than about half C size, can

* For example, a recent review (1) lists 162 references.

dergo thermal runaway and violent rupture when short circuited or subjected other abuse conditions such as overdischarge or crushing. Thus high rate cells are presently suitable for only a limited number of applications and all require substantial development until they can match the safety characteristics of low rate Li/SOCl₂ cells.

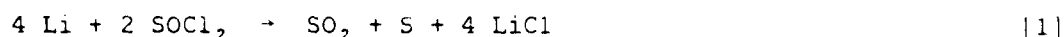
Safety issues with low rate cells will be given priority in this report because such cells are already in wide use and possible hazardous chemical reactions should be identified for the benefit of applications engineers and to encourage further design improvements. The most hazardous conditions encountered with high rate cells will also be given special attention. Such conditions include short circuit, overdischarge of carbon limited cells, and overdischarge of electrolyte and lithium limited cells.

2. CHEMICAL REACTIONS OCCURRING DURING LOW RATE DISCHARGE OF LITHIUM-THIONYL CHLORIDE CELLS

2.1 THE MAJOR CELL REACTIONS

2.1.1 The Stoichiometry of the Discharge Reaction

Experimental investigations carried out by a number of organizations (2-12) indicate that the overall cell reaction for the low rate discharge of lithium thionyl chloride cells with porous carbon cathodes at room temperature is:



Cogley and co-workers (2,3) analyzed dried cathodes for LiCl and entire cells for sulfur and found close to one mole of LiCl per equivalent of charge and close to one mole of sulfur per four equivalents of charge as predicted by Equation [1]. However, Schlaikjer and co-workers (7) found much less SO₂ in discharged 2000 Ahr cells than predicted by Equation [1]. Attia and co-workers (9) using an electrolyte flooded infrared flow cell more recently found 0.17 moles of SO₂/equivalent of charge passed compared to the 0.25 moles SO₂/equivalent expected. During the present contract (11) Li/SOCl₂ cells with the same high carbon-to-electrolyte volume ratios as commercial cells were multiply extracted with pure SOCl₂ at -20°C and the combined extracts analyzed for SO₂. The extraction procedure was used to collect all the SO₂ generated including the SO₂ adsorbed by the carbon cathode that was neglected by earlier studies. Quantitative FT-IR analysis of the combined extracts showed 0.22 moles of SO₂/equivalent of charge for cells discharged at 5 mA/cm² at 23°C in which 18% of the SOCl₂ was reduced.

It is thought (10,11) that much of the "missing" SO₂ is not detected by the chemical analysis because it reacts with the SOCl₂ electrolyte during the discharge to form a strongly solvated species with the Li cation in solution, Li(SO₂,SOCl₂)⁺. Part of the "missing" SO₂ could never have been formed or

3. HAZARDOUS CHEMICAL REACTIONS OCCURRING DURING LOW RATE AND SHORT CIRCUIT DISCHARGE OF LITHIUM-THIONYL CHLORIDE CELLS

3.1 THERMODYNAMICS OF PARASITIC AND SIDE REACTIONS

Numerous potentially hazardous reactions occurring in the Li/SOCl_2 cell have been investigated (13,14,24,26,29) and various conflicting opinions have been proposed as to which reaction or reactions are the most hazardous during abuse conditions. In principle, if one or two reactions could be identified as the most hazardous by a large margin, then the cell chemistry or design could be modified and the hazard eliminated. However, if a large number of reactions are found to be about equally hazardous then it may be impossible in practice to modify the cell to reduce the hazard. If this is found to be the case, a different approach may be necessary to prevent thermal runaway such as electrolyte additives, vents or fuses as discussed in Section 5.

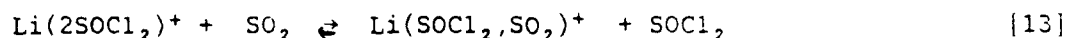
Thus, the major issue to be addressed involves the generation and evaluation of thermodynamic and kinetic data so that the hazards of the various reactions possible in the Li/SOCl_2 cell can be ranked quantitatively. Since the reaction kinetics depend on the concentration of the reactants, the presence of chemically active surfaces that may act as reaction sites, the presence of passivating films and the geometry of the cell which all complicate estimating concentrations. Therefore, it is very difficult to carry out experiments to obtain realistic kinetic data to compare the various potentially hazardous reactions. Cell geometry effects not only heat and mass transfer but also solubility, catalysis and absorption to name a few of the more important effects on the kinetics of hazardous side reactions.

Information about thermodynamic properties such as the free energy, enthalpy, solubilities and melting points can be obtained for many reactions from standard reference works and can be used to select those side reactions that may be potentially the most hazardous. Since kinetic studies of the reaction rate under practical conditions are much more difficult than thermodynamic calcula-

questionable since numerous infrared studies (1,7,9,11) have concluded that I_2 is not a product of the electrochemical reduction of $SOCl_2$. Thus further work is required to determine the exact composition of the intermediates, their lifetimes and their concentrations during the course of cell discharge at least at one set of temperature and rate conditions. A full characterization of the electrode and solution kinetics of the $SOCl_2$ reduction reaction at porous carbon electrode may take many years because of the rapid rate of reaction and the difficult analytical chemistry.

To define the intrinsic safety of the $Li/SOCl_2$ cell it may only be necessary to determine the overall cell reaction so that 95-99 Wt% of all the products can be accounted for within 10 to 15 minutes after the cell discharge has been terminated. This would be a more realistic task that could be completed within a year or less that should be given priority. The goals of this task have been largely achieved during the present contract (10,11) although considerable work remains to characterize the SO_2 solvation reaction with $SOCl_2$ electrolyte [13] under a wide range of temperature and concentration conditions.

tion of SO_2 . The decline in the SO_2 peak during approximately 24 hours storage was found by voltammetry, quantitative infrared and Raman spectroscopy to be due to a reaction between SO_2 and the SOCl_2 electrolyte. The exact nature of the products of this reaction are not yet known exactly but the Raman results suggest a strong solvation reaction



Williams and co-workers (12) have recently postulated the following mechanism for the reduction of SOCl_2 in the Li/SOCl_2 cell



They estimate that the lifetime of OClS and the triplet state dimers in equilibrium with it is ≈ 6 minutes at -46°C , and < 10 seconds at 24°C .

As discussed earlier in Section 2.1.2 short lived highly reactive intermediates such as OClS are of little significance relative to Li/SOCl_2 cell safety because they do not exist long enough so that a sufficient amount can possibly accumulate to constitute a safety hazard. Thus even at -46°C the intermediates detected by ESR do not appear to merit much attention as a safety hazard.

The work by Williams and co-workers (12) at JPL is currently still in progress and the mechanism proposed in Equations [14] to [18] is largely speculative since the composition of the intermediates has been deduced from ESR data. Reaction [18] involving the generation of SCl_2 as a discharge product is very

It was claimed that the delayed pressure rise due to the "missing" SO_2 , the excess heat evolution in discharged cells (19), the lower cell capacity at low temperature (30) and the voltammetry results all were consistent with the above reaction scheme.

A "hot spot" theory was proposed by Dey (Pgs. 195, 197 Ref. 26) to explain how the "spontaneous" explosion of discharged Li/SOCl_2 cells could be caused by exothermic reactions such as the decomposition of the SO intermediate (i.e., Equation 12) which creates a local "hot spot" inside the cell. This "hot spot" could then serve as a trigger to start reactions between other active cell components such as Li , S , SOCl_2 , Teflon and glass which produce heat to feed the thermal runaway. It was suggested that local hot spots could be involved in cell explosions during low current reversals. It was reported (Pg. 194, Ref. 26) that the decomposition of SO would generate 36.8 KCAL/mole of SO decomposed.

Since 1983 with the completion of new voltammetry (10,11), infrared (9,10,11,12) and ESR (12) investigations of the Li/SOCl_2 cell reaction, it has become clear that long lived intermediates (> 0.1 hour) are not formed during the reduction of SOCl_2 . In particular, the ESR measurements have indicated the presence of very short lived intermediates such as OClS and $(\text{OClS})_2$ and have more or less ruled out the presence of the SO intermediate. Furthermore, although SO has been observed in the vapor phase in the presence of a dilute gas, when condensation was attempted, a solid polymer resulted which decomposed to S and SO_2 when heated. Infrared absorption bands for " SO " or " S_2O_2 " were reported by Jones (31) for vapor phase samples at 1165 cm^{-1} and 679 cm^{-1} . However, Schlaikjer and co-workers (7) reported that when spectra were taken of used electrolyte and used electrolyte diluted with SOCl_2 immediately after discharge, no absorption was observed at the above " SO " frequencies. They also noted that no solutions of " SO " have ever been reported.

The voltammetry peak initially assigned (28) to the complexed intermediate $\text{SO}\cdot\text{SOCl}_2$ was found during the present contract (10,11) to be due to the reduc-

spontaneous explosions of partially discharged Li/SOCl₂ cells on casual storage was initiated by reactions involving such SOCl₂ reduction intermediates.

It was postulated by Bowden and Dey (28) that SOCl₂ undergoes two successive, one electron transfers to generate SO



Since SO is highly unstable it was proposed that during the early stages of discharge it was complexed by SOCl₂



It was believed that the species SO•SOCl₂ was detected in large amounts by linear sweep voltammetry in DMF supporting electrolyte (28) and that it was stable for many hours. On standing or warming of the solution it was thought that the complex disassociates to reform SO and SOCl₂



Dimerization and polymerization of the SO were suggested as part of the mechanism and were thought to occur during the latter part of the discharge when the concentration of SOCl₂ had decreased



Finally, it was postulated that these dimers and polymers may decompose on standing or heating to form S and SO₂



Frank (20) has measured the rate of decomposition of $1M LiAlCl_4/SOCl_2$ by storing sealed ampules of electrolyte at 40, 80, and 100°C and determining the SO_2 concentrations by IR after up to 100 days storage. The rate of $SOCl_2$ electrolyte decomposition was then calculated using the results of the SO_2 analysis, the stoichiometry of reaction [4] and the known storage time. The calculations showed that 12% of the $SOCl_2$ will decompose during ten years storage at 15°C.

More recently Babai and co-workers (25) have investigated the stability of $Li/SOCl_2$ cells discharged at temperatures up to 200°C. They found that $Li/SOCl_2$ cells could be discharged continuously for over six days at 200°C and for six months at 150°C while still yielding most of the available capacity. From open circuit measurements and infrared analysis of the electrolyte from cells stored at 150°C, they concluded that the presence of porous carbon in the cell probably caused the decomposition reaction to start at temperatures as low as 70-90°C. However, since the thermal decomposition reaction of thionyl chloride is reversible they believe that only small amounts of the thionyl chloride was decomposed because of the small capacity losses observed after six months of continuous discharge at 150°C.

The small rate of $SOCl_2$ decomposition observed by Frank (20) compared to the negligible rates predicted by thermodynamics suggests that the thionyl chloride he used may have been contaminated by traces of water and the SO_2 measured was simply a hydrolysis product. If the demand for $Li/SOCl_2$ cells for high temperature (> 150°C) long discharge applications continues to grow, then additional work may be required to determine the thermal stability of $SOCl_2$ and $LiAlCl_4/SOCl_2$ electrolyte with and without carbon cathode material present.

2.3 REACTION KINETICS

Until quite recently there was widespread concern (1,6,7,26-29) that the reduction of $SOCl_2$ during discharge produced substantial quantities of the long lived (28) unstable intermediate SO . It was thought (28,29) that the reported

