Safety of Li-$SOCl_2$ Cells

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The safety of lithium thionyl chloride cells has been a concern of JPL for some time in our development of these cells for NASA's use. Because the safety problems are complex and several issues are interrelated it was decided that it would be best to put together an organized review of the safety issues. This paper is intended to address these issues.

Figure 1

In the first viewgraph we point out that we are aware of certain problems that limit the use of Li-$SOCl_2$ cells. These include the unsafe behavior, poor performance at high rates and the fact that at the present time the cells do not meet the reliability requirements for space use.

Figure 2

Generally, hazards can be classified in three broad categories; 1) Cell leakage - a problem dealing with construction or materials, 2) venting of toxic gases through seals and welds - considered a mild hazard in which electrolyte and gas is released and 3) the unfortunate violent rupture or controlled rupture of cell with the possibility of explosion of the materials inside.

Figure 3

The next two viewgraphs are an overview of the areas by which hazards can occur. The first is the user-induced type which as you see from the figure involves the operation of the cell or its equipment. There are also two types of abuse:

1. Electrical
2. Mechanical/physical

As you can see the electrical and mechanical/physical type are considered hazardous.

Figure 4

In the next viewgraph we summarize the conditions for which the manufacturer has responsibility. These are in two areas which are referred to as cell design and/or quality control. We will be talking about these as we go along further in this paper.

Figure 5

The next viewgraph is quite simple in that it merely relates the fact that heat is generated, by drawing current out of the cell or battery; new chemical reactions are initiated and both add to the involvement of the potential hazards.

Figure 6

Here we present the influence of discharge rate on cell performance. First of all we know that the cell can be discharged at the C/10 discharge rate safely provided it is in an environment where the heat can dissipate. Secondly, we note that cell performance decreases as the discharge rate increases. This is seen in both capacity and voltage. The problem arises when we start to discharge at higher rates and here the cells, if not designed properly and especially without adaquate thermal dissipation, can undergo venting or explosion.

Figure 7

In this chart we break down the influence of discharge rate on safety. As you can see at less than the C/10 rate the cells are safe. At rates of C/10 – C/2 there is a probability of heat buildup as temperature increases, and if temperature increases the pressure increases. Both SO_2 gas and $SOCl_2$ vapor increase thus increasing the possibility of venting if the heat is not adequately dissipated. At very high discharge rates, e.g. > C/2, heat is obviously generated rapidly. The temperature increases, there is a greater possibility of lithium melting and reacting with the $SOCl_2$ and thus there is high probability of venting and violent rupture.

Figure 8

The various explanations reported for the unsafe behavior of Li-$SOCl_2$ cells during discharge fall into three categories. They are pressurization, thermal runaway and hazardous intermediates. The discharge rate causes the internal cell temperature to rise. The gaseous products and $SOCl_2$ vapor expand rapidly, thereby raising the internal pressure of the cell. Secondly, the thermal runaway mechanism is based on the fact that new exothermic reactions can occur at elevated temperatures resulting in a cell rupture or even explosion. Presently it is believed that thermal runaway of a Li-$SOCl_2$ cell is due to the reaction between molten lithium (MP > 181°C) and $SOCl_2$. It has been reported that hazardous intermediates such as SO, (SO)n, OCLS or Li_2O_2 are formed during discharge which may be responsible for the unsafe behavior of these cells. Many previously discussions have been held on these issues.

Figure 9

What is the affect of temperature? We see that at temperatures of −20 to 60°C cells operate safely as long as the current is less than the C/10 rate. They do lose capacity on storage, particularly at higher temperatures. They can undergo venting or even explosion if they are discharged at temperatures higher than +80°C. They may also exhibit poor performance at lower temperatures.

Figure 10

This chart breaks down the effect of temperture on safety. At low temperatures, conductivity and mass transport in the electrolyte decrease, resulting in increased cell internal impedance (polarization loss) and carbon electrode passivation (capacity loss). Safety problems have not been reported thus far for low temperature operation. For ambient temperature conditions, refer to figure 8. At the higher temperatures (> +80°C), even at low rates , gas expands, pressure increases and venting is probable. At +130°C, sulfur can react with $SOCl_2$ to give extra heat, again the pressure increases and venting probable. At +181°C or greater we know that the lithium melts and can react with the constituents of the cell, especially thionyl chloride. It is possible that there could be a violent rupture.

