(12)

GTE

INORGANIC ELECTROLYTES

by

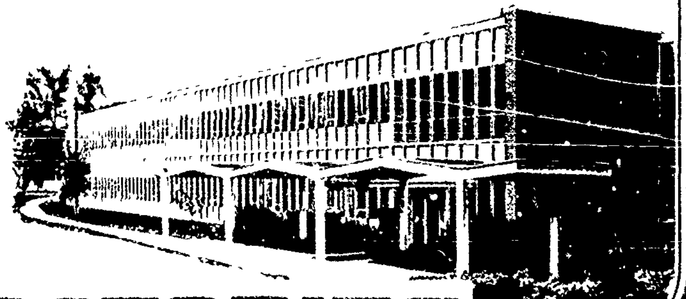
M. Domeniconi
K. Klinedinst
N. Marincic
C. Schlaikjer
R. Staniewicz
L. Swette

Contract No. N00014-76-C-0524 new

INTERIM REPORT
From January 1976 to October 1977

Submitted to

OFFICE OF NAVAL RESEARCH
Arlington, Virginia



GTE LABORATORIES
INCORPORATED

⑥
INORGANIC ELECTROLYTES,

by

⑩ M. Domeniconi,
K. Klinedinst,
N. Marincic,
C. Schlaikjer
R. Staniewicz
L. Swette

⑮ ~~Contract No~~ N00014-76-C-0524 ✓

⑨ INTERIM REP[redacted]T.
~~From~~ Jan[redacted] [redacted]76 [redacted] Oct[redacted] [redacted]77,

⑫ 104p.

Submitted to

OFFICE OF NAVAL RESEARCH
Arlington, Virginia

⑪ Oct 77

GTE LABORATORIES INCORPORATED
40 Sylvan Road
Waltham, Massachusetts 02154

406462

DISTRIBUTION STATEMENT A
Approved for public release;

ACCESSION for
NTIS White Section ☒
DDC Buff Section ☐
UNANNOUNCED ☐
JUSTIFICATION Letters on file
BY
DISTRIBUTION/AVAILABILITY CODES
Dist. AVAIL. and/or SPECIAL
A

ABSTRACT

A variety of subjects under the general heading of "Inorganic Electrolytes" have been investigated during the course of this program. These are presented as six separate studies summarized below.

PART I. ANALYSES OF THE HAZARD POTENTIALS OF VARIOUS REACTION MODES AND MATERIALS INCIDENTAL TO THE OPERATION OF $Li/SOCl_2$ CELLS

The hazards associated with the operation of $Li/SOCl_2$ cells arise upon disruption of the cell case by external physical damage, corrosion or internal over-pressurization. Only the last mechanism was examined in this study. Over-pressurization can proceed in a gradual manner resulting finally in failure of the cell case and the release of active cell materials, or the over-pressurization can occur rapidly resulting in violent disintegration of the cell. The mechanisms of over-pressurization can be separated into two general categories according to the source of pressure; (1) thermal mechanisms and (2) gas generation mechanisms.

Thermal mechanisms operate by vaporization and thermal expansion primarily, and the thermal sources may be external to the cell or internal. The internal thermal sources may be electronic short circuits, ohmic polarization effects, or exothermic chemical combination reactions (e.g., between the cell reactants, $Li + SOCl_2$; or between reactants and products or other materials, $Li + SO_2$, $SOCl_2 + Li_3N$ etc.). Any thermal source that does not raise the cell temperature above the boiling point of thionyl chloride produces a relatively low pressure increase ($\sim$15 lb/in.^{2}g), but could result in failure of the case in a prismatic cell configuration. Further heating to near the melting point of lithium would generate pressures in the range of 150 lb/in.^{2}g - 200 lb/in.^{2}g. Any thermal source that raises the cell temperature above the melting point of lithium could initiate any one of several exothermic chemical combination reactions resulting in explosive over-pressurization. Other exothermic chemical reactions, that do not involve lithium metal, probably can occur over a wide temperature range and are initiated or inhibited by other factors which have not been established.

Gas generation mechanisms of over-pressurization may be based on chemical sources or electrochemical sources. An electrochemical source is the gaseous discharge product, SO_2. Chemical sources could be gaseous thermal decomposition products (e.g., the decomposition of $SOCl_2$ producing SO_2 and Cl_2), or gaseous chemical reaction products (e.g., $SOCl_2 + S \rightarrow 2\, S_2Cl_2 + SO_2$). It appears that only the electrochemical generation of

gas is likely to occur, and this does not create significant pressure except during deep discharge of the cell.

In summary, the most hazardous conditions are generated by the two categories of exothermic chemical combination reactions. Materials that react directly with lithium ($SOCl_2$, SO_2, S) are in a metastable state that is relatively safe below the melting point of lithium. The other types of chemical combinations (involving Li_2S or Li_3N with $SOCl_2$) may occur at ambient temperature and present the greatest hazard potential.

PART II. PRELIMINARY SURVEY OF ALTERNATIVE ANODE MATERIALS COMPATIBLE WITH OXYCHLORIDE CATHOLYTES

The elements considered as alternatives to the lithium anode were aluminum, zinc, magnesium and calcium. Zinc, magnesium and calcium showed no signs of corrosion in the solvents. The aluminum, although it remained bright and shiny, gave rise to gelatinous precipitates. Magnesium and zinc exhibited relatively low open circuit voltages, approximately 1.8V and 1.35V, respectively. Calcium had an open circuit voltage of 2.6V to 2.8V but exhibited some discharge reaction limitations.

The alloys tested were aluminum based materials that were developed for the NUSCAL battery. These were various combinations of Al with Zn, Sn, Mg, In, Ga and Hg. None of these alloys was stable in thionyl chloride and all showed low open circuit voltages (approximately 1V).

In summary, of the various materials investigated, only calcium appears to be worth examining further as an alternative to the lithium anode.

PART III. PRELIMINARY SURVEY OF ALTERNATIVE CATHOLYTES FOR IMPROVED LITHIUM CELL PERFORMANCE

Alternatives to both the electrolyte salt ($LiAlCl_4$) and the solvent/oxidant ($SOCl_2$) were investigated. The electrolyte salt investigated was based on substitution of the Lewis Acid, SO_3, for $AlCl_3$, to form $LiSO_3Cl$. The suitability of this material was to be examined in four solvents, $POCl_3$, $SOCl_2$, SO_2Cl_2 and $S_2O_5Cl_2$. Various problems were encountered in preparing and dissolving the lithium chlorosulfonate which were not resolved during the course of the program. The only cell with sufficiently conductive electrolyte to be operated electrochemically (based on $POCl_3$) gave ambiguous results.

Alternative solvent/oxidants investigated were $S_2O_5Cl_2$ and nitrobenzene. Pyrosulfuryl chloride has a boiling point of 152°C (compared to 79°C for thionyl chloride), reacts with sulfur (which could be advantageous in removing discharge product sulfur), and does not react with lithium. However, $S_2O_5Sl_2$ did not dissolve sufficient $LiAlCl_4$ to form a usefully conductive electrolyte solution. Substitution of $LiSO_3Cl$ did not substantially alter the solubility or conductivity.

Nitrobenzene appears more attractive and may be useful as an organic cosolvent. This material was found to dissolve more than 1 mole/liter of $LiAlCl_4$ and showed an open circuit of 3.5V vs. lithium and the ability to sustain a current of approximately 0.5 mA/cm^2 above 1V. Thus nitrobenzene may be a potentially useful solvent/oxidant.

PART IV. RESERVE MODE CONFIGURATIONS OF THE $Li/SOCl_2$ CELL

Two reserve mode configurations of the $Li/SOCl_2$ cell were investigated, (1) a low rate semi-reserve electrolyte cell, and (2) a high rate reserve electrolyte cell. In the semi-reserve concept the cell contains thionyl chloride and the electrolyte salt ($LiAlCl_4$) is held in reserve. There are several advantages to this configuration; the thionyl chloride alone is sufficiently non-conductive so that the cell cannot be made to explode by short-circuiting, there is less severe passivation (voltage delay) and probably less self-discharge.

In the high rate configuration, lithium chloride is omitted and only $AlCl_3$ (the Lewis acid) is used together with thionyl chloride. The entire electrolyte solution must be held in reserve to prevent self-discharge of the lithium. The lithium chloride film which normally would protect lithium from direct reaction with $SOCl_2$ is removed by the aluminum chloride. However, corrosion of lithium by this mechanism is slow enough to allow a fast discharge after activation, as would be suitable in some applications (e.g., torpedo propulsion). Because the discharge product LiCl (which normally deposits in the cathode pores) is soluble in this electrolyte, high rate discharge is possible without premature clogging of the cathode. Rates up to 70 mA/cm^2 were achieved with simultaneous delivery of more than three times the capacity obtained in standard electrolyte. Polarization losses were severe at these rates, but the observed cell voltage (approximately 2.8V) may still be sufficient for short-run applications.

PART V. DETERMINATION OF THE DISCHARGE REACTION MECHANISMS IN $Li/SOCl_2$ CELLS

Qualitative observations and chemical analyses have verified that LiCl, S, SO_2, Li_2SO_3 and Li_2SO_4 are products of the discharge reaction in $Li/SOCl_2$ cells. The objective of this study was to establish the reaction stoichiometry. Two approaches were used: (1) chemical analyses of the discharge products by collection and analysis of gaseous materials, and analysis of the materials contained in the electrolyte and cathode; and (2) controlled potential coulometry of thionyl chloride in a supporting solvent ($POCl_3$).

The results of the chemical analyses indicate that at room temperature and above the predominant reaction is:

$$4Li + 2SOCl_2 \rightarrow 4LiCl + S + SO_2 \quad \text{(a)}$$

The quantity of Li_2SO_3 formed was generally about 1% of the theoretical amount predicted by the reaction:

$$8Li + 3SOCl_2 \rightarrow 6LiCl + 2S + Li_2SO_3 \quad \text{(b)}$$

This finding was supported by the coulometric analysis, in which thionyl chloride was observed to yield 2.00 equivalents/mole, as predicted by (a), and not 2.67, as predicted by (b).

The analysis of the stoichiometry of the reaction below room temperature has not been completed.

PART VI. INVESTIGATION OF INORGANIC LIQUID OXIDANTS AS CATHODE REACTANTS FOR SEA WATER BATTERIES

Various inorganic liquid oxidants were investigated for use as cathode reactants in place of AgCl in the AgCl/Mg sea water battery. The liquid oxidants (SO_2Cl_2, $SOCl_2$, $POCl_3$, S_2Cl_2, SCl_2) were fed to the back side of a porous carbon electrode in contact with an aqueous electrolyte and discharged vs. various magnesium alloy anodes (supplied by NUSC). The best performance was obtained with sulfuryl chloride in general; in particular, SO_2Cl_2 containing 1M $NaAlCl_4$ vs. MTA 75 alloy (7% thallium, 5% aluminum), with 3.5% NaCl electrolyte. This couple exhibited an open circuit voltage of 2.96V and sustained a 100 ohm load at 2.50V (compared to 1.61V for AgCl).

The reactive species involved may be decomposition products formed on contact with water, such as H_2SO_4 in the case of sulfuryl chloride. Investigation of the direct use of such decomposition products, in place of the oxyhalides, was not completed on this program.

ACKNOWLEDGMENT

We would like to acknowledge the initial work done in the areas of alternate anodes, alternate catholytes, semi-reserve electrolyte cells, and sea water batteries by Dr. James J. Auborn, formerly of GTE Laboratories, and the assistance in coordinating all the tasks by Mr. Francis G. Murphy, Program Manager.

Some of the work presented in this report was not performed specifically for this contract (e.g., Sec. I - Analyses of Hazard Potentials; Sect. V - Reaction Mechanisms), but has been included because of its relevance to the overall Li/$SOCl_2$ cell development program. In this regard, we would also like to acknowledge the assistance received from Mr. Franz Goebel (GTE/Sylvania - Communication Systems Division) in short circuit testing and electrolyte-SO_2 analyses.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. ANALYSES OF THE HAZARD POTENTIALS OF VARIOUS REACTION MODES AND MATERIALS INCIDENTAL TO THE OPERATION OF Li/$SOCl_2$ CELLS

1. INTRODUCTION

1.1 OBJECTIVES

Li/$SOCl_2$ cells of recent construction are all hermetically enclosed within stainless steel cases. Consequently the hazards associated with the storage, handling, and discharge of the cells (exclusive of the electrical hazards of large arrays of cells, common to all systems) can occur only by disruption of the cell case. Cell case failure could be caused by external physical damage, corrosion, or internal over-pressurization. Corrosion failure of the case is virtually eliminated through the use of 304L or 316L stainless steel, and the effects of physical damage are mostly predictable and controllable by proper handling; consequently, these mechanisms of cell case failure were not specifically analysed in this study. Internal overpressurization has been the only observed mode of cell case failure, and this mechanism was the principal subject of investigation in this study. The objective of this study, then, was to ascertain the approximate relative risk associated with various known and hypothetical mechanisms of pressure generation within a sealed lithium/thionyl chloride cell.

1.2 TECHNICAL APPROACH

Mechanisms of pressure generation within the cell were postualted on the basis of: 1) materials and reactions that are known to occur in Li/$SOCl_2$ cells; and 2) materials and reactions that might occur, or that have been suggested by other investigators to occur, in Li/$SOCl_2$ cells.

The mechanisms of pressure generation were separated into two categories according to the source of pressure: 1) thermal mechanisms, which operate primarily by vaporization of the solvent and thermal expansion of vapors and gases; and 2) gas generation mechanisms.

The technical approach was to perform a literature survey collecting qualitative and quantitative information and thermodynamic data on the postulated reactions, in order to evaluate the potential risks. Experimental verification was attempted in some cases for which the available information was inadequate for an approximate calculation or a qualitative judgement.

2. TECHNICAL PRESENTATION: INVESTIGATION OF THE SOURCES OF INTERNAL CELL PRESSURE

2.1 THERMAL MECHANISMS OF PRESSURIZATION

2.1.1 External Thermal Sources

2.1.1.1 Analytical Procedure — External thermal sources can be separated into two ranges: 1) room temperature to about 80°C, representing the normal environmental limit; and 2) above 80°C, representing accidental exposure to excessive heat or incineration. Above the melting point of lithium (180°C) the pressure generation mechanism will be altered drastically to an internal source (exothermic chemical combination reactions) as will be discussed in Section 2.1.2.3

Below the melting point of lithium the pressure generated will consist of vaporization of thionyl chloride according to the following equation, by Arii:[1,2]

$$\log_{10}P = 7.60844 - 1648.21/T \qquad (1)$$

(where P is in millimeters of mercury and T is in degrees Kelvin)

and by thermal expansion of any entrapped air according to the ideal gas law:

$$P = (nR/V)T \qquad (2)$$

The approximate pressure to be anticipated has been calculated for an increase in cell temperature upto the boiling point of thionyl chloride (79°C) and up to the melting point of lithium (180°C).

2.1.1.2 Results and Discussion — The vapor pressure of thionyl chloride has been plotted versus temperature in Figure 1, according to Eq. (1). From this plot the vapor pressure of thionyl chloride is seen to be about 120 mm Hg at 25°C. Thus the partial pressure of air entrapped in the cell is about 640 mm Hg. As the cell temperature is increased from 25° to 79°C the $SOCl_2$ partial pressure would increase to one atmosphere and the air partial pressure would increase to about 756 mm Hg or approximately one atmosphere (an increase of 0.15 atmospheres). Thus, by external heating of the cell to 79°C, the internal pressure anticipated would be about two atmospheres or a pressure differential of about 15 lb/in^2.

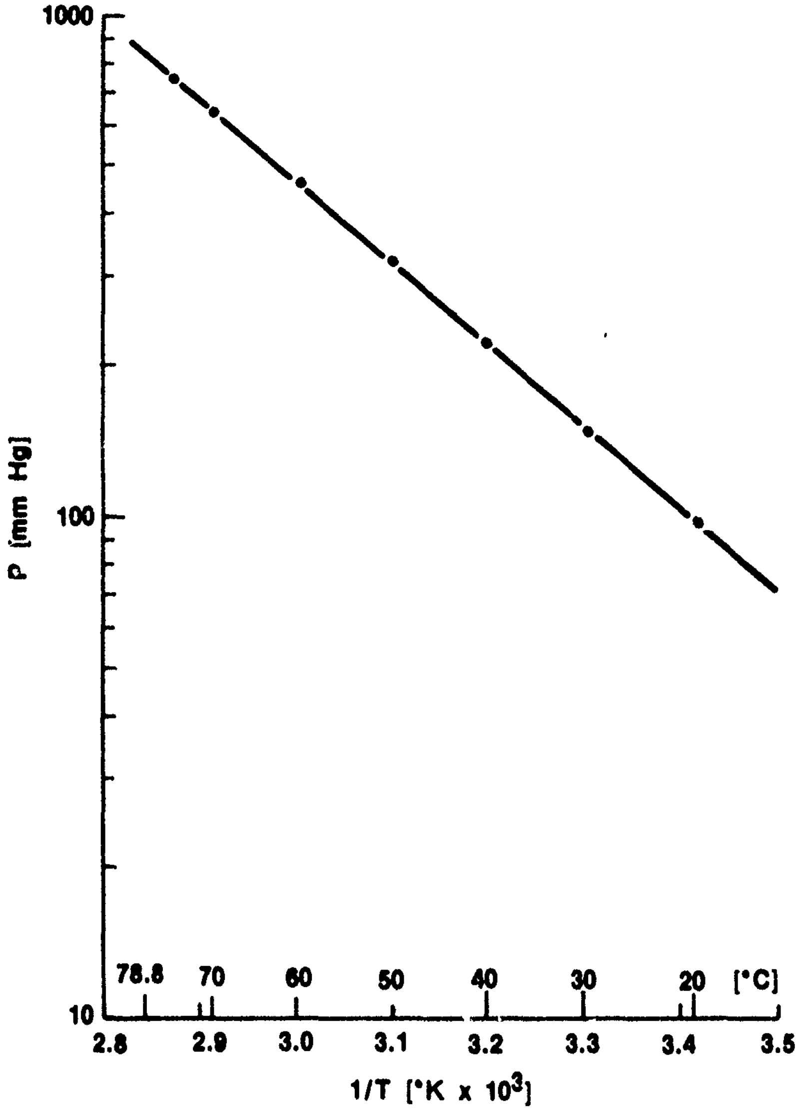


Figure 1. $SOCl_2$ Vapor Pressure vs. Reciprocal Temperature

Further heating to 180°C would cause the following increase in pressure of the trapped air, from Eq. (2):

$$P_2 = \frac{T_2}{T_1} \times P_1 = \frac{273.2 + 180}{273.2 + 25} \times 640 \text{ mm} = 973 \text{ mm}$$

If Eq. (1) is extrapolated beyond the boiling point of thionyl chloride, then the approximate pressure of the vapor over the liquid at 180°C is given by:

$$\text{Log}_{10} P = 7.60844 - \frac{1648.21}{273 + 180}$$

Thus P = 9333 mm or over 12 atmospheres. The combined total pressure is 10,310 mm or about 200 lb/in^2. The differential between the internal pressure and the atmosphere is 200 - 14.7 = 185.3 lb/in^2; this is reduced slightly by the presence of the electrolyte salt.

It is clear that serious deformation of a prismatic cell case would result from heating to slightly below the melting point of lithium. A small cylindrical cell such as AA can withstand over 6500 lb/in^2, so that such a cell could be heated to 180°C without significant risk in terms of vaporization of the solvent and thermal expansion of gases. The possible consequences of secondary effects due to heating will be considered in Section 2.2.

2.1.2 Internal Thermal Sources

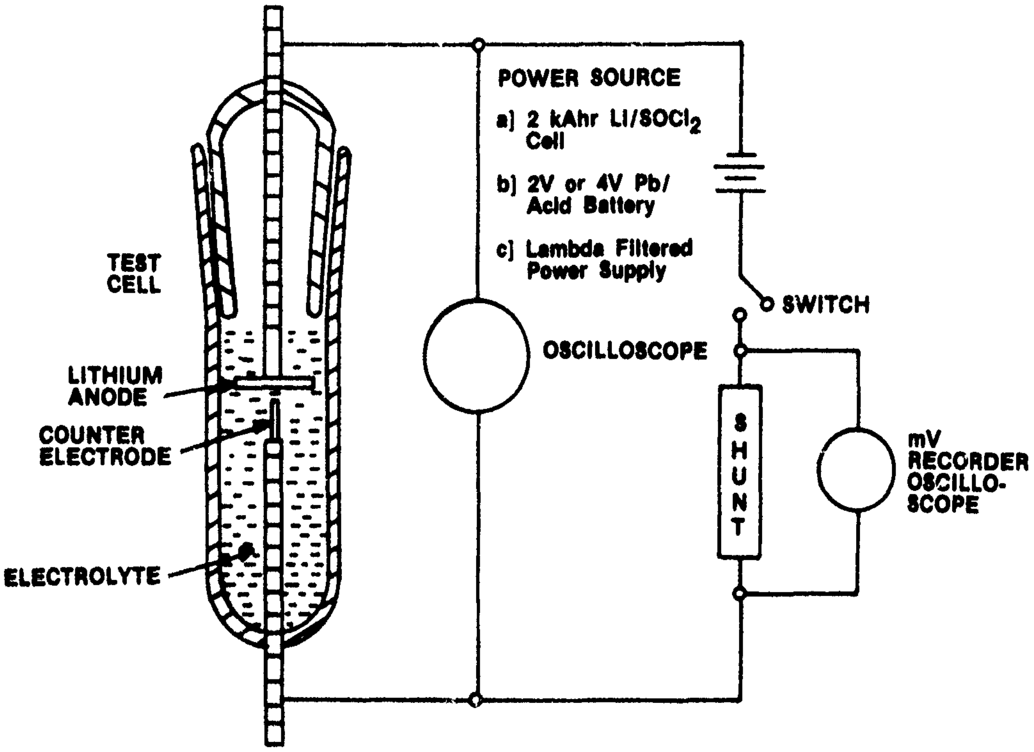
2.1.2.1 Electronic Short Circuits

2.1.2.1.1 Experimental Procedure — The term "short circuit" generally means unintentional electronic contact between the anode and cathode of a cell. There are three aspects of short circuiting to be considered: 1) arcing during partial contact, 2) local contact resistance heating and 3) ohmic polarization heating.

Arcing occurs during initiation of contact and when contact is broken. After contact is established resistance heating may occur. Arcing is considered to be potentially hazardous if lithium metal is involved. The resistance will be highest during partial contact and the heat generated in the area of the arc may be sufficient to spot-melt the lithium and initiate an exothermic combination reaction (of the types that will be discussed in Section 2.1.2.3). Similarly, the contact resistance heating produced by the passage of a large amount of current through a small contact area might also be hazardous if lithium metal is in the contact area. Either of the above short circuit modes would be expected to become critical rapidly. An arc will either initiate an instantaneous explosion or extinguish harmlessly; likewise contact resistance heating will produce melting and terminate either in an explosion or "burning off" of the contact in a matter of seconds.

If the short circuit contact has a low resistance, because of good contact in a large enough area, the mechanism will shift from localized rapid heating to slower generalized heating of the cell as a consequence of the sustained high discharge rate and the internal resistance of the cell (i^2R). The time to reach a critical temperature would be expected to expand from seconds to minutes in this case because of the thermal inertia of the cell. The effects of low-resistance short circuit heating will be the same as described for an external thermal source; i.e., vaporization of the thionyl chloride and expansion of the vapors and gases to approximately 200 lb/in^2, up to the melting point of lithium. Cells of prismatic configuration would be expected to sustain deformation and/or failure of the case with venting of the electrolyte (if pressure venting were not provided) before reaching the melting temperature of lithium. Cells of cylindrical configuration, on the other hand, would be expected to allow a higher temperature excursion on short circuit since they will withstand greater internal pressure, possibly allowing the temperature to reach the melting point of lithium, depending on the configuration of the electrodes and heat transfer characteristics.

In order to ascertain the magnitude of the hazard potential of the first two aspects of short circuiting, arcing and contact resistance heating, a special apparatus was designed 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 lithium/thionyl chloride battery (or other power source) could be safely passed through the controlled short circuit in the reactor, and any violent reactions produced were reduced to containable magnitude. The reactor consisted of two electrical contacts, one stationary and one moveable by remote operation, in a small glass vessel as shown in Figure 2. In designing the tests an effort was made to produce short circuits of plausible configuration involving lithium. Most of the tests were meant to simulate one type of short circuit most easily identified as a real possibility, namely, a filament of the cathode substrate (nickel expanded mesh) penetrating the separator and contacting the lithium. These tests were performed with the short circuit contact either completely submerged in thionyl chloride or partially wetted. Other configurations less likely to occur were also tested, such as a carbon-to-lithium short and contact between a cathode frame and a filament of lithium (the latter situation could only occur on accidental reversal of the cell and plating of dendritic lithium). The short circuit current and voltage were read directly on meters or, for some of the later tests, monitored on a high speed recorder.



ELECTRODE ARRANGEMENT

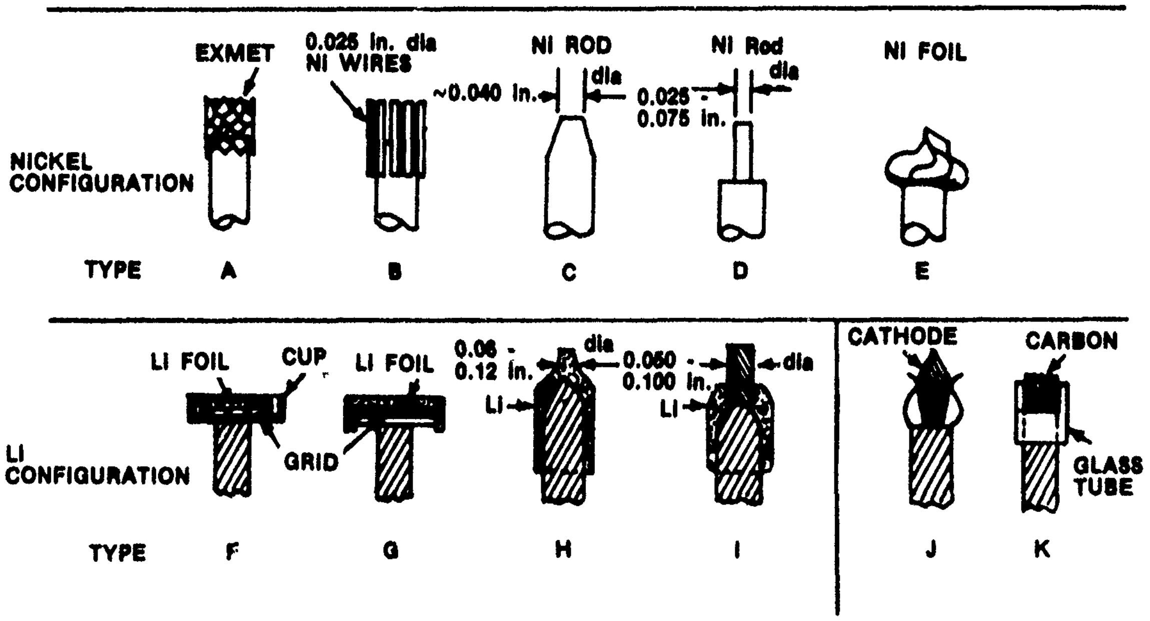


Figure 2. Remote Short Circuit Test Fixture and Electrode Configurations

An analysis of the consequences of a sustained short circuit (one that does not burn off immediately) is difficult because of the many variables involved. If the resistance of the contact area is near the design load range of the cell, the cell will discharge harmlessly (except at the end of discharge in some cases, as will be discussed in the next Section, 2.1.2.2). If the resistance of the contact area is low enough, the discharge rate will exceed the design rate of the cell and the consequences will depend upon the surface area of the electrodes, the capacity and state-of-charge of the cell, the conductivity of the electrolyte, the heat transfer characteristics of the cell configuration, the stress characteristics of the cell case, the starting temperature, and probably other factors as well. Consequently, a generalization about the effects of the short circuit, as well as experimental investigation, is complicated in this case.