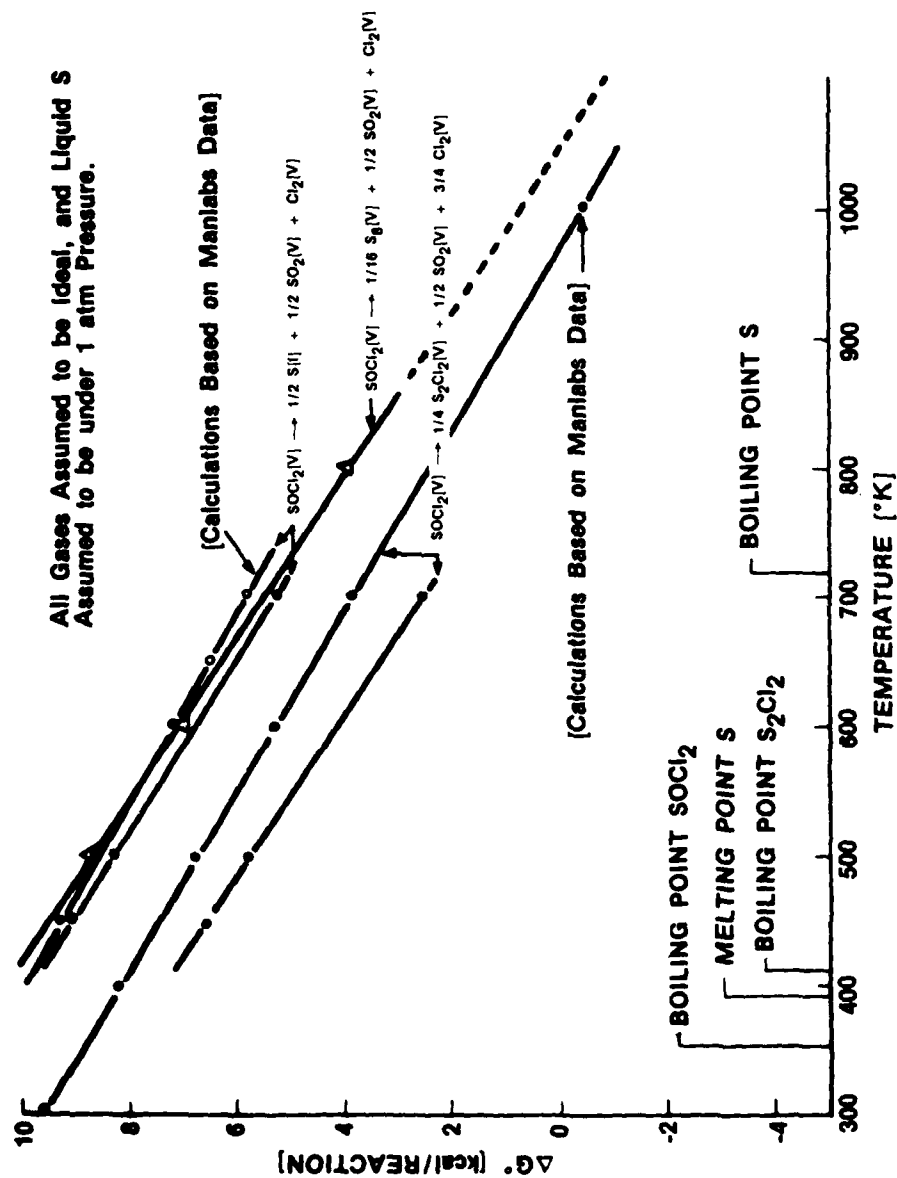


Figure 1: SOCl_2 Thermal Decomposition Thermodynamics

were plotted and are shown in Figure 1. Calculations for both reactions show that the decomposition reaction leading to the production of S_2Cl_2 is more favorable than that leading to the production of S. However, even that leading to S_2Cl_2 production does not proceed spontaneously at temperatures below about $580^{\circ}C$ (according to the data obtained from the available published literature) or about $690^{\circ}C$ (according to the data obtained from the MANLABS Data Bank). Further, even above these temperatures, the decomposition reaction is endothermic. It was concluded (24) that thermal decomposition of $SOCl_2$ to produce gaseous products does not present a hazard potential at any temperature of operation or storage for a $Li/SOCl_2$ cell.

For the Li/SOCl₂ cell, taking ΔS as -5.26 calories/degree-equivalent then the rate of heat production at low current densities close to reversible conditions would be 2.30 Kcal/equivalent at 25°C.

For cell discharge at practical current densities, the rate of heat generation is the sum of the heat generated by Equation [2] above, the heat generated by polarization and the heat generated by other reactions such as Li corrosion. The rate at which heat is released due to cell polarization is given by the difference between the open circuit potential E° and the potential under load, E

$$\frac{dj}{dt} = -4.184 \int (E^\circ - E) \frac{de}{dt} \quad [3]$$

By measuring the heat output of cells discharged at high current densities, then calculating the excess heat evolved above that expected on the basis of Equations [2] and [3], the heat generated by side reactions such as Li anode corrosion and intermediate decomposition can be calculated. Values for the excess heat evolution due to side reactions have been reported by several investigators (7,16,17,19) and the nature of the side reactions has been the subject of considerable discussion and debate.

The thermal decomposition of SOCl₂ has been reported (21,22) to occur by way of two alternative reactions



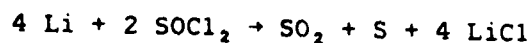
The decomposition has been reported to begin at temperatures as low as 150°C and to be virtually complete by 440°C (23°C). The thermodynamics of these two proposed reactions were examined during an earlier project at GTE Laboratories (24). The free energy changes accompanying these reactions were then calculated from readily available published thermodynamic data and by the use of the MANLABS-NPL Materials Data Bank. The resulting free energies of reaction

Table 1.

Thermodynamic Values for the Discharge Reaction of the Lithium Thionyl
Chloride Cell at 25°C*

	<u>Calculated Value +</u>	<u>Electrochemical</u>	<u>Calorimetric</u>
Free Energy - (Kcal/eq)	-84.4	-84.3	-83.9
Open Circuit Potential (V)	3.661	3.655	3.65
Enthalpy (Kcal/eq)	-86.1	-85.9	-87.4
Enthalpy (Cal/°K eq)	- 5.62	- 5.26	- 7.74
Reference	(18)	(16)	(16)

* Based on the Cell Reaction

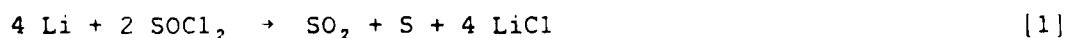


+ The calculated values were calculated by Miles (18) from standard thermochemical data from the National Bureau of Standards Circular 500 (1952) and W. M. Latimer's "Oxidation Potentials", 2nd Ed. (1952).

tributed to side reactions involving the corrosion of the Li anode to form LiCl during discharge and the decomposition of unstable intermediates (19). Some uncertainty and controversy exists concerning the existence of long lived intermediates and the heat produced during the decomposition of such intermediates.

Doubts have been raised concerning the stability of $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte during long term storage (20), that have proved to be largely unfounded. The thermodynamics of the SOCl_2 and $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte decomposition reactions will be discussed later in this section.

The free energies, entropies, enthalpies and open circuit potentials calculated from standard thermochemical data are listed in Table 1 based on the cell reaction



These calculated values are compared in Table 1 with the values obtained experimentally from electrochemical and calorimetric measurements with Li/ SOCl_2 cells. There has been considerable disagreement among various investigators in the value of the entropy with values ranging from +23.7 to -30.41 cal K^{-1} eq $^{-1}$. A very thorough discussion of the thermodynamic data obtained by six investigators for the Li/ SOCl_2 cell has been published by Godshall and Driscoll (16) and the values in Table 1 appear to be among the more reliable values.

In an electrochemical cell, such as the Li/ SOCl_2 cell, the rate at which heat is released in watts (W); i.e., joules per second (J s^{-1}) at vanishing low current densities close to reversible conditions is given by:

$$\frac{dj}{dt} = -4.184 T \Delta S \frac{de}{dt} \quad [2]$$

where T is the absolute temperature, ΔS is the entropy change of the discharge reaction in calories/degree-equivalent and de/dt is the discharge rate in terms of equivalent/second.

At the present time about 90% of the SO_2 produced at 25°C during the reduction of SOCl_2 , as predicted by the cell reaction of Equation [1] can be accounted for. Thus, it is clear that we are beginning to approach the limit of diminishing returns where greater and greater effort is required to achieve very small benefits.

Changing the subject to the relevance to safety of research on unstable SOCl_2 reduction intermediates, it is evident that it makes little sense to investigate reduction intermediates that are highly reactive with half lives less than a few minutes in solution. Such intermediates may be of interest in terms of improving high rate performance and selecting catalysts but they have little significance in terms of cell safety. Highly reactive short lived intermediates do not exist long enough so that a sufficient amount of the intermediate can possibly accumulate to constitute a safety hazard. If the intermediate could be concentrated into a single solid mass it is conceivable that perhaps a few tenths of a gram could decompose rapidly and set off a thermal runaway reaction. However, intermediates are without exception either soluble or adsorbed on surfaces and therefore widely dispersed at low concentrations.

2.2 THERMODYNAMICS

There have been a number of excellent investigations (1,7,16-18) of the thermodynamic properties of the cell reaction given by Equation [1] that occurs during the discharge of Li/SOCl_2 cells. The results of these studies are of fundamental importance in understanding the safety hazards of the cell. First of all, the heat generated by the discharge reaction which is given by the entropy term $T\Delta S$, is useful in the design of both active and reserve-activated batteries to achieve proper heat transfer and avoid thermal runaway under high load conditions. Second, discrepancies between the free energies, open circuit potentials, and entropy values obtained from thermodynamic tables (16,18) and those obtained experimentally from electrochemical and calorimetric measurements with Li/SOCl_2 cells have provided a sensitive method of detecting discrepancies due to side reactions. The excess heat produced has been at-

2.1.2 The Relevance of the Discharge Reaction Products to Cell Safety

A knowledge of the chemical composition and concentrations of the discharge products is invaluable (i) in determining the intrinsic safety of the Li/SOCl_2 system under various conditions and (ii) in developing new methods to improve the safety of the cell. However, the cell chemistry is complex, research is both time consuming and expensive and priorities must be established to identify those research topics that will yield the greatest benefit.

Information about the chemical composition and concentration of the discharge products is valuable because one can then separately study the thermodynamics and kinetics of each of the possible side reactions of each product with the major cell components and the other products. Using standard thermodynamic tables of free energies one can then decide which side reactions are most likely, the subsequent products and the heat produced by these reactions. Usually the reactions of the product with lithium, SOCl_2 , SOCl_2 electrolyte, carbon and the oxidation products produced during charging and lithium limited overdischarge are of most concern.

For those cases where thermodynamic values for the free energies for the reactions are not available then experimental work has been undertaken to characterize the thermodynamic properties of the various combinations of products and cell components. Determination of the free energies and enthalpies by standard calorimetric or electrochemical methods is quite lengthy, thus some fairly rapid technique such as differential thermal analysis (DTA) is generally used to identify and characterize the exothermic reactions.

If all the products of all the side reactions were investigated, a tremendous research effort would be required. However the importance of knowing the thermodynamic and kinetic properties of a particular product depend primarily on the amount present and to a lesser extent on its chemical reactivity. Thus if we can account for 95% to 99% of all the reduction products of SOCl_2 , then we can probably neglect the unknown 5% to 1% of the products. The unknown products may actually exist or may just be an artifact of the accumulated errors of the various techniques used for chemical analysis.

could be delayed due to generation of short lived intermediates such as OClS that undergo side reactions (12). The small discrepancies between the SO_2 predicted by Equation [1] and the concentrations actually found in discharged cells and the whole subject of intermediates, side reactions and the reactions of SO_2 with SOCl_2 electrolytes is currently an area of very active research in a number of laboratories (11,12). These matters and their relevance to safety will be discussed later in this section.

It is possible that the overall cell reaction for the discharge of the Li/SOCl_2 cell could change depending on the temperature, depth of discharge, rate of discharge, the acidity of the electrolyte, the nature of the cathode substrate and the presence of catalysts. Bailey and Kohut (8) determined the equivalent weight and elemental composition of the non-volatile components of cells discharged at -50 , -20 , $+25$, and $+71^\circ\text{C}$ at four depths of discharge and three rates. They found that under all of the conditions investigated the overall discharge reaction follows Equation [1]. They vacuum distilled the volatile products from discharged cells then performed elemental analysis for sulphur and chlorine. They note that the use of vacuum distillation may result in the decomposition of metastable intermediates such as lower sulfur oxides to produce the S and SO_2 found.

Bailey and Kohut (8) note that further reduction of the SO_2 produced does not occur. Debye-Scherrer x-ray diffraction analysis of carbon cathodes overdischarged over a wide range of conditions at GTE (13,14) also showed no sign of SO_2 reduction to $\text{Li}_2\text{S}_2\text{O}_4$ (lithium dithionite). The possible presence of $\text{Li}_2\text{S}_2\text{O}_4$ was initially of some concern because it could decompose and contribute to thermal runaway (15) under certain conditions.

Prototype cells were discharged at 0°C , 1.5 mA/cm^2 then extracted during the present contract (11) using the techniques described earlier and only 31.5% of the SO_2 theoretically expected from Equation [1] was found by IR analysis. Since the SO_2 solvation reaction with the SOCl_2 electrolyte is much slower at 0°C , it would appear that substantial adsorption of the SO_2 discharge product on the carbon electrode occurs at low temperature.

tions (or experiments), the use of thermodynamic data to rank the reactions and eliminate those that are not the most exothermic, allows the maximum effort to be focused on kinetic studies of the few most hazardous side reactions.

The free energies and enthalpies of some of the more likely side reactions expected in Li/SOCl₂ cells are listed in Table 2. The variation in the free energy with increasing temperature from 300 to 700°K for the reactions of Li with SO₂, S and SOCl₂ are shown in Figure 2 obtained from Ref. 24. Figure 3 shows the change in the free energy as a function of temperature for the reaction of S with SOCl₂. The list of reactions given in Table 2 is not complete because for many reactions the products are not known or the free energies are not readily available. For example, it has been reported (32) that Li reacts explosively with carbon black to form Li-C intercalation compounds. Table 2 would also have to be revised if it is found that the reduction of SOCl₂ during discharge generates substantial quantities of reactive long lived intermediates.

The reactions of Li with S, SO₂ and SOCl₂ are extremely energetic and should occur spontaneously with the release of large amounts of thermal energy. However, they do not occur for kinetic reasons below the melting point of lithium because the Li electrode surface is passivated with a protective layer of LiCl. Should the Li melt (m.p. 180.5°C) due to overheating caused by thermal or electrical abuse then the LiCl film would no longer be passivating and reactions [20] - [23] could occur leading to the sudden release of a large amount of thermal energy, overpressurization and explosion of the cell.

