LITHIUM-THIONYL CHLORIDE BATTERIES - PAST, PRESENT AND FUTURE

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Abstract

Lithium based batteries have the highest theoretical energy density of known battery types. Of the lithium batteries, the lithium-thionyl chloride electrochemistry has the highest energy density of those which have been reduced to practice. The characteristics, development status, and performance of lithium-thionyl chloride batteries are treated in this paper. Safety aspects of lithium-thionyl chloride batteries are discussed along with impressive results of hazard/safety tests of these batteries. An orderly development plan of a minimum family of standard cells to avoid a proliferation of battery sizes and discharge rates is presented.

Introduction

Dramatic progress has been made in the development of high performance batteries in recent years. Much of this development effort has concentrated on lithium-based batteries. The reason for the interest in lithium is that it has the highest potential of the metals in the electromotive series. Consequently, the theoretical energy density of lithium-based electrochemical couples is higher than other couples. As a result of research and development efforts carried out in industry and in government laboratories, the potential benefits of lithium-based batteries are now being realized in practical hardware. Lithium-sulfur and lithium-halogen couples are being developed for secondary (rechargeable) battery application and lithium-thionyl chloride, lithium-sulfur dioxide, and lithium-vanadium pentoxide are the better known couples being developed for primary (nonrechargeable) battery applications.

The lithium-thionyl chloride battery, which can be efficiently used in both high discharge rate and low discharge rate applications, has the highest demonstrated energy density of any battery available today. It is a relatively simple battery which does not require an externally circulated electrolyte, as do several other high energy density batteries. It can be operated in any orientation, it has good shelf life in the activated condition, and it can be stored nearly indefinitely in a reserve configuration. The development status, performance, safety, and availability of lithium-thionyl chloride batteries are addressed in this paper.

Lithium-sulfur dioxide batteries have also been developed and put into production by several companies. Although the energy density of lithium-sulfur dioxide batteries is about half of that of lithium-thionyl chloride batteries, they reached production first and they are less expensive. Consequently, they are presently in wider use. Lithium-sulfur dioxide batteries, which contain sulfur dioxide gas under pressure in the cell, have experienced several incidents involving fire and explosions in the field. As a result, these batteries have been removed from all U.S. registered civil aircraft, and from most U.S. Navy equipment pending further investigations.

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It is particularly important to realize that sulfur dioxide has been used as a refrigerant at one time because of its vapor pressure characteristics. At 20°C the internal pressure of a cell is ∿33 psig and at 100°C it is in excess of 392 psig. SO_2 cells should not be placed in sealed pressure containment equipment (i.e., deep-ocean equipment applications). The disallowance of these cells to vent freely can, and have, caused violent explosions. Table 1 presents other related $LiSO_2$ cell problems and hazards.

This unfortunate experience with lithium-sulfur dioxide batteries has given a tainted safety reputation to the entire lithium battery line. In addition, early lithium-thionyl chloride batteries were also prone to catching fire and exploding when subjected to abuse, which has added to the distrust of lithium batteries in the user community. The mechanisms causing the safety problems in lithium-thionyl chloride batteries are now generally understood, however, and quantum advances have been made in the safety of these batteries. Outstanding progress has been made in the safety area by the Altus Corporation. Large lithium-thionyl chloride cells produced by Altus have demonstrated the ability to withstand incineration, mechanical shock, bullet penetration, short circuits, and application of reverse voltage, without fire or explosion. Details of these abusive tests, and the results of an extensive test program which will be conducted shortly by the Naval Ocean Systems Center, should further verify the safety of lithium-thionyl chloride cells, and are discussed in this paper.

In an attempt to channel government sponsored development of lithium-thionyl chloride cells and batteries into useful hardware, a technical development plan is being generated by the Naval Ocean Systems Center. Highlights of that plan are presented in this paper.

Characteristics of Lithium-Thionyl Chloride Batteries

Cell Chemistry

Lithium-thionyl chloride cells typically contain a lithium anode, porous carbon cathode, and an interelectrode separator. The electrolyte, which also acts as a reducible catholyte, consists of a salt, such as $LiALCL_4$, dissolved in thionyl chloride. During discharge, the thionyl chloride is reduced at the carbon cathode. Initial contact of thionyl chloride with lithium during cell filling forms a layer of lithium chloride on the anode. This layer prevents further direct reduction of anodic and cathodic materials, thus eliminating self-discharge.