A D-size cell with concentric electrodes will not explode when externally short circuited in the open environment at ambient temperature. (The same is true for AA, C and DD size cells with concentric electrodes.) It will exhibit an initial current in the range of 15A and stabilize at 3A or 4A. The current is limited by the low electrode surface area (approximately 40 cm^2) and the resistivity of the electrolyte, and the temperature rise is limited by the high thermal conductivity of the electrode configuration; i.e., the lithium foil is in direct contact with the inside surface of the cell case. If the same cell were thermally insulated or short circuited at a very high starting temperature, it would be expected to approach the melting temperature of lithium and possibly explode.

A wound D-cell will explode when short circuited in the open environment at ambient temperature. This configuration has a high surface area (300 to 400 cm^2); the initial short circuit current reaches 40A to 60A and stabilizes at 10A to 15A. The outer windings of the electrode structure provide sufficient thermal insulation to allow the temperature of the inner windings to reach the melting point of lithium. The maximum safe discharge rate for a high surface area wound D-cell has been calculated and experimentally confirmed[3] to be 4A, at room temperature. It has also been reported that a wound D-cell can be safely shorted at room temperature in the open environment if the surface area is kept below about 150 cm^2 (7 in. long electrodes).[4] These examples give some indication of the complex interplay of factors governing the hazard potential of various cell configurations on short circuit, and the range of data available.

Any effect of a short circuit would be expected to be exaggerated for the prismatic configuration due to the lower pressure capability of the cell case. For this reason various sustained short circuit experiments were performed on prismatic cells on this program. A 2000 Ahr-cell, designed for a 5A to 8A discharge rate, was short circuited externally through a low resistant contact, and the cell voltage and current and the case pressure and temperature were monitored. Three 100 Ahr prismatic cells were subjected to internal short circuits: in one case a temporary barrier between a small area of the anode and cathode was removed generating a carbon-to-lithium short circuit; in two other cells, a metal ram was forced between the anode and cathode frames generating a metal-to-metal short circuit. In each test the voltage drop was monitored as a qualitative measure of the short circuit resistance and both pressure and cell case temperature were monitored.

2.1.2.1.2 Results and Discussion: Arcing and Contact Resistance Heating — The results of the testing to determine the effects of arcing and contact resistance heating are presented in Tables I-A through E. A variety of empirical short circuit configurations were tested as shown in Figure 2. The electrode and the power source were also varied. Most of the configurations involved lithium vs. a metal (usually nickel). A few configurations involved lithium vs. carbon.

The first three tables (I-A, B and C) summarize the results for what were considered the most realistic configurations. In Table I-A a piece of expanded nickel (Exmet) attached to a rod, as shown in Figure 2-A, was brought into contact with lithium foil bonded to a metal cup, as shown in Figure 2-F. In some cases, carbon cathode material was laid over the lithium. The lithium was either completely submerged in electrolyte ("flooded"), or partially wetted ("starved") for example, by placing saturated separator paper over the lithium. The power source for these tests was a single 2000 Ah Li/$SOCl_2$ cell. Generally, the nickel electrode was lowered slowly into the lithium and held in contact for a few seconds and then raised slowly (to produce arcing); if nothing significant happened this procedure would be repeated several times, (resulting in considerable local heating). Sparks, flashes and smoke were observed, but no explosions were initiated. Usually the expanded metal points burned off, terminating the test. The presence of carbon (over the Li) had no effect (#A-7, 8, 9). In the last two tests (#A-10, 11), for which the external wiring was changed to allow larger short circuit currents, the lithium was made to burn off, but without detonation.

TABLE I-A

SHORT CIRCUIT TESTING: Li FOIL (AND/OR CARBON) VS. EXMET SUBSTRATE
(POWER SOURCE— 2000 Ahr Li CELL)

TEST NUMBER	SHORT CIRCUIT CONFIG.	ELECTROLYTE CONDITIONS	POWER SOURCE	MAX. CURRENT ACHIEVED	DURATION OF TEST	# OF REP.	TEST RESULTS	REMARKS
A-1	0.010 in. Li Foil(10-15 mg Type F) vs. EXMET(Type A)	Flooded Conditions -Fresh Electrolyte	2K-Li-Cell 3.6V	42.24A	5s	6x	Flashes	Screen Used on Counter Electrode
A-2	(Same As #A-1)	Flooded Conditions - Fresh Elec.	2K-Li-Cell 3.6V		9s	6x	Spark	Lithium had Screen Protruding from Middle
A-3	(Same as #A-1)	Electrolyte-Saturated with Sulfur-Flooded Conditions-Sulfur Crystals on Lithium w/Paper over it	2K-Li-Cell 3.6V		5s	4x	Spark	Lithium had Screen Protruding from Middle
A-4	(Same as #A-1)	Starved Electrolyte Conditions-Sulfur Crystals Placed on Li, 2 Pieces of Paper Used	2K-Li-Cell 3.6V		5s	2x	Sparks and Flashes	Signs of Reaction; Lithium/Turned Black
A-5	(Same as #A-1)	Starved Conditions-Sulfur Crystals Used on Li- 26 mg-Paper over Crystals	2K-Li-Cell 3.6V	No Resistor Used	5s	5x	Spark and Flashes, Smoke	Screen on End of Counter Electrode Burned
A-6	No Lithium Involved. Discharged Carbon Cathode from "A" Cell, 1/8 in. Thick, (Type F) vs. EXMET (A)	Starved Conditions Fresh Electrolyte	2K-Li-Cell 3.6V	32A	5s	5x	Smoke only	
A-7	Used Carbon Cathode Over Li Foil (Type F) vs. EXMET Points(A)	Starved Conditions Fresh Elec.	2K-Li-Cell 3.6V	28A	3s	3x	Flash and Smoke	All Screen Burned off Counter Electrode
A-8	(Same as #A-7)	$SOCl_2$ Only-Starved Conditions	2K-Li-Cell 3.6V	30A	5s	3x	Smoke at First Bright Flash	
A-9	(Same as #A-8)	Same as #A-8,Separator Paper Between C/Li	2K-Li-Cell 3.6V	30A	5s	2x	Smoke and Flash	
A-10	0.044 in. Li Foil(32 mg Type F)vs. EXMET Points (Type A) (Wiring Changed to #2 Welding Cable)	$SOCl_2$ Only-Larger Cup Used-Level of $SOCl_2$ 0.060 in. Above Lithium	2K-Li-Cell 3.6V	120A	3s	1x	Red Glowing Wire	Li Sample Burned off Slowly; Test was not Reproducible; EXMET Burned off
A-11	(Same as #A-10)	Starved Electrolyte Conditions-Separator Paper Used over Li.	2K-Li-Cell 3.6V	130A	5s	1x	Li Burned off in Red Flame	

Table 1-B summarizes the tests in which small nickel wires were substituted for the Exmet at the end of the contact rod, as shown in Figure 2-B. This circle of wires was anticipated to withstand more arcing without burning off. The rest of the set-up was similar to that described for the tests in Table 1-A. The lithium foil was thicker and the short circuit currents were higher. Again sparks, flashes and smoke were observed, but no explosions were initiated. In one case (#B5), vaporization from overheating was sufficient to blow off the demountable top of the cell, and in several cases the lithium melted, but in no case was a violent reaction initiated.

For the tests summarized in Table I-C, the nickel rod terminating in a circle of small wires was changed to a nickel rod machined to terminate in a single short pin about 25 mils to 30 mils in diameter. The objective was to break the lithium surface and concentrate the power in a small area while retaining sufficient conductivity to carry a large current without burning off the contact. Simple tapering of the rod to a small point, as shown in Figure 2-C, was not suitable as indicated by the results of test #C-1. The more reactive configuration was the short 25 mil pin shown in Figure 2-D. Another significant change was the use of a lead/acid battery in place of the 2000 Ahr $Li/SOCl_2$ cell, both to increase the available current and to vary the applied potential. When one cell of the battery (2.1V) was used as the power source the current was in the range of 100A. Bright flashes were produced and the nickel pin was burned off, but no explosions were initiated. When two cells of the lead/acid battery (4.2V) were used the current range was raised to about 200A. For this configuration, an explosion was initiated in test #C-5 and repeated in test #C-6. On the third repetition of this configuration (C#-7), the electrolyte was heated to 50°C before contact. On short circuit the nickel pin burned off without producing an explosion. A repeat of this configuration (#C-8), again with electrolyte at 50°C, was tried with one cell of the battery (2.1V) to avoid burning off the pin. On the fourth contact the glass cell broke and lithium combustion was initiated; i.e., the equivalent of a mild explosion. The use of carbon cathode material in a sharp-edged or blunt configuration (Figure 2-J and K), in place of the nickel pin, did not allow passage of any significant current.

The short circuit configurations used in this set of tests (Table I-C); i.e., the special nickel pin configuration together with the use of a lead/acid battery, probably do not represent realistic possibilities for a short circuit in a $Li/SOCl_2$ cell. However, consideration of all three sets of data (A, B and C) indicates that, although an internal short circuit of a

TABLE I-B

SHORT CIRCUIT TESTING: Li Foil VS. 0.025 in. DIAMETER Ni WIRES (POWER SOURCE— 2000 Ahr Li/SOCl$_2$ CELL)

TEST NUMBER	SHORT CIRCUIT CONFIG.	ELECTROLYTE CONDITIONS	POWER SOURCE	MAX. CURRENT	DURATION OF TEST	# OF REP.	TEST RESULTS	REMARKS
B-1	0.030 in. Li Foil(Type F-116 mg) vs. 0.025 in. Dia. Ni Wires (Type B)	Flooded Conditions ¼ in. Above Li	2K-Li-Cell 3.6V	110A	4.5s	[illegible]	Sparks and Smoke	0.25 in. Nickel Wire Strands, Replaced Screen on Counter Electrode
B-2	0.045 in. Li Foil (F-184 mg) vs. Ni Wires (Type B)	Flooded Conditions ¼ in. Above Li	2K-Li-Cell 3.6V	115A	5s	4x	Flash and Smoke	
B-3	0.210 in. Li Foil (F-294 mg) vs. Ni Wires(B)	Starved Conditions Large Cup Used	2K-Li-Cell 3.6V	105A	5s	3x	Flash and Smoke	
B-4	0.030 in. Li Foil (F-113 mg) vs. Ni Wires (B)	Starved Conditions-Pure SOCl$_2$	2K-Li-Cell 3.6V	110A	5s	4x	Flashes only	Li had Hole in Middle-Half of Sample Melted
B-5	0.045 in. Li Foil (F-180 mg) vs. Ni Wires (B)	Starved Conditions-Pure SOCl$_2$	2K-Li-Cell 3.6V	110A	4s	2x	1.Blew Top off Cell 2.Flash into Top of Cell	Hole in Middle of Li, Li Distorted
B-6	0.160 in. Li Foil (F-630 mg) vs. Ni Wires (B)	Limited Volume -Pure SOCl$_2$-Large Cup Used SOCl$_2$ Covered Li in Cup	2K-Li-Cell 3.6V	130A	4s	2x	Flash and Flare	Li Rose up in Middle in Shape of Volcano, Sulfur on Top of Li
B-7	0.160 in. Li Foil (F-600 mg) vs. Ni Wires (B)	Same as #B-6	2K-Li-Cell 3.6V	125A	—		Sparks	Small Holes in Li; Cup Bent and Electrolyte Collector in Bottom of Cell, Yellow in Color
B-8	0.040 in. Li Foil (F-190 mg) vs. Ni Wires (B)	Flooded, Fresh Elec. ½ in. Above Li	2k-Li-Cell 3.6V	70A	3s	2x	Flash	No Distortion of Li
B-9	0.080 in. Li Foil (F-190 mg) vs. Ni Wires (B)	(Same as #B-8)	2K-Li-Cell 3.6V	68A	3s	3x	Flash Sparks	No Distortion of Li

TABLE I-C

SHORT CIRCUIT TESTING: Li FOIL VS. SINGLE Ni PIN (OR CARBON)
(POWER SOURCE-LEAD/ACID BATTERY 2V or 4V)

TEST NUMBER	SHORT CIRCUIT CONFIG.	ELECTROLYTE CONDITIONS	POWER SOURCES	MAX. CURRENT ACHIEVED	DURATION OF TESTS	# OF REP.	TEST RESULTS	REMARKS
C-1	0.030 in. Li Foil (80 mg Type G) vs. 0.035 in. Ni Rod (Type C)	(Same)	LEAD/ACID BATTERY (L.A.B.) 2V	110A	2s to 3s		No Reaction	Rod Buried in Li.
C-2	0.030 in. Li Foil (80 mg Type G) vs. 0.025 in. Ni Rod (Type D)	(Same)	L.A.B. 2V	80A	3s to 4s		White Flash	Ni Rod Burned off
C-3	(Same as #C-2)	(Same)	L.A.B. 2V	1st-80A 2nd-85A	4s 2s	1x 1x	Orange Flash Orange Flash	Tip of Rod Burned into the Surface of the Li
C-4	(Same as #C-2)	(Same)	L.A.B. 2V	100A	2s	2x	Orange Flash	Burned Rod Tip
C-5	0.030 in. Li Foil (80 mg-Type G) vs. 0.025 in. Ni Rod (Type D)	Flooded-Fresh Regular Electrolyte (Above Ni Rod)	L.A.B. 4V	200A	—	1x	Explosion	Li Electrode on Top Lowered into the Nickel Rod.
C-6	(Same as #C-2)	(Same)	L.A.B. 4V	180A	—	2x	Explosion	Red Spark on First Contact. Explosion 2nd.
C-7	(Same as #C-2)	Same Electrolyte, Heated to 50°C	L.A.B. 4V	200A	—	1x	Red Flash	Ni Rod Burned off
C-8	(Same as #C-2)	Same Electrolyte, Heated to 50°C	L.A.B. 2V	50-100A	—	4x	Flash, Cell Broke	Popped off Top, Li Burned in $SOCl_2$ Vapor
C-9	0.030 in. Li Foil (Type G) vs. Carbon (Type K)	Flooded-Fresh Electrolyte, Above Carbon Electrode	L.A.B. 4V	—	—	2x	No Reaction	Good Contact Cannot be Established Between Carbon and Li.
C-10	0.030 in. Li Foil (Type G) vs. Carbon Cathode (Type J)	(Same as #C-9)	L.A.B. 4V	—	—	4x	No Reaction	

TABLE I-D

SHORT CIRCUIT TESTING: Li FOIL VS. 0.025 in. DIAMETER Ni WIRES OR Ni ROD (POWER SOURCE-HIGH POWER DC POWER SUPPLY)

TEST NUMBER	SHORT CIRCUIT CONFIG.	ELECTROLYTE CONDITIONS	POWER SOURCE	MAX.CURRENT ACHIEVED	DURATION OF TEST	# OF REP.	TEST RESULTS	REMARKS
D-1	0.080 in. Li Foil(F-190 mg) vs. 0.025 in. Ni Wires (Type B)	Flooded, Fresh Elec. ½ in. above Li	dc Power Supply-30V	11A (30V)	2s	2x	Explosion	Flash on 1st and 2nd Contact. Explosion on Breaking of 2nd Contact.
D-2 19A	0.160 in. Li Foil(F-205 mg) vs. 0.025 in. Ni Wires (B)	(Same as #D-1)	dc Power Supply-30V	11A (30V)	—	3x	Explosion	Sparks on 1st and 2nd Contact. Popped off Top 2nd Contact Explosion at Initiation of 3rd Contact.
D-3	0.080 in. Li Foil(F-200 mg) vs. 0.025 in. Ni Wires(B)	Flooded, Fresh Elec. 1 in. above Li	dc Power Supply-30V	10A (30V)	—	1x	Explosion	2 Sparks Followed by Explosion.
D-4	(Same as #D-3)	(Same as #D-3)	dc Power Supply 30V	3000A (15V)	~3s	3x	Red Flash	Popped off Top on 2nd Contact.
D-5	0.040 in. Li Foil(F-200 mg) vs. Tapered Ni Rod (Type C)	Flooded, Fresh Elec. 1 in. above Li(0.08M SO_2 Added)	dc Power Supply-30V	3000A (15V)	~5s	7-8x	Sparks, Cell Broke	Top of Cell Taped, Bottom Blew out after 7-8 Sparks
D-6	(Same as #D-5)	(Same as #D-5)	dc Power Supply-30V	2000-3000A (10-20V)	—	3x	Sparks	Popped off Top 3rd Contact, Li Stuck to Ni Rod.

TABLE I-E

SHORT CIRCUIT TESTING: Li POINTS IN VARIOUS CONFIGURATIONS (POWER SOURCE-LEAD/ACID BATTERY 2V or 4V)

TEST NUMBER	SHORT CIRCUIT CONFIG.	ELECTROLYTE CONDITIONS	POWER SOURCES	MAX. CURRENT ACHIEVED	# OF REP.	TEST RESULTS	REMARKS
E-1	Li Point 1/8 in. Dia. (Type H) vs. S.S. Cup	Flooded (1 in. above Cup Regular Electrolyte	Lead/Acid Batt. (L.A.B.) 4V	800-1200A	4x	Explosion	Sparks Several Times, Then Explosion.
E-2	No Lithium. Ni Rod (Type C) vs. Cup	(Same)	L.A.B. 4V	—	—	—	Lead to Cell Burned off
E-3	(Same as #E-1)	(Same)	L.A.B. 4V	100A	3x	Explosion	Cell Heated on Initial Contacts
E-4	Li Rod 0.10 in. Dia. x ¼ in. Long (Type I) vs. S.S. Cup	(Same)	L.A.B. 4V	225A	2x	Explosion	Sparks on 1st Contact 2nd Contact ~1/50s
E-5	Li Rod 0.090 in. Dia. x ¼ in. Long (I) vs. S.S. Cup	(Same)	L.A.B. 4V	80A	2x	No Reaction	Li Rod Distorted
E-6	Li Rod 0.050 in. Dia. x ¼ in. Long (I) vs. S.S. Cup	(Same)	L.A.B. 2V	125A	1x	Explosion	Explosion on First Contact
E-7	(Same as #E-6)	(Same)	L.A.B. 2V	120A	6x	Explosion	Li Reshaped after 2nd Contact. Cell and Electrode Hot after 5th Contact
E-8	Li Rod 0.050 in. Dia. x 1/8 in. Long (I) vs. S.S. Cup	(Same)	L.A.B. 2V	—	4x	No Reaction Li Rod Stuck to Cup	Lithium was on Rod and Cup.
E-9	Li Rod 0.050 in. Dia. x ¼ in. Long (I) vs. S.S. Cup	Same Electrolyte Heated to 50°C	L.A.B. 2V	—	1x	No Reaction (Li Rod Distorted)	The Stainless Steel Cup was Believed to have Oxidized, Change to Nickel
E-10	(Same as #E-9)	Same Electrolyte Room Temp.	L.A.B. 2V	—		No Reaction	Poor Contact Between Electrodes
E-11	Li Rod 0.055 in. Dia. x ¼ in. Long (I) vs. Ni Foil	(Same)	L.A.B. 2V	Not Available	1x	No Reaction	Li Crushed-Poor Connection Between Electrodes
E-12	(Same as #E-11)	(Same)	L.A.B. 2V	Not Available	5x	No Reaction	3rd try L.A.B. Hooked in Series with Test Cell
E-13	(Same as #E-11)	(Same)	L.A.B. 2V	Not Available	2x	Gas Evolution	L.A.B. Hooked in Series. Electrolyte Bubbled Violently

TABLE I-E (Continued)

SHORT CIRCUIT TESTING: Li POINTS IN VARIOUS CONFIGURATIONS
(POWER SOURCE-LEAD/ACID BATTERY 2V or 4V)

TEST NUMBER	SHORT CIRCUIT CONFIG.	ELECTROLYTE CONDITIONS	POWER SOURCES	MAX. CURRENT ACHIEVED	# OF REP.	TEST RESULTS	REMARKS
E-14	Li Point 0.050 in. Dia. (Type H) vs. Ni Foil on Edge (Type E)	(Same)	L.A.B. 2V	100A	2x	Sparks	Lithium made Contact to Straight Edge of 0.025 in. Ni Strip.
E-15	(Same as #E-14)	(Same)	L.A.B. 2V	75A	6x	Sparks	Same as #E-14
E-16	Li Point 1/8 in. Dia. (Type H) vs. Ni Rod 0.050 in. Dia. (Type D)	(Same)	L.A.B. 4V		2x	No Reaction	Li Squashed, Straightened and Tried again.
E-17	Li Point 1/8 in. Dia. (H) vs. Ni Rod 0.075 in. Dia. (D)	(Same)	L.A.B. 4V	100A	2x	Sparks	Popped Top off Cell

critical configuration (i.e., a particular short metal fragment from the cathode repeatedly contacting the lithium anode in a very high power cell) may be unlikely to occur, there is some potential for an explosion to result from an internal short, and due consideration must be given to this hazard potential in the design of large cells.

A number of other tests were performed to evaluate two somewhat more remote possibilities of short circuits, representing possible events in a series string of cells. The first of these is a short driven at high voltage, representing the occurence of a critical internal short circuit after installation of the cell in a series string. A high power dc supply was used for these tests which unfortunately does not simulate a battery since it is capable of extremely high current pulses (caused by discharge of the filter capacitor of the power supply). These results are summarized in Table I-D. Explosions were initiated more readily but, surprisingly, they did not occur on first contact; rather some heating of the components always occurred before an explosion was initiated.

The second less likely type of short circuit configuration evaluated involved pointed lithium contacts (as opposed to a metal point contacting a sheet of lithium). Such a situation might occur if a cell in a series string reversed and lithium were plated forming dendrites; a dendrite might then penetrate the separator and short to the cathode. However, in earlier testing it was shown that lithium-to-carbon shorts were too resistive to produce a significant reaction. Consequently, only lithium-to-metal shorts were tested, making this configuration even less realistic. These tests are summarized in Table I-E. The power sources was again a lead/acid battery. Explosions were obtained several times, particularly when two cells of the battery were used. These results indicate that short circuits involving a lithium point and a metal are highly reactive; these configurations, however, are almost certainly not representative of a lithium dendrite-to-carbon short circuit.

In summary, several qualitative conclusions may be made regarding the effects of short circuit arcing and contact resistance heating:

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.

2.1.2.1.3 Results and Discussion: Sustained Short Circuits — A 2000-Ah prismatic cell, designed for discharge at 5A to 8A, was short circuited externally through 0.012Ω. The results of this test are shown in Figure 3. The cell sustained about 190A (at approximately 2.8V) for about 45 min. and dropped to about 50A to 100A for another hour. The surface temperature rose to approximately 90°C and the pressure, near the end of discharge, rose to approximately 20 lb/in^{2}g. An internal short circuit was apparently generated after about 90 min. and relieved again after about 100 min. After termination of the test the cell case was found to be quite distorted but it did not burst or vent.

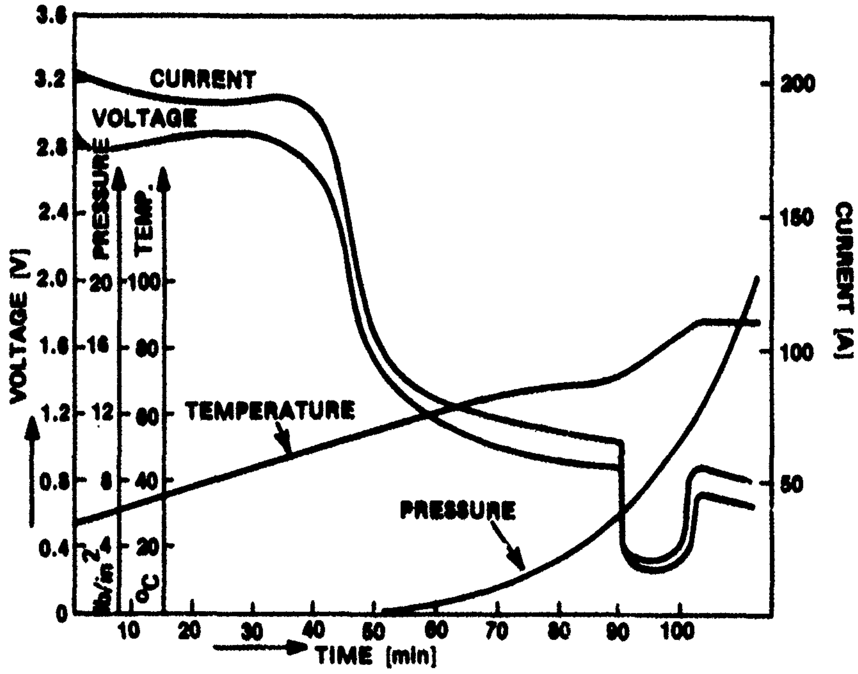


Figure 3. 2000-Ah Cell Short Circuit Test (0.012 Ohms)

Internal short circuits were produced in two 100 Ah cells as described previously. The carbon-to-lithium short was initiated by removing a temporary barrier between a portion of the two electrodes. The contact area was approximately 0.3 cm^2. On initiation of the short the cell voltage dropped from 3.6V to 3.5V, indicating that a high resistance contact was formed, as was found in spark testing previously (Table I-C). Consequently, the current drain was not excessive and the cell discharged near (or above) its design rate in a quite normal manner. The temperature rise was insignificant (1°C), and there was no indication of a pressure increase.

The metal-to-metal internal short circuit was induced by forcing a metal ram between the anode and cathode frames of a 100 Ahr cell. The voltage dropped from 3.6V to 0.38V in four minutes, indicating extremely good contact. The case temperature rose from 24° to 37°C in the first four minutes. The test was continued for 39 min., at which time the temperature had leveled off at 50°C. The maximum pressure increase was about 2 lb/in^2. A repeat of this test with another cell gave very similar results.

The following qualitative conclusions may be made regarding sustained short circuits:

1) Carbon-to-lithium shorts have quite high contact resistance and probably allow only low rate discharge of the cell.

2) $Li/SOCl_2$ prismatic cells can withstand quite low resistance short circuits, external or internal, without failure of the case or explosion. Distortion of the case under relatively low pressure would be expected; this might lead to additional internal short circuits and increased hazard potential.

3) The high current density characteristic of a short circuit has the effect of terminating the discharge prematurely i.e., the cell becomes completely polarized after delivering only 10% or even less, of its capacity.

2.1.2.2 Polarization Effects

2.1.2.2.1 Analytical Procedure — The amount of heat produced on normal discharge of a $Li/SOCl_2$ cell is minimal. The enthalphy of the reaction has been estimated from changes in the open circuit voltage versus temperature (from about -20° to 72°C) according to:

$$\Delta H = - nF\left(E-T \frac{\partial E}{\partial T}\right) \quad (3)$$

where:

ΔH = enthalpy, Kcal/mole

n = no. of equivalents/mole

F = 23.06 Kcal/V-equivalent

E = cell open circuit potential at temperature T

T = temperature, degrees K

The open circuit potential was found to vary linearly with temperature over this range, the value of $\partial E/\partial T$ being +1.026 mV/degree; ΔH is then -77 Kcal/equivalent.* Using this value, a "thermoneutral" voltage (V_H) can be calculated as:

$$V_H = \frac{-\Delta H}{23.06\ n} = 3.34 \text{ volts} \qquad (4)$$

This is the operating potential at which the heat generated by iR loss is just equal to that absorbed by the entropy change. Thus, for polarization from open circuit (approximately 3.65V) to 3.34V, which is below the typical discharge voltage of about 3.4V, there should actually be a slight net cooling effect. In practice the temperature of the cell tends to remain constant during discharge at moderate rates (< 2 mA/cm^2).

Near the end of discharge, cell polarization increases rapidly, with a corresponding increase in heat production. In the case of an anode limited cell (i.e., a cell in which the capacity is determined by the mass of lithium), the voltage tends to drop sharply at the end of discharge and the period of high heat production is short. In a cathode limited cell the voltage drop near the end of discharge is slower extending the period of higher heat production. The temperature in a cathode limited cell might rise to 40^0 or 50^0C at the end of discharge. This is not a significant change, as was discussed in Section 2.1.1. However, the concurrence of this temperature rise with the end of discharge has the secondary effect of expelling the dissolved SO_2 that was formed during the discharge. This will be examined further in Section 2.2.2. In order to determine the thermal characteristics of a cathode limited cell on discharge, a 2000 Ahr cell was designed to accomodate four thermocouples in the electrode stack and two on the cell case. The cell was then discharged on constant load, equivalent to 2 mA/cm^2, down to 1.0V, and the temperature at the various locations was monitored continuously.