Figure 11

In this figure we summarize the causes for unsafe behavior at low and high temperatures. At low temperatures, it suggests that an increase in polarization due to lR and an increase in stability of hazardous intermediates are possible which at high rates can lead to hazardous conditions. At high temperatures, higher pressures leading to venting is possible. Thermal runaway is also possible when violent reactions,such as molten lithium reacting with $SOCl_2$ occurs.

Figure 12

Here we address the subject of the effect of an external short-circuit on cell safety. In Bobbin type construction which has limited surface area, the rate is self limiting and there is little possibility for a short circuit to result in a serious problem. Spiral wound construction cells have been found to vent, or even explode in a short-circuit.

Figure 13

At high rates of discharge such as that occuring in a cell under a short-condition, cells experience large I^2R heating due to the relatively poor conductivity of the electrolyte. The increase in internal cell temperature can lead to melting of lithium, which in turn can react with $SOCl_2$.

Figure 14

The subject of the effect of forced overdischarge on safety is addressed in this figure. We know that venting or explosion can occur if a cell is reversed. This has been one of the more serious problems. During discharge one cell in a series string which is either not operating properly or has lower capacity can be forced into reversal by the other cells in the series. Certain results indicate that after a cell has been driven into reversal and allowed to stand for a time that it may be sensitive to shock as well.

Figures 15

The effect of forced overdischarge reversal on cell safety depends to significant extent on cell design which determines whether a cell is lithium limited, carbon limited, or $SOCl_2$ limited. The three different mechanisms are discussed in this figure. For the lithium limited cell, lithium is depleted first, resulting in substitute reactions taking place at the anode. The predominant reaction is the oxidation of the electrolyte ($SOCl_2$) producing Cl_2. SO_2Cl_2, SCl_2, and $AlCl_3$. Reducion of Cl_2 produced takes place at the cathode prefentially to $SOCl_2$ reduction resulting in the formation of LiCl. The LiCl reacts with $AlCl_3$ and $SOCl \cdot AlCl_4^-$ resulting in the formation of $LiAlCl_4$ and $SOCl_2$. These reactions being exothermic in nature, produces heat which raises the cell temperature during the reversal process. If reversal currents are very low the cell can be considered safe.

In carbon-limited cells, the end of cell life is brought about by the passivation of the carbon electrode. During reversal oxidation of lithium continues to take place at the anode while at the cathode the reduction of lithium ions (Li^+) is favored. Two possibilities exist relative to cell safety. It is possible for the lithium deposited by the carbon electrode to react with $SOCl_2$. If this occurs, depending on the reversal current, heat is generated and the temperature of the cell increases. At low rates the cells can be considered safe. An alternative mechanism that can occur in the carbon-limited cells is the formation of internal short-circuits formed by lithium dendrite bridging. In such a case the dendrites can carry the short-circuit current directly to the anode thus avoiding chemical and/or electrochemical reaction and I^2R heat generation. On open-circuit stand, it is reported that these dendrites are responsible for the observed shock sensitivity.

In the $SOCl_2$-limited cells the end of cell life is brought about by the depletion of $SOCl_2$. In such cells the I^2R heating results in an increased temperature of the cell. At elevated temperatures exothermic reactions are possible resulting in cell thermal runaway.

Figure 16

The various theories for unsafe behavior of Li-$SOCl_2$ cells on reversal are summarized in this viewgraph.

Figure 17

On the matter of the effect of charging on safety and performance, cells gain little or no additional capacity during the charge period. However, there is some increase in temperature and one would expect also some increase in pressure so that there could be some venting.

Figure 18

The problems associated with physical and mechanical abuse are shown here. We note that crushing or puncturing can either lead to venting or internal shorts which are a serious concern. Intense heat can generate undesirable reactions as we noted before with melting lithium reacting with sulfur and/or thionyl chloride. Obviously, these are of concern to us and care must be exercised in cell handling, storage and transportation.

Figure 19

Vibration and shock requirements must be considered for NASA missions. Cells must meet these requirements in order to be considered for use. Before use testing would be required to verify the structural integrity of the cell and battery over a range of vibration and shock regimes.

Figure 20

This is a look at the manufacturer-induced factors. In general, the cells are optimized for performance, not for safety. They may not have an adequate amount of electrolyte and current distribution may not optimized. The extremely important thermal dissipation requires improvement, additional "cell-overhead" volume to maintain the extra thionyl chloride would be desireable, and there is a possibility that redundant terminal connections could be an enhancement. In terms of Quality Control, material purity is always a concern, especially in performance, but sometimes in safety. Contamination by moisture and other constituents during the assembly of the components can occur.