At least two mechanisms have been identified for the discharge of the $LiSOCl_2$ cell. At low current densities the following reaction appears to predominate.

$$8\,Li + 3\,SOCl_2 \rightarrow 6\,LiCl + Li_2SO_3 + 2S$$

The products of reaction are all solid. The theoretical capacity of $SOCl_2$ for this reaction is 0.60 Ah/g.

At high current densities the overall discharge reaction is commonly accepted to be:

$$4\,Li + 2\,SOCl_2 \rightarrow 4\,LiCl + SO_2 + S$$

TABLE 1.

LITHIUM SULPHUR DIOXIDE CELL SAFETY PROBLEMS

- Lithium melting point 189°C - Very reactive when molten.
- SO_2 (~30 cc in "D" cell) - Boiling point: 0°C @ 1 atm.

  Vapor pressure: 3.2 atm. @ 20°C and 27.7 atm. @ 100°C.

  Critical pressure: 77.7 atm. @ 157.8°C (venting essential).
- Acetonitrile extremely toxic, limits disposal alternatives.
- Leakage thru seal & vent from corrosion in mild steel cases.
- Over-discharge results in lacey lithium which can fuse and initiate a reaction.
- Discharge after SO_2 loss produces I^2R heating and melting of lithium.
- Venting with flame produces chain reaction with adjacent cells.

The theoretical capacity of $SOCl_2$ for this reaction is 0.45 Ah/g.

Recent development have yielded reactions which substantially reduce the SO_2 generated over a wide range of discharge rates. The reduction of gaseous products is a significant factor in reducing the possibility of cell rupture at high temperatures.

The open circuit voltage of the cell is 3.65 volts, and typical voltages under load are 3.2 to 3.4 volts. For very high discharge rate applications, (current densities of more than one hundred mA per cm^2) the terminal voltage averages over 3.0 volts at normal battery operating temperatures. The output voltage is nearly constant during discharge until 95% of the active life is approached. These relatively high output voltages, in comparison to other battery types, contribute to the high specific energy of the battery.

Cell Construction

Small, flashlight type cells in sizes up to double D, are produced in "bobbin" and in the "jelly roll" configurations. The bobbin type cells consist of a central carbon cathode and a cylindrical anode which is attached to the cell container. This construction is used to obtain maximum energy at low discharge rates. Cells designed for maximum power are constructed by winding long strips of the two electrodes together in a jelly roll manner. The cathode is usually carbon which may contain a PTFE binder pressed onto a nickel or stainless steel current collector grid. The cells are usually hermetically sealed. Larger size batteries are made in prismatic form with a series of planar electrodes contained in a rectangular cell. GTE produces rectangular cells up to 10,000 Ah capacity and 44 x 31 x 25 cm (17.3 x 12.2 x 9.8 inches) in size. Honeywell produces cells up to 17,000 Ah capacity and 38 x 38 x 38 cm (14.9 x 14.9 x 14.9 inches) in size. Disc-like cell forms are being produced by Altus in sizes from 2.26 cm (0.89 inch) diameter to 43.2 cm (17 inches) in diameter. Battery systems can be made up from these cell types to meet particular applications. The disc cells, which can be stacked to achieve required power and energy requirements, allow efficient utilization of volume in cylindrical undersea vehicles. Several cylindrical, prismatic, and disc configuration lithium-thionyl chloride cells, ranging in capacity from 0.25 to 1500 ampere hours, are shown in Figure 1.

Figure 1. A Variety of Lithium-Thionyl Chloride Cell Configurations and Sizes.

Performance of Lithium-Thionyl Chloride Batteries

The theoretical specific energy of a lithium-thionyl chloride battery, considering only active material, is 1470 Wh/kg (666.6 Wh/lb). As in all batteries, practical factors such as a case, support structure, current collectors, and losses, reduce the available specific energy to a fraction of this value. A summary of presently available $LiSOCl_2$ cells in terms of capacity, type, dimensions, weight, and manufacturer is given in Table 2.

Commercially available D size cells offer specific energy of 340 to 420 Wh/kg (154.1 - 190.4 Wh/lb), depending on the manufacturer, and energy density of 680 to 800 Wh/liter (11.1 - 13.1 Wh/in^3).[1,2] Double D size cells offer specific energy of 480 Wh/kg (217.6 Wh/lb), and energy density of 900 Wh/liter (14.7 Wh/in^3), at a discharge time of 180 hours.[1] The shelf life of the above cells is typically specified as a capacity loss of 1% per year.