---

*See Figure 16, Section V.

2.1.2.2.2 Results and Discussion — The temperature profile across the stack is shown in Figure 4 at various stages of the discharge. It can be seen that there is a differential of 3^0 to 4^0C between the center of the stack and the case at the end of discharge. The complete discharge curve with the corresponding maximum cell temperature is shown in Figure 5. It is apparent that the cell temperature is only a few degrees above ambient throughout the discharge and fairly constant. While the operating potential is above the "thermoneutral" voltage, the temperature rise due to iR loss should theoretically be more than compensated for by the heat absorbed by the cathode during the entropy change. The apparent heating observed is probably due to poor heat conduction within the cathode. The temperature rise begins at the end of the discharge plateau, when the cell voltage drops below the "thermoneutral" voltage, and reaches a maximum of about 39^0 to 40^0C. (The cell was discharging on constant load so that the current diminished with the voltage, and heat production thus gradually diminished also.) This temperature rise in itself is not sufficient to cause a problem by vaporization and expansion of thionyl chloride, as mentioned above.

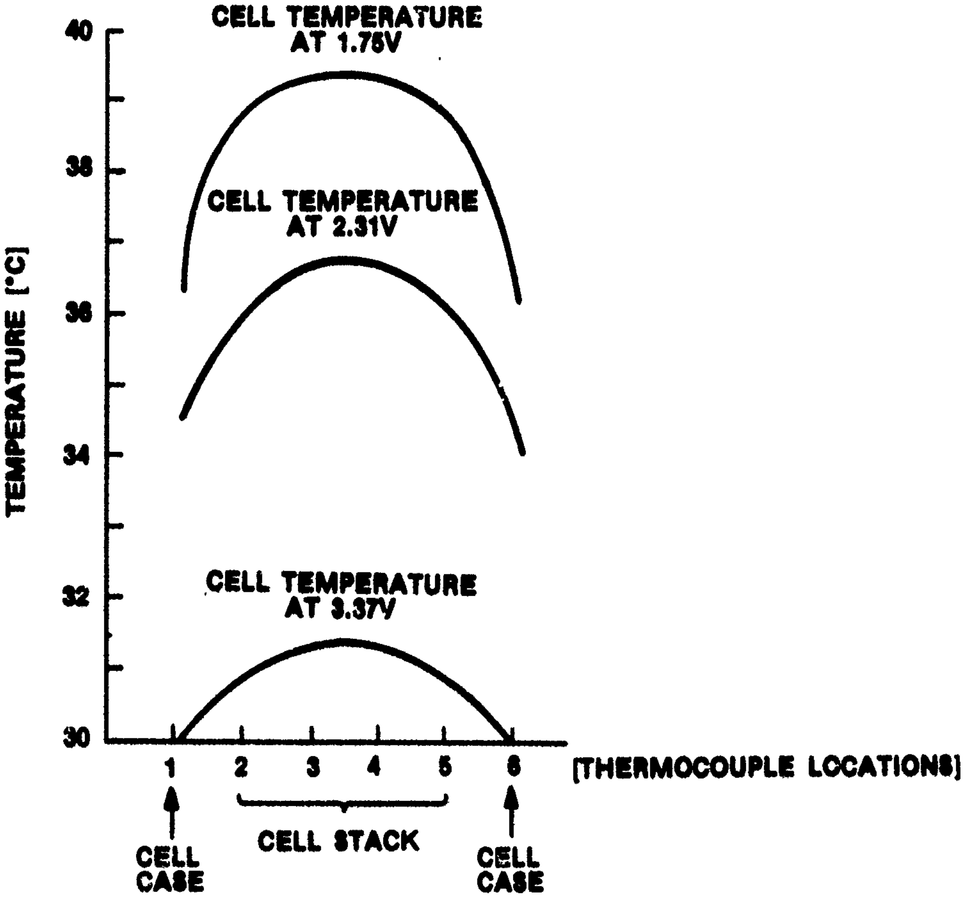


Figure 4. Temperature Profile of a Cathode Limited Prismatic Test Cell During Discharge at 10A ($2mA/cm^2$)

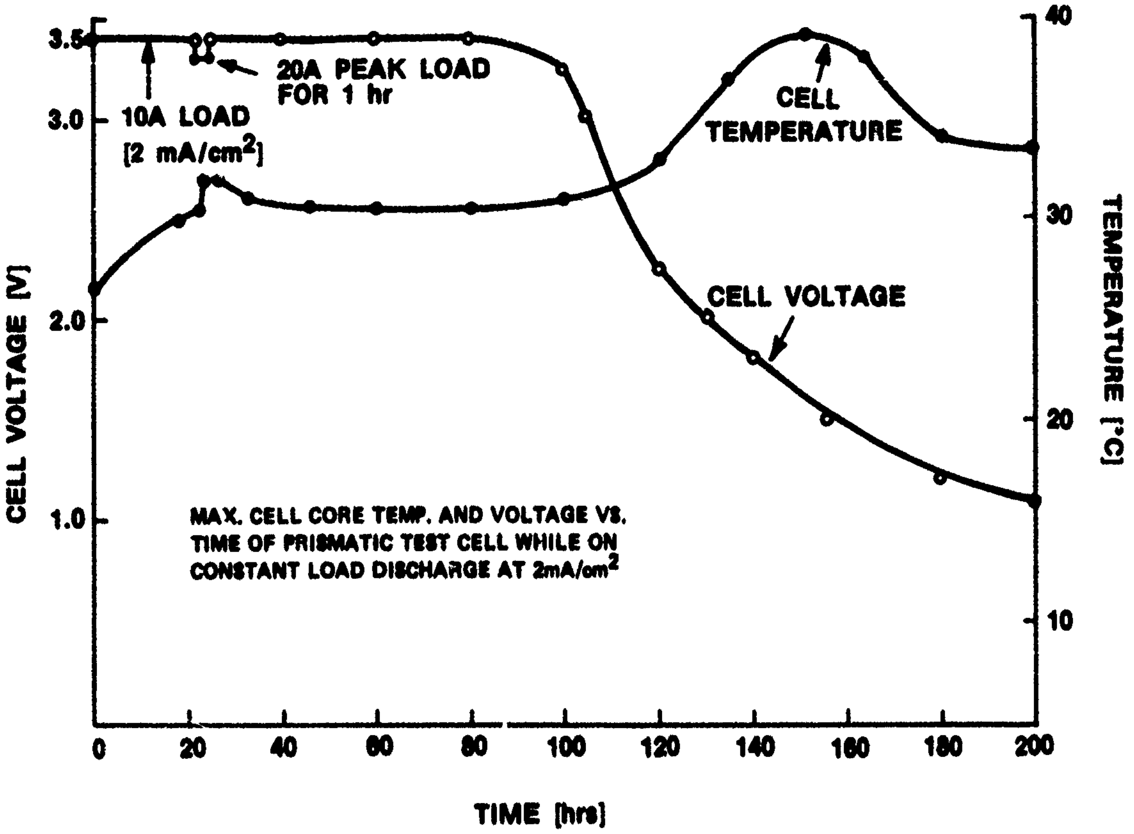


Figure 5. Maximum Profile Temperature and Voltage vs. Time for Prismatic Test Cell

It may be concluded that the heating that occurs at the end of discharge in a cathode limited cell has the potential hazard of releasing discharge-product SO_2 from solution and slightly overpressurizing a prismatic type cell. This effect can be mitigated by ending the discharge at 3V or by using an anode-limited configuration.

2.1.2.3 Exothemic Chemical Combination Reactions

2.1.2.3.1 Reactions with Molten Lithium — Lithium metal should react directly with various materials that occur in the cell such as the solvent/cathode reactant $SOCl_2$, and discharge products such as sulfur and sulfur dioxide. The free energy changes of such reactions have been calculated and are compared in Figure 6. All three reactions should occur spontaneously with the release of large amounts of thermal energy.

The room temperature heats of reaction are as follows:

$$6\ \text{Li} + \text{SOCl}_2 \rightarrow \text{Li}_2\text{O} + \text{Li}_2\text{S} + 2\ \text{LiCl} \quad (-394\ \text{Kcal/m}) \tag{5}$$

$$6\ \text{Li} + 3\ \text{S} \rightarrow 3\ \text{Li}_2\text{S} \quad (-320\ \text{Kcal/m}) \tag{6}$$

$$6\ \text{Li} + \text{SO}_2 \rightarrow \text{Li}_2\text{S} + 2\ \text{Li}_2\text{O} \quad (-321\ \text{Kcal/m}) \tag{7}$$

These reactions do not occur in actual cells because the lithium is always covered by a protective layer of LiCl. This layer has been determined by interfacial capacitance measurements (by Peled and Yamin[5]) to have a minimum thickness of about 2 nm to 4 nm. It is postulated that the LiCl acts as a cationic conducting solid electrolyte and discharge of Li proceeds by transport of Li+ through the LiCl.[6] Thus, the lithium is protected at all times from direct reaction with other materials, on open circuit or on discharge. However, if the cell temperature exceeds the melting temperature of lithium, the protective layer is apparently not maintained, and any of the above reactions may occur. The sudden release of large amounts of thermal energy accompanying these reactions results in drastic overpressurization and explosion of the cell.

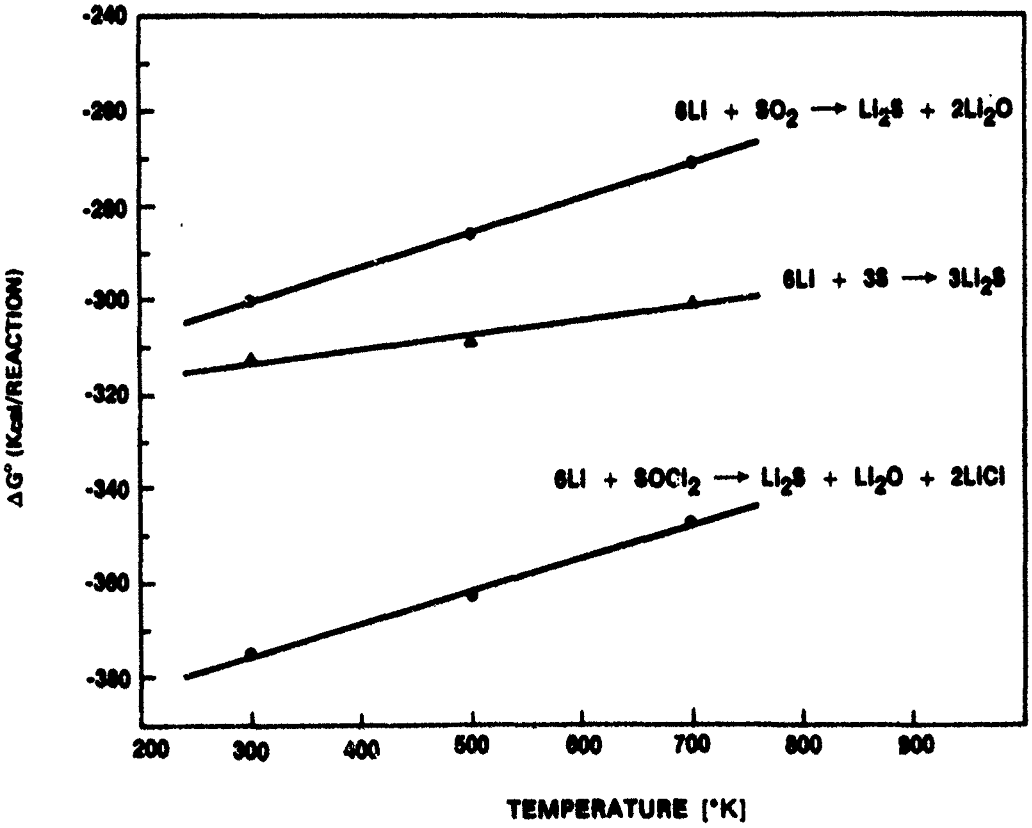


Figure 6. Free Energy Changes for Reactions of Li with SO_2, S, and $SOCl_2$

Thus, it may be concluded that although direct reactions with lithium do not occur under ordinary circumstances, any mechanisms which can raise the temperature of the cell to the melting point of lithium (180°C) present a serious hazard potential.

2.1.2.3.2 Other Types of Chemical Reactions — A survey of other reactive materials that might occur or be produced in a Li/$SOCl_2$ cell yielded hydrides of Li or Ni, Li_2S, and Li_3N.

A brief consideration of the possibility of the occurence of nickel hydride, on the expanded nickel substrate of the electrodes, indicates that it is not likely to be present in any significant quantity if at all. If the expanded nickel were annealed in hydrogen, some hydrogen might be retained as a hydride or a chemisorbed layer. The formation of a hydride appears unlikely since the accumulated evidence indicates a very low stability for the nickel hydride (ΔG_f^0 $NiH_{0.5}$ = + 5.64 Kcal/mole H_2; the unfavorable ΔG^0 results from a negative entropy of formation). That nickel hydride is exceptionally unstable is evidenced by a decomposition pressure of over 3000 atm at 25°C.[7,8] These preparative conditions are not present in ordinary hydrogen annealing of nickel and this strongly suggests that the nickel cermet is a single metallic phase. Chemisorption of a monolayer or hydrogen on the nickel surface, on the other hand, is possible. However, the expanded nickel would not present sufficient surface for the absorption of any significant quantity of hydrogen nor would it be retained through all the subsequent processing of the material in fabricating electrodes.

Lithium metal forms a well defined ionic hydride, LiH (a sodium chloride type lattice consisting of Li^+ and H^- ion); the free energy of formation is -16.16 Kcal/mole at 25°C.[7] It is highly reactive with water producing LiOH and H_2, and it is reported to react vigorously with oxidizing agents with some hazard of detonation with powerful oxidants.[9] Thus LiH might be expected to react violently with thionyl chloride (and/or SO_2). At least two such reactions are possibilities:

$$2\ SOCl_2 + 2\ LiH \rightarrow 2\ HCl + SO_2 + 2\ LiCl + S\ (\Delta H_f = -158) \qquad (8)$$

$$2\ SOCl_2 + 2\ LiH \rightarrow 2\ H_2 + SO_2 + S + LiCl\ (\Delta H_f = -24.8) \qquad (9)$$

Lithium hydride is prepared commercially by reacting molten lithium with hydrogen gas at 725°C and < 100 Torr pressure.[9] In a cell, lithium hydride might form on lithium by reaction with HCl in the electrolyte (HCl can be generated by hydrolysis of the thionyl chloride on contact with moist air):

$$Li + HCl \rightarrow LiCl + 1/2\ H_2\ (\Delta G_f^o = -69\ Kcal/mole) \tag{10}$$

$$2\ Li + HCl \rightarrow LiCl + LiH\ (\Delta G_f^o = -85.4\ Kcal/mole) \tag{11}$$

Since both Li^+ and H^+ can be transported through the protective film of LiCl on the lithium, LiH might form under the LiCl layer, protected from immediate reaction with $SOCl_2$, and thus accumulate. The quantity of LiH that could be present by any mechanism, however, would be expected to be limited by two factors: 1) the amount of HCl in a sealed cell is extremely limited (ppm range), and 2) any LiH formed would be expected to react further with HCl according to:

$$LiH + HCl \rightarrow H_2 + LiCl\ (\Delta G_f^o = -52.6\ Kcal/mole) \tag{12}$$

Commercially prepared lithium hydride powder (Pfaltz & Bauer, Inc.) was exposed to thionyl chloride in the open atmosphere, in a dry argon atmosphere, at room temperature and at the boiling temperature of thionyl chloride to determine its reactivity. There was no observable reaction under any of the above conditions. It is concluded therefore, on both theoretical and experimental grounds, that the occurrence or reaction of LiH does not present a significant hazard potential.

Holleck, Turchan and Cogley have reported[10] that anhydrous Li_2S reacts violently with $SOCl_2$ generating considerable heat, gas and elemental sulfur. A possible reaction may be:

$$2\ Li_2S + 2\ SOCl_2 \rightarrow SO_2 + 3S + 4\ LiCl\ (\Delta H_f = -147.6\ Kcal/mole) \tag{13}$$

A.N. Dey has reported that lithium and sulfur react at 178°C (by DTA analysis), presumably to form Li_2S.[11] Apparently the lithium is covered by a layer of lithium sulfide which prevents further reaction until either the lithium melts (180°C) or the Li_2S dissolves in the molten sulfur, exposing the lithium surface. Lithium sulfide is not a discharge product and its presence has not been detected in $Li/SOCl_2$ Cells. Sulfur, which is a discharge product (formed at the cathode and soluble in the electrolyte upto about 1.1M), would not be expected to react with the lithium because of the protective film of LiCl on its surface. However, this film is formed by the direct reaction of lithium and thionyl chloride and sulfur is formed along with the lithium chloride:

$$4\ Li + 2\ SOCl_2 \rightarrow S + SO_2 + 4\ LiCl \tag{14}$$

A trace of sulfur has been reported in this film;[12] consequently, it may be possible for some Li_2S to form on the surface of the lithium. The quantity would be expected to be very small, and none has been detected or reported.

In order to determine the reactivity of Li_2S, commerically prepared material (Foote Mineral Company) was exposed to $SOCl_2$. (The material was gray rather than white. It is prepared by slowly adding H_2S to finely divided lithium in a coordinating solvent such as THF. The material is dried at 200°C, and subsequently sintered at a higher temperature to decompose the residual solvent. The decomposition of the solvent produces carbon and gives the material its gray color.) The Li_2S was insoluble in $SOCl_2$ and did not react at room temperature or at the boiling temperature of $SOCl_2$. The experiments were performed under dry argon and in the open atmosphere without effect. Thus the hazard potential of Li_2S in contact with $SOCl_2$ is probably minimal, but remains uncertain.

Lithium reacts directly with atmospheric nitrogen to form lithium nitride:

$$3\ Li + 1/2\ N_2 \rightarrow Li_3N\ (\Delta G_f^0 = -37\ Kcal/mole) \qquad (15)$$

This reaction occurs only very slowly in dry nitrogen; however, the reaction proceeds readily in moist air and, once initiated, continues in dry nitrogen.[13] Evidence of this reaction has been observed in the form of purplish-black spots on the surface of lithium stored in air at 1% to 4% relative humidity (dry room conditions). Although Li_3N has not been reported to react with thionyl chloride, it might well be expected to; finely divided Li_3N is stated to be flammable in air.[14] Li_3N is also reported to react with sulfur to form cyclic sulfur imides:[15]

$$S_8 + Li_3N \rightarrow S_7N^- + S_4N^- \qquad (16)$$

Two sources of Li_3N were tested for reactivity with $SOCl_2$: 1) commercially prepared powder obtained from Polyresearch Corp. (98.9%) and, 2) particles of lithium nitride removed from old lithium foil (dark spots 1 mm to 2 mm in diameter on the surface of Lithium). The latter were ground to a powder in a dry argon atmosphere (1 ppm H_2O dry box). Neither of those materials was soluble in thionyl chloride and showed no reactivity with $SOCl_2$ in the dry argon atmosphere. However, both materials, when added to $SOCl_2$ in the normal atmosphere, reacted violently burning even in the vapor above the liquid. Similarly, Li_3N powder exposed to the normal atmosphere briefly (a few seconds), and then added to thionyl chloride in the dry argon atmosphere, also reacted violently. A larger piece of Li_3N exposed to the atmosphere, unlike the ground powder, did not react with $SOCl_2$. The mechanism of this reaction has not been established, but possibly the Li_3N reacts with moisture in the air to form a more reactive amide:

$$Li_3N + H_2O \rightarrow LiNH_2 + Li_2O \tag{17}$$

Clearly, the reactivity of Li_3N with $SOCl_2$ presents a potential hazard since Li_3N can form on the lithium under the normal assembly conditions. However, no real danger would be anticipated for any operations with a sealed cell except for the unusual circumstance of disassembly of a discharged cell, containing residual lithium, in normal humid air.

In summary, the following conclusions may be made regarding the hazard potential of these materials:

1. Ni_2H, LiH and Li_2S do not appear likely to occur in any significant quantity in the cell and LiH and Li_2S were not found to be reactive in $SOCl_2$. Based on other reports however, the reactivity of Li_2S remains uncertain.
2. Li_3N might form on lithium during cell assembly and thus could be present in a cell. This material was found to be highly reactive with $SOCl_2$ but only under the peculiar conditions of exposure to moist air in a finely divided state. Lithium nitride would not be expected to present a hazard in a sealed $Li/SOCl_2$ cell.

2.2 GAS GENERATION MECHANISMS OF PRESSURIZATION

2.2.1 <u>Chemical Sources</u>

2.2.1.1 Gaseous Thermal Decomposition Products — Two reactions by which $SOCl_2$ might be thermally decomposed have been reported in the literature:[16,18]

$$4\ SOCl_2 \rightarrow S_2Cl_2 + 2\ SO_2 + 3\ Cl_2 \tag{18}$$

$$2\ SOCl_2 \rightarrow SO_2 + 2\ Cl_2 + S \tag{19}$$

The decomposition has been reported to begin at temperatures as low as 150°C and to be virtually complete by 440°C.[19] We have examined the thermodynamics of these proposed thermal decompostion reactions. The free energy changes accompanying these reactions have been calculated from readily available published thermodynamic data and by the use of the MANLABS-NPL Materials Data Bank. The resulting free energies of reaction have been plotted in Figure 7. Both calculations 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°C (according to the data obtained from the available published literature) or about 690°C (according to the data obtained from the MANLABS Data Bank). Further, even above these temperatures, the decomposition reaction is endothermic.

It may be concluded 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.

2.2.1.2 Gaseous Chemical Reaction Products — The reaction of $SOCl_2$ with sulfur has been reported in a number of sources,[20,24] and since sulfur is a discharge product and soluble up to 1.1M in thionyl chloride this possibility was examined:

$$2\ SOCl_2 + 3\ S \rightarrow 2\ S_2Cl_2 + SO_2 \qquad (20)$$

The reaction is reported to be catalyzed by $AlCl_3$[21] and by $FeCl_3$.[24] In References 20 and 22 the experiments were carried out in glass tubes without a catalyst. At 100°C, the S was found to dissolve in the $SOCl_2$ to form a clear solution, but upon cooling it separated in the form of crystals. At temperatures between 150° and 180°C, the $SOCl_2$ and S reacted to produce SO_2 and S_2Cl_2. In Reference 24, it was reported that when pure $SOCl_2$ was refluxed with sulfur for 45 min, no sulfur chlorides were formed. However, upon adding 200 ppm Fe (as $FeCl_3 \cdot 6\ H_2O$) and refluxing further, S_2Cl_2 was formed (about 8% after refluxing for about 4 hr.)

As in the case of the thermal decomposition of $SOCl_2$, thermodynamic calculations were performed in two ways. In the first case, the readily available published thermodynamic data were used, while in the second case the MANLABS-NPL Materials Data Bank was employed. The resulting free energies of reaction have been plotted in Figure 8. The results of the first calculation show that the S-$SOCl_2$ reaction will proceed spontaneously at temperatures above about 120°C, while the MANLABS data indicate that the reaction will proceed spontaneously above 290°C. The experimental results reported suggest that the free energy changes calculated using the published

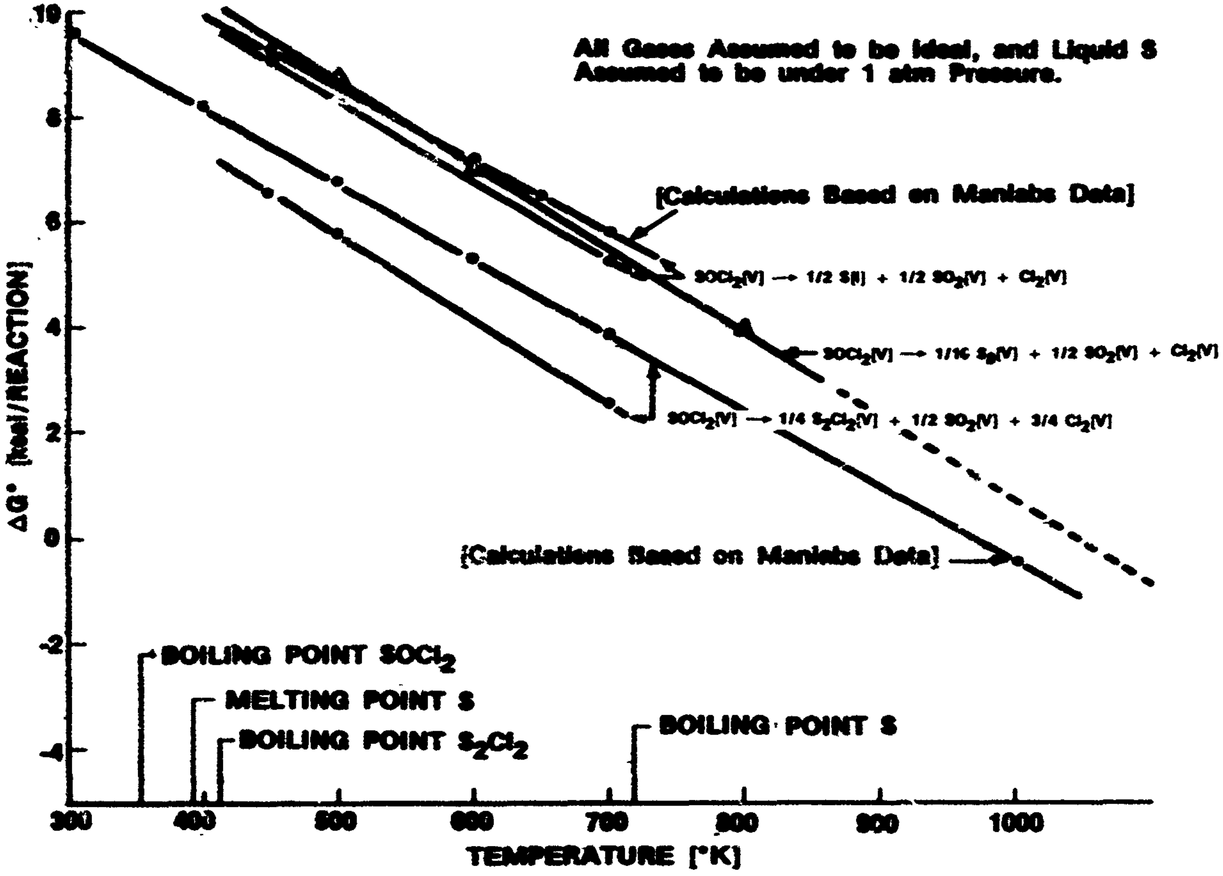


Figure 7. $SOCl_2$ Thermal Decomposition Thermodynamics

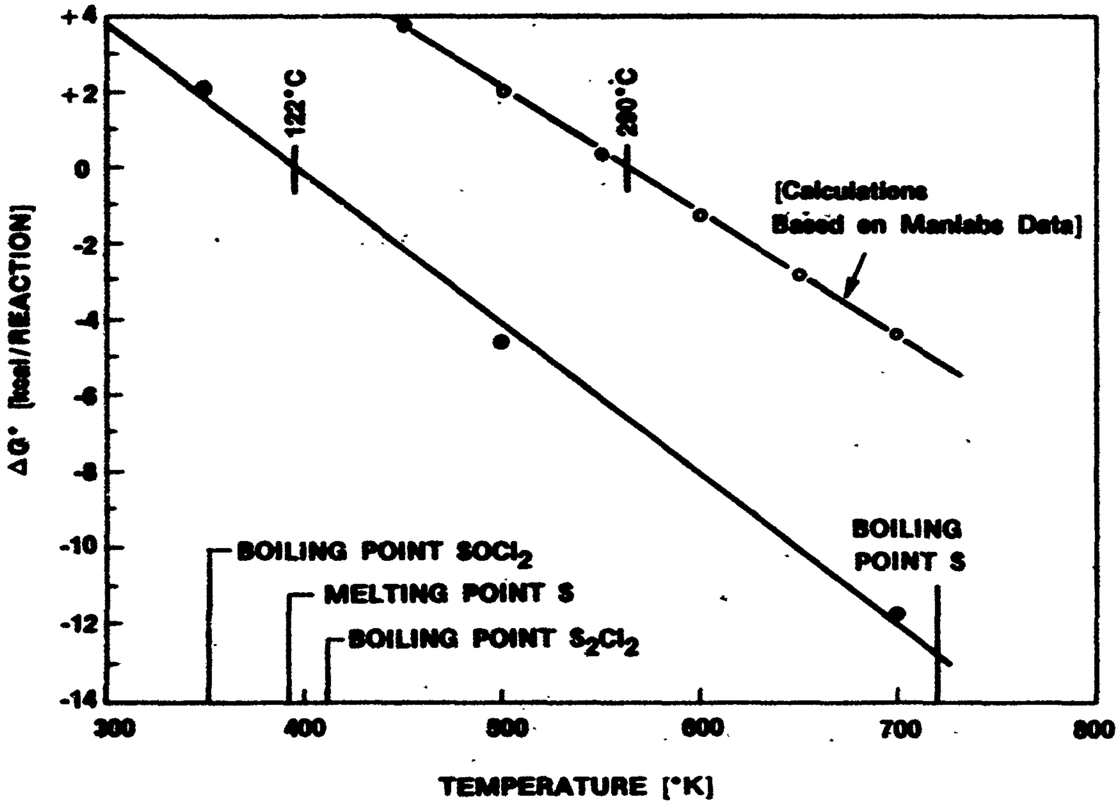


Figure 8. Free Energy Change for the Reaction 2 $SOCl_2 + 3 S \rightarrow 2 S_2Cl_2 + SO_2$

Thermodynamic data are more accurate than those obtained by the use of the MANLABS Data Bank. However, both calculation have indicated that the reaction proceeds endothermically once the mixture is heated beyond the required temperature. ΔH^{0}_{298} = 18.6 Kcal by the first calculation and ΔH^{0}_{298} = 22.6 Kcal by the second calculation. On heating mixtures of sulfur and $SOCl_2$ to a temperature where reaction may proceed, ΔH^{0} would change somewhat, but still likely remain positive. Thus, heat energy should be required to sustain the reaction.