Below the melting point of lithium the reaction of SO₂ with Li by either Reaction [20] or more likely Reaction [24] is unlikely to be hazardous because the SO₂ is dissolved in the electrolyte and has to diffuse to the Li surface to react where it produces solid products. On the other hand sulfur can precipitate out as large crystals on the high surface area Li dendrites formed during carbon limited overdischarge which in principle could lead to Reaction [20] and a thermal runaway hazard should a Li dendrite short circuit occur. Thus,

Table 2.
Thermodynamic Values for Possible Side Reactions of the
Lithium-Thionyl Chloride Cell*

Reaction	Eq. No.	ΔH_{298}^0 (Kcal/m)	ΔF_{298}^0 (Kcal/m)	Ref.
$2 \text{SOCl}_2 + 3\text{S} \rightarrow 2\text{S}_2\text{Cl}_2 + \text{SO}_2$	19	-18.6 to -22.6	-120	24,26
$6 \text{Li} + 3\text{S} \rightarrow 3\text{Li}_2\text{S}$	20	-320	-	24
$6 \text{Li} + \text{SO}_2 \rightarrow \text{Li}_2\text{S} + 2\text{Li}_2\text{O}$	21	-321	-	24
$6 \text{Li} + \text{SOCl}_2 \rightarrow \text{Li}_2\text{O} + \text{Li}_2\text{S} + 2\text{LiCl}$	22	-391	-	24
$\text{Li}_2\text{S} + 2\text{SOCl}_2 \rightarrow \text{SO}_2 + 3\text{S} + 4\text{LiCl}$	23	-147.6	-	24
$4 \text{SOCl}_2 \rightarrow \text{S}_2\text{Cl}_2 + 2\text{SO}_2 + 3\text{Cl}_2$	4	-	10	24
$2 \text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$	24	- 69.5		33
$\text{S}_2\text{Cl}_2 + 2 \text{Li} \rightarrow 1/4\text{S}_8 + 2 \text{LiCl}$	25	-	-174.18	12
$\text{SO}_2 + \text{Li}(2\text{SOCl}_2)^+ \rightleftharpoons \text{Li}(\text{SOCl}_2, \text{SO}_2)^+ + \text{SOCl}_2$	13	-	-11 ?	11

* The free energies and enthalpies are given as Kcal/mole of product.

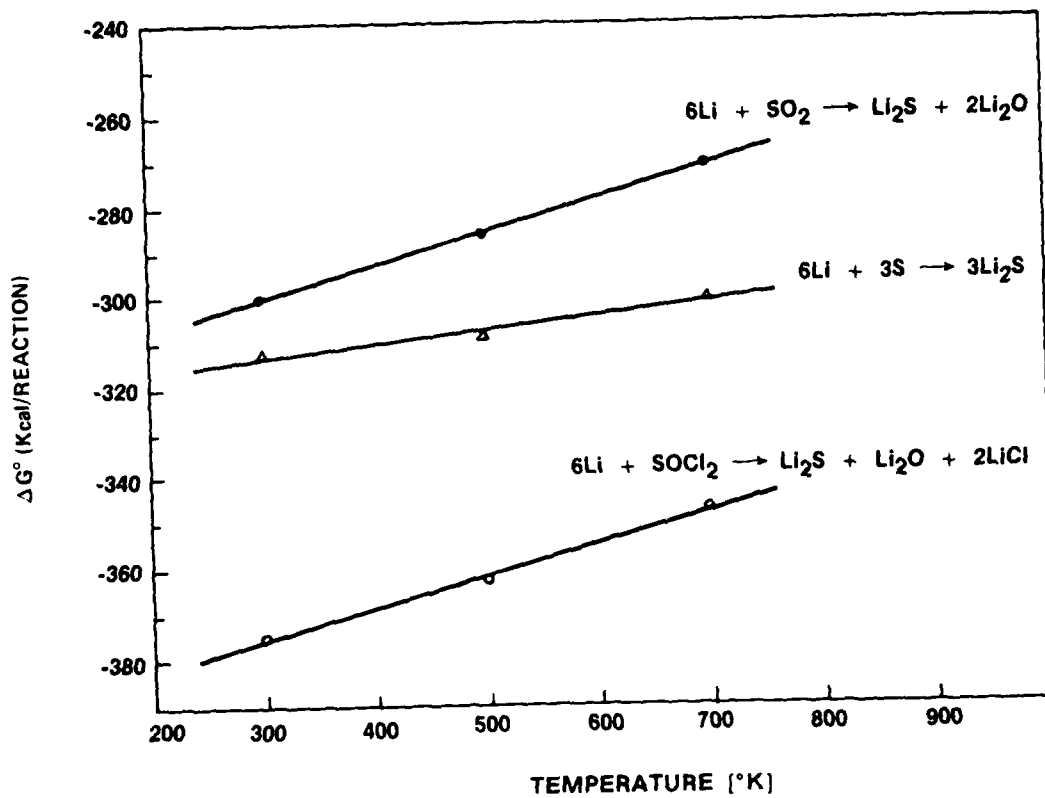


Figure 2: Free Energy Changes for Reactions of Li with SO_2 , S, and SOCl_2

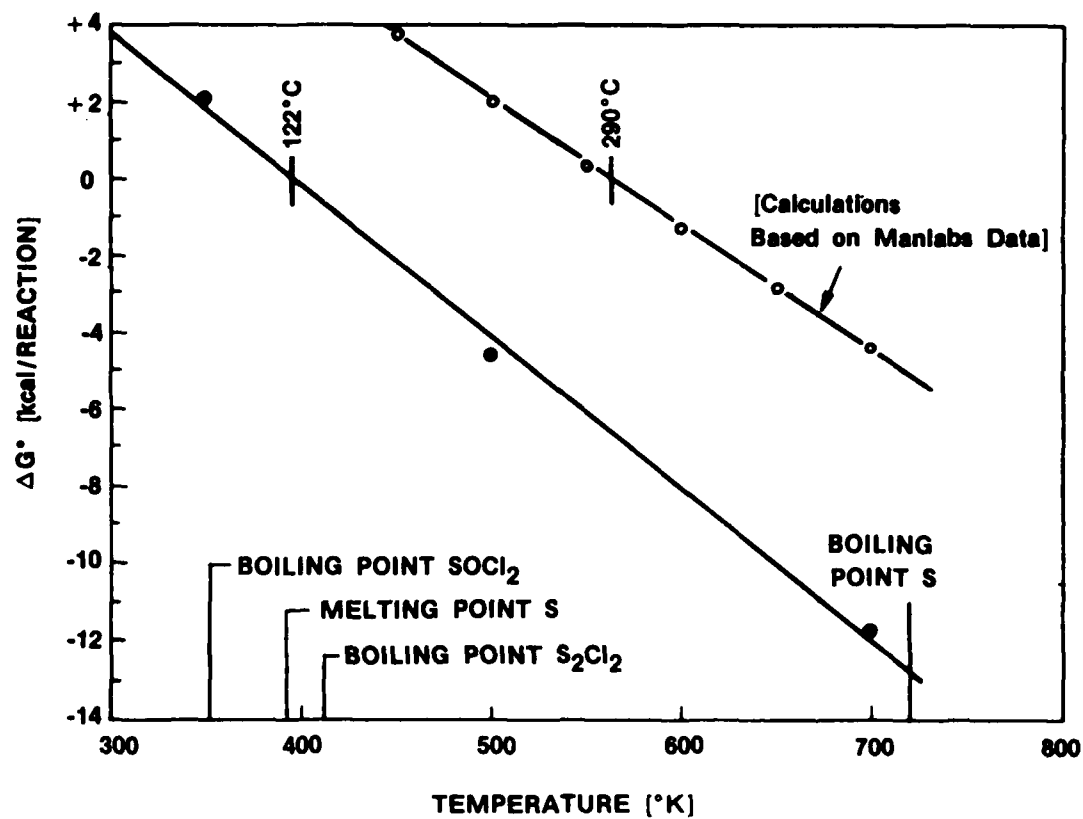


Figure 3: Free Energy Change for the Reaction $2 \text{SOCl}_2 + 3 \text{S} \rightarrow 2 \text{S}_2\text{Cl}_2 + \text{SO}_2$

there are at least three hazardous reactions that could occur in Li/SOCl_2 cells at room temperature on the basis of thermodynamic data and the inertness of the cell is entirely due to a kinetic block caused by a passivating self-healing film.

3.2 KINETICS OF PARASITIC AND SIDE REACTIONS

3.2.1 Summary of DTA, DSC and Other Kinetic Results

The reaction kinetics of the various combinations of cell components and discharge products present in Li/SOCl_2 cells have been investigated using differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The DTA exothermic transition temperatures found by Dey (29) and those found by Dalleck, James and Kilroy (34) for a majority of the components studied are listed in Table 3.

During a DTA measurement, the temperature difference between a sample and a reference material is recorded as a function of time as the sample and a reference are heated at the same rate (36). A DSC measurement involves recording the energy input into a substance and a reference material as a function of time. DSC normally consists of measurement of the power input required to keep the sample and the reference at the same temperature. Thus, the total DSC peak is associated with the enthalpy of transition (37).

The data in Table 3 reveals that Li and sulfur and $\text{Li} + \text{C} + \text{LiAlCl}_4/\text{SOCl}_2$ are the most easily initiated reactions between cell components with DSC exotherms at 121 and 54°C, respectively. There has been some disagreement among various workers whether Li_2S reacts with SOCl_2 (24,29,35). Work at GTE Laboratories is consistent with the DSC measurements (35) which indicate that Li_2S is essentially unreactive with SOCl_2 up to a 276°C cutoff and with 1.6M $\text{LiAlCl}_4/\text{SOCl}_2$ up to a 367°C cutoff.

Table 3 summarizes the DTA and DSC results only for some of the simpler combinations of cell components. It is recommended that the original publications (26,29,35) be consulted for a full description of the experimental techniques, the thermograms and an analysis of the results.

Table 3.

Summary of DTA and DTA Results for Li/SOCl₂ Cell Components

Reactants	Transition Temperatures (°C) ⁺		
	DTA Exothermic	DSC Exothermic	DSC Endothermic
1. SOCl ₂	-	214	212
2. LiAlCl ₄	-	-	143
3. Li + SOCl ₂	-	217, 231	176
4. Li + LiAlCl ₄	n/a	137	181
5. SOCl ₂ + C	n/a	-	-
6. Li + LiAlCl ₄ /SOCl ₂	-	-	177
7. S + LiAlCl ₄ /SOCl ₂	-	-	236
8. S + Li	150	121	185
9. Li ₂ S + LiAlCl ₄ /SOCl ₂	109, 118	-	-
10. Li + SOCl ₂ + C	n/a	-	169
11. Li + LiAlCl ₄ + C	n/a	137	179
12. Li + LiAlCl ₄ /SOCl ₂ + C	n/a	54, 326	-
13. Li + LiAlCl ₄ /SOCl ₂ + S	273	395	184
14. LiAlCl ₄ /SOCl ₂ + C + S	n/a	-	-
15. SOCl ₂ + S	-	n/a	n/a
16. Li + S + SOCl ₂	-	n/a	n/a
17. Li + S + LiAlCl ₄ /SOCl ₂	273	395	184
18. Li + Carbon Cathode	197	**	**
19. Li + Glass Separator	208	n/a	n/a

⁺ The differential scanning calorimetry (DSC) values are those of Dallek, James and Kilroy (34) and the differential thermal analysis values (DTA) are those of Dey (29).

* n/a indicates not available

** See References (32) and (35).

Differential thermal analysis measurements have been carried out (39; P. 174, Ref. 26) in which the differential temperature response between fresh and discharged spiral wound Li/SOCl₂ D size cells were measured. The technique was found to be a very effective method to identify and characterize the nature of the instabilities that are generated as a result of the discharge of Li/SOCl₂ cells. The DTA thermogram at 0.8°C/minute is shown in Figure 4 for a D cell completely discharged at 0.25A to a capacity of 12.7 Ahr compared to a fresh D cell as reported by Dey (26). A similar test at less than half the heating rate (i.e., 0.35°C/minute) for a D cell discharged 6 Ahr subjected to DTA then discharged further at 0.25A for an additional 7.1A hr showed exothermic peaks at 92° and 103°; and a third smaller one at 148°C. A repeat run showed no transitions. Rhombic and monoclinic sulfur melt at 112.8°C and 119.0°C, respectively, and the large exothermic transition seen in Figure 4 is most probably due to the reaction of sulfur crystals precipitated on the surface of the Li anode at the end of discharge. The solubility of sulfur in 1.8M LiAlCl₄/SOCl₂ is 1.16M at 23°C, therefore, it is likely that sulfur would precipitate from the electrolyte toward the end of discharge in cells with only a small excess of electrolyte because the SOCl₂ would be in large part consumed.

The cause of the exotherms at 92°C and 103°C observed during the second DTA for the cell subjected to a DTA half way through discharge as discussed above is difficult to account for at this time. The exotherms could be due to the incorporation of some impurity into the sulfur crystals leading to depression of the melting point of sulfur or reaction of some unknown product or intermediate of the discharge reaction with lithium.