Developmental 500 Ah prismatic cells built by Honeywell provide specific energy of 642 Wh/kg (291.1 Wh/lb) and energy density of 2100 Wh/liter (34.4 Wh/in^3) at a discharge time of about 1000 hours.[3] Their experimental 17,000 Ah cells provide specific energy of about 480 Wh/kg (217.6 Wh/lb) and energy density of about 920 Wh/liter (15.0 Wh/in^3) at a discharge time of about 425 hours. Developmental 0.2 Ah disc cells built by Altus have demonstrated specific energy of 780 Wh/kg (353.7 Wh/lb), and energy density of 1200 Wh/liter (19.6 Wh/in^3), at a discharge time of 90 minutes. Altus 1500 Ah disc cells have a specific energy of 370 Wh/kg (171.8 Wh/lb) and energy density of 960 Wh/liter (15.7 Wh/in^3).[4] The 2000 Ah prismatic cell developed by GTE provides specific energy of 460 Wh/kg (208.6 Wh/lb), and energy density of 910 Wh/ liter (14.9 Wh/in^3), over a discharge time of 250 hours.[1] GTE is producing 10,000 Ah cells which provide 480 Wh/kg (217.6 Wh/lb) and 950 Wh/liter (15.5 Wh/in^3) at a current of 40 amperes for 250 hours.[1] The 10,000 Ah GTE cell weighs 78.8 kg (173.7 lbs) and occupies 36.3 liters (2215 in^3).

A 180 kWh High Energy Density Battery (HEDB) system is being developed by the Naval Ocean Systems Center. The battery contains 38-43.2 cm (17 inches) diameter disc cells built by Altus. The cells are stacked to form a battery system with overall external dimensions of 0.53 meters (21 inches) diameter and 1.52 meters (60 inches) long. The projected weight of the overall battery system is about 523 kg (1150 pounds). Results of cell testing indicate that at least 180 kWh will be delivered by the battery over a 1600 hour mission. The net specific energy of the battery system, including substantial support structure, is 363 Wh/kg (164.6 Wh/lb) and the net energy density is 681 Wh/liter (11.16 Wh/in^3). The 1500 Ah cells are 43.2 cm (17 inches) in diameter and 3.5 cm (1.4 inches) thick. Each cell weighs 13.3 kg (29.3 lbs). A photograph of the HEDB and a

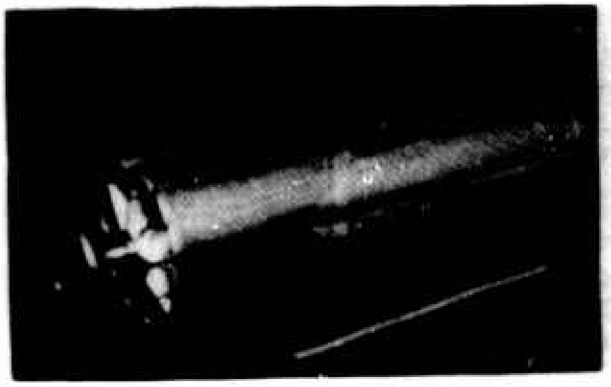
1 GTE Sylvania Data Sheets
2 Tadiran (Israel Electronics Industries) Data Sheets
3 Honeywell Data Sheets
4 Altus Model 1700-1400 Data Sheet

Table 2.