The following qualitative conclusions may be made:

1) The reaction shown in Eq.(20) has been observed to occur in the vicinity of 150°C, generating gaseous products.

2) The reaction may be catalysed at lower temperature by materials occurring in the cell such as $AlCl_3$ and $FeCl_3$ (the concentration of Fe is normally very low - a few ppm).

3) The conditions necessary to initiate the reaction between S and $SOCl_2$ are approached only at the end of discharge (high concentration of sulfur from the discharge reaction, consumption of the $SOCl_2$ raising the level of the solute, $AlCl_4^-$, and any catalytic impurities such as Fe, and an increasing temperature), but even then the temperature is unlikely to be sufficient to initate and sustain the reaction. Consequently, this mechanism of gas generation is not considered to present a serious potential hazard for any normal operating conditions.

2.2.2 Electrochemical Sources: Gaseous Discharge Products

2.2.2.1 Analytical Procedure — At ambient temperature and above, the predominant reaction that occurs on discharge in a $Li/SOCl_2$ cell appears to be (the discharge mechanism will be discussed in Section V):

$$4\,Li + 2\,SOCl_2 \rightarrow 4\,LiCl + S + SO_2 \qquad (21)$$

Thus a gaseous product is clearly formed on normal discharge of the cell. The rate is 0.933 moles of SO_2/100 Ah (0.6 g SO_2/Ahr). In order to determine the relative potential hazard associated with this reaction, the solubility of SO_2 in thionyl chloride was determined, and the SO_2 dissolved and expelled by cells on discharge was monitored during the operation of 2000 Ah prismatic cells.

The solubility of sulfur dioxide gas in thionyl chloride was determined according to the following procedure.

An Erlenmeyer flask was fitted with a sidearm bubbler through which SO_2 could be passed from a lecture bottle into $SOCl_2$ contained within the flask. The flask itself was contained within an oil or cold water bath by which the $SOCl_2$ was maintained at a preselected temperature between 0^o and 60^oC. A glass wool-packed water-jacketed condenser was employed to prevent the significant loss of $SOCl_2$ during its saturation with SO_2. Initially, the flask was fitted with ground glass stoppers and weighed. Twice distilled $SOCl_2$ was then transferred (under argon) into the flask, the flask was re-stoppered, and the volume of $SOCl_2$ was calculated from its density and the gain in weight of the flask upon the addition of the $SOCl_2$. The condenser was then connected to the flask, and the $SOCl_2$ was saturated with SO_2 as described above. The condenser was then removed, and the stoppered flask containing the SO_2-saturated $SOCl_2$ was weighed. Another condenser was then connected to the flask, and dry argon was slowly bubbled into the $SOCl_2$ as it was heated to reflux the liquid, thus driving off the previously dissolved SO_2. Finally, the condenser was removed, the flask was again stoppered, and the amount of SO_2 previously contained in the saturated solution was determined gravimetrically.

SO_2 generation in cells on discharge was determined by monitoring the discharge of 2000 Ah prismatic cells at room temperature. The cells were discharged on constant load equivalent to 1.8 mA/cm^2. Samples of electrolyte were withdrawn periodically and the SO_2 concentration was analysed by quantitative infra-red spectroscopy. The cells were also connected to chemical scrubbers containing 4M K_2CO_3 solution, to absorb any SO_2 expelled at atmospheric pressure during the discharge. This was carried out by passing dry nitrogen through the cell vent, as shown in Figure 9, and periodically analysing the scrubbers for chloride and sulfite. The $SOCl_2$ emitted is equal to half the chloride content, and the quantity of SO_2 collected is equal to the total sulfite less half the chloride content.

2.2.2.2 Results and Discussion — Assuming regularity, the solubility of the SO_2 (expressed as mole fraction, x) is related to the heat of solution (ΔH_{sol}) and the temperature (T, ^oK) by an equation of the form:

$$\ell n\ x = -(\Delta H_{sol}/R)(1/T - \alpha) \qquad (22)$$

(R is the ideal gas constant and α is a proportionality factor.) Thus, over a sufficiently narrow temperature range, a plot of lnx vs. 1/T should be approximately linear. This was found to be the case for SO_2 in 1.8M $LiAlCl_4/SOCl_2$. A best fit (least squares) line is shown in Figure 10 corresponding to the following equation:

$$\ln x = \frac{(2.417 + 0.184) \times 10^3}{T} - (0.863 \pm 0.613) \qquad (23)$$

For convenience, the same line has been replotted in Figure 11 expressed as the molar solubility of SO_2 vs. T (°C). (The dotted lines are data for pure $SOCl_2$.) From this curve it can be seen that the solubility of SO_2 in 1.8M $LiAlCl_4/SOCl_2$ at room temperature is about 3 moles/liter (approximately 0.2 g/cm^3). Lithium thionyl chloride cells are normally designed to contain about 2 cm^3 of electrolyte/Ah. According to Eq. (21), about 1.36 cm^3 of $SOCl_2$/Ah would be consumed and about 0.6g of SO_2/Ah (1.37g/cm^3 at 25°C) would be generated on discharge. This would leave about 0.64 cm^3 of electrolyte/Ah and 0.436 cm^3 of SO_2/Ah. The final concentration would be 0.6g SO_2/1.076 cm^3 or 8.7 moles/liter. Clearly, if Eq. (21) represents the only reaction occurring above room temperature, the SO_2 solubility in the electrolyte would be exceeded some time after the midpoint of the discharge. The problem would be aggravated toward the end of discharge by the increase in temperature (discussed in Section 2.1.2.2.), reducing the SO_2 solubility to perhaps less than 2 moles/liter.

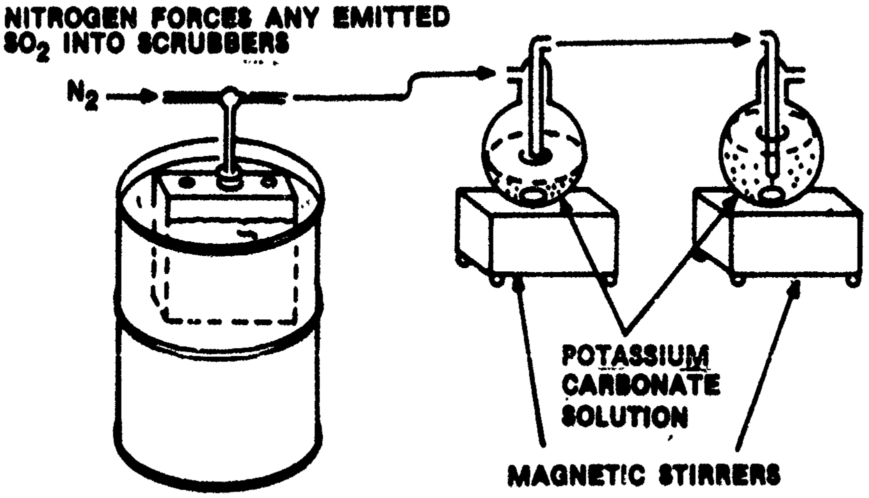


Figure 9. Apparatus for Collecting SO_2 Expelled from Discharging Cells

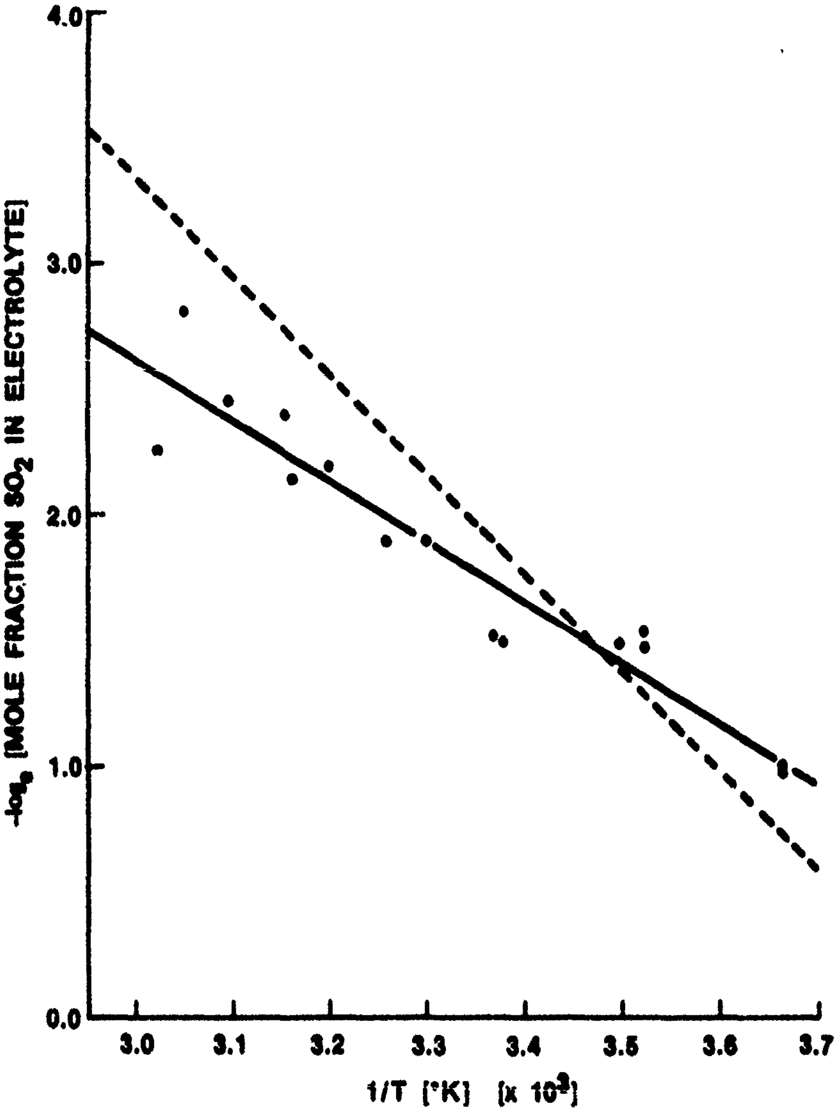


Figure 10. SO_2 Solubility in Standard Electrolyte vs. 1/T

The results obtained for the discharge of the 2000 Ah cells are shown in Figure 12 for an anode-limited cell and in Figure 13 for a cathode-limited cell. These cells contained about 5000 cm^3 of electrolyte, or 2.5 cm^3/Ah, which is a little more than usual. After about 1100 Ah of discharge, 660g (482 cm^3) of SO_2 should have been generated and 1500 cm^3 of electrolyte should have been consumed, net volume 4008 ml. This represents about 0.165g of SO_2/cm^3 (2.57M). For the anode-limited cell, the end of discharge started at this point and no SO_2 was detected in the scrubber after about 1350 Ah total capacity. The analysis of the electrolyte for SO_2 showed a great deal of scatter, but the final concentration of SO_2 was near 3.5 moles/liter (theoretical, 3.37 moles/liter). The cathode-limited cell

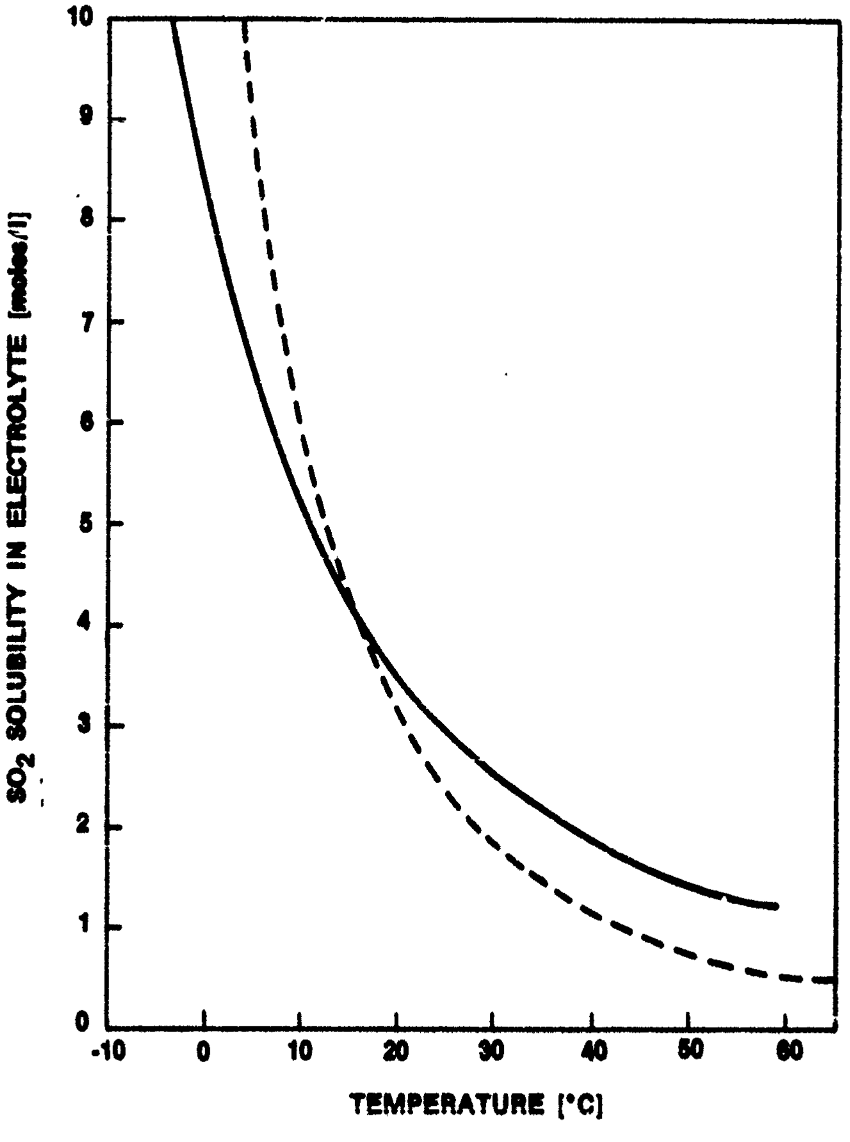


Figure 11. SO_2 Solubility in Standard Electrolyte vs. T

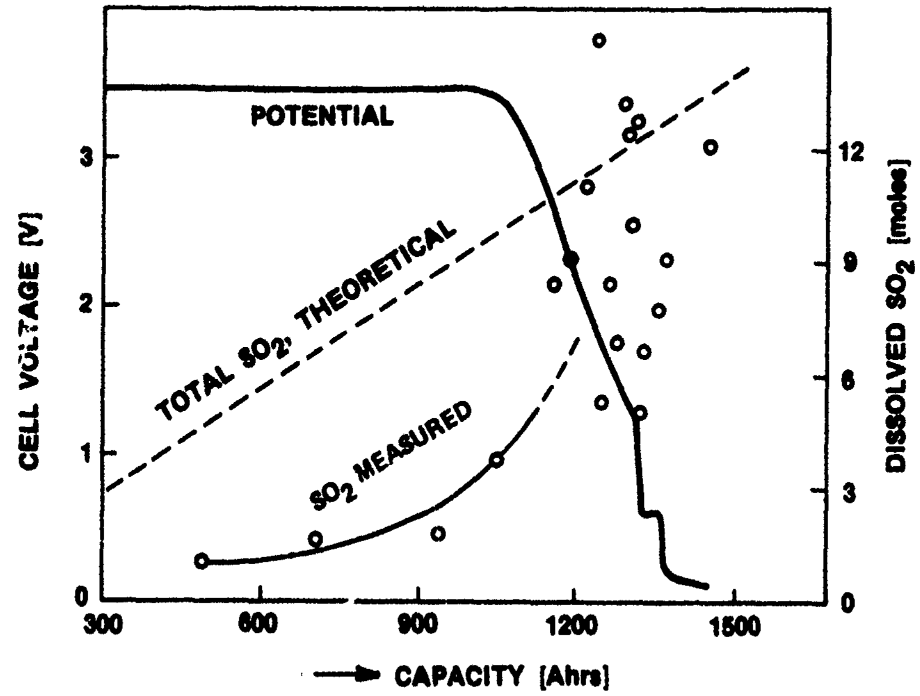


Figure 12. Anode Limited SO_2 Test Cell

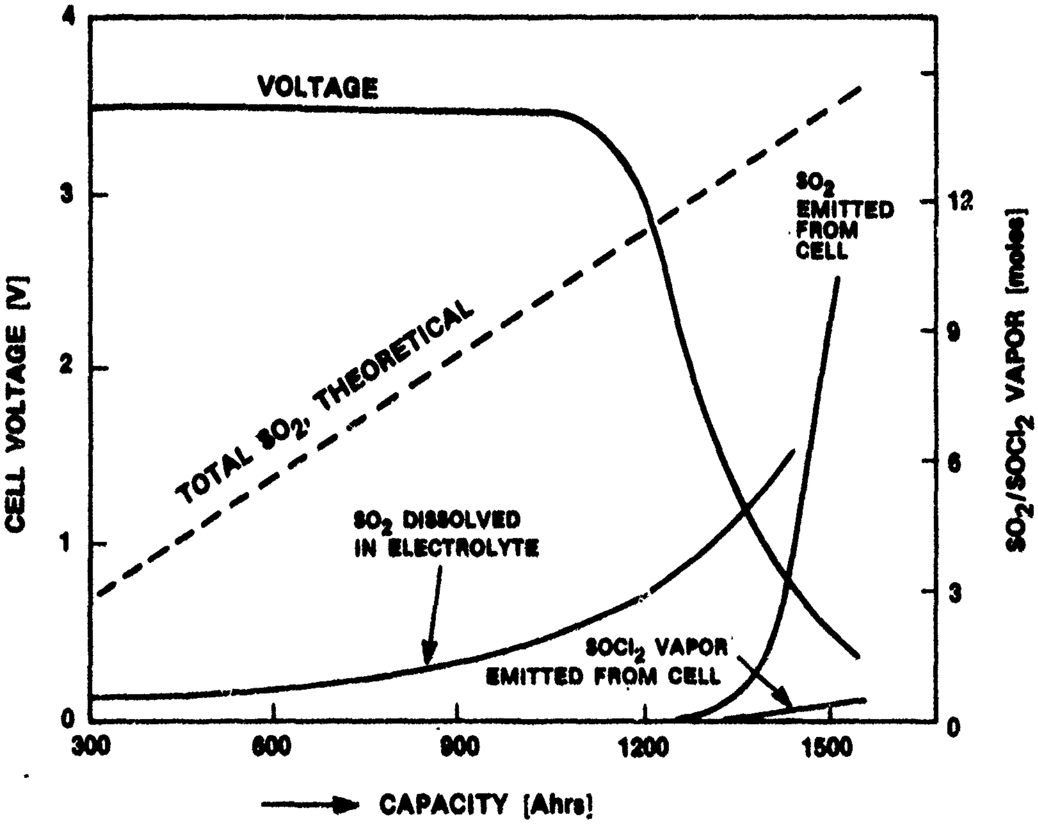


Figure 13. Cathode Limited SO_2 Test Cell

delivered more capacity. The end of discharge started around 1200 Ah and continued to about 1500 Ahr. SO_2 was detected in the scrubber sometime after the 1200 Ah point, (2.88 moles SO_2/liter) as would be expected from the SO_2 solubility data. The anaylsis of the electrolyte for SO_2 did not show a good correlation with the theoretical SO_2 production. This could indicate that some other product such as Li_2SO_3 or SO was produced in addition to SO_2, but it would not explain why SO_2 was expelled after 1200 Ah at an apparent (measured) concentration of about 1 mole/liter (calculated, 2.88M); even at the higher temperature at this point (approximately 40°C) the solubility would still be about 2 moles/liter. Sulfur dioxide was measured using the infrared absorption band at 1333 cm^{-1}, and a 0.1 mm cavity NaCl cell on a Perkin Elmer #621 spectrophotometer. Calibration curves showed good agreement with Beer's law throughout the measured range to 0.10M. Standard curves were taken for every sample run, to correct for any variations in cell thickness. We thus have no explanation as to why SO_2 began to escape at 1200 Ahr to 1300 Ahr.

These results indicate that some SO_2 pressure can be expected at the end of discharge. In a sealed cell the SO_2 solubility will be higher than at atmospheric pressure, and the discharge is usually terminated at about 3V, reducing the magnitude of any temperature effects. This would only be of significance in cells of prismatic configuration, and significant pressurization has never been observed. There is the potential hazard of prismatic cell case deformation for high rate discharge below the 3V cut-off in cathode limited cells.

3. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The analyses of the thermal mechanisms of cell pressurization indicate the following hazard potentials:

1) Any thermal sources that raises the cell temperature to about 80°C (the normal environmental limit) will produce an internal pressure of about 15 lb/in^{2}g. This would not have any effect in a cylindrical cell design but could cause deformation of a prismatic cell case if a vent were not provided.

2) Any thermal source that raises the temperature of the cell, even locally, to the melting point of Li (180°C), may initiate an exothermic reaction between lithium and other cell reactants or products. A particular kind of internal short circuit involving arcing to lithium in a very large cell could be an adequate thermal source to initiate an explosion. A low resistance short circuit is probably not an adequate thermal source to initate an explosion, (except in special configurations like spiral wound electrode structures) but would cause deformation of a prismatic cell case. These potential hazards can be greatly minimized by proper cell design.

3) Of the reactive materials that might occur in the cell, LiH, Li_2S and Li_3N, only Li_3N is likely to occur in any appreciable amount. Li_3N is potentially a hazard since it may form on lithium that is not stored properly, and it was found to be highly reactive with $SOCl_2$ at room temperature. However, reaction of Li_3N with $SOCl_2$ only occurred after the peculiar circumstances of exposure to moist air in a finely divided state, and this is not expected to be a realistic hazard in a sealed Li/$SOCl_2$ cell.

The analyses of the gas generation mechanisms of pressurization indicate the following hazard potentials:

1) Of the various gas generation mechanisms of pressurization, only the electrochemical generation of SO_2 on discharge presents a hazard potential. This problem is minimal for a low rate discharge that is terminated at 3V, or for anode limited cells.

2) Heating of the cell by any means near the end of discharge (such as discharging a cathode limited cell below 3V) reduces the solubility of SO_2 and presents some potential hazard of cell case deformation for the prismatic configuration if no vent is provided.

It is recommended that the reaction of Li_3N with $SOCl_2$ be investigated further to establish the nature of the reactants and the mechanism of the reaction. Although neither the reactivity of Li_2S nor its occurrence in the cell was established, it would also be advisable to further investigate this material.

II. PRELIMINARY SURVEY OF ALTERNATIVE ANODE MATERIALS COMPATIBLE WITH OXYCHLORIDE CATHOLYTES

1. INTRODUCTION

1.1 OBJECTIVES

Lithium metal has proved to be an excellent anode material in almost every respect, and its advantages are generally well known. Its most serious deficiency is its relatively low melting temperature of 180°C; the potential hazards related to this property have been discussed in Section I. In addition, lithium can exhibit severe passivation in 1.8M $LiAlCl_4/SOCl_2$ after storage at elevated temperature, if various preventative measures are not taken.

It is not very likely that a material which is superior to lithium in all respects will be found. However, if a metal or alloy with a higher melting temperature and perhaps better passivation characteristics can be found, some sacrifice of electrochemical performance may be acceptable

The objective of this study then was to examine various candidate materials and ascertain their potential suitability as alternative anode materials.

1.2 TECHNICAL APPROACH

Both metal alloys and elements were considered as candidate alternate anode materials. The elements were selected from eleven possibilities according to the following characteristics: melting point, E^0 vs. Cl_2, specific gravimetric capacity, and specific volumetric capacity. The candidate metals are shown ranked by decreasing value for each characteristic in Table II. On this basis, Ca, Mg and Al were chosen for study. Beryllium was not considered, in spite of some very favorable characteristics, because of its known tendency to passivate in nonaqueous solvent, its scarcity, and the high toxicity of beryllium oxides. Zinc was also examined, but only superficially, in conjunction with the alloys.

The investigation of alloys as alternative anode materials was limited to four aluminum alloys developed for the NUSCAL battery, based on their ready availability. These had the following compositions:

(1) Al, Zn (1.4%), Hg (0.019%)

(2) Al, Zn (3.52%), In (0.03%)

(3) Al, Zn (4.19%), Mg (0.46%), In (0.04%)

(4) Al, Mg (0.79%), Sn (0.13%), Ga (0.05%)

TABLE II

CHARACTERISTICS OF POSSIBLE ANODE METALS
(RANKED BY DECREASING VALUE)

RANK	MELTING POINT		E^o VS. Cl_2 (THEOR.)		GRAVIMETRIC CAPACITY		VOLUMETRIC CAPACITY	
	Metal	(°C)	Metal	(Volts)	Metal	(Ah/g)	Metal	(Ah/cm^3)
1	Be	1278.0	K	4.24	Be	5.948	Be	10.992
2	Ca	839.0	Na	4.00	Li	3.863	Al	8.043
3	Al	660.4	Li	3.95	Al	2.980	Ga	6.809
4	Mg	648.8	Ca	3.92	Mg	2.205	Zn	5.849
5	Zn	419.6	Mg	3.07	Ca	1.337	Cd	4.125
6	Pb	327.5	Be	2.31	Na	1.166	Mg	3.832
7	Cd	320.9	Al	2.18	Ga	1.153	Pb	2.936
8	Li	180.5	Zn	1.91	Zn	0.820	Li	2.062
9	Na	97.8	Cd	1.78	K	0.685	Ca	2.060
10	K	63.7	Pb	1.63	Cd	0.477	Na	1.132
11	Ga	29.8	Ga	1.59	Pb	0.259	K	0.591

The suitability of these materials as alternatives to lithium vs. $SOCl_2$ was established by determining their stability in thionyl chloride (and sulfuryl chloride in some cases), their open circuit potentials vs. $C/SOCl_2$, and if possible, their discharge characteristics vs. $C/SOCl_2$. The last task included investigation of suitable electrolytes.

2. TECHNICAL PRESENTATION

2.1 ALTERNATIVE ANODES: ELEMENTS

2.1.1 Experimental Procedure

In order to determine the stability of the selected metals in the solvents, samples of Ca, Mg and Al (and Li, as a control) were exposed to both $SOCl_2$ and SO_2Cl_2 at 72°C for extended periods of time. The metal/solvent combinations were sealed in glass ampules, for visual observation, according to the following procedure: in a dry argon atmosphere the metals were first cleaned with emery paper to remove oxides and then inserted into the ampules containing the solvents; the ampules were then stoppered to keep out moisture, removed from the dry box, frozen in liquid nitrogen and fused at the neck of the ampule. Samples thus prepared were stored in an oven at 72°C and observed periodically.