The handling and assembly process itself needs to be better controlled.

Figures 21 & 22

The conclusions are summarized in the following two viewgraphs. With regard to fundamental issues there are a number of items listed that require further attention to explain what is happening in the cell. We consider the fact that the cell design may not be optimized for the application at high rate and we need to better involve ourselves in the actual design whether it be thermal, structural or the most significant one, the optimization of the ratio of lithium, carbon and thionyl chloride.

Figure 23

Finally, the processing and Quality Control of materials require adequate consideration. Material purity and handling of quality control is important to us as well as the use of some nondestructive methods to determine the health of the cell. The last item is one that we feel is extremely important. Education is an extremely important facet of this effort. We believe that it is important that all people that come in contact with these cells or the materials, whether it be on the assembly line, quality control, operation, test, the user or the equipment designer be aware of the safety issues and that all understand fully the problems associated with these devices. This may be relatively straight forward for a NASA mission which is a controlled activity but more difficult for other applications. However, educating all those involved can enhance the safety and reliability of cells in the future. We need to better understand the chemistry and the safety issues as they develop and we believe, as we have indicated in this particular discussion, that the lithium thionyl chloride cell can be built safely and operate safely when all of the concerns are addressed. Further, the design is such that the hazard conditions described will not be reached in the applications. Thank you

Present Limitations of Li-$SOCl_2$ Cells

<u>CELLS REPORTEDLY</u>:

- EXHIBIT UNSAFE BEHAVIOR UNDER CERTAIN CONDITIONS
- EXHIBIT POOR PERFORMANCE AT HIGH RATES OF DISCHARGE
- DO NOT MEET THE RELIABILITY REQUIREMENTS OF NASA

Figure 1.

Classification of Hazards of Li-$SOCl_2$ Cells

- LEAKAGE OF ELECTROLYTE THROUGH SEALS AND WELDS
- VENTING OF TOXIC GASES AND ELECTROLYTE THROUGH SEALS AND WELDS
- VIOLENT OR CONTROLLED RUPTURE OF CELL WITH EXPULSION OF TOXIC MATERIALS SOMETIMES EXPLOSIVELY WITH FIRE

Figure 2.