The relative stability of the undischarged D size Li/SOCl₂ cells was demonstrated by the lack of exothermic transitions in the DTA thermogram of undischarged cells against an Al₂O₃ reference. This agrees with the DTA results for mixtures of components which show the absence of any exothermic interactions between the materials present in a fresh cell at temperatures below the melting point of lithium. Thus the instability of discharged Li/SOCl₂ cells seen in the DTA measurements is probably caused by some of the discharge products generated in the cell during discharge such as sulfur. Additional DTA studies

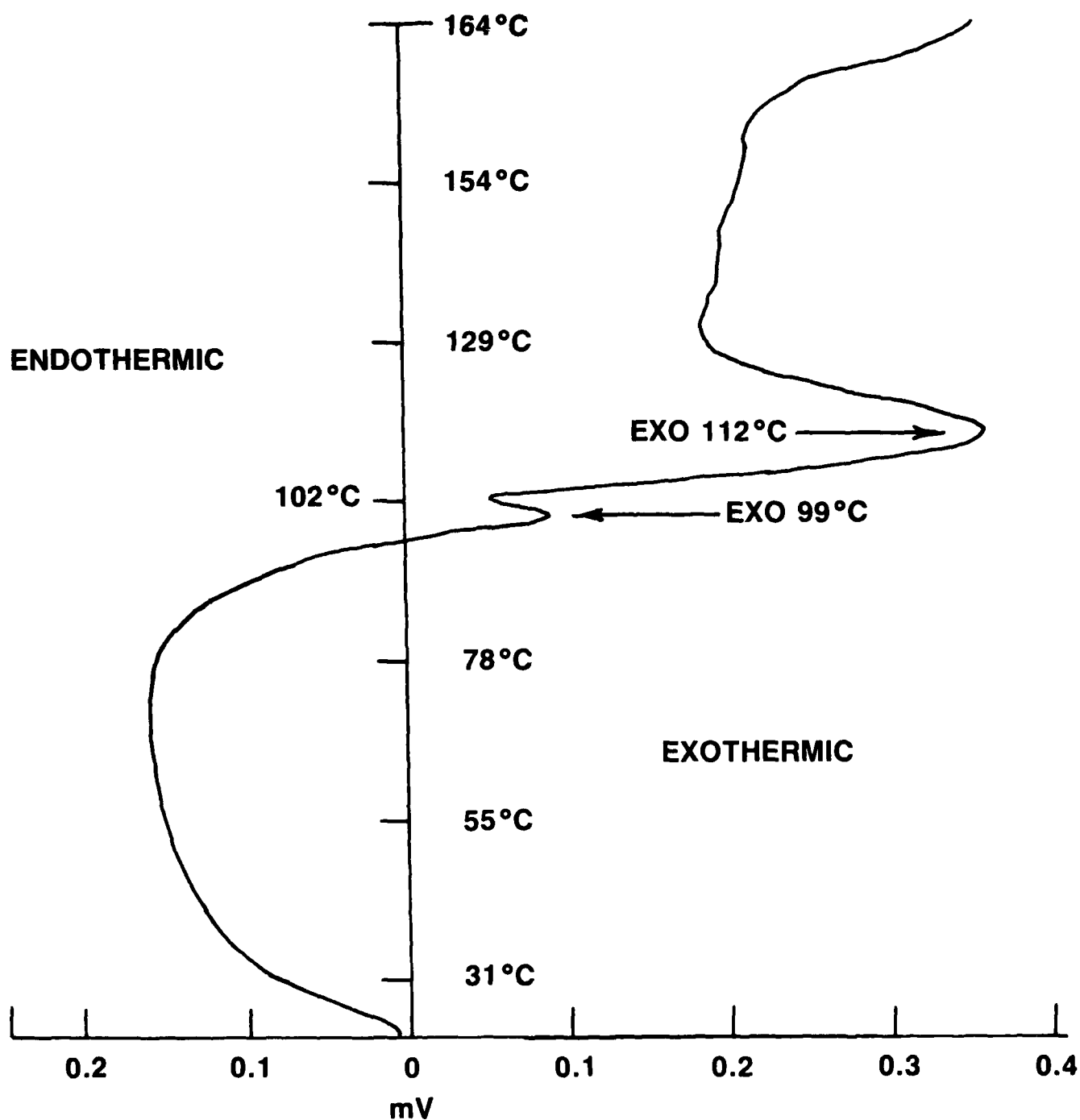


Figure 4. Thermogram from Differential Thermal Analysis of a Completely Discharged (12.7 Ahr) Spiral Wound D Cell Against a Fresh Cell Reported by Dey (26).

of prototype Li/SOCl₂ cells with systematic variations of the Li area, cathode and electrolyte over the complete range of discharge, overdischarge, rate and temperature conditions would clearly be of great value.

The hot spot theory of thermal runaway was investigated by Dey (cf. Pg. 197, Ref. 26) using spiral wound hermetically sealed D size cells fitted with internal heating wires and spark gaps. Six cells were tested having the heating wires located near the cathode side within the electrode spiral and in many of them the heating wire corroded and developed a discontinuity during the test. Cells were generally found to be very abuse resistant and were able to withstand internal temperatures up to 175°C at the heating wire. However, explosions were initiated in several cases. Having reviewed the available kinetic results for, both mixtures of cell components and prototype cells, the results for specific reactions between cell components will now be discussed in greater detail.

3.2.2 Reaction Kinetics of Molten Lithium with SOCl₂ Electrolyte

Spiral wound 1/2C size Li/SOCl₂ cells equipped with thermocouples have been short circuited at GTE Laboratories for several minutes and returned to open circuit several seconds before the cell was expected to explode. Disassembly of the cells after they had cooled showed that portions of the Li anode had melted and flowed to form a large puddle of lithium. Thus it appears that molten lithium can be stable in LiAlCl₄/SOCl₂ electrolyte in the cell environment for at least the several seconds required for the lithium to melt and flow. This finding is consistent with the DTA and DSC results for Li in LiAlCl₄/SOCl₂ listed in Table 3.

Further evidence for the short term stability of molten lithium in the cell environment comes from an extensive series of 53 experiments carried out at GTE Laboratories (24) to investigate arcing and other heating processes during electronic short circuits between Li and various substrates while immersed in SOCl₂ electrolyte. In order to determine the magnitude of the hazard poten-

tial of two aspects of short circuiting, arcing and contact resistance heating, a special apparatus was constructed in which short circuits of various configurations and power densities could be produced in a small reactor separated from the power source. In this way the full power of a Li/SOCl_2 battery (or other power source) could be safely passed through the controlled short circuit in the reactor, and any violent reactions produced could be reduced to a containable magnitude. The reactor consisted of two electrical contacts, one stationary and one movable by remote operation, in a small glass vessel. Most of the tests were meant to simulate a filament of nickel expanded mesh penetrating the separator and contacting the lithium. Other configurations less likely to occur were also tested such as a carbon-to-lithium short and contact between a nickel sheet (cathode frame) and a filament of lithium which could only occur during carbon limited reversal.

Using lead acid batteries as a power source, currents as high as 200A were generated to simulate some of the Li short circuit tests. To evaluate the possible effects of a high voltage short circuit in a cell in a series string of cells, a series of tests with a 30V power supply were carried out with currents as high as 3000A at 15V. These currents were too high to properly simulate a battery because of the extremely high current pulses caused by the discharge of the filter capacitor. Explosions were initiated more readily at high voltage, but surprisingly, they did not occur on first contact; rather some heating of the components always occurred before an explosion was initiated.

A full description of the Li and alternate electrode geometries and the results of the 52 tests is beyond the scope of the present report. However, the qualitative conclusions reached regarding the effects of lithium short circuits in brief were:

1. An arc or spark between Li/SOCl_2 cell components does not necessarily initiate an explosive reaction. Explosions can be produced in particular configurations, but not nearly as readily as might be anticipated.

2. Contact resistance heating alone appears more likely to terminate by burning off of the contact point than by explosion; the heating produced probably lowers the threshold for a subsequent spark-induced explosion.
3. Spot-melting of lithium was observed to occur without initiation of an explosion; an explosion could be produced more readily with a short circuit involving a lithium point rather than lithium foil, indicating that the high thermal conductivity of an anode plate may significantly reduce the potential for an explosion on short circuit in an actual cell.
4. The influence of electrolyte conditions was not clearly established.

3.2.3 Reaction Kinetics of Sulfur with Lithium

The DSC and DTA results listed in Table 3 both confirm a violent reaction between Li and S in the absence of SOCl_2 at sulfur's melting point (i.e., 112.8°C for rhombic sulfur). The thermal analysis tests show that SOCl_2 protects Li from reacting with both molten and dissolved S by virtue of the passivating film of LiCl as in the battery. A belated reaction of Li with S in the presence of SOCl_2 only occurs at 400°C (34).

Dey (P. 216, Ref. 26) has postulated that the mixture of finely divided Li dendrites and sulfur in overdischarged carbon limited Li/ SOCl_2 cells causes the cells to become shock sensitive. The shock sensitivity of such mixtures should be quantitatively evaluated. It is also recommended that additional DSC experiments be carried out with mixtures of sulfur and Li dendrites without SOCl_2 and with SOCl_2 and $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte.

3.2.4 Reaction Kinetics of Carbon with Lithium

The reactivity of carbon with lithium in SOCl_2 electrolyte has been studied in some detail by Kilroy, James and co-workers (32,34,35). Carbon reacts exothermically with Li at temperatures as low as 54°C (34) in SOCl_2 electrolyte if the carbon is mechanically ground into the lithium. The above reaction occurs because the lithium-carbon mixture in SOCl_2 electrolyte is essentially a multitude of short circuited Li/ SOCl_2 cells. Although the reaction is very exothermic, it is not likely to lead to thermal runaway during normal cell operation unless the cell is crushed, punctured, or otherwise subjected to severe mechanical abuse.

When the reactivity of carbon-lithium mixtures was first investigated there was some concern that the C-Li reaction could initiate thermal runaway during the overdischarge of carbon limited cells when lithium dendrites are deposited on the carbon cathode. However, x-ray diffraction and scanning electron microscope (SEM) studies of carbon electrodes from overdischarged carbon limited cells carried out at GTE Laboratories (13,14) showed that metallic Li is not deposited in the interior of the carbon electrodes. The x-ray diffraction results showed no sign of carbon-lithium intercalation compounds over a wide range of overdischarge rates and temperatures within the 5% detection limit of the procedure.

3.3 CONCLUSIONS AND RECOMMENDATIONS

In addition to the recommendations that have already been made in this section, several additional recommendations are suggested.

The reactivity of sulfur with lithium could be further characterized by measuring the polarization characteristics of lithium microelectrodes in SOCl_2 electrolytes from 50°C to 170°C with increasing amounts of dissolved sulfur. The LiCl film on the Li electrode could be exfoliated off by anodic dissolution at elevated temperature in half cells and the composition of the new film

formed at elevated temperature determined by EDAX, AUGER and ESCA. Such studies of the composition and structure of the new LiCl film formed at elevated temperatures could reveal if such films are less passivating than the LiCl film formed at room temperature.

Lithium could be stored in electrolyte with various additives selected to modify the LiCl film. DSC tests could be carried out to determine whether the transition temperature for the S + Li reaction was increased. If effective additives were identified, they could be evaluated further in sealed Li/SOCl₂ prototype cells over a range of abuse conditions.

(53,59,61,67). However, the subject remains a matter of some controversy (1,64). The electrolyte limited design is hazardous (63) but the thermal problems associated with electrolyte limitation can be avoided by providing cells with a slight excess of electrolyte and a hermetic closure. Thus the issue of the preferred design to withstand overdischarge becomes a choice between the carbon and lithium limited designs.

Even though a lithium limited design is preferred to reduce the possibility of thermal runaway during overdischarge information about carbon limited overdischarge is of vital importance because lithium limited cells can become carbon limited under certain operating conditions such as low temperature discharge. Carbon limited overdischarge in a nominally lithium limited cell can also occur if a low rate cell with a low cathode area is discharged at high rate. Thus information about the processes leading to thermal runaway in carbon limited cells during overdischarge would be extremely useful in order to decide which design changes or chemical modifications to adopt in order to decrease the possibility of thermal runaway in lithium limited Li/SOCl_2 cells during electrical abuse.

Situations where overdischarge of carbon limited cells have resulted in thermal runaway with venting or "explosions" have been reported widely (26,52,62). For example, the behavior of the temperature and potential as a function of time during overdischarge at constant currents of 0.5 and 0.25A (i.e., 0.55 mA/cm^2) have been reported by Dey (52,26) for spiral wound carbon** limited D size cells. It was found that the potentials become slightly negative (i.e., -0.3 to -0.5V) on overdischarge and oscillated just before the cells "exploded". The cell overdischarged at 0.25A "exploded" when the cell had been

** It was not stated explicitly that the D cells were carbon limited but from the Li anode dimensions it was calculated that the Li anode volume was 6.357 cm^3 and the Li anode capacity 17.2 Ahr. The 45g of electrolyte (Pg. 29, Ref. 26) could provide 30.6 Ahr. From Figure 9 of Ref. 26, a D size cell delivered 11.6 Ahr to 3.00V at 0.1A (0.22 mA/cm^2). Thus their D cells were carbon limited.

is utilized in many applications because the technology for a high rate cell that can withstand a short circuit is not available. Various design modifications and approaches that have been used to improve the safety of high rate cells under short circuit and other electrical abuse conditions were discussed previously in Section 5.0.

The short circuit currents of Li/SOCl_2 cells are very high immediately after filling and decrease rapidly during the first hours and weeks of storage to a plateau value. Even after months or years of storage the short circuit currents of high rate Li/SOCl_2 cells are still large enough to cause the cells to explode if shorted. The storage time after filling is very frequently not specified for much of the short circuit test data in the literature and care must be taken when evaluating such results. In particular, the time after filling must be known when evaluating the short circuit test results for design improvements that are claimed as substantial improvements in safety. It is recommended that further work should be carried out to characterize the current, temperature, and cell potential behavior during short circuit of high rate C or D size cells as a function of the time after filling during the first hours or days of such storage.

6.2 OVERDISCHARGE

6.2.1 Overdischarge of Carbon Limited Cells

Overdischarge or reversal of Li/SOCl_2 cells through series string discharge or constant current discharge with an external power supply can result in thermal runaway depending on the design of the cell. Considerable evidence (26,47,52,62,63) indicates that carbon* limited cells may undergo thermal runaway during high rate reversal and that the anode limited design is preferred.