The sample of zinc was exposed to 1.8M $LiAlCl_4/SOCl_2$ at room temperature for a relatively short period of time to measure the open circuit potential.

Open circuit potentials of Al and Zn were measured by constructing complete cells consisting of the metal and a carbon cathode in 1.8M $LiAlCl_4/SOCl_2$ enclosed in a glass tube. Ca and Mg were investigated by assembling complete "AA" configuration cells in stainless steel cans. These consisted of a carbon cathode and the metal foil separated by glass fiber paper. The assembled cells were enclosed in glass tubes (rather than welding a metal feedthrough/cover assembly). Various solutes were investigated as electrolytes for these cells, e.g., $LiAlCl_4$, $NaAlCl_4$, $Ca(AlCl_4)_2$ and $Ca(SbCl_6)_2$.

The polarization characteristics of cells were determined by connecting one of the electrodes to the "working electrode" terminal and the other electrode to both the "counter" and "reference electrode" terminals of a potentiostat (PAR 173). The cell was then polarized following a linear sweep signal (PAR 175 Universal Programmer) from open circuit to 0.0V at a rate of 50 mV/s to 100 mV/s. The resulting E vs. I curve was plotted on an X-Y recorder (Hewlett-Packard 7001A).

Discharges at constant load were carried out by applying a load resistor across the cell and monitoring the voltage on a strip chart recorder (Varian 5A).

2.1.2 Results and Discussion

After about three months of storage in $SOCl_2$ and SO_2Cl_2 at 72°C, both lithium and calcium had turned slightly dull but magnesium showed no obvious signs of reaction; there was no evidence of solvent decomposition for any of these combinations. The aluminum retained its original surface luster in both solvents but ultimately gelatinous precipitates formed indicating corrosion of the Al. These precipitates had the same appearance as aluminum chloride-sulfur dioxide or aluminum chloride-thionyl chloride adducts, which were synthesized in separate experiments. Thus the corrosion process might follow one or more of the following reactions:

$$8Al + 13SOCl_2 \rightarrow 6AlCl_3 \cdot SO_2 + Al_2Cl_6 \cdot SOCl_2 + 6S \qquad (24)$$

$$2Al + 3SO_2Cl_2 \rightarrow 2AlCl_3 \cdot SO_2 + SO_2 \qquad (25)$$

$$8Al + 12SO_2Cl_2 \rightarrow 3Al_2Cl_6 \cdot SOCl_2 + 9SO_2 + Al_2O_3 \qquad (26)$$

These adducts show remarkable high temperature stability. The $AlCl_3 \cdot SO_2$ adduct is a colorless viscous liquid or gelatinous precipitate at ambient temperature without excessive vapor pressure. The $Al_2Cl_6 \cdot SOCl_2$ adduct is a yellow oil that can be distilled at 215°C at one atmosphere pressure without decomposition. The high temperature stability of metallic aluminum in the presence of these adducts was not determined.

The initial open circuit potentials of the metals measured vs. $C/SOCl_2$ (1.8M $LiAlCl_4$) at room temperature are as follows:

Li	3.65V
Ca	2.85V
Mg	1.95V
Zn	1.35V
Al	1.04V

Because of their favorable open circuit potentials, Ca and Mg were investigated further. This entailed the development of solutes other than $LiAlCl_4$, such as $NaAlCl_4$, $Mg(AlCl_4)_2$, $Ca(SbCl_6)_2$, and $Ca(AlCl_4)_2$. The conductivities of these solutions are similar to those based on $LiAlCl_4$; i.e., in the range of 10^{-3} to 10^{-2} $\Omega\text{-cm}^{-1}$.

Solutions were prepared in the same manner as for $LiAlCl_4$; i.e., a Lewis acid such as $AlCl_3$ or $SbCl_5$ was dissolved in thionyl chloride or sulfuryl chloride and the desired salt (anhydrous LiCl, NaCl, $CaCl_2$ or $MgCl_2$) was then added to form the complex. $LiAlCl_4$ was easily soluble up to 2.0 m/l in both thionyl and sulfuryl chloride (the solubility of $LiAlCl_4$ exceeds 4 m/l in thionyl chloride). $NaAlCl_4$ was similarly soluble with ease up to 2.0M in $SOCl_2$ and approximately 1.0M in SO_2Cl_2. $Ca(SbCl_6)_2$ was readily soluble in both thionyl and sulfuryl chlorides up to about 2 m/l. $Ca(AlCl_4)_2$, however, went into solution very slowly (only after continuous stirring for three days), and dissolved up to 1 m/l in thionyl chloride. The Mg salts were found to be relatively insoluble. Possibly the $MgCl_2$ was not dried sufficiently since Peled and Straze have recently reported[6] that $Mg(AlCl_4)_2$ is soluble up 0.5 m/l in thionyl chloride.

An "AA" size $Mg/SOCl_2$ cell, as described previously, was tested using standard electrolyte, 1.8M $LiAlCl_4/SOCl_2$. Using a linear potential sweep in the range of 100 mV/s, the cell was polarized from its open circuit (1.95V) down to 0V. The cell gave about 1 mA/cm^2 at 1.5V, about 5 mA/cm^2 at 1.0V, and a short circuit current density of about 15 mA/cm^2 (200 mA).

Calcium was tested in various electrolytes. The results are summarized in Table III showing polarization from open circuit vs. current density, and in Table IV showing actual cell voltage vs. current density; some results for lithium are included for comparison. Cells using $Ca(SbCl_6)_2$ - $SOCl_2$ electrolytes gave the lowest performance. The best results were obtained in 1.8M $LiAlCl_4$ - $SOCl_2$: the open circuit voltage was about 2.85V; at a polarization of approximately 1000 mV from open circuit the current density, for the better of the two cells tested, was 14.5 mA/cm^2. A lithium cell at equivalent polarization, shows more than twice this rate. Ca anodes in $NaAlCl_4$ - $SOCl_2$ showed similar performance. Ca anodes in sulfuryl chloride and $NaAlCl_4$ exhibited higher open circuit potentials (approximately 3.1V), but did not perform as well as in thionyl chloride. Cells with $Ca(AlCl_4)_2$ - $SOCl_2$ electrolyte were not made during the course of this program because of the initial difficulty in dissolving the solute, as discussed above.

One of the cells with $Ca(SbCl_6)_2$ - $SOCl_2$ electrolyte (#5) was discharged for several hours and maintained about 2V at about 2 mA/cm^2. Both of the cells with $LiAlCl_4$ - $SOCl_2$ were discharged on constant load also. Cell #6 ran at about 1.5 mA/cm^2 for about 50 hrs at 2V. Cell #7, in which the electrode spacing was closer, ran at 0.75 mA/cm^2 and about 2.7V for 35 hrs. Cells #8 and #9, with $NaAlCl_4$ - $SOCl_2$ gave similar performance but less capacity. The cell with the dilute electrolyte was discharged across a 2565Ω load at approximately 1 mA (0.075 mA/cm^2). It exhibited a very flat voltage plateau at 2.65V and then rapidly dropped toward a second plateau at 1V after approximately 230 hrs. The cell with the more concentrated electrolyte was discharged across a 262Ω load at approximately

TABLE III

ELECTROCHEMICAL CHARACTERISTICS OF Ca ANODES: POLARIZATION FROM OPEN CIRCUIT VS. CURRENT DENSITY

			SURFACE AREA	CELL	OCV	CELL POLARIZATION (mV) VS. CURRENT DENSITY(mA/cm^2)							
NO.	ELECTROLYTE/CATHODE	ANODE	(cm^2)	CONFIG.	VOLTS	500	1000	1500	2000	2500	3000	3500	(mV)
1	1.8M $LiAlCl_4$ - $SOCl_2$/C	Li	10.0	(1)	3.65	10.0	33.0	50.0	80.0	118.0	160.0	210.0	
2	0.5M $Ca(SbCl_6)_2$ - $SOCl_2$/C	Ca	10.0	(1)	2.65	1.6	5.2	9.0	12.8	16.8			
3	2.0M $LiAlCl_4$ - $SOCl_2$/C	Li	5.0	(1)	3.65	10.0	28.0	50.0	72.0	96.0	122.0	146.0	
4	0.2M $Ca(SbCl_6)_2$ - $SOCl_2$/C	Ca	5.0	(1)	2.5	2.4	6.8	11.0	16.4	21.0			
5	0.5M $Ca(SbCl_6)_2$ - $SOCl_2$/C	Ca	13.8	AA	2.85	0.7	0.29	0.51	0.80	1.38			
6	1.8M $LiAlCl_4$ - $SOCl_2$/C	Ca	13.8	AA	2.84	—	6.0	11.8	19.2	26.8			
7	1.8M $LiAlCl_4$ - $SOCl_2$/C	Ca	13.8	AA(2)	2.85	0.7	14.5	26.8	40.6	53.6			
8	1.0M $NaAlCl_4$ - $SOCl_2$/C	Ca	13.8	AA	2.78	—	12.0	23.0	35.0	49.0			
9	0.1M $NaAlCl_4$ - $SOCl_2$/C	Ca	13.8	AA	2.59	—	0.8	1.7	2.5	3.6			
10	SULFURYL CHLORIDL 1.0M $NaAlCl_4$ - SO_2Cl_2/C	Ca	13.8	AA	3.09	1.0	2.4	4.4	6.5	8.7	10.6		
11	1.0M $NaAlCl_4$ - SO_2Cl_2/C	Ca	13.8	AA	3.16	—	0.7	4.7	15.3	28.3	39.8		

(1) Flat electrodes about 0.5 cm apart immersed in electrolyte.

(2) Closer electrode spacing (less resistance) than cell #6.

TABLE IV

ELECTROCHEMICAL CHARACTERISTICS OF Ca ANODES: CELL VOLTAGE VS. CURRENT DENSITY

			SURFACE AREA	CELL	OCV	CELL VOLTAGE VS. CURRENT DENSITY (mA/cm^2)						
NO.	ELECTROLYTE/CATHODE	ANODE	(cm^2)	CONFIG.	VOLTS	3.0V	2.5V	2.0V	1.5V	1.0V	0.0	VOLTS
1	1.8M $LiAlCl_4$ - $SOCl_2/C$	Li	10.0	(1)	3.65	15.0	35.0	55.0	85.0	130.0	225.0	
2	0.5M $Ca(SbCl_6)_2$ - $SOCl_2/C$	Ca	10.0	(1)	2.65	—	—	2.8	6.4	10.2	18.0	
3	2.0M $LiAlCl_4$ - $SOCl_2/C$	Li	5.0	(1)	3.65	14.0	34.0	56.0	80.0	104.0	150.0	
4	0.2M $Ca(SbCl_6)_2$ - $SOCl_2/C$	Ca	5.0	(1)	2.5	—	—	2.4	6.8	11.0	21.0	
5	0.5M $Ca(SbCl_6)_2$ - $SOCl_2/C$	Ca	13.8	AA	2.85	—	—	0.22	0.45	0.73	2.46	
6	1.8M $LiAlCl_4$ - $SOCl_2/C$	Ca	13.8	AA	2.84	—	—	4.0	9.4	16.7	31.5	
7	1.8M $LiAlCl_4$ - $SOCl_2/C$	Ca	13.8	AA	2.85	—	—	11.2	22.8	37.0	62.3	
8	1.0M $NaAlCl_4$ - $SOCl_2/C$	Ca	13.8	AA	2.78	—	—	7.25	18.0	30.4	59.4	
9	0.1M $NaAlCl_4$ - $SOCl_2/C$	Ca	13.8	AA	2.59	—	—	—	1.0	2.0	4.0	
10	SULFURYL CHLORIDE 1.0M $NaAlCl_4$ - SO_2Cl_2/C	Ca	13.8	AA	3.09	—	1.2	2.8	4.9	7.1	11.0	
11	1.0M $NaAlCl_4$ - SO_2Cl_2/C	Ca	13.8	AA	3.16	—	—	0.8	5.0	29.0	40.0	

(1) Flat electrodes about 0.5 cm apart immersed in electrolyte.

(2) Closer electrode spacing (less resistance) than cell #6.

10 mA (0.72 mA/cm^2) and exhibited a flat plateau at 2.65V, but dropped below 2V after 23 hrs. The discharge voltage continued to drop slowly below 0.5V after 88 hrs when the experiment was terminated. Both of these cells delivered only about 0.23 Ahr above a 2V cut-off. Disassembly of the discharged cells revealed a normally wet and active cathode structure without evidence of hardening or accumulation of discharge products. The discharge products appeared to have precipitated out on the surface of the calcium anode facing the cathode. This apparent passivation of the calcium anode was not observed with cells using $Ca(SbCl_6)_2$ electrolyte but the cells were not specifically examined in this regard (cells using $Ca(AlCl_4)_2$, unfortunately, were not investigated). Driscoll and Holleck[25] have reported similar results for the discharge of calcium, also in $LiAlCl_4$ -$SOCl_2$; i.e., the formation of a white crystalline precipitate on the surface of the calcium and discharge capacities of about 50% of theoretical. In cells with sodium or lithium tetrachloraluminate, it would be expected that the alkali metal ions, because of their higher mobility, would deposit as LiCl or NaCl at the cathode and be replaced in the electrolyte by calcium ions:

$$2Ca + 4Na^+ + 2SOCl_2 \rightarrow S + SO_2 + 4NaCl + Ca^{2+} \qquad (27)$$

For the two cells with $NaAlCl_4$, the point of depletion of the Na+ ions would correspond to 0.107 Ah for the 1 M $NaAlCl_4$, and to 0.0107 Ah for the 0.1M $NaAlCl_4$. Since both cells delivered about 0.230 Ah before passivation, there is no obvious correlation with the sodium ion concentration; rather it would appear to be related to the thickness of the passivating layer on the calcium.

In separate experiments with reserve cell electrolytes, Ca was discharged in thionyl chloride containing only $AlCl_3$(2.3M). The calcium showed an initial open circuit voltage of 3.5V vs. C/$SOCl_2$ and sustained a current density of about 19 mA/cm^2 at 2.5V for about 10 min before anode passivation; the calcium was mostly black with a small shiny spot in the center. A lithium anode in the same electrolyte (2.3M $AlCl_3$ - $SOCl_2$) ran at about 70 mA/cm^2 at 2.8V for 30 min; the discharge was terminated in this case by clogging of the cathode. These results again suggest differences in the calcium/solution interface.

Peled[6] has reported that the alkali and alkaline earth metals are covered by a metal chloride layer at all times in thionyl chloride and that electrochemical processes occur by migration of ions through this solid electrolyte interphase. The transference number for the Li+ cation through LiCl is 1.0. However, it is well known that the transference number for Ca++ in $CaCl_2$ (or Mg in $MgCl_2$) is less than 1.0 and the transference number for anions is greater than zero.[26] Thus on discharge of a Ca anode in $SOCl_2$, part of the current would be carried through the solid electrolyte interphase by the cations and part would be carried by the anions. Such a mechanism would be anticipated to promote growth of the passivation layer,[27] and may account for the increased polarization and ultimate passivation of calcium anodes on discharge in thionyl chloride.

2.2 ALTERNATIVE ANODES: ALLOYS

2.2.1 Experimental Procedure

The NUSCAL-battery aluminum alloys were investigated by fabricating small cells in demountable glass containers. The electrolyte was 1.8M $LiAlCl_4$ - $SOCl_2$. Storage and all measurements were at room temperature. Pure zinc (99.99%) and pure aluminum (99.99%) were examined in similar cells. Zinc was examined because it is one of the alloying elements; it also showed some favorable characteristics in Table II, and it was anticipated to be corrosion resistant since it is used as the liner in shipping containers of $SOCl_2$.

2.2.2 Results and Discussion

The open circuit potentials measured in 1.8M $LiAlCl_4$ - $SOCl_2$ are as follows:

	Alloy	OCV vs. C/$SOCl_2$(V)
1)	Al, Zn (1.47%), Hg (0.01%)	1.10
2)	Al, Zn (3.52%), In (0.03%)	1.11
3)	Al, Zn (4.19%), Mg (0.46%), In (0.04%)	1.07
4)	Al, Mg (0.79%), Sn (0.13%), Ga (0.05%)	1.04
5)	Al, (99.99%)	1.04
6)	Zn, (99.99%)	1.35

Pure aluminum and all of the alloys exhibited substantial pitting after only two days of exposure to the electrolyte. The rate seemed to slow down after the initial rapid corrosion: however, all samples showed severe corrosion after several months. Zinc did not show any obvious signs of corrosion after three weeks of storage at room temperature (i.e., no discoloration of metal or solution and no precipitated material). No attempt was made to discharge any of these cells.

3. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Of the various metals and alloys tested, only calcium, magnesium and zinc were sufficiently corrosion resistant to examine further. All of these have higher melting temperatures than lithium, but only calcium shows a high enough potential vs. $C/SOCl_2$ to be a potentially viable alternative to the lithium anode. The calcium anode may also be subject to less activation inhibition ("voltage delay") than Li after storage at elevated temperature,[25] but it appears that, unlike lithium, calcium may passivate on discharge due to differences in the anion transfer characteristics of the $CaCl_2$ solid electrolyte interphase on the calcium surface.

In summary, as an alternative anode material, calcium remains an intriguing possiblity. However, many aspects of the $Ca/SOCl_2$ reaction mechanism remain unanswered; therefore, further investigation is recommended. It would be of particular interest to examine the solid electrolyte interphase and the discharge characteristics of calcium in $Ca(AlCl_4)_2$, $Ca(FeCl_4)_2$ and other solutes in $SOCl_2$.

III. PRELIMINARY SURVEY OF ALTERNATIVE CATHOLYTES FOR IMPROVED LITHIUM CELL PERFORMANCE

1. INTRODUCTION

1.1 OBJECTIVES

The lithium cell currently produced commercially by GTE Laboratories is based on thionyl chloride as the solvent/oxidant and $LiAlCl_4$ as the electrolyte solute. This has proved to be a very successful combination, yielding a high energy density battery with excellent discharge characteristics. The properties which could be the most productively improved are the conductivity ($2 \times 10^{-2} \Omega\text{-cm}^{-1}$ for 1.8M $LiAlCl_4$ - $SOCl_2$), the boiling point (79°C for $SOCl_2$), the capacity for dissolving the discharge reaction products (at 25°C, sulfur = 1.63 m/l of $SOCl_2$ and 1.16 m/l of 1.8M $LiAlCl_4$ - $SOCl_2$; sulfur dioxide = 2.4 m/l of $SOCl_2$ and 3.0 m/l of 1.8M $LiAlCl_4$ - $SOCl_2$; LiCl is insoluble in $SOCl_2$), and the extent of voltage delay after storage at elevated temperature.

The objective then was to investigate various alternatives to both the solvent/oxidant and the solute to obtain an improved catholyte for the lithium cell.

1.2 TECHNICAL APPROACH

The original investigations of the lithium cell were based on the solvent $POCl_3$. One approach to finding alternative solvents has been to simply explore related members of the phosphorous and sulfur oxyhalide families. This approach has yielded the currently favored solvent $SOCl_2$. Other possibilities are listed in Table V. It can be seen that many of the compounds containing fluorine have low boiling points; even the more promising fluorine compounds may also decompose to lower boiling compounds (e.g., $POFBr_2 \rightarrow POF_3$ and $PSFBr_2 \rightarrow PSF_3$). $POCl_3$, $SOCl_2$ and SO_2Cl_2 have been investigated, and $SOBr_2$ is unstable. The remaining possibilities, then, are $S_2O_5Cl_2$, $P_2O_3Cl_4$ and $PSCl_3$.

Another approach is to consider the fundamental solvent characteristics of various solvents. The ability of a solvent to function as an electron pair donor (EPD) toward a Lewis acid such as antimony pentachloride, $SbCl_5$, has been represented by the negative heat of reaction of the EPD solvent with $SbCl_5$ in a dilute solution of an inert cosolvent such as 1,2-dichloroethane and is quantitatively called the donor number (DN). Gutman

TABLE V

MELTING POINTS AND BOILING POINTS OF VARIOUS SOLVENTS

SOLVENT	MELTING POINT (°C)	BOILING POINT (°C)
SOF_2	-110.5	-43.8
POF_3	-68	-39.7
$SOCl_2$	-105	78.8
$POCl_3$	2	105.3
$SOBr_2$	-52	138
$POBr_3$	56	189.5
SOClF	-139.5	12.2
$POFCl_2$	-80.1	52.9
$POFBr_2$	-117.2	110.1
SO_2F_2	-136	-55.4
SO_2Cl_2	-54	69.1
SO_2FCl	-125	7
SO_2FBr	-86	41
$S_2O_5F_2$	-46	51
$P_2O_3F_4$	--	71
$S_2O_5Cl_2$	-38	152.5
$P_2O_3Cl_4$	-165	212
PSF_3	-148.8	-52.2
$PSCl_3$	-35	125
$PSBr_3$	38	212
$PSFBr_2$	-75.2	125.3

and Mayer have tabulated donor numbers for various EPD solvents along with their dielectric constants as represented in Table VI.[28] Those solvents with higher DN's and dielectric constants would be expected to dissolve a larger number of electrolyte salts and yield electrolyte solutions with higher conductivities. For example, $POCl_3$ is a much better EPD solvent than $SOCl_2$, and it has been found that several more lithium salts are soluble in $POCl_3$ than in $SOCl_2$.[29]

For every equivalent of charge passed in a cell, one mole of Li^+ ions is added to the electrolyte at the anode ($Li \rightarrow Li^+ + e^-$) and one mole is removed at the cathode ($Li^+ + 1/2\ SOCl_2 + e \rightarrow 1/4\ S + 1/4\ SO_2 + LiCl$); thus some

TABLE VI

DONOR NUMBERS (DN) AND DIELECTRIC CONSTANTS (ε) OF VARIOUS EPD-SOLVENTS

SOLVENT	DN	ε	MELTING POINT (^{o}C)	BOILING POINT(^{o}C)
1, 2-Dichloroethane	-	10.1	-35.0	84.0
Sulphuryl chloride	0.1	10.0	-54.1	69.1
Benzene	0.1	2.3	5.5	80.1
Thionyl chloride	0.4	9.2	-105.0	78.8
Acetyl chloride	0.7	15.8	-112.0	∿51.0
Tetrachloroethylene carbonate	0.8	9.2		
Benzoyl fluoride	2.0	22.7		∿155.0
Benzoyl chloride	2.3	23.0	-1.0	197.2
Nitromethane	2.7	35.9	-29.0	101.0
Dichloroethylene carbonate	3.2	31.6		
Nitrobenzene	4.4	34.8	5.7	210.0
Acetic anhydride	10.5	20.7	-73.1	140.0
Phosphorus oxychloride	11.7	14.0	2.0	105.3
Benzonitrile	11.9	25.2	-13.0	190.7
Selenium oxychloride	12.2	46.0	8.5	176.4
Acetonitrile	14.1	38.0	-45.0	81.6
Sulpholane	14.8	42.0	∿22.0	
Propanediol-1,2-carbonate	15.1	69.0	-48.8	240.0
Benzyl cyanide	15.1	18.4	-23.8	234.0
Ethylene sulphite	15.3	41.0		∿60.0(10 mm)
iso-Butyronitrile	15.4	20.4	-71.5	103.9
Propionitrile	16.1	27.7	-92.9	97.35
Ethylene carbonate	16.4	89.1	∿36.0	
Phenylphosphonic difluoride	16.4	27.9		
Methylacetate	16.5	6.7	-98.1	57.0
n-Butyronitrile	16.6	20.3	-112.0	118.0
Acetone	17.0	20.7	-95.35	56.2
Ethyl acetate	17.1	6.0	-83.6	77.06
Water	18.0	81.0	0.0	100.0
Phenylphosphonic dichloride	18.5	26.0		258.0
Diethyl ether	19.2	4.3	-116.2	34.6
Tetrahydrofuran	20.0	7.6	-65.0	∿64.0
Diphenylphosphonic chloride	22.4	-		
Trimethyl phosphate	23.0	20.6		197.2
Tributyl phosphate	23.7	6.8		289.0
Dimethylformamide	26.6	36.1	-61.0	153.0

TABLE VI (Continued)

DONOR NUMBERS (DN) AND DIELECTRIC CONSTANTS (ε) OF VARIOUS EPD-SOLVENTS

SOLVENT	DN	ε	MELTING POINT (^{o}C)	BOILING POINT (^{o}C)
N-methyl-ε-caprolactam	27.1	-		
N-methyl-2-pyrrolidone	27.3	-	-17.0	197.0
N, N-Dimethylacetamide	27.8	38.9	-20.0	165.0
Dimethyl sulphoxide	29.8	45.0	18.45	189.0
N, N-Diethyformamide	30.9	-		∿177.0
N, N-Diethylacetamide	32.2	-		∿185.0
Pyridine	33.1	12.3	-42.0	115.5
Hexamethylphosphoricamide	38.8	30.0	7.0	∿100.0 (6 mm)

lithium salt must be dissolved or generated in the solvent to sustain the ionic current through the electrolyte.

The Lewis Base EPD solvents, upon which inorganic lithium cells depend for the cathode reaction, exhibit markedly different properties with different salts. Devynck and Tremillon[30] applied a chloro-acid/chloro-base theory to the oxychlorides $POCl_3$ and $SeOCl_2$ that is also applicable to other oxyhalide solvent systems and helps explain some of the chemistry. Phosphorus oxychloride can be considered to be an ionic solvent with an ionic product $K_i = \left[POCl_2^+\right]\left[Cl^-\right] = 10^{-19\pm0.3}\ mol^2 \ell^{-2}$ at 25°C. A scale of chloroacidities in $POCl_3$, determined by Devynck and Tremillon[30] is shown in Figure 14. The solubility of basic electrolytes such as the alkali metal halides can be achieved through the addition of chloroacid SO_3, $SbCl_5$, BCl_3 or $AlCl_3$ to yield a slightly acidic electrolytic solution capable of being reduced at a carbon cathode vs. an alkali metal anode. If these electrolyte solutions are made basic through the addition of a chlorobase such as a tetralkyl ammonium chloride, the anodes can no longer be oxidized and the cells cease to function. We also suspect that the anode passivation is strongly dependent on the acidity of the electrolyte salts.

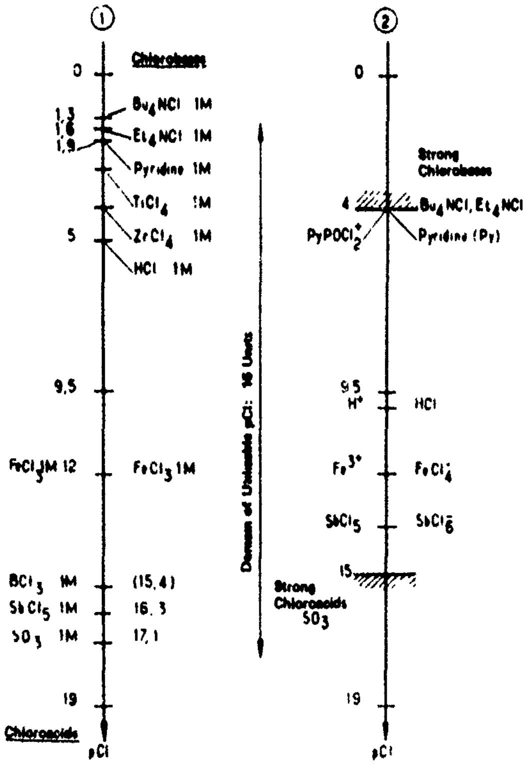


Figure 14. Order of Chloroacids and Chlorobases in $POCl_3$ (1) 1M Solution, (2) 10^{-4}M Solutions.

2. TECHNICAL PRESENTATION

2.1 ALTERNATIVE SOLVENT/OXIDANTS

2.1.1 Experimental Procedure

Two solvents, pyrosulfuryl chloride and nitrobenzene, were selected for preliminary investigation. Pyrosulfuryl chloride ($S_2O_5Cl_2$) has a boiling point of 152.5°C and a melting point of -38°C. Nitrobenzene has a boiling point of 210°C and a melting point of 5.7°C; thus, this material would require a cosolvent to lower its freezing point to a more reasonable value.