Analysis of the Factors Responsible for Unsafe Behavior of Li-$SOCl_2$ Cells

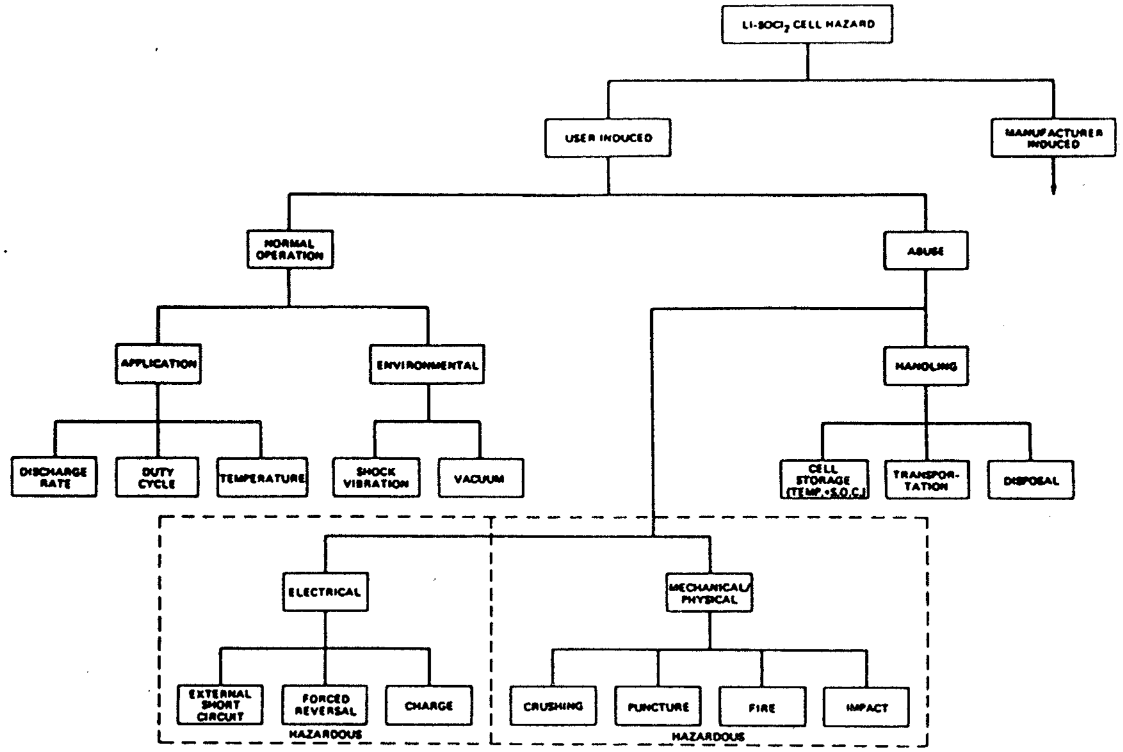


Figure 3.

Analysis of the Factors Responsible for Unsafe Behavior of Li-$SOCl_2$ Cells

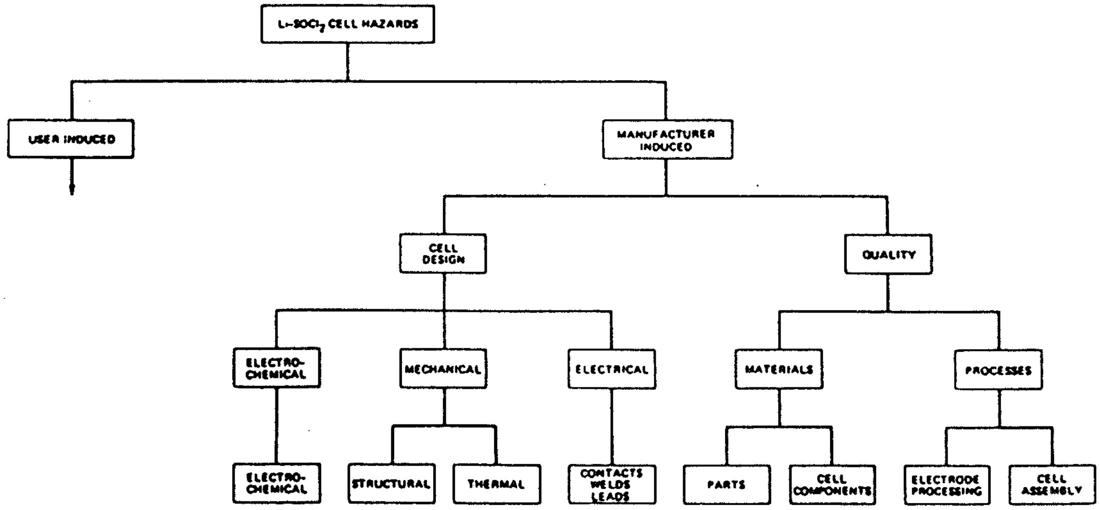


Figure 4.

Proposed Mechanism for the Unsafe Behavior of Li-$SOCl_2$ Under High Rates of Discharge/Short Circuit/Forced Over Discharge

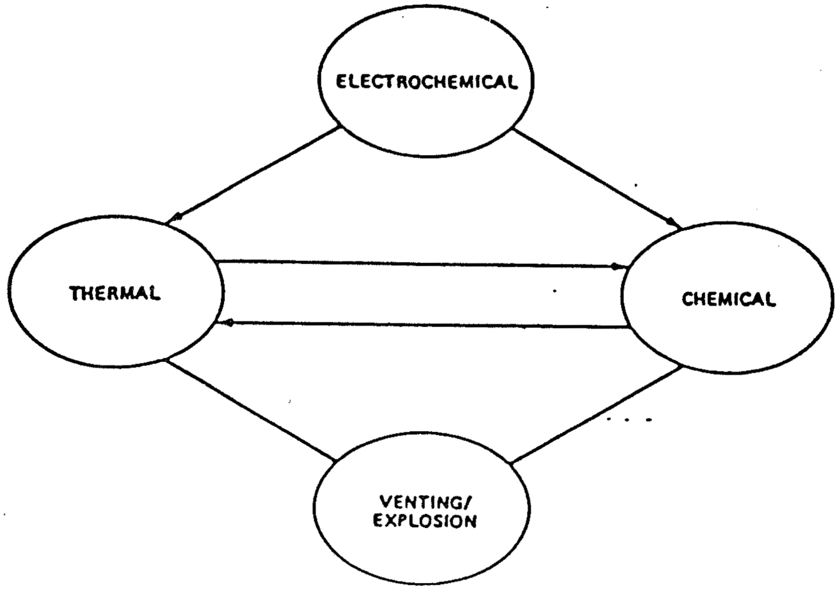


Figure 5.