The terminology carbon limited instead of cathode limited is used to avoid confusion between electrolyte and carbon limitation since SOCl_2 is both the cathode material and the electrolyte solvent.

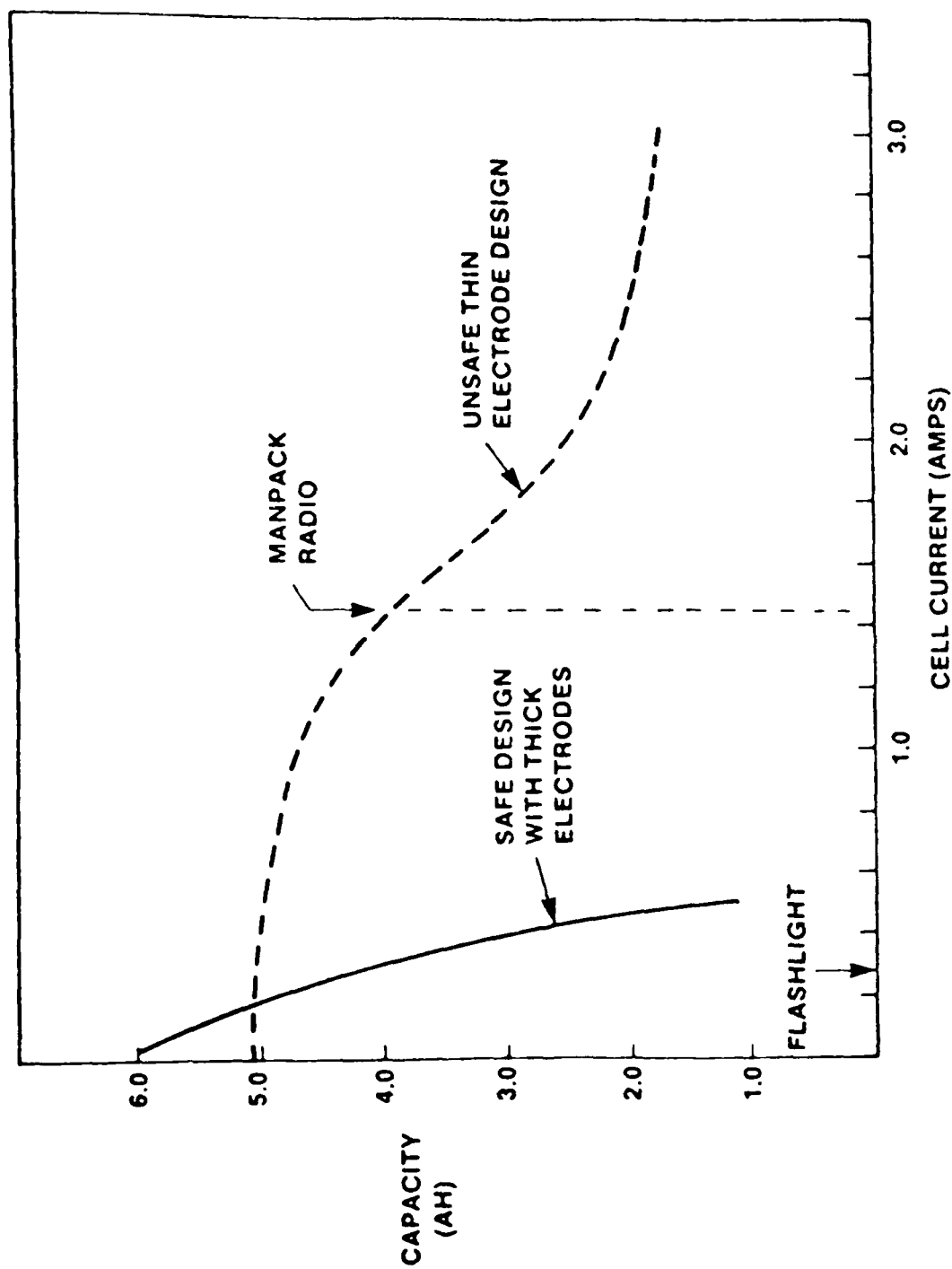


Figure 5: Capacity and Power Capabilities of Low and High Rate C Size Li/SOCl_2 Cells

6. ELECTRICAL ABUSE HAZARDS

6.1 SHORT CIRCUIT

Low rate Li/SOCl_2 cells with thick cathodes of either cylindrical bobbin design or prismatic design show a temperature increase when short circuited but do not undergo thermal runaway or explode. This fact has been confirmed in tests with hundreds of AA size (57,58,53) and D size cylindrical cells (47,59) and a more limited number of tests with prismatic cells up to 16.5 KAh (47,60,61). For AA cells the maximum short circuit current and can temperatures were 2.70A and 65°C (58). When 10 KAh cells were short circuited (60) a current of approximately 700A was maintained for almost two hours above 2V before a gradual and then a sudden drop in both the current and the voltage was observed. The temperature increased to a maximum of 60°C and the pressure increased to slightly above 136 KNI (20 Psig) during the first hour of short circuit, followed by a decrease after a brief venting through a preset check valve into the scrubber at the temperature maximum.

High rate cells with thin electrodes undergo thermal runaway and explode when short circuited. The results of short circuit test with spiral wound D cells where the cell potential, current, case temperature and in many cases the pressure were recorded have been widely reported (26,52,49). The dividing line between the safe and unsafe designs depends on the size of the cell and the internal configuration of the electrodes but a safety hazard on short circuit begins for cells which can deliver their nominal capacity at a power density greater than approximately 45 watts/liter for a C size cell. The safe power density would be expected to decrease proportionally the larger the cell is compared to C size. The capacities for low and high rate C size cells are shown in Figure 5. Cells that were constructed with larger but thinner electrodes so that their current capability was improved, thereby moving their capacity-current curve even a small amount to the right of the "safe design" curve in Figure 5 were found to explode on short circuit. Thus as Figure 5 illustrates the Li/SOCl_2 cell has considerable power capabilities that can not

To facilitate fabrication and to increase their mechanical strength, the non-woven glass fiber separators used in Li/SOCl_2 cells contain up to 9 Wt% of organic binders such as polyvinyl alcohol and polyacrylates. The rate of hydrolysis of these binders by $\text{LiAlCl}_4/\text{SOCl}_2$ was investigated during the present contract (10). Possible safety hazards caused by the hydrolysis products and the dissolved organics have been discussed earlier in Section 4.2.

The safety of these new high rate designs with vents and fuses over a full range of electrical, mechanical, and thermal abuse conditions has yet to be demonstrated by an independent testing laboratory to verify the manufacturer's claims.

5.3 ELECTROLYTE ADDITIVES AND ELECTRODE POISONS

Mixed success has been achieved in controlling thermal runaway in spiral wound Li/SOCl₂ cells by the use of electrolyte additives that dissolve at approximately 90°C, raise the electrolyte viscosity and prevent thermal runaway. One such additive, a PVC gel emulsion developed at GTE Laboratories (46) has been successfully demonstrated and has been found not to have detrimental effects upon cell capacity, potential, rate and storage characteristics. However, the additive is not effective 100% of the time and improved quality control and development work will be required to improve its reliability.

The concept of electrode poisons microencapsulated in plastics that will melt during the early stages of thermal runaway has been described in a patent by Fritts (56). To our knowledge, experimental results concerning the latter approach have not been published involving lithium cells.

5.4 SEPARATOR INTEGRITY

The mechanical strength of the separator in Li/SOCl₂ cells to shear, puncture, dendrite penetration and other types of forces is a very important factor in determining the ability of the cell to safely withstand mechanical and electrical abuse. The tradeoffs between the performance gains possible by using thinner, weaker separators and the increased probability of short circuits during mechanical abuse are well understood by most battery engineers.

To be able to accurately specify the safety hazards of various designs of high rate Li/SOCl₂ cells over a full range of conditions, it is evident that comprehensive heat transfer models will be required. Prior to testing, the unique internal electrode spacings for individual cells could be determined by three dimensional x-ray tomography and the dimensions could be used to predict the thermal behavior of the cells during electrical abuse conditions. The agreement between the predicted and observed thermal behavior could be used to evaluate the accuracy of the heat transfer model.

Heat transfer in large Li/SOCl₂ reserve batteries with bipolar electrodes has been modeled by Chua and co-workers (33) using a computer model. Heat management in large Li/SOCl₂ reserve cells has also been discussed by Hall (50), and Marincic (51). Since the heat management problems of reserve cells are very application dependent the topic is outside the scope of this report.

5.2 VENTS AND FUSES

Early work at GTE Laboratories (49) and at Duracell (26,52) showed that high rate spiral wound D size cells exploded on shorting in spite of vents. In recent years a number of manufacturers have developed high rate Li/SOCl₂ cells using both a vent and an internal fuse that will blow if the cell is short circuited or subjected to electrical abuse. The latter design however is vulnerable to thermal runaway caused by mechanical abuse such as crushing, internal shorts, and overdischarge if additional measures are not taken.

Union Carbide (53) employs a resealable vent operating in the 400 psi range in their 1.25 Ahr cylindrical low rate bobbin design. Tadiran (54) however uses a vent activated at 100-150 psi, a slow blow fuse and a diode in their moderate rate disc design cylindrical cell. Their cell is similar to a D size cell only shorter with a height of 23 mm and a diameter of 32.6 mm.

A spiral wound Li/SOCl₂ cell design of limited effectiveness incorporating a thermal switch to prevent thermal runaway in the event of a short circuit is described in a patent by Goebel and co-workers (55).

5. DESIGN FACTORS INFLUENCING THE SAFETY OF LITHIUM-THIONYL CHLORIDE CELLS

5.1 HEAT TRANSFER AND DISSIPATION

High rate Li/SOCl₂ cells above the 1/2C size with thin cathodes undergo thermal runaway when short circuited or subjected to electrical abuse because of heat transfer problems not encountered in low rate cells with thick cathodes. A high rate C size cell using a stacked disc design with heat transfer characteristics superior to the conventional spiral wound design has been discussed by Goebel and co-workers (47).

An expression was derived by Marincic and co-workers (48,49) for the maximum time a spiral wound cell would take, T, to reach a certain temperature, t, measured above ambient temperature, during discharge:

$$T = \frac{GC(t)}{0.239 \Delta VI - (a + bt + ct^2)} \quad [38]$$

where G is the cell weight; C, the specific heat capacity of the cell; ΔV , the voltage drop on discharge; I, the discharge current; and a, b, c, coefficients of the polynomial relating the cooling rate to the cell surface temperature.

It was calculated that a D size cell discharged at 10A constant current at 2.0V would reach the melting point of sulfur in 23.65 minutes. The above calculation compares well with the results of Dey (26) for a spiral wound D cell that exploded after 28.49 minutes of 10A discharge.

In other calculations, it was found that cells exploded sooner during high rate discharge than predicted by the heat transfer calculations. The premature explosions were attributed to local overheating effects that were not included in the calculations.

Lithium hydride forms a well defined ionic hydride, LiH that might be expected to react violently with SOCl_2 by either Reactions [28] or [29] in Table 4. It could be formed by reacting with H_2 produced during the hydrolysis of water by Reaction [27]. However, tests (24) showed that LiH does not react with SOCl_2 at either room temperature or at the boiling point of SOCl_2 . Thus, it was concluded that LiH does not present a significant hazard potential.

The chemistry of lithium nitride and its formation during lithium storage in dry air have been discussed in some detail elsewhere (24, 43). It was found that Li_3N might form on lithium during cell assembly and thus could be present in Li/ SOCl_2 cells. It was found experimentally to be highly reactive with SOCl_2 but only under the peculiar conditions of exposure to moist air in a finely divided state. It was concluded (24) that lithium nitride would not be expected to present a hazard in a sealed Li/ SOCl_2 cell.

with diethyl ether and GC/MS and FT-IR analysis during the present contract and less than 1.0 Wt%, 30 ppm, 100 ppm, and 20 ppm of soluble organic impurities were detected, respectively.

The pressure generated by the reaction of the separator binder with SOCl_2 electrolyte with and without Li present was measured in sealed glass tubes containing closed end Hg manometers over a period of 915 hours at 23°C during Task II of the present program. Pressures equivalent to 33.6 psi in a 10,000 Ahr prismatic cell were generated. Further separator gassing studies at room temperature in bobbin-type commercial D-size cells equipped with closed end Hg manometers are currently underway at GTE Products Corporation. Since binderless separators such as the Lydall No. 991 glass fiber separator are available which do not evolve gas in SOCl_2 electrolyte it is possible that such separators may find wider use if their mechanical properties are acceptable.

The polyvinyl alcohol binder used in the Crane separator is thought to react with SOCl_2 electrolyte to form polyvinyl chloride (PVC) which is very soluble in the electrolyte. Short circuit tests with spiral wound 1/2C cells and other work in connection with PVC electrolyte additives at GTE Laboratories has shown that PVC does not have detrimental effects on the stability of the LiCl film on the Li anode at high temperatures. However, other organic binders such as the polyacrylics could react with SOCl_2 electrolyte to generate products which make the LiCl film unstable towards sulfur or $\text{LiAlCl}_4/\text{SOCl}_2$ at elevated temperatures. It is suggested that DSC or DTA tests similar to those in Section 3.3 be carried out with Li, S and SO_2 in SOCl_2 electrolytes containing organic impurities to further investigate potentially destabilizing and hazardous effects of soluble organic compounds on the LiCl anode film.