Pyrosulfuryl chloride was synthesized from carbon tetrachloride and sulfur trioxide according to the following reaction:

$$CCl_4(\ell) + 2\ SO_3(\ell) \rightarrow S_2O_5Cl_2(\ell) + COCl_2(g) \tag{28}$$

With both solvents attempts were made to dissolve $LiAlCl_4$ to make conductive solutions, and to build experimental cells.

2.1.2 Results and Discussion

Pyrosulfuryl chloride was refluxed over lithium with no apparent corrosion or decomposition of the solvent. It was not possible to dissolve enough lithium chloride and aluminum chloride in $S_2O_5Cl_2$ to yield a usefully conductive electrolyte solution in the solvent itself. Pyrosulfuryl chloride is miscible with both thionyl chloride and sulfuryl chloride, however, and might be used as an inorganic cosolvent with either of these materials in an electrolyte solution. It cannot be used with the aluminum chloride containing electrolytes, however. The addition of 25% by volume $S_2O_5Cl_2$ to a 1.8M solution of $LiAlCl_4$ in thionyl chloride or a 2.0M solution of $LiAlCl_4$ in sulfuryl chloride results in the formation of a gelatinous precipitate in the case of $SOCl_2$, or a crystalline precipitate in SO_2Cl_2. These precipitates are probably not simply $LiAlCl_4$, but most likely involve adducts of the solvents or their decomposition products with aluminum chloride. An attempt was made to check the solubility of elemental sulfur (10% by weight) in pyrosulfuryl chloride. No immediate reaction was noted at room temperature, but bubbles of gas were evolved as the mixture was heated and the solution changed from colorless to yellow. Upon reaching the melting point of sulfur (120°C), the bubbling stopped and the globule of molten sulfur in the bottom of the solution slowly dissolved. The reaction noted between sulfur and pyrosulfuryl chloride is probably:

$$S_2O_5Cl_2(\ell) + 2S(s) \rightarrow S_2Cl_2(\ell) + SO_2(g) + SO_3(g) \qquad (29)$$

or

$$2S_2O_5Cl_2(\ell) + 5S(s) \rightarrow 2S_2Cl_2(\ell) + 5SO_2(g) \qquad (30)$$

This reaction between pyrosulfuryl chloride and elemental sulfur might be used "in situ" in an inorganic electrolyte cell based on reduction of thionyl chloride or sulfuryl chloride to consume the elemental sulfur formed during discharge and extend the life of the cathode.

Nitrobenzene was found to dissolve up to about 1.5 m/l of $LiAlCl_4$. A small lithium/carbon cell was built with this electrolyte using a glass cell. The open circuit voltage was about 3.5V and the application of various load resistors gave the following results:

CURRENT DENSITY (mA/cm^2)	CELL VOLTAGE (V)
0.13	2.57
0.23	2.25
0.25	2.08
0.32	1.91
0.41	1.62
0.50	1.08
OCV	3.32

Thus, it appears that the nitrobenzene was being reduced at the cathode. It should be pointed out that these are preliminary results and no attempt to optimize this system was made.

2.2 ALTERNATIVE ELECTROLYTE SOLUTES

2.2.1 Experimental Procedure

Sulfur trioxide was investigated as a substitute Lewis acid for the $AlCl_3$ presently used to make the conductive lithium salt. Sulfur trioxide is a very strong Lewis acid and can be used to solubilize lithium chloride in phosphorus oxychloride. The reaction proceeds as follows to form lithium chlorosulfonate:

$$LiCl + SO_3 \rightarrow LiSO_3Cl \qquad (31)$$

This material is soluble in phosphorus oxychloride and renders the solution ionically conducting. Unfortunately, sulfur trioxide is also a strong oxidant and will oxidize thionyl chloride. We have demonstrated, however, that sulfuryl chloride and sulfur trioxide are completely miscible and do not react. Initial attempts to form alkali metal or alkaline earth metal chlorosulfonates in sulfuryl chloride solutions by reaction of the respective chlorides and sulfur trioxide were not successful. An appropriate cosolvent may have to be used or other measures taken to insure ionic conductivity in SO_2Cl_2/SO_3 solutions. Simple compatibility studies indicated that solutions of SO_3 in SO_2Cl_2 are not reactive toward lithium metal and this solution therefore might form the basis for a much more powerful soluble depolarizer than sulfur dioxide or even thionyl chloride itself.

An attempt was made to synthesize approximately 1M $LiSO_3Cl$ in each of four inorganic solvent systems (phosphorus oxychloride, $POCl_3$; thionyl chloride, $SOCl_2$; sulfuryl chloride, SO_2Cl_2; and pyrosulfuryl chloride, $S_2O_5Cl_2$) by reacting stoichiometric quantities of chlorosulfonic acid, HSO_3Cl, with lithium metal according to:

$$2\ Li\ (m) + 2\ HSO_3Cl\ (sol'n) \rightarrow 2\ LiSO_3Cl\ (sol'n) + H_2(g) \qquad (32)$$

The reaction did not go to completion in any of the four solvent systems attempted, even when the mixtures were heated to boiling and refluxed under an inert atmosphere. Simple electrochemical cells in glass tubes were constructed utilizing a 1.25 cm x 4 cm Teflon-bonded carbon cathode wrapped with glass mat filter paper and lithium ribbon to yield a 10 cm^2 active electrode area. The polarization characteristics of these cells were determined by subjecting them to controlled voltage sweeps from open circuit to 0V in the same manner as described in Section II-2.1.1.

2.2.2 Results and Discussion

Discharge of the cells described above, containing $LiSO_3Cl$ as the electrolyte solute, gave the following results:

SOLVENT	OPEN CIRCUIT VOLTAGE	AC RESISTANCE	SHORT CIRCUIT CURRENT
$POCl_3$	3.84V to 3.81V	0.44K	83.0 mA
$SOCl_2$	2.16V to 3.22V	1.0 K	0.41 mA
SO_2Cl_2	1.54V to 1.50V	1.0 K	0.17 mA
$S_2O_5Cl_2$	3.22V to 2.67V	1.0 K	0.102 mA

The only cell of the group that had a sufficiently conductive electrolyte solution to show electrochemical performance was that utilizing $POCl_3$ as a solvent. This cell was capable of delivering 1.6 mA/cm^2 at 3.0V when fresh. Since we know the open circuit potential of the lithium-phosphorus oxychloride cell reaction is below 3.0V, we see that we were discharging another component of the solution, possibly the $LiSO_3Cl$ or unreacted HSO_3Cl. This hypothesis was confirmed by discharging the cell across a 180Ω resistor. The discharge voltage was initially above 3.0V, but finally stabilized at 2.2V after the active component was reduced and the normal $POCl_3$ discharge reaction became predominant.

A small quantity of crystalline $LiSO_3Cl$ was synthesized from lithium chloride and boiling chlorosulfonic acid according to:

$$LiCl\ (s) + HSO_3Cl\ (\ell) \rightarrow LiSO_3Cl\ (sol'n) + HCL\ (g) \qquad (33)$$

The $LiSO_3Cl$ was precipitated from the cooled chlorosulfonic acid solution with dry thionyl chloride and washed several times with thionyl chloride to yield a relatively pure product. This material was soluble in $POCl_3$ but not in $SOCl_2$, SO_2Cl_2 or $S_2O_5Cl_2$, which correlates with the above results.

3. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

No suitable alternatives to the present catholyte, $LiAlCl_4$ - $SOCl_2$ were developed in this investigation. $LiSO_3Cl$ was soluble in $POCl_3$ (which is not an acceptable cathode reactant) but gave ambiguous results when tested in a lithium/C cell. Pyrosulfuryl chloride was stable to lithium but did not dissolve enough $LiAlCl_4$ or $LiSO_3Cl$ to make a sufficiently conductive electrolyte for testing. Nitrobenzene was more promising as a solvent/oxidant; $LiAlCl_4$ was soluble to about 1.5 m/l. A lithium/C cell in this electrolyte exhibited an open circuit of 3.5V and nitrobenzene appeared to be reduced at the cathode. This solvent, however, has an unacceptably high freezing point and thus could only be used with a cosolvent. On this basis, nitrobenzene may merit further investigation.

IV. RESERVE MODE CONFIGURATIONS OF THE $Li/SOCl_2$ CELL

1. INTRODUCTION

1.1 OBJECTIVES

The objective of this study was to explore reserve electrolyte configurations of the $Li/SOCl_2$ cell to ascertain the potential advantages for improved performance and/or for prolonged storage.

1.2 TECHNICAL APPROACH

Two reserve mode configurations of the $Li/SOCl_2$ cell were investigated; 1) a low-rate (standard) semi-reserve electrolyte cell and, 2) a high-rate reserve electrolyte cell. In the semi-reserve concept the cell contains thionyl chloride but the electrolyte salt ($LiAlCl_4$) is held in reserve. There could be some advantages to this configuration: the thionyl chloride alone is known to be sufficiently nonconductive to prevent high currents on accidental short-circuiting, and there should be less direct reaction between lithium and pure thionyl chloride, reducing self-discharge and possibly reducing voltage delay.

In the high-rate configuration, only the $AlCl_3$ (Lewis Acid) component of the electrolyte is used, and the entire electrolyte solution is held in reserve. The electrolyte must be held in reserve to prevent self-discharge of the lithium in the presence of aluminum chloride ($AlCl_3$ continuously dissolves the LiCl film covering the lithium surface). However, this reaction may be slow enough to allow a fast discharge after activation, as would be suitable in some applications (e.g., torpedo propulsion). Because the discharge product LiCl (which normally deposits in the cathode pores) is soluble in this electrolyte, high rate discharge may be maintained without the usual premature clogging of the cathode.

2. TECHNICAL PRESENTATION

2.1 SEMI-RESERVE ELECTROLYTE CELLS

The concept of chemical activation of a reserve cell containing thionyl chloride stored in contact with lithium and carbon electrodes was demonstrated in small glass cells. The cell consisted of two 1.25 cm × 4.0 cm lithium electrodes on either side of a similarly sized Teflon-bonded carbon electrode assembled in glass tubes filled with 1.8M $LiAlCl_4$ in $SOCl_2$ or with $SOCl_2$ alone. The cell containing the $LiAlCl_4$ salt was capable of delivering an initial short circuit current in excess of 2.2A when potentiostatically swept from its open circuit voltage (3.63V) to 0V at 100 mV/s. After aging six days at 70°C, the short circuit current obtained under similar conditions at ambient temperature was limited to 0.22A, the majority of the passivation being observed on the lithium electrode. The simple addition of 0.1g $AlCl_3$ to the approximate 15 ml of electrolyte solution did not depassivate the anode; the short circuit current observed after this treatment was only about 0.25A. A similar cell, after storage at 70°C in thionyl chlordie alone, had sufficient lithium chloride and aluminum chloride added to make 1.8M $LiAlCl_4$ before discharge. This cell was potentiostatically polarized in a similar manner and exhibited a short circuit current of 1.4A. These experiments demonstrate that the addition of a small amount of Lewis acid $AlCl_3$, is not sufficient to depassivate a lithium anode aged in an electrolytic solution originally containing electrolyte salts, $LiAlCl_4$; however, anodes aged in solvent alone ($SOCl_2$) show much less passivation and the cell can be activated by the addition of the electrolyte salt before use. A.N. Dey has also reported that Li stored in pure thionyl chloride for 624 hrs at 78°C shows (by SEM analysis) a much thinner small-grained film.[31]

2.2 HIGH-RATE RESERVE ELECTROLYTE CELLS

2.2.1 Experimental Procedure

For testing of the high rate reserve concept, small cells were built in glass containers. The lithium electrode had an area of 16 cm^2 (0.05 × 4 × 4 cm) and a theoretical capacity of about 1.7 Ah. The cathode was a carbon-Teflon structure on nickel expanded mesh substrate; it had an area of 25 cm^2 (0.095 × 5 × 5 cm) and a carbon loading of approximately 0.55 g/cm^3. These two electrodes were separated by glass fiber paper and placed horizontally at the bottom of a shallow glass cell. The electrodes were held in place by covering them with a glass block. Electrolyte was added immediately before initiation of discharge in each case. The cells were discharged at room temperature at a constant rate of 70 mA/cm^2 in thionyl chloride solutions of the following compositions:

$AlCl_3$	LiCl	
1.8M	1.8M	(standard electrolyte)
2.3M	1.8M	
1.8M	0.0M	
2.3M	0.0M	

2.2.2 Results and Discussion

The discharge performance observed in the various electrolytes tested are summarized in Figure 15. For a normal discharge (1 to 2 mA/cm^2) in standard electrolyte (1.8M $LiAlCl_4$), the cell would have been cathode limited. The lithium had a theoretical capacity of 1.7 Ahr and the cathode had a normal-rate capacity of approximately 1 to 1.2 Ah; at this very high discharge rate (about 70 times the normal rate), the capacity obtained in 1.8M $LiAlCl_4$ was about 0.17 Ah to a 2.0V cutoff (plateau at about 2.4V). In the electrolyte containing 2.3M $AlCl_3$ alone the capacity obtained was about 0.55 Ah above 2.0V (initial plateau at about 2.8V). Similarly improved results were obtained with 1.8M $AlCl_3$: about 0.33 Ah but with more polarization. It is apparent that the use of $AlCl_3$ alone in the electrolyte produces a significant increase in the high rate performance of a lithium/thionyl chloride cell. The rate of lithium loss over the discharge period was not quantitatively determined but appears to be low enough for practical application.

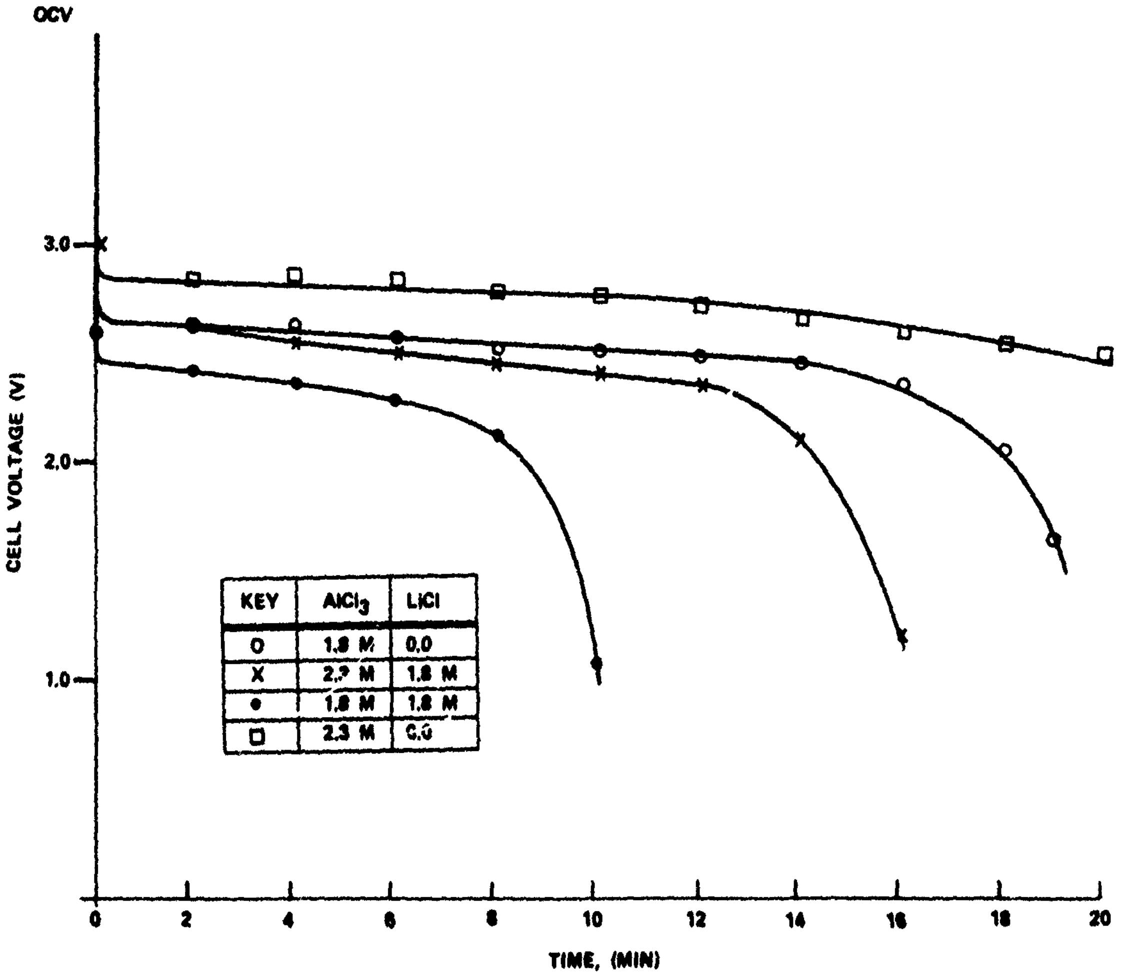


Figure 15. High Rate Li/$SOCl_2$ Cell. Effect of Solute Ratios and Concentrations on Discharge at Current Density of 70 mA/cm^2

3. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The low-rate semi-reserve cell in which the electrolyte solute ($LiAlCl_4$) is held in reserve, appears to be a viable concept in terms of reduced self-discharge and voltage delay after storage at elevated temperature. The engineering problems in reducing this concept to pratice and the cost in terms of energy density, complexity and reliability were not evaluated but are anticipated to be substantial. Since there are no present applications that would utilize the prolonged storage capabilities of this configuration, and because progress has been made in other simpler approaches, no further investigation is recommended.

The second reserve electrolyte concept, in which all of the electrolyte is held in reserve and contains only the $AlCl_3$ component of the solute, has proved capable of delivering more than three times the capacity and energy obtained with standard electrolyte at about 70 times the normal rate (70 mA/cm^2 for 30 min at 2.5V to 2.8V). Thus, this system may be suitable for some high rate applications, such as undersea weapons propulsion, and it is recommended that the engineering aspects of such a reserve system be evaluated.

V. DETERMINATION OF THE DISCHARGE MECHANISMS IN $Li/SOCl_2$ CELLS

1. INTRODUCTION

1.1 OBJECTIVES

The determination of processes occurring during the discharge of $Li/SOCl_2$ cells is of both theoretical and practical interest. Understanding of these processes can help in estimating the ultimate capability of the system and in determining design parameters.

The reactions occurring at the lithium electrode are reasonably well established. Lithium metal reacts superficially with thionyl chloride to produce a coating of lithium chloride; this film of LiCl is insoluble and prevents further direct attack. The LiCl acts as a solid electrolyte interphase: it has a very low electronic or anionic conductivity, but a cationic conductivity sufficient to allow discharge of the lithium.[6] At the anode, lithium ions are furnished to the electrolyte and electrons are furnished to the external circuit. Electrical conduction in the electrolyte involves no net transfer of the anion (tetrachloroaluminate) but the lithium ion must transfer from the anode through the electrolyte and into the cathode. In the cathode, transfer of electrons from the external circuit to the thionyl chloride must take place on the carbon surface with the entrance of the lithium ions, to preserve the balance of charge. The processes by which this occurs, however, have not been so clearly established. The purpose of this work then has been to determine the nature of the electrochemical processes occurring in the cathode during cell operation.

1.2 TECHNICAL APPROACH

Since lithium ions are involved in the cathode process, the formation of a lithium salt or salts is indicated. At the same time, the sulfur in $SOCl_2$ must be reduced (the oxygen and chlorine are already reduced to their lowest oxidation states). Examples of known compounds with reduced sulfur, which could be present include:

SCl_2,	sulfur dichloride
S_2Cl_2,	sulfur monochloride
Li_2S,	lithium sulfide
$Li_2S_2O_3$,	lithium thiosulfate

S,	elemental sulfur
$Li_2S_2O_4$,	lithium dithionite
$Li_2S_{(2+n)}O_6$	lithium polythionates

Compounds of sulfur with an oxidation state the same as or higher than that in $SOCl_2$ could exist as products by exchange or disproportionation:

Li_2SO_3,	lithium sulfite
$Li_2S_2O_5$	lithium pyrosulfite
SO_2,	sulfur dioxide
$Li_2S_2O_6$,	lithium dithionate
Li_2SO_4,	lithium sulfate

In addition to the compounds already mentioned to account for the chloride and oxide present in $SOCl_2$, there is also:

LiCl,	lithium chloride

There have been several attempts to define the reaction mechanism based on known cell reactions, on qualitative analyses, and on some quantitative work. Behl et al.[32] postulated that the sulfur was ultimately reduced to lithium dithionite, based on the known reaction for the Li/SO_2 soluble cathode cell. Auborn et al.[29] found Li_2SO_3 by x-ray analysis of crystals present on a cathode taken from a discharged cell; it was assumed that the reduced form of sulfur was the element, since sulfur crystals were also found throughout cells after discharge. Dey and Schlaikjer [12] discharged C-size cells with neoprene closures and noted deformation of the closures for cells which had been discharged, but not for cells stored without discharge. The pressurized vapor phase of the discharged cells was found, by infrared spectroscopy, to contain SO_2. Qualitative confirmation of the presence of sulfur, along with the essential absence of sulfur oxyacid salts in the cathode, led to the hypothesis that the products were LiCl, S, and SO_2. Confirmation of this reaction was attempted by Cogley et al.[33] They performed quantitative analyses of discharged cathodes for lithium chloride, and of complete discharged cells for sulfur and sulfur dioxide. Wet chemical analyses for LiCl and S showed one mole of LiCl per equivalent of charge, and one mole of sulfur per four equivalents of charge. Analyses of cell electrolytes by gas chromatography showed that SO_2 was present and increased with cell discharge, but that one mole of SO_2 appeared for every two equivalents of charge. This is twice the amount expected for the reaction:

$$4\ Li + 2\ SOCl_2 \rightarrow S + SO_2 + 4\ LiCl \qquad (34)$$

The observed amounts of sulfur and LiCl however, correspond to the predicted values.

Several conflicting observations then, needed to be resolved at the beginning of this work. If the production of LiCl had a one-to-one correspondence with the amount of Li consumed,[33] production of Li_2SO_3[29] would be impossible, although this material had apparently been positively identified in the cathode. If no lithium compounds other than LiCl could form, then SO_2 would be the only known compound in which the oxygen could occur after discharge. Yet, twice the amount of SO_2 predicted by Eq. (34) was actually observed.[33]

Table VII shows the calculated open circuit potentials and the number of equivalents per mole of $SOCl_2$ predicted by a number of possible discharge reactions. For the first six reactions the products are assumed to be sulfur, lithium chloride, and various compounds containing oxygen. For the remaining reactions the products are assumed to be sulfur monochloride, lithium chloride, and various oxygen compounds. The predicted open circuit potentials are all similar and close to the observed potential (3.645V at 25°C, see Figure 16). Thus these values alone are not sufficient to confirm a reaction. The predicted numbers of equivalents per mole, however, are substantially different in many cases; this information, which can be determined without chemical analyses, can be combined with information obtained from quantitative chemical analyses, and offers another means of studying the discharge process. For this reason we developed a method of measuring the number of electrical equivalents passed per mole of $SOCl_2$ reduced, based on controlled potential coulometry.

Procedures were also developed for detecting qualitatively, and then measuring quantitatively, any lithium-oxyacid-sulfur salts which might have been present in the cathodes of discharged cells. In the work by Cogley et al.,[33] the objective was to measure chloride in the cathode but not sulfite or sulfate, etc. If lithium-sulfur-oxyacid salts are present in the cathode, as Auborn claimed,[29] the quantities might be too low to be detected by difference, using this chloride analysis method. The presence of non-stoichiometric amounts of Li_2SO_3, Li_2SO_4, etc. in the cathode might indicate that more than one discharge reaction occurs, and that predominance of one or another could be affected by electrolyte concentration, temperature, or other parameters.

TABLE VII

EQUIVILENTS PER MOLE OF $SOCl_2$ AND OPEN CIRCUIT POTENTIALS PREDICTED BY CELL REACTIONS

	EQUIVALENT PER MOLE $SOCl_2$	CALCULATED POTENTIAL (V)
$4\ Li + 2\ SOCl_2 \rightarrow 4\ LiCl + S + SO_2$	2.00	3.72
$14\ Li + 6\ SOCl_2 \rightarrow 12\ LiCl + 4\ S + Li_2S_2O_6$	2.33	3.70
$10\ Li + 4\ SOCl_2 \rightarrow 8\ LiCl + 2\ S + Li_2S_2O_4$	2.50	3.57
$10\ Li + 4\ SOCl_2 \rightarrow 8\ LiCl + 3\ S + Li_2SO_4$	2.50	3.73
$8\ Li + 3\ SOCl_2 \rightarrow 6\ LiCl + S + Li_2S_2O_3$	2.67	3.56
$8\ Li + 3\ SOCl_2 \rightarrow 6\ LiCl + 2\ S + Li_2SO_3$	2.67	3.60
$6\ Li + 4\ SOCl_2 \rightarrow 6\ LiCl + S_2Cl_2 + 2\ SO_2$	1.50	3.68
$10\ Li + 6\ SOCl_2 \rightarrow 8\ LiCl + 2\ S_2Cl_2 + Li_2S_2O_6$	1.67	3.64
$7\ Li + 4\ SOCl_2 \rightarrow 5\ LiCl + 3/2\ S_2Cl_2 + Li_2SO_4$	1.75	3.68
$6\ Li + 3\ SOCl_2 \rightarrow 4\ LiCl + S_2Cl_2 + Li_2SO_3$	2.00	3.52
$8\ Li + 4\ SOCl_2 \rightarrow 6\ LiCl + S_2Cl_2 + Li_2S_2O_4$	2.00	3.50
$7\ Li + 3\ SOCl_2 \rightarrow 5\ LiCl + 1/2\ S_2Cl_2 + Li_2S_2O_3$	2.33	3.52

The measurement of sulfur dioxide in the electrolyte of discharging or discharged cells was performed by Cogley et al., using gas chromatography. In their technique, the injector was at 150°C and the column at 80°C. A reaction of sulfur with the solvent to form SCl_2 and SO_2 is thermodynamically favored at 127°C (i.e., below the injector temperature):

$$S + 2\ SOCl_2 \rightarrow SO_2 + 2\ SCl_2\ \Delta F_{400^\circ K} = -12\ \text{Kcal mole}^{-1}\ \ldots \qquad (35)$$

The investigators reported that over 90% of the sulfur, theoretically predicted from the $SOCl_2$ discharge, had been found previously in the electrolyte.

Thus, reaction of sulfur with $SOCl_2$ at the injector could account quantitatively for the observed two fold excess of SO_2 over that predicted by Eq. (34). For our experiments, sulfur dioxide was measured by quantitative infrared spectroscopy at room temperature to avoid chemical or thermal decomposition of any of the material present in the electrolyte.

The vapor pressure as a function of temperature was measured for mixtures containing thionyl chloride with lithium tetrachloroaluminate, sulfur, sulfur dioxide, and carbon, when it was found that the amount of sulfur dioxide generated by cell discharge was less than that predicted by Eq. (34). Carbon was suspected of absorbing the sulfur dioxide from the electrolyte until the discharge products displaced the sulfur dioxide near the end of discharge. Thionyl chloride itself was studied to compare measured vapor pressure with literature data.[1] Fresh electrolyte, simulated-discharged electrolyte (saturated with sulfur dioxide and sulfur), and discharged electrolyte taken from spent cells were all tested without and with fresh cathode material and cathodes taken from spent cells.