Effect of Discharge Rate

- CELL CAN BE USED SAFELY UP TO C/10 DISCHARGE RATES
- CELL PERFORMANCE DECREASES (CAPACITY AND OPERATING VOLTAGE) WITH THE INCREASE OF DISCHARGE RATE
- CELLS MAY VENT OR EXPLODE IF DISCHARGED AT RATES HIGHER THAN C/3

Figure 6.

Influence of Discharge Rate on Safety

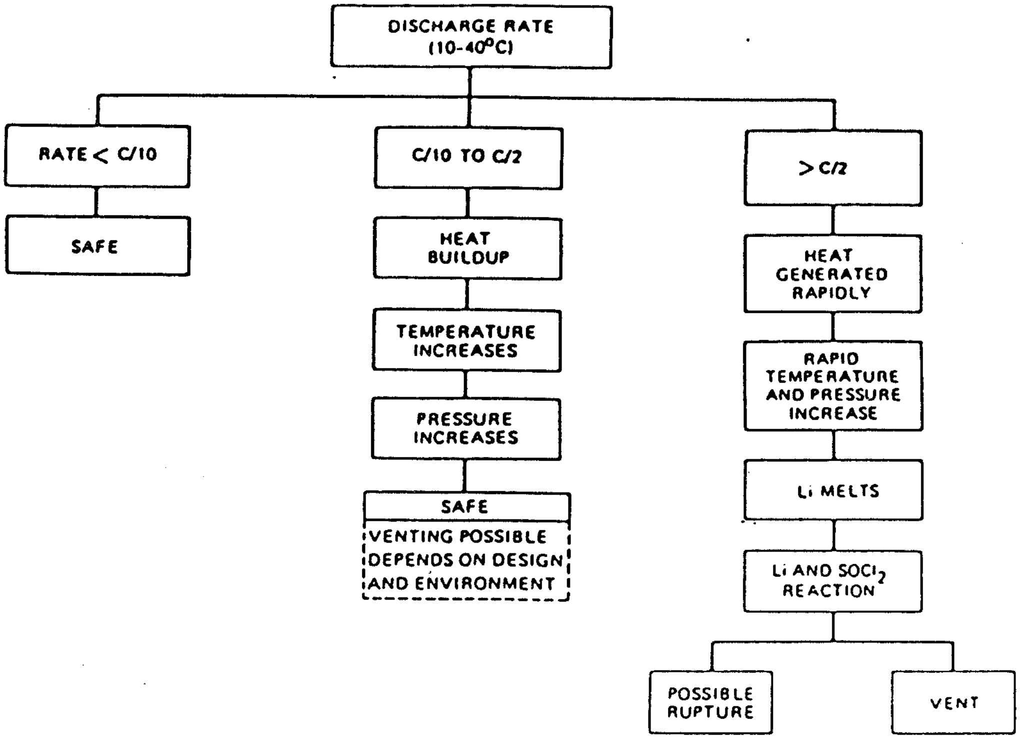


Figure 7.

Proposed Theories to Explain the Unsafe Behavior of Li-$SOCl_2$ Cells During Discharge

PRESSURIZATION

- CELL PRESSURE INCREASES DUE TO $SOCl_2$ VAPORIZATION AT HIGHER TEMPERATURES AND FORMATION OF GASEOUS DISCHARGE PRODUCTS

THERMAL RUNAWAY

- ELECTROCHEMICAL AND OTHER PARASITIC CHEMICAL REACTIONS RAISE THE CELL INTERNAL TEMPERATURE
- AT ELEVATED TEMP EXOTHERMIC REACTIONS POSSIBLE (Li + S, S + $SOCl_2$, MOLTEN Li + $SOCl_2$)
- FORMATION OF GASEOUS PRODUCTS AND TEMPERATURE LEAD TO CELL VENTING/EXPLOSION

HAZARDOUS INTERMEDIATES

- SO, (SO)N OCIS, AND Li_2O_2 ARE REPORTED TO BE FORMED DURING DISCHARGE AND THEY MAY LEAD TO UNSAFE BEHAVIOR

Figure 8.