PRESENT LITHIUM THIONYL CHLORIDE BATTERY SUMMARY

CAPACITY (AH)	TYPE	DIMENSIONS (in.)	WEIGHT (oz.)	MANUFACTURER
0.08	DISC*	0.80 × 0.12	0.12	ALTUS
0.14	DISC	0.79 × 0.10	0.08	ALTUS
0.18	CYLINDRICAL	0.63 × 1.00	0.35	HONEYWELL
0.19	WAFER	0.110 × 0.985	0.13	GTE
0.20	DISC	0.80 × 0.12	0.12	ALTUS
0.22	DISC	0.80 × 0.12	0.12	ALTUS
0.45	CYLINDRICAL	0.63 × 2.20	0.88	HONEYWELL
0.70	DISC	0.80 × 0.12	0.12	ALTUS
0.75	CYLINDRICAL	1.03 × 0.75	0.81	HONEYWELL
1.50	DISC	1.27 × 0.28	0.61	ALTUS
1.80	CYLINDRICAL	0.60 × 1.30	0.63	HONEYWELL
1.70	"AA"	1.98 × 0.56	0.50	GTE
2.00	"AA"	0.28 × 1.97	0.58	TADIRAN
5.00	"C"	1.98 × 1.00	1.85	TADIRAN
5.00	"C"	1.93 × 1.03	1.82	GTE
5.50	DISC	2.50 × 0.28	3.17	ALTUS
6.00	CYLINDRICAL	0.98 × 1.87	1.86	TADIRAN
9.00	CYLINDRICAL	1.28 × 2.29	3.31	TADIRAN
10.00	"D"	2.42 × 1.29	3.38	TADIRAN
12.00	"D"	2.40 × 1.34	3.24	GTE
17.00	PRISMATIC	1.18 × 1.14 × 2.48	——	HONEYWELL
18.00	DISC	4.50 × 0.30	10.58	ALTUS
30.00	"DD"	4.72 × 1.34	6.70	GTE
186.0	PRISMATIC	2.30 × 4.20 × 5.0	——	HONEYWELL
400.0	PRISMATIC	3.63 × 4.30 × 5.5	——	HONEYWELL
800.0	PRISMATIC	3.63 × 4.25 × 6.18	——	HONEYWELL
1 500.00	DISC	17.00 × 1.40	464.00	ALTUS
2 000.00	PRISMATIC	19.8 × 3 × 13.4	640.00	GTE
10 000.00	PRISMATIC	19.8 × 11.5 × 13.5	2720.00	GTE
17 000.00	PRISMATIC	15 × 15 × 15	3200.00	HONEYWELL

*DENOTES HIGH RATE



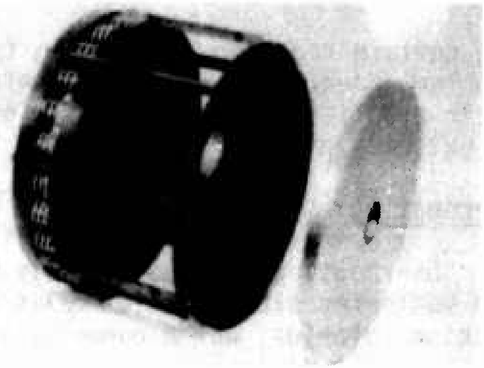


Figure 2. The High Energy Density Battery (HEDB) and a Single Cell

Figure 3. 28-volt Short Stack HEDB

single cell is shown in Figure 2. Design specifications for the HEDB are summarized in Table 3. A 28-volt "short stack" version of the HEDB which uses 9-1500 Ah cells is illustrated in Figure 3.

Table 3. HEDB Specifications

Total energy	200 kw-hr
Peak power	1.5 kw (combined electronic & electro-mechanical load)
Envelope	.53 m dia & 1.52 m in length
Weight	~500 kg
Endurance	Up to 6 months
Operating depth	600 meters
Safety	Full compliance with appropriate Mil specs/standards & special requirements for lithium batteries
Stand by to full power	< 5 minutes
Start up/shut down	<1/2 hour to full power/instantaneous
Storage life	Dry - 5 years; wet - 1 year
Operating attitude	Prefer vertical attitude ±35°
Environmental	Shock, vibration, pressure, penetration, etc
Temperature:	
Operate	-2°C to 27°C
Storage & transport	-40°C to 60°C activated; -40°C to 74°C dry
Replenishment	Accomplish in a closed, manned shipboard space
Disposal	At-sea with no pollution

Safety Aspects of Lithium-Thionyl Chloride Batteries

Early lithium-thionyl chloride batteries responded violently in the form of fire and explosion when subjected to abuse such as overheating, physical damage, short circuits, and reverse voltage conditions. The causes of the violent reaction are generally well understood. These mechanisms are briefly reviewed in the following paragraphs. Additives have been found to be effective in preventing certain reactions. However, the most satisfactory solution to the safety problem appears to have been developed by the Altus Corporation. Cells made with their proprietary technology, do not explode, or catch fire, even when subjected to extremes of the forms of abuse listed above.