The possibility of hazardous reactions involving lithium and nickel hydride and lithium nitride was considered by Schlaikjer and co-workers (24). The formation of nickel hydride $\text{NiH}_{0.5}$ was thought to be very unlikely because it has a very low stability with a $\Delta G^\circ_f = 5.64 \text{ Kcal/mole H}_2$. That nickel hydride is exceptionally unstable is evidenced by a decomposition pressure of over 3000 atmos at 25°C . These preparative conditions are not present in ordinary hydrogen annealing of nickel.

are hermetically sealed. Carbon has excellent absorption characteristics and could pick up moisture from the breath of workers assembling cells even in a dry room at < 3% R.H.. Cells can be vacuum dried after assembly but this is not always possible for a number of reasons.

The slowness of the hydrolysis reaction is somewhat insidious because the pressure buildup would not occur for many weeks and, therefore, could not be detected by the manufacturer as bulging prior to shipment. Slight pressure buildups in cylindrical cells probably pose no safety hazard in D size cells or smaller because such cells can easily withstand pressure up to 200 psi without bulging and over 800 psi without rupture. However, large prismatic cells can bulge at much lower internal pressures which can indirectly lead to problems in batteries where bulging could cause inter-cell short circuits. To avoid the generation of pressure in Li/SOCl₂ batteries due to traces of moisture in the carbon and separator, an SO₂ flushing technique has been developed by McDonald (43) that has proven very effective.

The effect of 0, 20, and 100 ppm water added to standard and reverse polarity cells was investigated during the present contract (see Section 1.3, Ref. 10) and no detrimental effects were observed in terms of voltage delay or capacity. Safety problems due to reactions of hydrogen generated during hydrolysis have never been reported to our knowledge and probably are a negligible hazard. The reactions of hydrogen in Li/SOCl₂ cells should be investigated at some time in the future but in our opinion such a study has a low priority.

Protic organic compounds are an important group of impurities that could have a detrimental effect on cell safety that have received little attention until the present contract (10). Certain glass fiber separators widely used in Li/SOCl₂ cells were found to contain over 7 Wt% of organic binder materials such as polyvinyl alcohol which reacts with the electrolyte to generate hydrolysis products. The amount of hydrolysis products generated by such reactions with organic compounds is very likely considerably greater than that due to traces of water adsorbed by the carbon electrode. The organic impurities in the carbon electrode, AlCl₃, LiCl and SOCl₂ electrolyte were determined by extraction

Infrared measurements by Staniewicz (42) agree with earlier work by Driscoll (45) that thionyl chloride reacts with water to produce SO_2 and HCl .

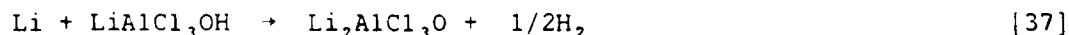


It is now evident that HO-SOCl is not a product as previously reported (41). Very recently, using quantitative infrared techniques, Staniewicz and Dixon (44) have shown that water added to 1.35M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte reacts exclusively with the AlCl_4^- anion rather than with the SOCl_2 .



The reaction is much slower than expected requiring five days to go to 50% completion and five weeks to 100% completion.

The subsequent reaction of Li with a known concentration of HCl in SOCl_2 electrolyte was found to be extremely slow and only a 10% decrease in the HCl concentration was observed after two months storage at room temperature.



The expected reaction to form H_2 and LiCl



is thermodynamically feasible but kinetically inhibited due to the LiCl layer on the Li . Staniewicz (44) reports a $\Delta H = -151.28$ Kcal/mole for Reaction [26] which appears to contradict the $\Delta F = -69$ Kcal/mole value in Table 4.

The concentration of hydrolysis products in SOCl_2 electrolytes used for cell production is closely monitored and maintained at very low levels by all experienced manufacturers. However, it is more difficult to monitor the water content of the carbon cathode and traces of water introduced after the cathodes are vacuum dried could generate H_2 gas pressure in the cells after they

TABLE 4

Thermodynamic Values for Reactions of Possible Impurities in the
Lithium-Thionyl Chloride Cell*

Reaction	Eq. No.	ΔH^0_{298} (Kcal/m)	ΔF^0_{298} (Kcal/m)	Ref.
$\text{Li} + \text{HCl} \rightarrow \text{LiCl} + \frac{1}{2} \text{H}_2$	26	-	-69	24
$2 \text{Li} + \text{HCl} \rightarrow \text{LiCl} + \text{LiH}$	27	-	-85	24
$\text{LiH} + \text{HCl} \rightarrow \text{H}_2 + \text{LiCl}$	28	-	-52.6	24
$2 \text{SOCl}_2 + 2 \text{LiH} \rightarrow 2 \text{HCl} + \text{SO}_2 + 2 \text{LiCl} + \text{S}$	29	-158	-	24
$2 \text{SOCl}_2 + 2 \text{LiH} \rightarrow 2 \text{H}_2 + \text{SO}_2 + \text{S} + \text{LiCl}$	30	- 24.8	-	24
$3 \text{Li} + \frac{1}{2} \text{N}_2 \rightarrow \text{Li}_3\text{N}$	31	-	-37	24
$\text{S}_8 + \text{Li}_3\text{N} \rightarrow \text{S}_7\text{N}^- + \text{S}_4\text{N}^-$	32	-	-	24
$\text{H}_2 + \text{S (RHOMBIC)} \rightarrow \text{H}_2\text{S}$	33	-	- 7.8	40
$\text{H}_2 + \text{SO}_2 \rightarrow 2 \text{H}_2\text{O} + \frac{1}{2} \text{S}_2$	34	-	-16.9	40

* The free energies and enthalpies are given as Kcal/mole of product.

4. POTENTIALLY HAZARDOUS PROCESSES DUE TO IMPURITIES OCCURRING IN LITHIUM THIONYL CHLORIDE CELLS

4.1 IMPURITIES AND THEIR EFFECTS

Four classes of impurities that could have an effect on Li/SOCl_2 cell safety are (i) hydrolysis products from traces of water or organics, (ii) hydrides and nitrides (e.g., Li_3N , LiH and $\text{NiH}_0.5$), (iii) dissolved transition metals (e.g., Fe , Co or Ni) and (iv) soluble organic compounds. Hydrolysis products such as HCl and H_2 could increase the internal cell pressure if present in large enough concentrations leading to cell rupture. In principle, the hydrogen produced by the reaction of HCl with the lithium anode could cause hydrogen embrittlement of the can and welds or form LiH but in practice these reactions have not caused any difficulties. Lithium nitride, Li_3N is occasionally found as small nodules, several mm in diameter in Li foil that has been manufactured and/or stored improperly. It was found (24) to react explosively with SOCl_2 and $\text{LiAlCl}_4/\text{SOCl}_2$ at room temperature in the presence of moisture or electrolyte hydrolysis products. However, in the absence of moisture or hydrolysis products, it was found that Li_3N would not react with SOCl_2 or SOCl_2 electrolyte even when finely divided. Dissolved transition metals reduce cell safety hazards indirectly by increasing the voltage delay after storage and reducing the short circuit current.

4.2 REACTION THERMODYNAMICS AND KINETICS FOR IMPURITIES

The free energies and enthalpies for reactions of impurities in Li/SOCl_2 cells that could effect cell safety are listed in Table 4 for those reactions where published values are available. The details of the reaction of protic compounds such as water, alcohols, and other protic organic compounds with SOCl_2 and $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte have been widely investigated (10,41-45). Although much research remains to be carried out, the general nature of the hydrolysis reactions are now understood qualitatively.

overdischarged 12.7% (i.e., 6.5 hrs) at which time the cell wall temperature was 39°C.

During overdischarge of carbon limited cells the electrode reaction at the Li anode continues to be the oxidation of Li metal to Li cations. However, the carbon cathode becomes totally passivated with LiCl upon reversal and instead of the reduction of SOCl_2 , the cathode reaction changes to the reduction of Li cations from the electrolyte to form Li dendrites on the surface of the carbon electrode that grow out into the solution (13,14). In principle, on further overdischarge, the Li anode will eventually become depleted of Li and the carbon limited cell will become both carbon and lithium limited.

The precise reaction that occurs during overdischarge that leads to thermal runaway in high rate Li/ SOCl_2 cells is not known although a variety of likely reactions have been suggested (1,24,26,29,32,52,63). On overdischarge the Li dendrites growing towards the Li anode could make contact with the anode and short circuit the cell. The Li dendrites would then heat up and could react exothermically with sulfur deposited on the dendrites (26,63) or melt and react with the SOCl_2 electrolyte (26), carbon (32) or other cell components.

During a recent investigation of Li deposition in Li/ SOCl_2 cells (13,14) carried out at GTE Laboratories for the Naval Surface Weapons Center (NSWC), it was found that Li deposits as fine filaments. The Li dendrites were examined by scanning electron microscopy (SEM) and were observed to be made up of a coiled spaghetti-like structure of Li filaments with a diameter of $4 \cdot 10^{-3}$ mm. The morphology of the Li filaments was very similar for cells overdischarged at 2, 5, and 20 mA/cm² at 25°C. Thus it was concluded that the Li dendrites would have such a high electrical resistance that they could not carry a large enough current to reach the melting point of Li (i.e., 180.5°C) when Li dendrite shorting occurred.

To learn about the reactions between Li dendrites and other cell components during dendrite shorting brought about by overdischarge, in situ studies of dendrite shorting were undertaken using optical microphotography during the

present contract and are discussed in Section 1.4.1.2 of the final report (11).

Incidents have been reported (65) in which 5 Ahr carbon limited (66) prototype Li/SOCl_2 cells that were overdischarged at -40°F vented violently when they were allowed to warm to room temperature. To investigate cell reversal during such conditions, carbon limited Li/SOCl_2 cells were investigated at -40°C during our earlier NSWC Study (13,14). It was found that when carbon limited cells are overdischarged at -40°C then allowed to warm to room temperature, the Li dendrites only become detached from the cathode between 3.5 and 16 hours after the cell has warmed up. The detached Li dendrites then dissolved in the electrolyte which was puzzling since they are usually very stable. For example, Li dendrites deposited on the cathode of carbon limited cells at 25°C are stable for over 300 hours after the end of discharge.

The stability of the Li dendrites for over three hours after the cell had warmed up to 25°C from -40°C is an indication that the species attacking the Li builds up slowly as is the case with the product of the $\text{SO}_2\text{-SOCl}_2$ electrolyte reaction (see Section 2.3). The $(\text{OClS})_2$ dimer intermediate postulated by the group at JPL (12) has a lifetime of only five minutes at -40°C and 10 seconds at 25°C and thus could not account for such a slow reaction.

In Section 1.4.1.3 of the final report of the present contract (11) work is described in which carbon limited cells were overdischarged at -40°C , then the corrosion and detachment of the Li dendrites photographed over a period of 24 hours. There was a need for a photographic record to document the reaction rate since previously our only evidence was two qualitative observations at 3.5 and 19 hours (13). The solid product that was produced and settled to the bottom of the cell as the Li dendrites dissolved was collected and analyzed since the composition of this compound could indicate the composition of the unknown compound in solution responsible for the unusual high rate of corrosion of the Li deposits. It was found from the analysis that the solid product was LiCl .

It was concluded (11) that Li dendrites deposited at -40°C are more reactive towards the electrolyte than those deposited at 25°C because of the greater amount of SO_2 in the SOCl_2 electrolyte at -40°C . At -40°C , the reaction of SO_2 with SOCl_2 electrolyte proceeds much more slowly and the SO_2 concentration becomes greater. Furthermore, the solubility of SO_2 in SOCl_2 electrolyte is greater at -40°C . It is well known that voltage delay at the Li anode in Li/ SOCl_2 cells can be reduced by adding SO_2 to the electrolyte which increases the rate of Li corrosion at the anode. It is thought that the corrosion of Li dendrites deposited at -40°C is caused by the same phenomenon. By some unknown process high concentrations of SO_2 reduce the effectiveness of the LiCl film in preventing SOCl_2 from reacting with Li. It is known that SO_2 is more strongly adsorbed on the carbon electrode at low temperatures, thus warming the cell from -40°C to 25°C would release SO_2 into the SOCl_2 electrolyte. These explanations are of course very tentative because this phenomenon has not been fully investigated.

It has been noted earlier in the literature (34) that carbon limited cells can be overdischarged for long periods of time during which the charge input greatly exceeded the Li originally present in the cell, similar to results obtained during the present contract (11). No transients in the potential were noted and a short circuit mechanism was proposed to account for the low Li utilization. However, quantitative data were not given (34) concerning the Li utilization or the proportion of the current carried by an electronic pathway during overdischarge.

The results of the overdischarge tests carried out during the present contract (11) tend to suggest that carbon limited cells form Li dendrite shorts by a benign mechanism and that overdischarge does not constitute a specific hazard. This impression was reinforced by observations during cell disassembly which revealed no sign of overheating such as burn marks. However, spiral wound D size cells have been reported (52,26) to "explode" when overdischarged 12.7% at which time the cell wall temperature was only 39°C . Other situations where the overdischarge of carbon limited cells has resulted in thermal runaway have been widely reported (26,52,62). The occurrence of thermal runaway in spite

of evidence that Li dendrite short circuits are benign supports the long held idea that some unknown reaction occurring during overdischarge triggers the thermal runaway process.