Effect of Temperature

- CELLS CAN BE DISCHARGED SAFELY AT RATES < C/10 AT -20 TO 60°C
- CELLS LOSE CAPACITY ON STORAGE AT TEMPERATURES HIGHER THAN 45°C
- CELLS MAY VENT OR EXPLODE IF DISCHARGED AT TEMPERATURES HIGHER THAN 80°C
- CELL EXHIBIT POOR PERFORMANCE AT LOWER TEMPERATURES
- CELLS KEPT AT LOWER TEMPERATURES WERE REPORTED TO VENT (OR EXPLODE) WHEN WARMED UP

Figure 9.

Influence of Temperature on Safety

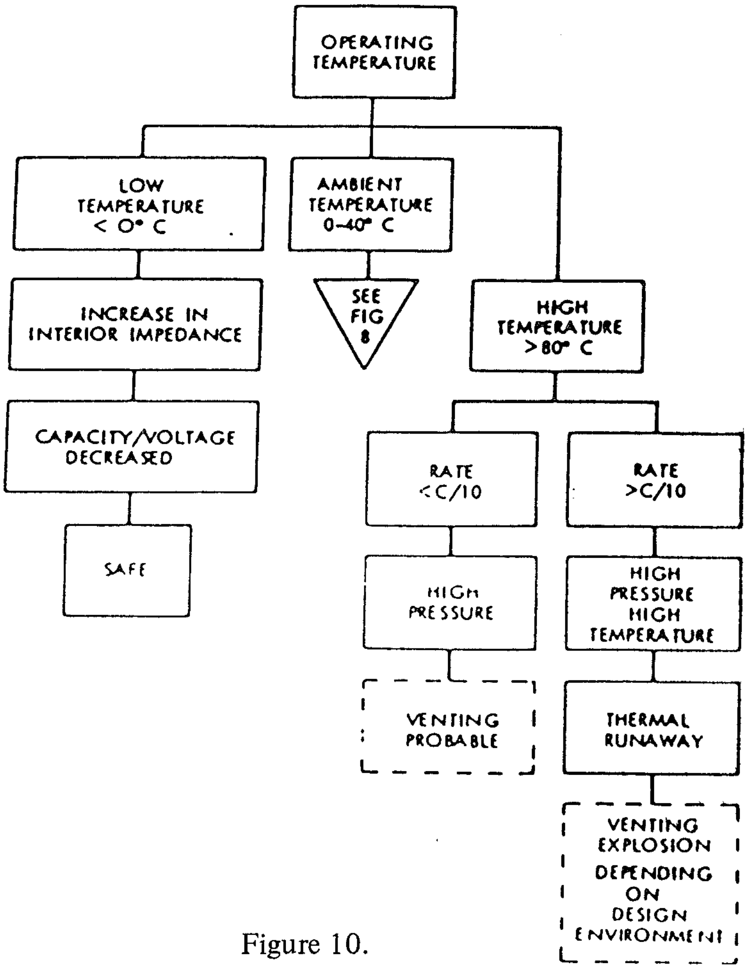


Figure 10.

Proposed Theories to Explain the Unsafe Behavior of Cells at Low and High Temperatures

LOW TEMPERATURE

- THE INCREASE IN IMPEDANCE LEADS TO POLARIZATION AND EARLY FAILURE
- INCREASE IN STABILITY OF HAZARDOUS INTERMEDIATES MAY LEAD TO UNSAFE BEHAVIOR

HIGH TEMPERATURE

- INCREASE IN INTERNAL PRESSURE
- > 80°C VENTING
- THERMAL RUNAWAY DUE TO
  - (S + $SOCl_2$ REACT EXOTHERMICALLY (130°C)
  - (MELTED Li REACTS WITH $SOCl_2$ (190°C)

Figure 11.

Effect of Short Circuit on the Safety of Li-$SOCl_2$ Cells

- CELLS OF BOBBIN TYPE CONSTUCTION POSE NO PROBLEMS UPON SHORT CIRCUIT
- CELLS OF SPIRAL WOUND CONSTUCTION WILL VENT/EXPLODE UPON SHORT CIRCUIT

Figure 12.