Overheating

Overheating is a potentially hazardous condition for lithium-thionyl chloride batteries since lithium melts at about 186°C, and the passivating film of lithium chloride, which normally isolates the lithium from the other components of the cell, no longer provides protection. Highly exothermic reactions can take place between molten lithium, and thionyl chloride and/or elemental sulfur. The later component is commonly considered to be a product of normal battery reaction. Sulfur monochloride has been found to be an effective additive by some manufacturers to solubilize the elemental sulfur as it is formed in the cell, thus avoiding the possibility of a lithium-sulfur reaction. Sulfur monochloride can also form slowly from the reaction of elemental sulfur and thionyl chloride at elevated temperature. The generation of sulfur dioxide in the cell can be held to low levels by appropriate cell chemistry. This has a two-fold benefit; first, the possibility of reaction between lithium and sulfur dioxide is minimized; and second, it avoids the problem of high concentrations of gas in the cell which would expand with increasing temperatures and cause build up of dangerously high pressures within the cell. Cells built by Altus have demonstrated the ability to withstand temperatures well above the melting point of lithium without violent reaction.

Short circuiting the terminals of the cell causes internal heating, with the consequences attendant with overheating, as described above. In addition, it is possible that localized high concentrations of heat and reaction products could be generated which accentuates the possibility of a violent reaction. Short circuit testing of early lithium-thionyl chloride cells often produced an explosion. However, the major manufacturers of large lithium-thionyl chloride cells, Altus, GTE, and Honeywell, have now all demonstrated that their cells can be short circuited without causing explosion or some other violent reaction.

Reverse Voltage

One or more cells of a series-connected battery can experience a reverse voltage condition if they become discharged before the other cells in the battery. Applying reverse voltage to lithium-thionyl chloride cells can cause lithium in dendritic form to grow from the anode to the cathode. This is a potentially hazardous situation, since the dendrite can burn out and arc when it contacts the cathode, and in so doing initiate a reaction between the lithium and other cell components. A second deleterious effect of reverse voltage conditions is that electrolysis of the electrolyte can take place which can generate oxyanions such as ClO_2. These oxyanions can spontaneously react with the carbon electrode and cause high pressures within the cell.

One method which has been suggested to protect cells in a series battery arrangement from reverse voltage is to place Schottky diodes around each cell. Although the techniques used to achieve safe operation are proprietary to each company, cells built recently by Altus have demonstrated the ability to withstand 200% of cell rated ampere hours in reversed voltage condition. Cells built by GTE have successfully withstood 150% of their rated capacity in reverse voltage.

Physical Abuse

Penetration of the cell by sharp objects can break the passivating film on the lithium and allow reaction between it and other cell components to take place. Nail penetration of early lithium-thionyl chloride cells resulted in fire or explosion. Likewise, bullet penetration, which causes local heating as well as deformation leading to internal short circuit, resulted in fire or explosion in early cells. Cells built by Altus have been subjected to nail penetration without ensuing fire or explosion. They have also been penetrated with .30 caliber bullets. When fired at with soft nose bullets, which caused extensive damage to the cell, local fires were generated which soon went out.

Hazard/Safety Testing of Lithium-Thionyl Chloride Batteries

A hazard/safety test program was conducted for the Navy by Wyle Laboratories in Norco, CA in May 1978 on 43.2 cm (17 inch) diameter, 500 Ah lithium-thionyl chloride cells built by Altus. These cells were developed for the High Energy Density Battery program under contract with the Naval Ocean Systems Center. The tests, which were designed to determine the safety of these cells under conditions of extreme abuse, included exposure to a fuel-oil fired bonfire (Figure 4), nail penetration (Figure 5), punching a 2.5 cm (1 inch) diameter hole through a cell (Figure 6), multiple bullet penetrations (Figure 7), and drop testing from 12.2m (40 feet) onto a steel plate (Figure 8). No cases of explosion resulted from these tests. Under the extreme overheating tests, the cells merely vented.

During bullet penetration tests, using soft nosed bullets which caused extensive internal damage to the cell, fire occurred in the immediate area of the damage. Repeated penetration eventually destroyed the cell structure and the cell was consumed by fire. Solid nose bullets cleanly penetrated the cell without causing fire.

A crush test was performed by applying 1000 psi local pressure to the cell without noticeable effect on performance. At a pressure of 20,000 psi over a 1-inch diameter area, the cell was punched through, and a local cell fire resulted.

Short circuit testing was performed without incident, although the negative terminal melted off after sustaining 100 amperes for one (1) minute.

During reverse voltage testing, one cell vented. Changes were made in the cell desigh, and later cells have demonstrated an ability to withstand reverse voltage conditions, without adverse reaction.