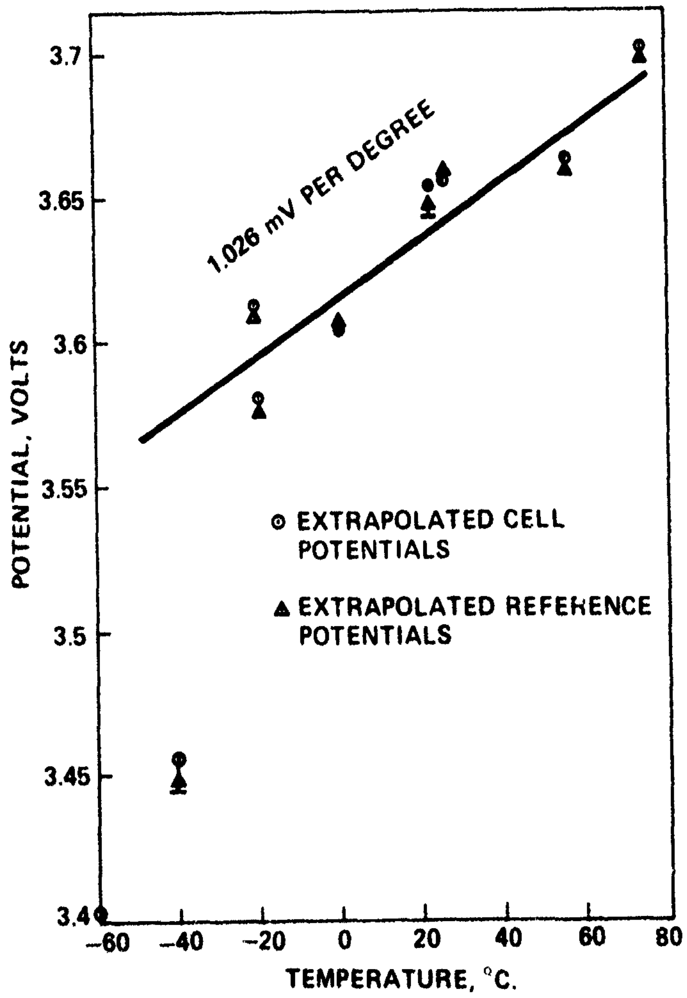


Figure 16. Open Circuit Potential of a $Li/SOCl_2$ Cell vs. Temperature

2. TECHNICAL PRESENTATION

2.1 EXPERIMENTAL PROCEDURE

The controlled potential coulometry was carried out in a cylindrical pyrex vessel containing about 100 ml of supporting electrolyte, to which was added a small weighed amount of $SOCl_2$. A 1 ml pipette was used to measure two samples, one for the test cell, the other for a weighing bottle to establish the weight of the sample. The $SOCl_2$ had been purified according to the procedure of Friedman and Wetter,[34] and checked for hydrolysis products according to French et al.[35] The amount of $SOCl_2$ used was about 1.6g, equivalent to 1 Ahr, assuming 2.67 equivalents per mole, the highest value predicted in Table VII. The cell had a working electrode about 3.5 cm^2 with carbon in excess, usually 500 mg to 600 mg; a lithium reference electrode, and a counter electrode with lithium in excess. The counter electrode was also about 3.5 cm^2 (two pieces of 30 mil foil). The electrolyte was $POCl_3$ with either $LiAlCl_4$ or $LiBCl_4$ as the electrolyte salt. The phosphorus oxychloride was refluxed from 12 to 14 hrs over lithium and distilled under dry air. It was checked for hydrolysis products prior to use.[35] The supporting electrolyte was chosen for the following desirable features: it did not react with $SOCl_2$, lithium, or the nickel screen used to support the carbon working electrode. However, $POCl_3$ also discharges on a carbon surface at about 2.5V to 3V anodic to lithium; therefore the coulometric reduction of $SOCl_2$ had to be performed at a controlled potential.

In order to determine the lower potential limit for the coulometry, the open circuit potential of the $Li/SOCl_2$ system had to be determined as a function of temperature (see Figure 16). (This information was also useful in determining the "thermoneutral" potential; see Section I-2.1.2.2.) A hermetically sealed D-size cell was used for these measurements. It had a cylindrical lithium anode pressed against the inside surface of the can and an inner concentric carbon cathode. Part of the cathode was removed at the bottom to permit introduction of a second lithium electrode. This electrode was attached to the center pin of a second cover/feed through assembly welded to the bottom of the can. This cell was about half discharged using a low current density at room temperature. The cell was equilibrated at 25°C. The dependence upon applied current of the terminal potential, and of the potential of the cathode vs. the reference, was recorded for a stepwise series of ascending and descending currents. The data were fitted to polynomial functions and extrapolated to zero current to obtain the open circuit potential. The process was repeated for a number of temperatures. The final results are presented in Figure 16. A value of 3.30V was chosen as the limiting potential for the coulometric reduction based on the approximate average of the measured $SOCl_2$ cell potentials and the test cell without $SOCl_2$ added to the supporting electrolyte. With the limiting potential chosen, another constraint was needed. A potentiostat could be used to fix the potential above the lower limit selected, but the resulting initial current might be high enough to passivate the cathode surface. Current limitation was therefore necessary also. The apparatus and method used to achieve both potential and current control are shown in Figure 17. The potentiostat was a Wenking Model 61R. With the diode in place, the potentiostat was not capable of discharging the cell, only of charging it. Since the set potential was below the open circuit potential however, charging could not occur, and no net current could pass through both the cell and the potentiostat. Instead, the potentiostat impressed a current through the load resistor which prevented the potential between the carbon working electrode and the lithium reference from falling below the set value. The recording ammeter (A) measured only the current through the cell; the current through the resistor consisted of the cell current plus that impressed by the potentiostat. When the switch was first closed at time t_1, the cell discharged through the load resistor without any participation by the potentiostat. The resistor was chosen such that the initial current was below 1 mA/cm^2 of cathode. When the potential fell to the set value at time t_2, the potentiostat then sent current through the resistor, gradually reducing the fraction of current through the cell. The measured quantity is the total charge passed, $(i \times t)$, i.e., the shaded area under the curve shown in Figure 17. The cell was placed in a thermostatically controlled chamber 12 hrs before beginning a run. A magnetic stirrer was used to keep the solution agitated. Predischarge of the supporting electrolyte, to remove impurities such as Cl_2, was carried out prior to adding the $SOCl_2$ to the cell.

Chemical analyses of cathodes from discharged wound-D and bobbin 2-D cells were performed as follows. Cells were discharged at constant current at various temperatures to a 1V cutoff. Temperature equilibration before discharge was typically 12 to 14 hrs. Discharged cells were drilled near the top, where there is void volume, and all volatile materials were then removed by evacuating the cells at ambient temperature. The cells were disassembled in the dryroom. The cathodes were separated and subjected to further vacuum drying under gentle heating (40° to $50^\circ C$). Qualitative testing of these cathodes for lithium-sulfur-oxyacid salts, Li_2O, and Li_2S was carried out using wet chemical methods. Solutions were handled under argon to avoid air oxidation of sulfite, sulfide, and dithionite. Cathodes were leached in aqueous buffer solutions or in distilled water. Detection of sulfate in solution (obtained by leaching of cathodes with distilled water) was accomplished by precipitation with barium chloride solution, followed by x-ray analysis of the dried salt. Quantitative analysis for sulfite was carried out by oxidation to sulfate using hydrogen perioxide in a boiling carbonate-bicarbonate buffer, followed by precipitation of $BaSO_4$ from an acetate buffer. Standard samples demonstrated this method to be superior to redox titration or other methods of oxidation.

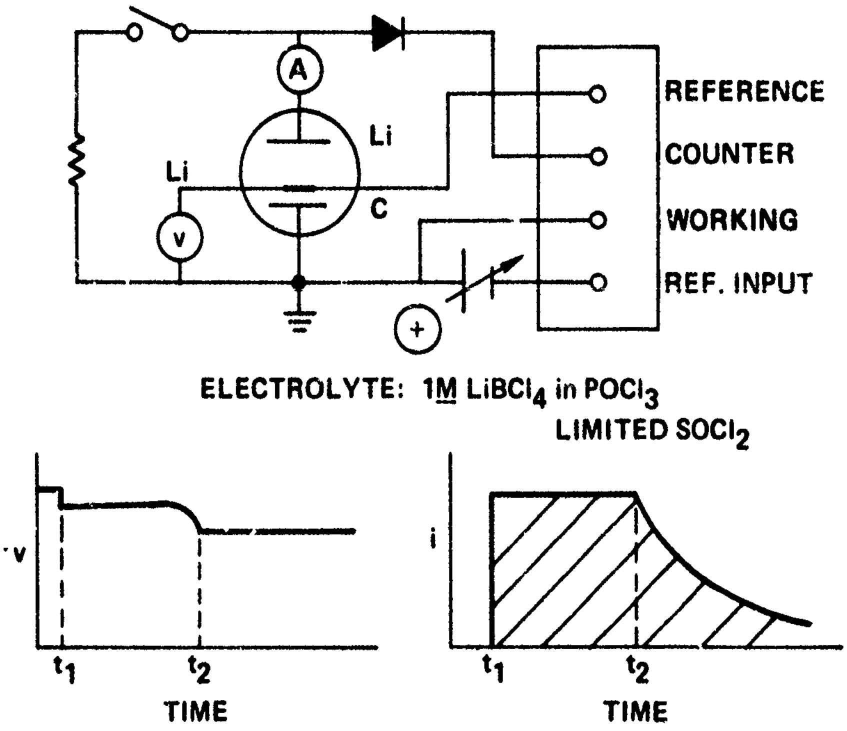


Figure 17. Controlled Potential Electrolysis

Two thousand Ah prismatic cells were used to follow concentration of sulfur dioxide dissolved in the electrolyte and cell vapor effluents (SO_2 and $SOCl_2$) as a function of discharge (Figure 9). The cell electrodes were 12 in. × 12 in. plates. Each cell had three cathodes, two full anodes and two half anodes, one at either end of the stack. Cells were discharged at 10A (1.8 mA cm^{-2}) at ambient temperature. The cell case was welded and provided with a filling port through which vapors could escape into a tightly fitted Teflon tube. Vapors were led from the cell to a scrubbing apparatus assembled from standard laboratory equipment. Each flask was one liter in capacity. The total volume was one liter of 4M aqueous K_2CO_3. If the cell ejected SO_2 and $SOCl_2$ slightly above atmospheric pressure, the carbonate would absorb both gases forming K_2SO_3 and KCl. For sampling, dry nitrogen was led through the system as shown, to purge any acid vapors out of the connecting tubing. (A "Drierite" trap between the cell and the first flask was found to be unnecessary; the double flask system prevented any hazard of back-flow of the aqueous mixture into the cell.) After purging, the flasks were removed, the solutions were mixed and then distributed between the two flasks again. At regular intervals, samples were taken, one from one of the flasks and one from the cell through the filling port, with the short plastic tube to the Y-joint disconnected. K_2SO_3 in the aqueous sample was determined by oxidation to the sulfate and precipitation as $BaSO_4$. KCl was determined argentimetrically and the $SOCl_2$ collected was equal to half the KCl; the SO_2 collected was then equal to the total K_2SO_3 minus half the KCl.

Sulfur dioxide dissolved in the electrolyte was determined by infrared spectroscopy according to the following procedure. Solutions of SO_2 in $SOCl_2$ will absorb in the infrared region at 1333 cm^{-1} and, to a lesser extent, at 1140 cm^{-1} (Figure 18). The former is useful for analysis. For calibration standards, $SOCl_2$ free of SO_2 must be prepared. This can be done by fractionating the purified solvent, discarding the first fractions. Gravimetric standard solutions of SO_2 may be then prepared and appropriate dilutions made. The net absorption vs. concentration is linear, following Beer's law, up to at least 0.1 molar, (Figure 19). A Perkin Elmer Model 621 infrared spectrophotometer was used, with Barnes Engineering NaCl micro-cavity cells (nominal thickness 0.10 mm). Path lengths increased with cell use, so that standards had to be run following every measurement. One milliter electrolyte samples were pipetted into 50 ml flasks containing 25 ml of SO_2- free $SOCl_2$ and then filled to the mark with SO_2-free $SOCl_2$.

The vessel used to measure the vapor pressure of electrolyte mixtures as a function of temperature is shown in Figure 20. It was constructed of stainless steel. Its internal volume was 70 ml; 51 ml was the typical sample size of the liquid under test. Table VIII shows the mixtures used for the tests performed. The used cathode material had 5g of carbon to 51 ml of liquid, to repeat the ratio used in the cells. Used electrolyte presumably was saturated with sulfur and SO_2, having been taken from completely discharged 2000 Ahr prismatic cells.

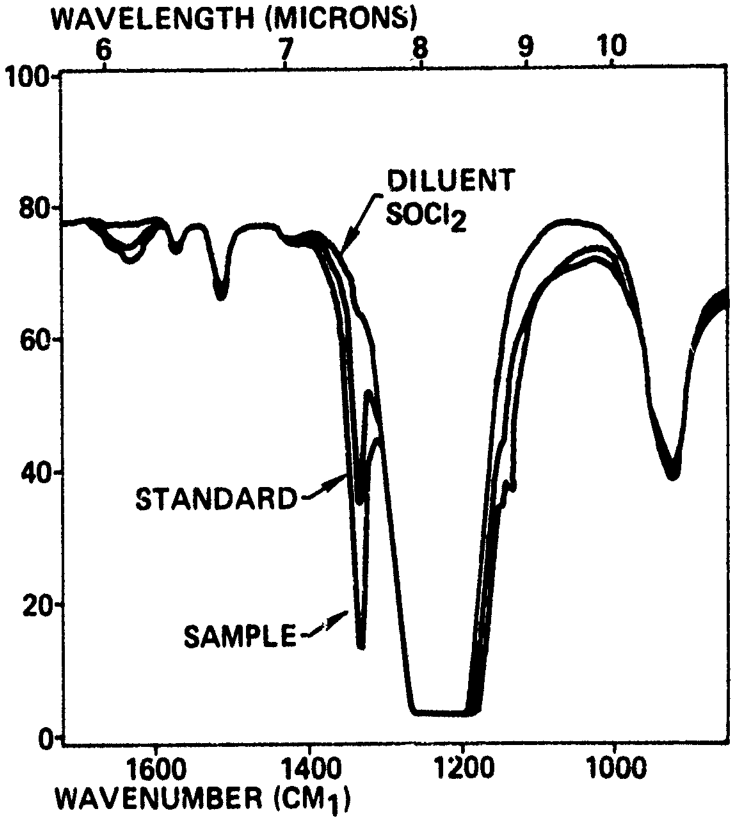


Figure 18. SO_2 in $SOCl_2$, Infrared Spectrum

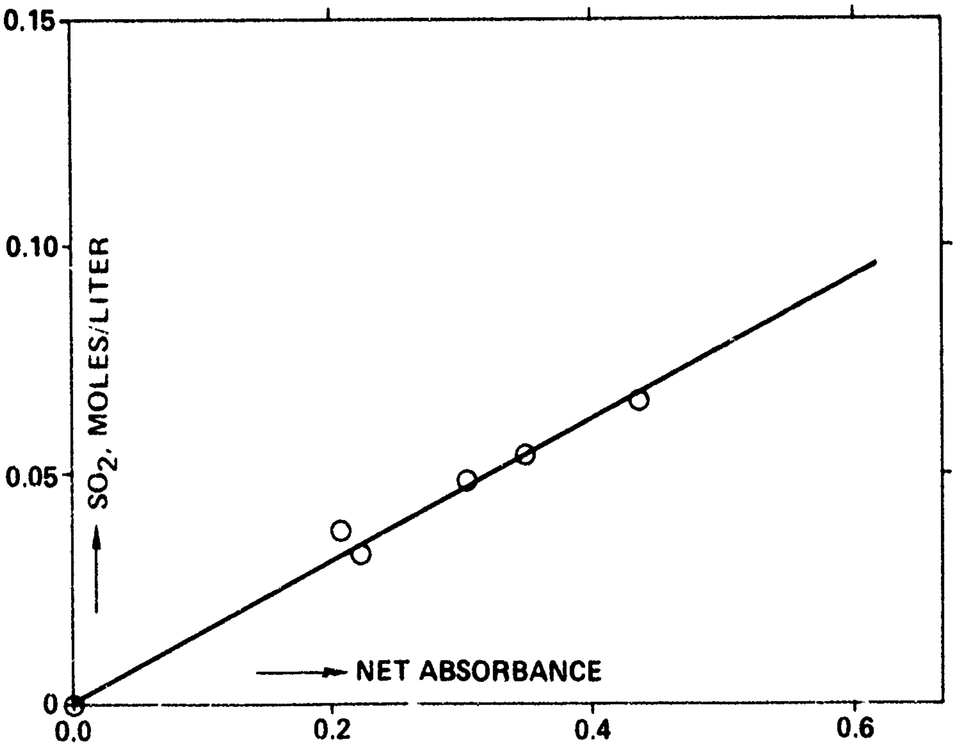


Figure 19. Beer's Law Plot SO_2 in $SOCl_2$

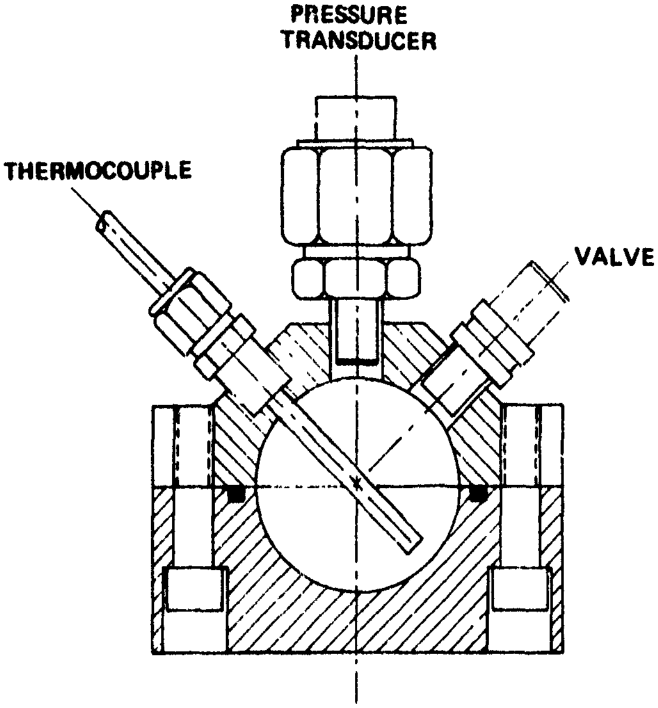


Figure 20. Vapor Pressure Vessel Configuration

TABLE VIII

SAMPLES OF $SOCl_2$ WITH CARBON, SO_2, S, AND $LiAlCl_4$ USED IN PRESSURE VESSEL TESTS

SAMPLE NO.	CARBON	SO_2	S	$LiAlCl_4$
1	None	None*	None	None
2	None	3.5M	None	None
3	None	3.5M	1.1M	None
4	None	3.5M	1.1M	1.8M
5	None	USED ELECTROLYTE		
6	Fresh	3.5M	1.1M	None
7	Fresh	3.5M	None	1.8M
8	Fresh	None*	None	1.8M
9	Fresh	USED ELECTROLYTE		
10	Used	3.5M	None	None
11	Used	3.5M	None	1.8M
12	Used	USED ELECTROLYTE		

*∿0.08M SO_2, no SO_2 added.

The vessel was charged with a sample in the dry room, sealed, and placed in a stirred oil bath at ambient temperature. The temperature was slowly raised to a maximum value, either 70^0 or 100^0C over a three hour period, then held at that temperature for three hours, or allowed to cool again to ambient temperature while readings were taken.

2.2 RESULTS

The controlled potential coulometry gave the following information:

TABLE IX

CONTROLLED POTENTIAL COULOMETRY OF $SOCl_2$ IN A SUPPORTING ELECTROLYTE AT 3.30V

TEMPERATURE °C	ELECTROLYTE	EQUIVALENTS PER MOLE $SOCl_2$
25	$POCl_3$; 1.0M $LiAlCl_4$	1.82
25	$POCl_3$; 0.85M $LiBCl_4$	2.00
10 to 13	$POCl_3$; 0.36M $LiBCl_4$	1.856
-2.6 to +2.6	$POCl_3$; 0.36M $LiBCl_4$	1.527

Qualitative tests of dried D and 2D cathodes for the materials outlined in Section V, 1.2 revealed that small amounts of sulfate were present in the aqueous leach solution, identified by x-ray analysis of precipitates reclaimed after the addition of $BaCl_2$ solution to the leach. A substance was present which would reduce MnO_4^- at pH = 5 for cells discharged at -20^0C, but not at -10^0, $+12^0$, or 25^0C. This could not have been dithionite, sulfide, or thiosulfate since tests specific for these anions was negative. The species present could have been sulfite or pyrosulfite. X-ray analysis of the barium salt reclaimed from the neutral leach solution revealed only $BaSO_4$, but the control sample of authentic $BaSO_3$ demonstrated that barium sulfite was partially oxidized to $BaSO_4$ during analysis in the diffractometer. These experiments must be repeated using the Debye-Scherrer technique, where the samples can be protected from the atmosphere. Specific tests for, and analyses of sulfur and lithium chloride were not carried out. Quantitative analyses of sulfur-oxyacid salts were expressed as cathode sulfate found (after oxidation of sulfur oxyacid species to sulfate by H_2O_2 at pH = 10) divided by sulfate expected according to:

$$7Li + 4SOCl_2 \rightarrow 3/2\ S_2Cl_2 + Li_2SO_4 + 5LiCl \ldots \qquad (36)$$

$$(1.75 \text{ eq. per mole } SOCl_2)$$

and according to the observed cell capacity. For the control cells (which were not discharged at all), the capacity was taken as the average of the bobbin 2D cells discharged at 25°C. The % sulfate, or sulfate found divided by that expected, is plotted against discharge temperature in Figure 21. The amount of sulfate found at room temperature or 12°C is near that for the control samples, implying that sulfate formed as much through handling as through cell discharge. At -10°C, more sulfate appeared, and at -20°C, a significant amount of sulfur-oxyacid-salt was produced by discharge, possibly a mixture of sulfite and sulfate.

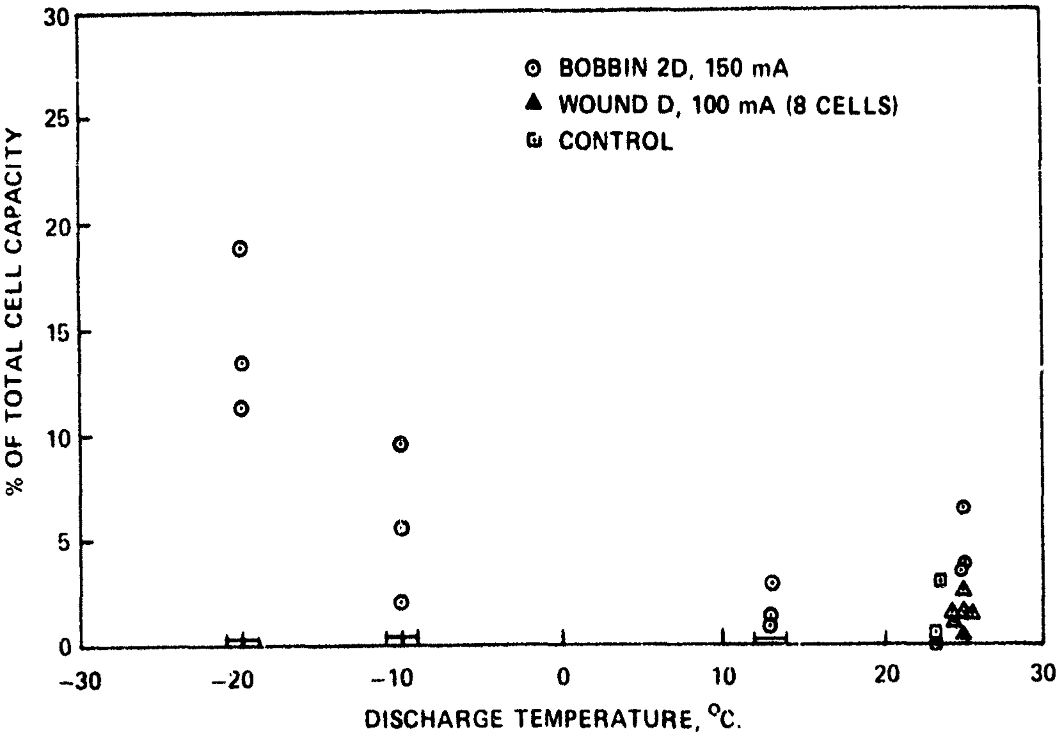


Figure 21. %Cell Capacity Accounted for Based on $7\ Li + 4\ SOCl_2 \rightarrow 3/2\ S_2Cl_2 + Li_2SO_4 + 5\ LiCl$

The measurements of SO_2 in the electrolytes of anode limited and cathode limited 2K Ahr prismatic cells, and the amount of SO_2 and $SOCl_2$ vapors which escape from such cells, have been plotted as a function of electrical capacity. These were shown and described above in Section I, 2.2.2, and Figures 12 and 13. In both the anode and cathode limited cells, SO_2 concentration built up more slowly than that indicated in Figures 12 and 13 as predicted by Eq. (34), until near the end of discharge. At this point, electrolyte sulfur dioxide increased rapidly and about 10.5 moles of SO_2 were finally expelled to the scrubber in the case of the cathode limited cell, beginning shortly after 1200 Ahrs. The anode limited cell also expelled SO_2 to the scrubber shortly after 1200 Ahrs, but the amount expelled never exceeded 90 millimoles. Scatter in electrolyte SO_2 measurement was in excess of that expected from the uncertainty (±5%), as noted in the data of Figure 12. When the cell was redesigned to allow for greater electrolyte mixing by thermal convection, the scatter was greatly reduced, but the SO_2 generation was still less than predicted by Eq. (34) until near the end of discharge. The time required for discharge was about 1350 Ahr/10A = 135 hours or 5.6 days.

The pressure tests were performed to determine whether the carbon was responsible for absorbing some of the generated SO_2, therefore explaining why the amount found was less than that expected according to Eq. (34). Figure 22 shows the result when pure thionyl chloride saturated with SO_2 at room temperature (3.56M) was introduced into the pressure vessel with or without unused cathode material, in the same ratio as that present in the 2K Ahr cells. The carbon made no significant difference in the vapor pressure vs. temperature curve, indicating that it did not absorb SO_2. Figure 23 shows the result when electrolyte taken from a completely discharged 2K Ahr cell was temperature cycled to 70°C without carbon, at a measured SO_2 concentration of 3.01M. The pressure at 70°C (about 18 lb/in^2 gauge) was less than that for SO_2-$SOCl_2$ mixture (about 33 lb/in^2 gauge), possibly because of the dissolved electrolyte salt (see Figure 10). However, on cooling the vessel, the pressure was higher than it had been during heating. On the second thermal cycle, the pressure rose even higher. The experiment was repeated using carbon and cycling to 100°C (Figure 24). Pressure hysteresis was also observed as the temperature was cycled five times. No hysteresis occurred when fresh electrolyte saturated with S and SO_2 was used in place of the electrolyte from the discharged cells, whether carbon was present or not. This demonstrated that reactions such as Eq. (35) or Eq. (20) were not responsible for the pressure increase observed on temperature cycling below 100°C.