Causes for the Unsafe Behavior of Li-$SOCl_2$ Cells Under Short Circuit Conditions

- POOR ELECTRICAL CONDUCTIVITY OF THE ELECTROLYTE
- LOW MELTING POINT OF LITHIUM
- POOR THERMAL DISSIPATION

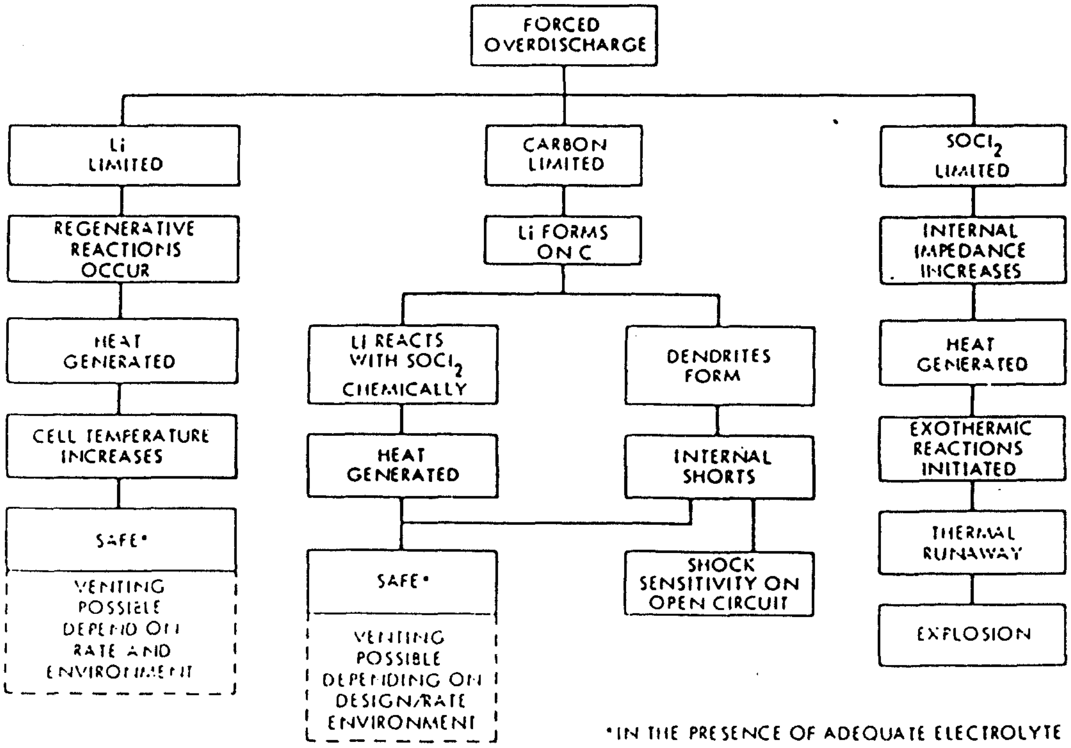
Figure 13.

Effect of Forced Over Discharge on the Safety of Li-$SOCl_2$ Cells

- **CELLS MAY VENT OR EXPLODE**
- **CERTAIN RESULTS INDICATE THAT CELLS DRIVEN INTO REVERSAL ARE SENSITIVE TOWARDS SHOCK**

Figure 14.

Influence of Cell Reversal on Safety



*IN THE PRESENCE OF ADEQUATE ELECTROLYTE

Figure 15.

Proposed Theories to Explain the Unsafe Behavior of Li-$SOCl_2$ Cells During Forced Over Discharge

CARBON LIMITED CELLS

- o HIGH REACTIVITY OF Li DENDRITES WITH $SOCl_2$ AT THE CARBON ELECTRODES
- o FORMATION HAZARDOUS INTERMEDIATES (Li_2O_2)

LITHIUM LIMITED CELLS

- o FORMATION OF HAZARDOUS INTERMEDIATES (Cl_2))
- o COMPLEX CHEMICAL REACTIONS

$SOCl_2$ LIMITED CELLS

- o FORMATION OF DRY SPOTS
- o MANY EXOTHERMIC REACTIONS POSSIBLE (EX Li + S, Li + GLASS PAPER ETC.)

Figure 16.

Effect of Charge Rate on the Performance and Safety of Li-$SOCl_2$ Cells

- o LITTLE OR NO ADDITIONAL CAPACITY
- o MARGINAL INCREASE IN CELL TEMPERATURE
- o CELLS WITH CRIMPED SEALS MAY VENT

Figure 17.