Various chemical reactions and processes have been proposed (26,30,32,52) to account for thermal runaway in carbon limited cells during overdischarge. Of the various explanations, we think evidence is growing stronger that thermal runaway occurs due to the reaction of sulfur which has precipitated from the electrolyte with the high surface area Li dendrites. The reaction of sulfur with Li is highly energetic with a free energy (see Table 2) $\Delta F = -120$ Kcal/mole of Li_2S . Differential thermal analysis (DTA) measurements (26,29) have shown that the $\text{Li} + \text{S}$ reaction has a strong exothermic transition and undergoes thermal runaway at 153°C . Sulfur normally does not react with the Li anode because the sulfur is dissolved in the SOCl_2 electrolyte. However, it has recently been found by scanning electron microscope studies (35,36) that the Li dendrites formed in Li/SOCl_2 cells during overdischarge are fine filaments (i.e., 4 μm diameter) coiled in a spaghetti-like structure with an extremely high surface area. During overdischarge it is possible that some of these fine Li dendrites covered with a layer of precipitated sulfur or near a large sulfur crystal could either mechanically break or be corroded and the fresh Li surface could come in contact with solid sulfur and begin to react. Alternatively, the Li dendrites could undergo a substantial temperature rise due to IR heating during short circuit and react with nearby sulfur crystals initiating a thermal runaway reaction.

In 1978 it was proposed (30) that discharged carbon limited cells could undergo thermal runaway due to reaction of Li with unstable SOCl_2 reduction intermediates such as SO which were believed to exist. It is now known that long lived intermediates are not formed, as discussed in detail in Section 2.3 thus exothermic reactions of discharge intermediates can be ruled out as a cause of thermal runaway for carbon limited cells during overdischarge.

Assuming that thermal runaway in carbon limited cells occurs during overdischarge due to a reaction of solid sulfur with the high surface area Li den-

drites, it is not surprising that the small prototype cells used to investigate overdischarge (11) during the present contract did not show signs of excessive heating or undergo thermal runaway. First, the cells contained a somewhat higher electrolyte to carbon cathode mass ratio than commercial cells and it is likely that the electrolyte volume was large enough so that all the sulfur produced from the discharge reaction dissolved.* Thus no solid sulfur was present to react with the Li dendrites. Second, even if an exothermic reaction occurred, thermal runaway did not take place probably because of the small size of the cell and the excellent heat transfer properties of the prismatic configuration.

Because overdischarged carbon limited cells can explode with only a 15°C temperature rise before the explosion, it appears that the chemical reactions responsible for thermal runaway can be identified and safely studied in small laboratory prismatic cells. This is in contrast to thermal runaway brought about by short circuit in high rate cells which is caused by both poor heat transfer and exothermic chemical reactions and which can only be investigated effectively in high rate cells at least as large as C-size. Thus it appears that it will probably be much easier to study thermal runaway in overdischarged cells than short circuit in high rate cells. Since small cells may be adequate to identify the cause of thermal runaway during carbon limited overdischarge, the investigation could progress more rapidly to yield designs to eliminate the thermal runaway hazard.

It is therefore recommended that additional overdischarge tests should be carried out with small carbon limited prismatic cells with small electrolyte-to-carbon mass ratios at temperatures from 25°C to approximately 60°C. The electrolyte and components from the overdischarged cells should be analyzed for unusual products that could be generated from exothermic side reactions such as Li_2S and the cell components inspected for burn marks or other signs of excessive heating. If small exothermic reactions can not be detected then additional tests in somewhat larger multiple cathode prismatic cells could be

* The solubility of sulfur in 1.8M LiAlCl_4 is 1.326M at 24°C (38).

carried out.

It is also recommended that DTA measurements of the properties of lithium dendrites and sulfur should be carried out since earlier measurements did not use finely divided Li. Information is also needed concerning the chemical and electrical behavior of compressed slurries of Li dendrites in SOCl_2 neutral electrolyte while high current densities are passed through the slurry. The use of metal tabs on the anode and cathode to localize Li dendrite growth and prevent thermal runaway as described in a recent patent (66) should also be thoroughly investigated since little information has been published about this design modification.

6.2.2 Overdischarge of Lithium Limited Cells

As discussed earlier in the previous section, most of the results currently available indicate that anode limited Li/ SOCl_2 cells are less likely to undergo thermal runaway during high rate overdischarge than carbon or electrolyte limited cells (53,59,61,67). GTE (59,67) and Honeywell (61) have carried out overdischarge tests with large anode limited cells with capacities up to 16,500 Ahr and incidents involving thermal runaway were not experienced with any of the cells. Union Carbide (53) carried out safety tests on over 8,000 cylindrical cells slightly smaller than a standard 'AA' size and no safety problems or hazards were identified as a result of the tests.

During the overdischarge of anode (i.e., lithium) limited cells, the electrode reaction at the carbon cathode continues to be the reduction of SOCl_2 to produce SO_2 , Cl^- , and S as described by Equation [1]. However, the $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte is oxidized at the bare nickel anode screen as soon as the lithium is consumed by anodic dissolution. The predominant reaction of $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte oxidation at the anode substrate is:



The AlCl_3 and Cl_2 produced can then react further with the SOCl_2 discharge products SO_2 and S



The dissolved chlorine produced by reaction [39] could also undergo reduction at the carbon cathode where it would be reduced in preference to SOCl_2 .



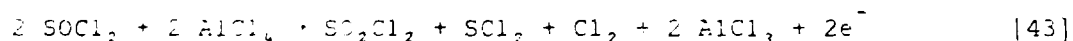
The existence and relative importance of the side reactions of Equations [40], [41], [42] under various conditions of charging are still a subject of active research that will be discussed later in this section.

The AlCl_3 produced by oxidation of the SOCl_2 electrolyte at the anode screen diffuses to the carbon cathode where it reacts with LiCl inside the cathode produced by the reduction of SOCl_2 and Cl_2 (i.e., Equation [42]). For every equivalent of charge passed, one mole of AlCl_3 will be produced at the anode substrate and one mole of LiCl will be produced at the cathode by the reduction of SOCl_2 , SO_2Cl_2 or Cl_2 that will eventually react to form soluble LiAlCl_4 . Thus the carbon cathode will not be filled up with LiCl and become passivated but will remain active indefinitely, provided that the cell has sufficient electrolyte. Electrolyte is consumed during anode limited over-discharge because the S and SO_2 produced by the reduction of SOCl_2 are not re-generated.

The above qualitative description of the reactions occurring during anode limited overdischarge generally agrees with the electrochemical behavior and the early exploratory infrared and voltammetric analysis of the electrolyte (1,64). However, the explosions of several anode limited spiral wound "C" size cells overdischarged at 1 mA/cm^2 reported by Abraham and Mank (64) and the claims by Salmon et al (68) that chlorine monoxide, Cl_2O , a highly oxi-

dized explosive compound is produced has stimulated further research (9,69). This research has used a variety of very sensitive techniques such as "in situ" electron spin resonance (ESR), infrared spectroscopy and mass spectroscopy to determine the composition of all the minor products and intermediates formed during anode limited overdischarge. No new compounds such as Cl_2O were detected. The investigations were generally semi-quantitative and quantitative analytical data has yet to be obtained to accurately describe the stoichiometry of the reactions occurring during anode limited overdischarge at even one set of standard conditions at room temperature. Ultimately, to be assured that no hidden safety hazards exist, it will be necessary to know the reaction stoichiometry during anode limited overdischarge over a broad range of conditions of temperature, rate, and overdischarge time for both flooded and electrolyte limited cells.

Attia and co-workers (9) using an "in situ" IR flow cell detected SOCl^+ , SO_2Cl_2 , and species giving rise to absorptions at 1070 and 665 cm^{-1} that were interpreted as indirect evidence for Cl_2 or SCl_2 formation. They obtained direct evidence for SCl_2 formation on anode limited overdischarge by mass spectroscopy. Carter et al (69) used gas chromatography (GC) atomic adsorption, IR and ESR spectroscopy to analyze the electrolyte during and after anode limited overdischarge. They found by ESR that ClO_2 is not present in sufficient concentrations to be observed. Their analytical results agreed well with those reported earlier by Abraham and Mank (64) and they proposed a similar overall cell reaction for the oxidation of $\text{LiAlCl}_4/\text{SOCl}_2$.



They proposed that there is no safety hazard due to intermediates or products formed by the oxidation of $\text{LiAlCl}_4/\text{SOCl}_2$ during anode limited overdischarge. They limited their conclusions however to flooded cells at room temperature.

It is now thought (70) that the explosions of spiral wound anode limited Li/SOCl_2 cells that were observed by Abraham and Mank (64) during overdischarge were caused by intermittent electrical contact between the anode screen and

dislodged lithium rather than unstable oxidation products. Schlaikjer has noted (1) that the proper design and construction of anode limited Li/SOCl₂ cells is essential to their successful use and that the lithium must be applied to the screen such that it does not become detached during discharge.

Although the reactions occurring during lithium limited overdischarge are beginning to be understood qualitatively, additional quantitative data is required to characterize the stoichiometry of the cell reactions. It is recommended that additional investigations should be carried out in which the electrolyte from overdischarged lithium limited cells is extracted at least four times with distilled SOCl₂ and analyzed by quantitative FT-IR using the techniques developed during the present contract (11). Cells would have to be analyzed quantitatively for SO₂Cl₂, Cl₂, AlCl₃, and S₂Cl₂ after various times, rates, and temperatures of overdischarge.

6.3 CELL CHARGING

Charging of Li/SOCl₂ cells of a variety of designs has been widely investigated by a number of organizations. Discharged and fresh lithium limited D size bobbin type cells were charged at GTE Products Corp. (47,59) at currents up to 100 mA for two to eight hours and no rupture, leakage, bulging or explosion was experienced with any of the cells. Charging tests at 40A for 100 hours with three 10 KAh cells by GTE (67) showed only a small pressure increase to $\approx$ 18 psig and a temperature increase to 66°C. Similar results with no instances of thermal runaway or venting were found by Honeywell during charging tests with 16.5 KAh cells (61). However, Zupancic and co-workers (53) at Union Carbide found that 1.25 Ahr Li/SOCl₂ cells slightly smaller than an 'AA' size cell underwent a high pressure gas release through a vent assembly on the cell when charged at greater than 100 mA for a discharged cell and 1.0A for an undischarged cell. The vent operated in the 2.7MPa (400 psi) range.

When Li/SOCl₂ cells are charged, lithium is electrodeposited at the lithium negative electrode. Present analytical results (64) indicate that the predominant reaction at the carbon electrode is



The Cl₂ can then react with the Li electrode



and the AlCl₃ can react with the LiCl film on the Li electrode.



For each equivalent of charge passed during "charging" one equivalent of Li is deposited and one equivalent each of Cl₂ and AlCl₃ is generated. The metallic Li then reacts with the Cl₂ and AlCl₃ to regenerate the LiAlCl₄ that was electrolyzed during charging. This sequence of reactions has been postulated (64) to account for the observation that Li/SOCl₂ cells could be charged for very long periods in which the total coulombs passed considerably exceeded the amount of SOCl₂ or Li originally present in the cell. Such cells could then be discharged to yield capacities equivalent to those obtainable from fresh cells.

Abraham and Mank (64) identified SO₂Cl₂, SO₂ and SCl₂ in the electrolyte of Li/SOCl₂ cells that were "charged". Cells that were discharged prior to charging would contain SO₂ and S which could react with the chlorine and aluminum chloride produced at the carbon electrode during charging



Sulfur dichloride (SOCl_2) is normally somewhat unstable (71) thus it is peculiar that it has been observed in both "charged" and overdischarged anode limited cells (69).

It was noted earlier that small Li/SOCl_2 cells, that have been discharged, vent when charged at currents ten times smaller than those required to cause fresh cells to vent (58). It is not known whether discharged cells vent simply due to the effect of moderate heating and the pressure of SO_2 produced as a discharge product or due to exothermic chemical reactions involving either SO_2Cl_2 , S_2Cl_2 , or Li . It is also possible that in discharged cells Cl_2 and AlCl_3 would be more likely to be consumed by reactions such as [40], [41] and [45] (LiCl in the carbon pores) in the vicinity of the carbon electrode, therefore allowing greater growth or buildup of Li dendrites at the lithium electrode. The morphology of the Li deposits could be effected by the composition of the electrolyte.

Charging of primary Li/SOCl_2 cells involves less hazard than overdischarge of carbon limited cells. Charging does not cause thermal runaway and it can be prevented by the inclusion of a diode in the circuit. However, charging is a matter of some concern in the design of reserve batteries where charging can occur via the common electrolyte fill path between a series stack of cells. In large, high rate reserve batteries, charging is thought in some cases to produce dendrite shorts resulting in thermal runaway.

There is some similarity between the products produced during oxidation of $\text{LiAlCl}_4/\text{SOCl}_2$ in overdischarged anode limited cells and those produced during "charging". However, in anode limited overdischarge, the oxidation occurs at the bare grid of the Li anode which is usually nickel whereas during charging the oxidation occurs at a high surface area carbon electrode. In charging the Cl_2 can attack the Li electrode whereas during anode limited overdischarge no metallic Li is present and the chlorine could either be reduced at the carbon electrode, undergo reactions [40] and [41] or other reactions currently under investigation (9,69). Thus the chemical stability of high surface area Li dendrites in an electrolyte containing SOCl_2 oxidation products is a potentially hazardous situation unique to charging.