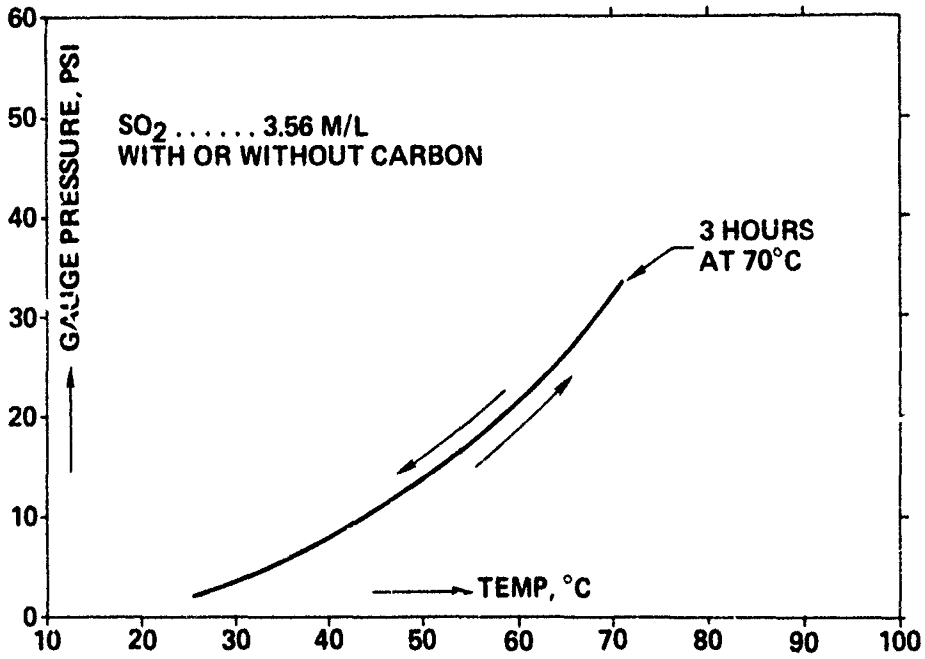


Figure 22. Pressure-Temperature Behavior, $SOCl_2$ with SO_2

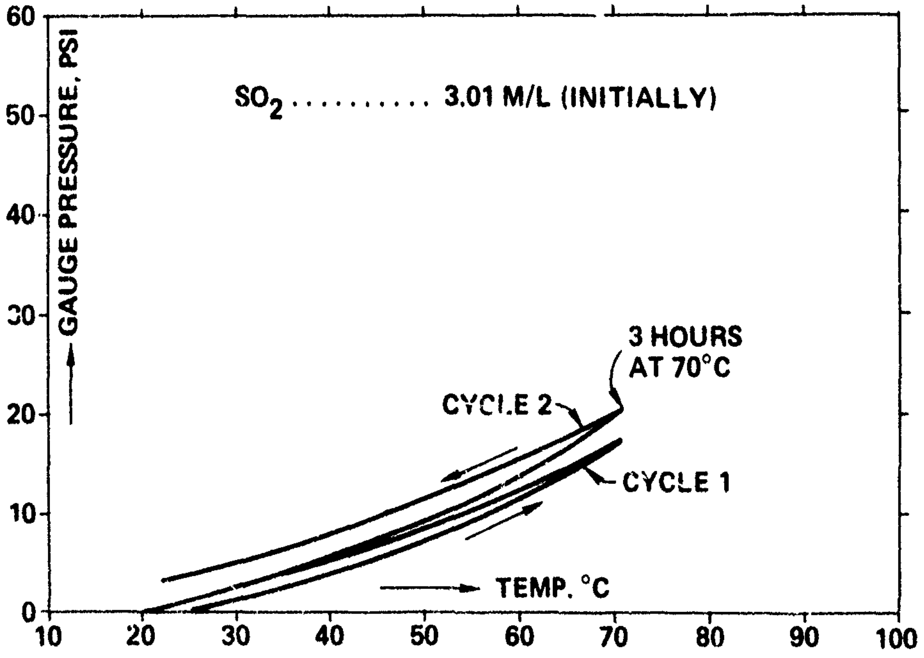


Figure 23. Pressure-Temperature Behavior, Electrolyte from Discharged Cell

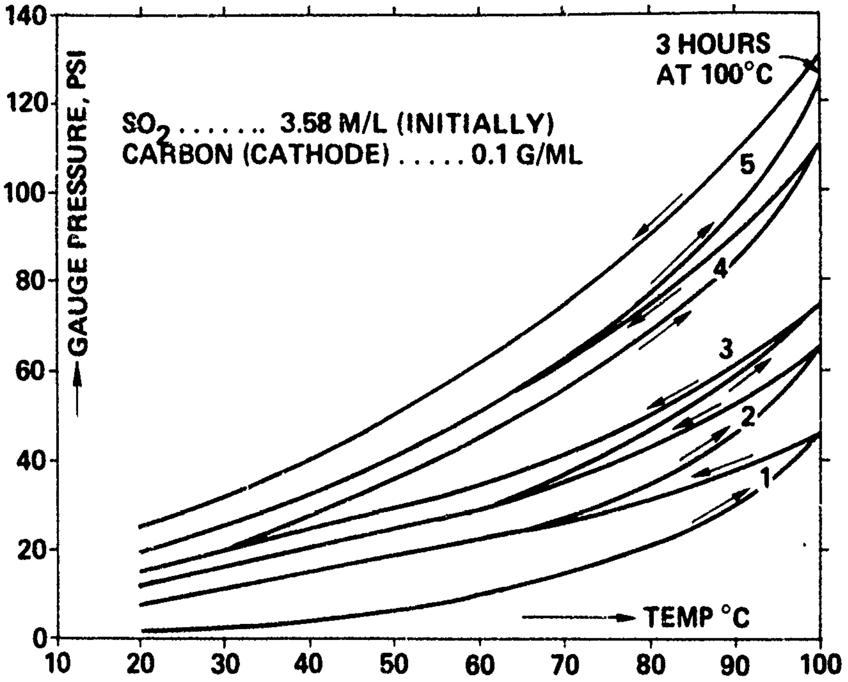


Figure 24. Pressure-Temperature Behavior, Electrolyte from Discharged Cell

2.3 DISCUSSION

The reconciliation of the coulometric data with the noted production of SO_2 is the most important problem in the analysis of these data. Examination of dried cathodes showed that at room temperature, production of lithium-sulfur-oxyacid salts does not account for a significant fraction of the discharge mechanism. This correlates with the data of Cogley et al.,[33] so it is assumed that the lithium ions are consumed in the cathode as lithium chloride. The only other possible products are SO_2, SCl_2, S_2Cl_2, and elemental sulfur. However, when these possible reactions are considered

$$2\ Li + 2\ SOCl_2 \rightarrow SCl_2 + SO_2 + 2LiCl\ \ldots \tag{37}$$

$$1\ \text{eq. mole}^{-1}\ SOCl_2$$

$$2\ \text{eq. mole}^{-1}\ SO_2$$

$$6\ Li + 4\ SOCl_2 \rightarrow 6\ LiCl + S_2Cl_2 + 2SO_2\ \ldots \tag{38}$$

$$1.5\ \text{eq. mole}^{-1}\ SOCl_2$$

$$3\ \text{eq. mole}^{-1}\ SO_2$$

$$\mathrm{4\,Li + 2\,SOCl_2 \rightarrow 4\,LiCl + S + SO_2} \qquad (34)$$

$$\mathrm{2.00\ eq.\ mole^{-1}\ SO_2}$$

$$\mathrm{4\ eq.\ mole^{-1}\ SO_2}$$

the available data do not correspond to the predicted electrical equivalents per mole of $SOCl_2$ or of SO_2. From 0° to 25°C, the equivalents per mole $SOCl_2$ is at least 1.5, closer to 2.0 (Table IX), ruling out Eq. (37). The predicted amount of SO_2 is even higher for Eq. (37) and (38) than for Eq. (34), thus likely ruling out Eq. (38). There is one other possibility which has not been explored:

$$\left\{\begin{array}{ll} \mathrm{6\,Li + 3\,SOCl_2 \rightarrow S_2O + SO_2 + 6\,LiCl} & (39) \\ \mathrm{2\,Li + SOCl_2 \rightarrow SO + 2\,LiCl} \quad \text{(on discharge)} & (40) \end{array}\right.$$

$$\left\{\begin{array}{ll} \mathrm{2\,S_2O \rightarrow 3S + SO_2} \quad \text{(slow)} & (41) \\ \mathrm{2\,SO \rightarrow S + SO_2} & (42) \end{array}\right.$$

The formation, properties, and infrared spectra of "SO" and S_2O have been described in the literature. (See for example "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie, Weinheim (1953), Volume 9, part B, pages 167-178.) Sulfur monoxide has been observed in the vapor phase in the presence of a diluent gas. When condensation is attempted, a solid polymer results which decomposes on heating to sulfur and sulfur dioxide. No solutions of S_2O or SO have ever been reported. The infrared absorption bands at 1165 and 679 cm^{-1} observed by A.V. Jonas in 1950 were sought in dilutions of electrolyte taken from discharged 2K Ahr cells, but nothing was found. Formation of "SO" in solution according to Eq. (40) followed by decomposition according to Eq. (42) would conveniently explain all the other observed phenomena: electrical capacity of two equivalents per mole; low electrolyte SO_2 content when compared with that predicted by Eq. (34); more rapid buildup of SO_2 as the concentration of "SO" increased (decomposition rate by bimolecular reaction would be proportional to the square of the concentration); pressure buildup or hysteresis on temperature cycling to 100°C in a closed vessel which cannot be duplicated with $SOCl_2 + S + SO_2 + LiAlCl_4$; sulfur stoichiometry as found by Cogley[22] in discharged cells from which $SOCl_2$ was removed; absence of significant quantities of lithium sulfur oxyacid salts in the cathodes of cells discharged at room temperature.

The presence of reducing species in the aqueous leach of dried cathodes taken from cells discharged at -20°C can explain the results reported by Auborn,[29] where x-ray analysis of a dried cathode identified Li_2SO_3. However, more work in this area is needed. Analysis of cells discharged at temperatures lower than -20°C are underway. Changes in the principal reaction stoichiometry could alter the ΔF and ΔH for the cell reaction, changing also the dependence of the open circuit potential upon temperature, as reported in Figure 16.

Cathode limited cells ejected SO_2 at atmospheric pressure, while anode limited cells did not (Figures 12 and 13). The heat generated at the anode of an anode limited cell near the end of discharge is due to polarization of remaining lithium as the surface area decreases. Uniform discharge of lithium was found to occur making this transition period short. The surface is always close to bulk electrolyte, facilitating heat transport away from the surface. In the passivating cathode of a cathode limited cell, the heat produced is trapped inside the pores where there is less opportunity for convection to remove or distribute it. The time between the onset of passivation and the end of discharge is longer for a cathode than for an anode limited cell, so that more heat is produced. Thus, an anode limited cell is better, both because heat and pressure generation are less likely, and because a discharged cell contains no lithium to pose an explosion hazard during disposal or recycling of cell materials.

3. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The prinicpal cell reaction at room temperature in the Li/$SOCl_2$ system does not involve the formation of lithium-sulfur-oxyacid salts, Li_2S or Li_2O, under the conditions of these experiments. Sulfur dioxide is produced by cell discharge, but at a rate lower than that predicted by a stoichiometric reaction producing suflur, sulfur dioxide and lithium chloride. The difference may be the production of an unstable lower oxide of sulfur, which decomposes on heating below 100°C to generate equal amounts of sulfur and sulfur dioxide.

At -20°C, electrochemical production of sulfur-oxyacid salts during discharge becomes significant, and may include sulfite or pyrosulfite as well as sulfate. The dependence of open circuit potential upon temperature is linear from 72° to -20°C but falls steeply at lower temperatures, possibly because of a change in the principal reaction stoichiometry. It is recommended that further studies be conducted on discharge reaction mechanisms at low temperatures by analysis of discharged cathodes.

The coulometric equivalence of $SOCl_2$ is near 2.00 equivalents per mole at room temperature. The method should be refined and the procedure repeated to establish whether this value really changes as the temperature is lowered. The present limitation is the freezing point of the supporting electrolyte solvent, about 2°C.

Since sulfur dioxide is produced during discharge, cell design should deal with the possible increase of pressure as the result of increasing electrolyte SO_2 concentration. Cathode limited 2K Ahr prismatic cells were found to eject SO_2 at atmospheric pressure near the end of discharge, when polarization occurred. Anode limited cells did not do so. It is recommended that anode limited cells be designed, particularly when large prismatics are needed, to avoid pressure increases near the end of discharge and to eliminate explosion hazard during reclamation of materials from spent cells.

VI. INVESTIGATION OF INORGANIC LIQUID OXIDANTS AS CATHODE REACTANTS FOR SEA WATER BATTERIES

1. INTRODUCTION

1.1 OBJECTIVES

There are numerous electrically powered devices that operate in sea water such as sonobuoys, electric torpedoes and emergency/rescue equipment. The most widely used power source is the magnesium/silver chloride sea water battery. Recently, F. Solomon[36] has reported on the characteristics of this cell, and a more economical version based on copper halide; the advantages attributed to these systems are as follows:

1) Simplicity. The Mg/AgCl cell consists of simple bipolar plates which are stored dry. Sea water flowing between the plates provides a conductive electrolyte and carries out the discharge and corrosion products. The system will also function in fresh water, generating electrolyte from discharge products. The copper halide battery is reported to be of similar simple construction and operation.

2) Durability. In a dry condition the cells can be stored indefinitely and are mechanically rugged.

3) Voltage regulation. The silver chloride system gives excellent voltage regulation from 0 mA/cm^2 to 10 mA/cm^2; the polarization curve is essentially flat at about 1.57V over this range in 3.5% salt solution. Above 10 mA/cm^2 the polarization is still low; about 1.37V at 100 mA/cm^2 (137 mW/cm^2). The copper halide system exhibits a steeper polarization curve, but operates over the same approximate voltage range. A variation of the copper halide system that was being developed for electric torpedo propulsion was reported to sustain about 150 mA/cm^2 at 1.4V (210 mW/cm^2), which is actually better than the silver chloride system.

4) Energy density. The Mg/AgCl system may be capable of energy densities of 30 Wh/Dm^3 and 120 Wh/Kg. For the sonobuoy application the reported volumetric energy densities are in the range of 7 Wh/Dm^3 to 15 Wh/Dm^3 and the gravimetric energy densities are in the range of 83 Wh/Kg to 111 Wh/Kg. For the copper halide systems these values are 9 Wh/Dm^3 to 12 Wh/Dm^3 and 75 Wh/Kg.

5) Cost. The major disadvantage of the AgCl based system is the cost of the cathode material. The silver chloride cost was estimated to be about \$0.52/Wh. (This was based on \$5.50 per troy ounce of silver and \$0.30 per troy ounce for conversion to the chloride-1974. The current price of silver is about \$5.00 per troy ounce.) In this respect the copper halide has a significant advantage. The material cost of the copper halide mix was estimated to be about \$0.04/Wh. However, development of this system has apparently been discontinued.

The use of a liquid oxidant/carbon cathode vs. the magnesium electrode in sea water might produce a more powerful electrochemical couple than the halide cells described above. The use of an inexpensive liquid oxidant (e.g., sulfuryl chloride at approximately \$0.03 to \$0.05/Wh) with a carbon electrode might in addition be economically favorable. The purpose of this investigation then was to explore the potential feasibility of active metal-sea water cells using inorganic liquid oxidant cathodes. The ultimate goal is to develop economically feasible sea water battery systems in which the peak power density exceeds that of the Mg/AgCl system.

1.2 TECHNICAL APPROACH

In order to explore a number of possibilities in a preliminary manner, state-of-the-art materials and technology were used whenever possible. Various sea water cell magnesium alloy anodes were obtained from NUSC (Newport), and the cathodes were carbon-Teflon structures. The inorganic liquid oxidants examined were several of the materials investigated in the course of the $Li/SOCl_2$ cell development; SO_2Cl_2, $SOCl_2$, S_2Cl_2, SCl_2 and $POCl_3$. AgCl electrodes, obtained from NUSC, were used to generate comparison data. Only laboratory type cells were investigated and no attempt has yet been made to evaluate energy densities or cost.

2. TECHNICAL PRESENTATION

2.1 EXPERIMENTAL PROCEDURE

The magnesium anode materials obtained from NUSC had the following allow compositions.

1) MTA75 Mg, Tl (7%), Al (5%)
2) AZ61 Mg, Al (6%), Zn (1%)
3) AZ31 Mg, Al (3%), Zn (1%)
4) AP65 Mg, Al (6%), Pb (5%)

In addition, pure magnesium, pure aluminum (99.99%), and an aluminum alloy were tested:

5) MRLA6 Al, Sn (0.12%), Ga (0.06%), Mg (0.06%)

Most of the electrode couples were evaluated in 3.5% aqueous NaCl to simulate sea water. A few systems were tested in 40% KOH.

The cells were arranged in a horizontal configuration; the anode was placed at the bottom of a glass dish and covered with aqueous NaCl, and the carbon cathode was laid over a circular glass frit or attached directly to the end of the glass tube. For operation, the liquid oxidant was added to the carbon through a rubber septum and the glass tube was lowered into the aqueous solution over the anode. Open circuit voltages were measured, and the cells were polarized from open circuit to 0.0V with a linear potential sweep in the manner described in Section II-2.2.1. Usually a 100Ω load was placed across each cell and the voltage was monitored on a strip chart recorder to determine the voltage under a sustained load.

2.2 RESULTS AND DISCUSSION

In the first group of experiments performed, MTA-75 magnesium anodes were used in 3.5% NaCl electrolyte; cathodes were constructed by adding various inorganic liquid oxidants to carbon powder on a 0.5 cm^2 fritted glass support. The open circuit voltage and voltage under a 100Ω load are summarized in the following table. These are compared with a standard AgCl cathode in a similar configuration:

TABLE X

PERFORMANCE OF MTA MAGNESIUM ALLOY VS. SULFURYL CHLORIDE (AQUEOUS NaCl)

CATHODE REACTANT	OPEN CIRCUIT VOLTAGE	VOLTAGE ON 100Ω LOAD
AgCl	1.87V	1.64V
1 M $NaAlCl_4$ SO_2Cl_2	2.54V	1.52V
SO_2Cl_2	2.70V	1.69V
1 M $AlCl_3$ SO_2Cl_2	2.70V	0.90V

These results indicate that the electrochemical properties of the sulfuryl chloride type oxidants compare favorably with the more expensive silver chloride cathode. No significant voltage changes were seen upon addition of a few drops of sulfuric acid to the aqueous electrolyte or by increasing the ratio of oxidant to carbon (1 ml catholyte to 0.1g carbon). This latter observation would seem to indicate that the available "active sites" on the carbon were completely occupied by the oxidant.

The second group of experiments also used MTA-75 magnesium anodes and 3.5% NaCl electrolyte, but 20% Teflon-bonded carbon was used in the cathode and open glass tubing with a nickel screen conductor was used instead of a fritted glass support. The geometric area of these cathodes was 0.332 cm^2. The results for a standard AgCl cathode are also given:

TABLE XI

PERFORMANCE OF MTA MAGNESIUM ALLOY VS. VARIOUS CATHODE REACTANTS IN 3.5% AQUEOUS NaCl

CATHODE REACTANT	OPEN CIRCUIT VOLTAGE	VOLTAGE ON 100Ω LOAD
AgCl	1.876V	1.642V
SO_2Cl_2	2.842V	0.440V (?)
1 M $NaAlCl_4$ SO_2Cl_2	2.958V	2.504V
1 M $AlCl_3$ SO_2Cl_2	2.834V	1.624V
S_2Cl_2	2.722V to 1.713V	0.503V
SCl_2	2.703V to 2.538V	0.047V
$POCl_3$	2.462V	1.462V

SCl_2 and S_2Cl_2 formed sulfur deposits which clogged the porous cathodes; these materials were not investigated further. 1M $NaAlCl_4$ in SO_2Cl_2, SO_2Cl_2 and 1M $AlCl_3$ in SO_2Cl_2 showed no sign of sulfur deposits and had high open circuit potentials, about 2.9V. The 1M $NaAlCl_4$ in SO_2Cl_2 system showed an especially promising peak power density of 550 mW/cm^2. This compares with a peak power density of 145 mW/cm^2 for the control experiment run with the silver chloride cathode.

In the third group of experiments AZ 61 magnesium anodes were tested in 40% aqueous KOH electrolyte vs. 20% Teflon-bonded carbon cathodes. The cathode reactants used in this group of experiments were Ag_2O, SO_2Cl_2, $SOCl_2$, $POCl_3$, SCl_2 and S_2Cl_2. None of these gave open circuit potentials greater than 1.5V or short circuit currents greater than 20 mA. This indicates that a basic electrolyte is unsuitable, and does not reflect oxidant performance.

Similarly, the fourth group of experiments using AP 65 magnesium anodes and 40% aqueous KOH or 3.5% aqueous NaCl electrolytes gave low open potentials and low short circuit currents. The oxidants used here were SO_2Cl_2, $POCl_3$ and $SOCl_2$. These results suggested that AP 65 alloy was not a suitable anode.

Pure magnesium, pure aluminum and various alloys were also tested in 3.5% NaCl vs. SO_2Cl_2 alone. The best performance was obtained with GTE carbon-Teflon cathodes. The results are summarized below:

TABLE XII

PERFORMANCE OF VARIOUS METALS AND ALLOYS VS. SO_2Cl_2 IN 3.5% AQUEOUS NaCl

ANODE	OCV	SHORT CIRCUIT CURRENT (mA)	PEAK POWER DENSITY (mW/cm^2)
Pure Mg	2.876	128	450
Magnesium Alloy MTA75	2.650	180	650
Magnesium Alloy AZ61	2.316	80	320
Pure Al	1.421	38	80
Aluminum Alloy MRLA6 (at 50°C)	1.510	90	290

Of all the anode materials tested, the MTA75 magnesium alloy gave the best results, and sulfuryl chloride gave the best performance as an oxidant. This combination was tested further in a larger cell using sea water electrolyte replenishment and with SO_2Cl_2 alone, with 1M $AlCl_4$ added, and with 1M $NaAlCl_4$ added. These cells had a 3 cm x 3 cm MTA-75 anode separated from the cathode by 0.5 cm, and a 20% Teflon-bonded carbon cathode containing 0.2g carbon powder with 1 ml of oxidant. Among these three cells, the one containing $NaAlCl_4$ in SO_2Cl_2 gave the best performance. This cell was discharged across a 32Ω load for 70 min at a power density of 140 mW/cm^2. The objective of the electrolyte replenishment was to remove the discharge products and expose a clean electrode surface. The anodes were corroded considerably at the end of the test. This corrosion usually started directly under the cathode (this problem is common to several sea water battery systems). The amount of oxidant and the amount of carbon present did not seem to affect the initial performance significantly.

3. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

In terms of peak power density, the liquid oxidant sulfuryl chloride on a carbon electrode vs. various anode materials gave higher performance than commercial Mg/metal-halide sea water cells. The best results obtained were 650 mW/cm^2 for SO_2Cl_2 vs. MTA75 magnesium alloy in 3.5% NaCl; this compares to about 145 mW/cm^2 for Mg/AgCl. Engineering complexity and cost of a sulfuryl chloride/carbon-cathode based system were not evaluated; however, the initial results are sufficiently promising to justify further investigation of the system. Since SO_2Cl_2 reacts with water to form H_2SO_4, it is recommended that sulfuric acid and other aqueous solutions be tested in addition.

VII. REFERENCES

1. K. Arii, Bull, Inst. Phys. Chem. Tokyo 8, 719 (1929).

2. K. Arii, Science Repts. Tohoku Imp. Univ., First Ser., 22, 182-99 (1933).

3. N. Marincic, A. Lombardi and C.R. Schlaikjer, "Progress in the Development of Lithium/Inorganic Batteries," Proceedings of the 27th Power Sources Symposium, pp. 37-42 (1976).

4. A.N. Dey, ECOM-74-0109-5 (August 1975).

5. E. Peled and H. Yamin, Submitted to 28th Power Sources Symposium (June 1978).

6. E. Peled and H. Straze, JECS 124, 1030 (July 1977).

7. K.M. McKay, Comprehensive Inorganic Chemistry, A.F. Trotman-Dickenson (Ed.), Pergamon Press, 1, 23-76 (1973).

8. Z. Szklarksa-Smialowski, JECS 110, 444 (1963).

9. K.M. McKay, Hydrogen Compounds of the Metallic Elements, E. & F.N. Spon Ltd. London (1966).

10. G.L. Holleck, M.J. Turchan and D.R. Cogley, ECOM-74-0030-7 (January 1975).

11. A.N. Dey, ECOM-74-0109-10 (December 1976).

12. A.N. Dey and C.R. Schlaikjer, Proceedings of the 26th Power Sources Symposium, p. 47 (1974).

13. W.A. Hart and O.F. Beumel, Jr., Comprehensive Inorganic Chemistry, A.F. Trotman-Dickenson (Ed.), Pergamon Press, 1, 336 (1973).

14. Ibid., 1, 358.

15. J. Boyes and J. Chivers, J. Chem. Soc. Dalton, 1715 (1975).

16. W.C. Schumb, et al., J. Am. Chem. Soc. 57, 260-266 (1935).

17. H. Staudinger, et al., Helv. Chim. Acta, 71-74 (1925).

18. R. Cherton, Bull. Soc. Roy. Sci. Liege 11, 54-60 (1942).

19. K. Heumann, et al., Ber. 16, 1625-1631 (1883).

20. H. Prinz, Lieb. Ann. 223, 355-371 (1884).

21. O. Ruff, Ber. 34, 1749-1758 (1901).

22. H.B. North, et al., J. Am. Chem. Soc. 40, 774-777 (1918).

23. W.C. Schumb, et al., J. Am. Chem. Soc. 57, 260-266 (1935).

24. T. Harrington, et al., J. Soc. Chem. Ind. 64, 209-211 (1945).

25. J.R. Driscoll, G.L. Holleck, D.E. Toland and S.B. Brummer, ECOM-74-0030-12 (April 1977).

26. L. Heyne, Electrochimica Acta 15, 1251-1266 (1970).

27. E. Peled, "The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Non-Aqueous Battery Systems -- The Solid Electrolyte Interface Model," presented at the 152nd Meeting of the Electrochemical Society, Atlanta, GA (October 1977).

28. U. Mayer and V. Gutmann, Structure and Bonding 12, 113 (1972).

29. J.J. Auborn, K.W. French, S.J. Liberman, V.K. Shah and A. Heller, JECS 120, 1613 (1973).

30. J. Devynck, Thesé de DS, Faculté des Sciences de Paris (April 1971).

31. A.N. Dey, Electrochimica Acta 21, 377-382 (1976).

32. W.K. Behl, J.A. Christopulos, M. Ramirez, S. Gilman, J. Electrochem. Soc. 120, 1619 (1973); U.S. Army Electronics Command, Fort Monmouth, NJ, Report ECOM-4101 (April 1973).

33. D.R. Cogley, M.J. Turchan, ECOM-74-0030-2 (May 1974).
D.R. Cogley, M.J. Turchan, G.L. Holleck, ECOM-74-0030-3 (September 1974).
G.L. Holleck, M.J. Turchan, D.R. Cogley, ECOM-74-0030-4 (January 1975).
G.L. Holleck, J.J. Turchan, D.E. Toland, ECOM-74-0030-5 (April 1975).
G.L. Holleck, J.R. Driscoll, D.E. Toland, ECOM-74-0030-6 (July 1975).
J.R. Driscoll, G.L. Holleck, Abstract 34, Electrochem. Soc., Fall Meeting, Dallas, Texas (1975).

34. L. Friedman and W.P. Wetter, J. Chem. Soc. (A), p. 36 (1967).

35. K. French, P. Cukor, C. Perisiani, J. Auborn, J. Electrochem. Soc. 121, 1045 (1974).

36. F. Solomon, "Performance of a New Non-Silver Sea Water Battery," Proceedings of the 9th Intersociety Energy Conversion Engineering Conference, pp. 660-66 (1974).

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2
Office of Naval Research Arlington, Virginia 22217 Attn: Code 1021P 1	6
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. Jerry Smith	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R.J. Marcus	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P.A. Miller	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L.H. Peebles	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1
Dr. Paul Delahay New York University Department of Chemistry New York, New York 10003	1

	No. Copies
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W.S. Haynes	1
Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A.L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Library P.R. Mallory and Company, Inc. P.O. Box 706 Indianapolis, Indiana 46206	1
Dr. P.J. Hendra University of Southampton Department of Chemistry Southampton SO9 5NH United Kingdom	1
Dr. Sam Perone Purdue University Department of Chemistry West Lafayette, Indiana 47907	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. R.A. Osteryoung Colorado State University Department of Chemistry Fort Collins, Colorado 80521	1
Dr. E. Yeager Case Western Reserve University Department of Chemistry Cleveland, Ohio 41106	1
Dr. D.N. Bennion University of California Energy Kinetics Department Los Angeles, California 90024	1
Dr. R.A. Marcus University of Illinois Department of Chemistry Urbana, Illinois 61801	1
Dr. J.J. Auborn Bell Laboratories Murray Hill, New Jersey 07974	1
Dr. Adam Heller Bell Telephone Laboratories Murray Hill, New Jersey 07974	1
Dr. T. Katan Lockheed Missiles & Space Co., Inc. P.O. Box 504 Sunnyvale, California 94088	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1
Dr. S.B. Brummer EIC Corporaion 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02912	1
Dr. R.C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1

	No. Copies
Dr. Royce W. Murray University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1
Naval Ocean Systems Center San Diego, California 92152 Attn: Technical Library	1
Dr. J.H. Ambrus The Electrochemistry Branch Materials Division, Research & Tech. Dept. Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. G. Goodman Globe-Union Inc. 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. J. Boechler Electrochimica Corporation Attn: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. P.P. Schmidt Oakland University Department of Chemistry Rochester, Michigan 48063	1
Mr. D.L. Warburton The Electrochemistry Branch Materials Division, Research & Tech. Dept. Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1