Causes for the Unsafe Behavior of Li-$SOCl_2$ Cells During Physical/Mechanical Abuse

- CRUSHING OR PUNCTURING LEADS TO
  - RELEASE OF TOXIC MATERIALS
  - INTERNAL SHORTING - VENTING
- INTENSE HEATING WITH FLAME
  - PRESSURE INCREASE DUE TO VAPOR PRESSURE OF Li-$SOCl_2$
  - EXOTHERMIC REACTIONS BETWEEN ..

    Li, S, AND $SOCl_2$ (AT 130°C)
    Li AND $SOCl_2$ (AT 190°C)

Figure 18.

Influence of Vibration, Shock and Spin on the Performance and Safety of Li-$SOCl_2$ Cells

- CELLS CAN MEET THE REQUIREMENTS OF MOST LAUNCH ENVIRONMENTS
- CELLS DRIVEN INTO REVERSAL ARE REPORTED TO BE SENSITIVE TOWARDS SHOCK

Figure 19.

Analysis of Manufacturer-Induced Factors on the Safety of Li-$SOCl_2$ Cells

DESIGN

- NOT OPTIMIZED FOR SAFETY
- INADEQUATE QUANTITY OF ELECTROLYTE
- NON-UNIFORM CURRENT DISTRIBUTION
- POOR THERMAL DESIGN
- INSUFFICIENT OVERHEAD VOLUME
- NO REDUNDUNCY OF TERMINAL CONNECTIONS

QUALITY CONTROL

- IMPURE MATERIALS
- CONTAMINATION OF ELECTRODES AND OTHER COMPONENTS DURING STORAGE AND/SPACE HANDLING
- INEFFECTIVE OF QUALITY CONTROL PROCEDURES

Figure 20.

Conclusions

SAFE Li-$SOCl_2$ CELLS CAN BE DEVELOPED FOR NASA APPLICATION

FUNDAMENTAL ISSUES: TO BE ADDRESSED

- CHEMISTRY OF THE OELLS DURING DISCHARGE AND REVERSAL AT VARIOUS TEMPERATURES AND DISCHARGE RATES
- ROLE OF INTERMEDIATES (OCIS, Li_2O_2 ETC.) IN CELL SAFETY
- CHEMISTRY OF ELECTROLYTE LIMITED CELLS
- THERMAL ANALYSIS OF Li-$SOCl_2$ CELLS DURING REVERSAL
- CORRELATION OF CARBON ELECTRODE CHARACTERISTICS AND ITS PERFORMANCE
- INVESTIGATION OF NEW ELECTROLYTES WITH IMPROVED CONDUCTIVITY
- INFLUENCE OF ADDITIVES/CATALYSTS FOR IMPROVING PERFORMANCE AND SAFETY

Figure 21.

Conclusions (Con't)

CELL DESIGN: CONSIDERATIONS

- **DESIGN FOR SAFETY, FIRST -- THEN PERFORMANCE**
  - **OPTIMIZATION OF ELECTROLYTE COMPOSITION AND QUALITY**
    - **TO ACCOUNT FOR NORMAL DISCHARGE**
    - **TO SUSTAIN CONDUCTIVITY DURING DISCHARGE AND REVERSAL**
    - **TO KEEP DISCHARGE PRODUCTS IN SOLUTION**
- **OPTIMIZATION OF ELECTRODE CAPACITY (Li/C) RATIO**
  (LITHIUM LIMITED DESIGN POSSIBLE ONLY FOR LOW RATE CELLS)
  (CARBON LIMITED DESIGN IS THE ONLY CHOICE FOR HIGH RATE CELLS)
- **MINIMIZE CURRENT DISTRUBUTION PROBLEMS**
- **OPTIMIZE THERMAL MANAGEMENT**
- **UTILIZE CORROSION RESISTANT SEALS**
- **USE THERMAL RESISTANCE FUSES**

Figure 22.

Conclusions (Con't)

- PROCESSING AND QUALITY CONTROL: CONSIDERATION
  - MATERIAL PURITY REQUIREMENTS
  - IMPROVEMENT OF HANDLING, PROCESSING AND ASSEMBLY TECHNIQUES
  - DEVELOPMENT AND IMPLEMENTATION OF A EFFECTIVE QUALITY CONTROL PROGRAM
  - DEVELOPMENT OF N.D.T. METHODS TO DETERMINE THE HEALTH OF THE CELL
- EDUCATION OF THE USER

Figure 23.