In view of the exothermic nature of the reaction of Li with Cl_2 , SO_2Cl_2 , and other oxidation products and the potentially hazardous effects of Li dendrite shorts, an investigation was undertaken during the present contract(11) of the growth and reactions of Li dendrites during charging. Previously very little attention had been given to exothermic reactions that could occur at Li dendrites during charging and clearly this was a subject that merited investigation. Of particular interest was the rate of corrosion by AlCl_3 and Cl_2 of the Li dendrites produced during charging and shape changes and energetic chemical reactions that occur when the Li dendrites reach the carbon electrode surface causing a short circuit. Using a glass cell with a 4.0 cm diameter optical glass window designed for "in situ" optical microscope studies, shape changes and corrosion of the Li dendrites formed during charging were recorded by photography during subsequent open circuit storage. The microphotographs revealed no dimensional changes greater than ± 0.05 mm during 3.0 hours on open circuit after charging.

It was concluded that charging at current densities up to 20.0 mA/cm^2 appears to involve no safety hazards other than the usual problems of heat management related to cell design and external heat transfer. Thus it is recommended that further investigations of safety hazards during charging for cells using SOCl_2 neutral electrolyte should be given a low priority. However, safety hazards involving Li dendrite short circuits that occur due to intercell charging in Li/ SOCl_2 series connected batteries using SOCl_2 acid electrolytes is a high priority area that merits much further attention.

7. MECHANICAL AND THERMAL ABUSE HAZARDS

7.1 VIBRATION AND IMPACT

A broad range of mechanical abuse tests involving vibration, shock and impact have been carried out by GTE and other manufacturers on cylindrical (47,53,54,59,60) and prismatic (47,59,61,72) Li/SOCl₂ cells. Bobbin type cylindrical DD cells were subjected at GTE Products Corporation (47) to vibration tests in accordance with MIL-STD-810C for 90 minutes each in the horizontal and vertical positions and no changes in the open circuit voltage, skin temperature or closure seal were noted. Partially discharged 10 Kahr prismatic cells (60) were subjected to 100 g shocks along each of the three axes without any change of the cell voltage, pressure or temperature. The ability of cells to withstand vibration and impact is almost entirely determined by the mechanical design since there appear to be no shock sensitive chemical reactions. However, overdischarged carbon limited cells have been reported (26) to be shock sensitive as discussed earlier in Section 3.2.3 and it is recommended that further work to determine the sensitivity threshold of such cells should be given a high priority.

The shock sensitivity of AA size Li/SOCl₂ cells was investigated during the present contract (76) at cryogenic temperatures and it was found that the cell reactivity decreased with decreasing temperature.

7.1.1 PUNCTURE AND CRUSHING

The results of puncture and crushing tests for a broad range of low rate Li/SOCl₂ cells have been widely reported (47,54,59,61). Both tests are basically short circuit tests but the crushing test is more severe because the lithium anode is sheared and scraped removing any protective LiCl film and increasing the area. Such tests are by their nature very uncontrolled and it is not recommended that more than a few cells of any new design be subjected to crushing and puncture tests.

Generally high rate Li/SOCl₂ cells would be expected to undergo thermal runaway during crushing whereas low rate cells would undergo some heating but would not explode. For example, lithium limited bobbin-type D size cells were subjected to a crush test by Goebel and co-workers (47) and no venting or explosion was observed.

7.3 THERMAL ABUSE

Thermal abuse tests have been reported for both cylindrical (53,59,47) and prismatic (60,59,47) Li/SOCl₂ cells. In the future it is recommended that such tests should be carried out for smaller cells using the whole cell differential thermal analysis technique described by Dey (26,39).

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2. The test program recommended earlier to evaluate the hazards of electrolyte limited low rate Li/SOCl₂ cells should be continued and expanded to include a similar matrix of tests with high rate spiral wound C size cells.
3. The test program recommended earlier to evaluate the shock sensitivity of overdischarged low rate carbon limited cells should be continued and expanded to include a similar matrix of tests with high rate spiral wound C size cells.
4. The safety hazards associated with charging and overdischarge should be investigated by carrying out DTA studies with high rate D size cells over a range of lithium areas and electrolyte-to-carbon volume ratios. The DTA measurements would be carried out using both carbon and lithium limited overdischarged cells using undischarged cells as references.
5. The use of metal tabs on the anode and cathode to localize Li dendrite growth and prevent thermal runaway during carbon limited discharge as described in a recent patent (41) should also be investigated. Very little information about this interesting design modification has been published and a thorough study would help resolve some of the doubts about the hazards of overdischarged carbon limited cells.
6. Heat transfer processes in high rate Li/SOCl₂ cells with neutral electrolyte should be investigated with an equal amount of time devoted to mathematical modeling and experimental work. The internal dimensions of individual cells should be measured by x-ray tomography and the data put into the model prior to short circuit tests to predict the thermal behavior of the cell. A number of new approaches based on the above work should be evaluated to improve thermal management during high rate discharge.

4. Basic studies of the chemistry of the Li/SOCl_2 cell would be of general value for both low and high rate applications but should be given a lower priority because such work will require much work to achieve what is expected to be minimal benefits. However, it is difficult to anticipate the benefits of research of this type.

The heat evolved by the SO_2 solvation reaction with $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte (see Eq. 13, Section 3.3) should be measured by standard calorimetric techniques and the composition of the products determined by Raman spectroscopy and/or other techniques. The stoichiometry of electrolyte oxidation and the side reactions that occur during anode limited overdischarge and charging should be investigated using the multiple low temperature extraction procedure developed during the present contract (11). The electrolyte extracts should be analyzed by quantitative FT-IR to determine the concentrations of SO_2 , AlCl_3 , Cl_2 , SO_2Cl_2 , and S_2Cl_2 .

Recommendations for High Rate Cells. -

1. The outstanding high rate capabilities of the Li/SOCl_2 electrochemical system can not be safely utilized in active (i.e., none reserve) cells because high rate cells undergo thermal runaway and explode if short circuited or subjected to other types of abuse. It is recommended that a substantial priority effort be undertaken to develop new technology to eliminate the thermal runaway hazard so that the outstanding high rate capabilities of the Li/SOCl_2 cell can be utilized. The new technology required to control thermal runaway would probably take the form of electrolyte additives, microencapsulated electrode poisons, or special thermally sensitive separators similar to those described in several recent patents (46,56). Since much progress has already been achieved in developing this emerging technology that has not been published, it is likely that some practical method of controlling thermal runaway could be demonstrated with a program requiring between two- to six-person years to complete.

safety hazard begins for high rate cells which can deliver their nominal capacity at a power density of approximately 45 watts/liter for a C size spiral wound cell. The safe power density would be expected to decrease proportionally with larger cells.

The type of future investigations to reduce the hazards of Li/SOCl_2 cells that should be given priority will depend a great deal on the specifications of the battery application for which new work is directed. Accordingly, our recommendations will be organized into two large groups. The first group will be of general benefit and of benefit to low rate cells. The second group will be of benefit for high rate active cells.

Recommendations for Low Rate Cells.-

1. The possibility that overdischarged carbon limited cells may be shock sensitive is a safety hazard that needs to be investigated. Low rate cells fitted with thermocouples should be overdischarged at various rates at temperatures from -40°C to 25°C then subjected to increasing shock forces. Cells with electrolyte-to-carbon ratios close to the minimum electrolyte required up to an excess of approximately 50% should be included in the test matrix. The cells should be disassembled and examined for burn marks.
2. Very little data has been published concerning the safety hazards of electrolyte limited cells during overdischarge. A full range of abuse tests should be carried out with electrolyte limited cells overdischarged at various rate and temperature conditions. Full cell DTA tests would be especially valuable and should be given priority.
3. Differential scanning calorimetry (DSC) should be undertaken with Li dendrites formed in $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte. The Li dendrites would be mixed with SOCl_2 or $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte and other components such as S, C, Li_2S , and glass separator added in a systematic series of tests. The studies outlined in Items 1-3 above, probably could be completed with an effort of one person-year or less.

10. CONCLUSIONS AND RECOMMENDATIONS

Low rate Li/SOCl_2 cells with thick cathodes have a negligible safety hazard under even the most severe mechanical or electrical abuse conditions such as short circuit or crushing. Small cells up to 1.8 Ahr are seriously being considered for consumer applications (73). However, high rate Li/SOCl_2 cells with thin electrodes, capable of power densities over approximately 45 watts/liter, can undergo thermal runaway and explode if subjected to electrical abuse such as short circuit or high rate cathode limited overdischarge. A number of other mechanical and thermal abuse conditions can also initiate thermal runaway in high rate cells.

The only intrinsic safety hazard of low rate Li/SOCl_2 cells is the possibility that a very young or thoughtless person might try and open the steel cell case while trapped in a small enclosed space and might suffer the toxic effects of SOCl_2 vapor. Exposure to SOCl_2 vapor causes an intense burning irritation of the mucous membranes of the eyes, nose, and throat which is usually sufficient to initiate prompt evacuation from contaminated atmospheres long before severe effects are produced (see Section 9.1). Only a few additional laboratory studies of low rate Li/SOCl_2 cells are recommended to clear up the few minor doubts about the hazards of low rate cells.

The safety hazards of high rate cells can be reduced by the use of vents, internal fuses and diodes. However, such cells must still be regarded as extremely dangerous because the effectiveness of such devices has not been established over the entire range of abuse conditions such as crushing, overdischarge and shock. Even if such devices are demonstrated to be effective the margins of safety will probably be small and high standards of manufacturing quality control will have to be determined and maintained.

The dividing line between the safe low rate design and the hazardous high rate designs depends mainly on the cathode thickness but the size of the cell, the internal configuration of the electrodes, and the presence of cathode catalysts also determines whether the cell is safe during abuse conditions. A

The human toxicology of lithium compounds has been thoroughly investigated relative to their use to treat manic depressive illness. The therapeutic level of 300 mg of lithium carbonate is close to the toxic level (81).

9. THE TOXICITY OF LITHIUM-THIONYL CHLORIDE BATTERY COMPONENTS

9.1 THIONYL CHLORIDE ELECTROLYTE

The environmental and health hazards that may be encountered after the accidental release of the electrolyte from batteries of 10,000 Ahr Li/SOCl₂ cells have been presented by Rydz (77). Concentrations high enough to cause serious acute health hazards are preceded by intense, burning irritation of the mucous membranes of the eyes, nose, and throat. This is usually sufficient to initiate prompt evacuation from contaminated atmospheres long before severe effects are produced. Exceptions to this occur when victims are prevented from escaping or when hypersensitive personnel are exposed.

Unfortunately, very little information regarding the specific dose-response relationship exists for thionyl chloride. Sax (78) states that SOCl₂ is more toxic than SO₂, noting that a 20 minute exposure of 17.5 ppm is fatal to cats. However, the validity of this figure is questionable due to the lack of additional data to confirm it. The only other dose - specific information for SOCl₂ is its well accepted threshold limit value (TLV) of 5 ppm for humans (79). A TLV is the lowest concentration having toxic effects.

9.2 LITHIUM AND OTHER BATTERY COMPONENTS

The main health hazard associated with lithium and other battery components is the possibility of fire if lithium is exposed to water or ignited by sparks. Lithium scrap from battery assembly, if reacted with water for disposal, can create a cloud of steam containing LiOH/H₂O droplets that are very irritating to the mucous membranes of the nose and throat. Rapid hydrolysis of lithium should be generally avoided because of the hazard of a hydrogen explosion. However, should rapid lithium hydrolysis become necessary, it should be carried out in a fume hood.

A disposal procedure (74) has also been developed for 10 KAh cells that have become damaged due to mechanical abuse which involves cooling the cell with liquid nitrogen so that it can be safely transported to a deactivation site. The physical and chemical characteristics of the Li/SOCl₂ electrochemical system between ambient and 77°K were investigated during the present contract (75,76) and it was found that the system is totally inactivated at liquid nitrogen temperatures. Liquid nitrogen can also be used to freeze small numbers of Li/SOCl₂ cells which can then be cut open so that the SOCl₂ can be removed.

Since the cost of disposal rather than the technology is the major area requiring improvement, no further research is recommended at the present time. However, improved documentation of procedures for the disposal of intermediate size cells (i.e., 1.5 to 100 Ahr) and reserve cells would be valuable.

8. SHIPPING AND DISPOSAL

8.1 SHIPPING

The packaging and shipment of lithium cells depends on the size of the cell and the applicable government regulations are described in the ninth revision of the Department of Transportation Regulation DOT-E 7052, dated August 29, 1980.

8.2 DISPOSAL AND DISASSEMBLY

The technology of cell disposal is very well developed (74,80) and currently the only areas of improvement involve cost, documentation of procedures and the availability of trained personnel. Very small Li/SOCl₂ cells can be disposed of in sanitary landfill and recently Altus Corporation announced (73) that they received permission from the State of California for disposal of 1.8 Ahr, 9V, Li/SOCl₂ 1604 size consumer batteries in sanitary landfill.

The disposal of lithium batteries is now a commercial business and Radiac Research Company of Brooklyn, NY will dispose of lithium cells shipped to them in 30 gallon steel barrels. The barrels are limited to six lbs of batteries per 30 gallon barrel and the cost of disposal is \$160 per barrel. Radiac is EPA approved (EPA License No. NY D049178296) and they in turn have the batteries disposed of by Battery Disposal Technology, Inc., of Clarence NY.

A number of techniques were evaluated by GTE for the disposal of lithium limited 10 KAh cells and it was found that low rate resistive discharge to 0.00V followed by a hydrostatic burst of the cell was the safest and most convenient technique (74). The cell is held in special fixtures and splits at the bottom and is flushed with sodium carbonate/water solutions for 21 days. Finally, the acid solution is neutralized to the correct pH to meet EPA disposal regulations.

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