An exhaustive test program to demonstrate the safety of lithium-thionyl chloride batteries for naval applications will be undertaken shortly by Code 631 of the Naval Ocean Systems Center. It is planned to subject a total of 41-1500 Ah cells to a rigorous environmental, and hazard/safety test sequence. These cells have higher capacity than the cells previously tested, and incorporate the latest refinements in the technology. In addition to performance and characterization tests, the following tests will be performed:

Figure 4. Fuel-oil fired bonfire.

Figure 5. Nail penetration.

Figure 6. Punching a 2.5 cm (1 inch) diameter hole through a cell.

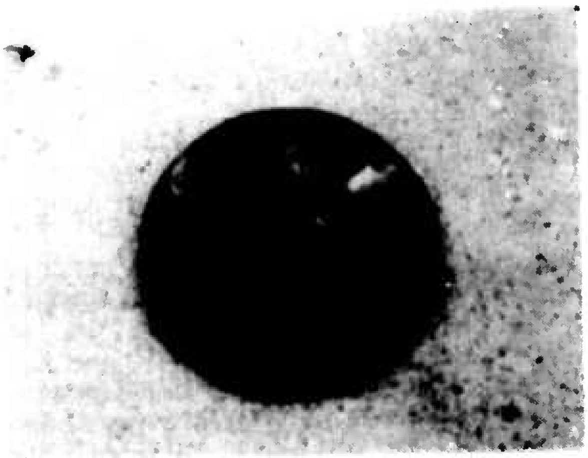


Figure 7. Multiple bullet penetration.

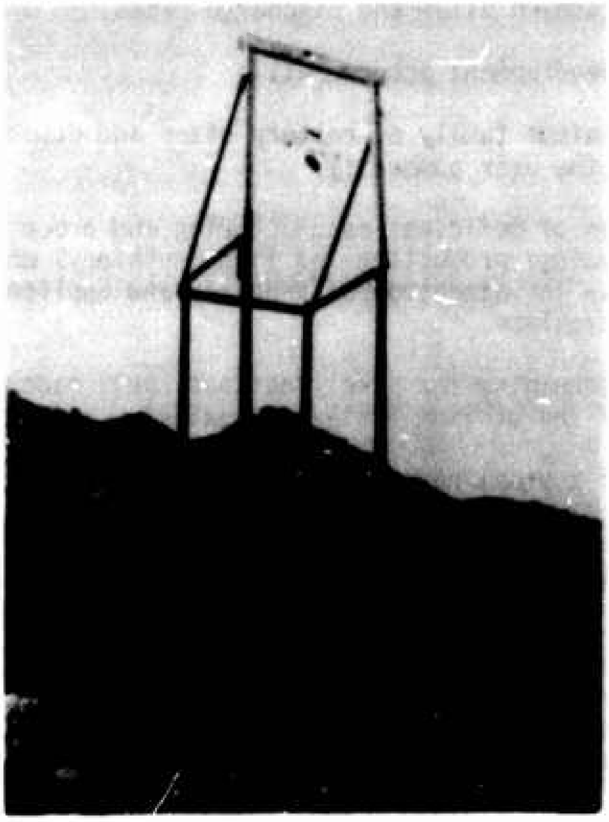


Figure 8. Drop testing from 12.2 m (40 feet) onto a steel plate.

Environmental	Hazard/Safety
Vibration	External Heat
Shock	Reverse Voltage
Hydrostatic	Post-Reverse Voltage Shock
Overcurrent	Penetration
Drop (3')	Drop (6')
Altitude	Short Circuit
	Disposal

Following cell testing, three short stack batteries (shown in Figure 3), each containing 9 cells, will be assembled and subjected to performance and hazard/safety testing. These tests will include overcurrent, short circuit, and sympathetic influence of one cell rupturing in a battery stack.

It is anticipated that this test program will provide a conclusive demonstration of the inherent safety of advanced lithium-thionyl chloride battery technology.

High Energy Density Battery Technical Development Plan

A technical development plan for lithium-thionyl chloride batteries has been generated by the Naval Ocean Systems Center. The objectives of the High Energy

Density Battery Development Program are to promote and focus the development of safe, "off-the-shelf" lithium-thionyl chloride batteries for government use into and orderly array of standard sizes and discharge rates.

In essence, the development program will:

1. Identify a minimum family of battery sizes and discharge rates which will meet the needs of the user community.

2. Identify areas of deficient manufacturing and processing technology that presently retards the volume production of lithium-thionyl chloride batteries at low cost, and will focus the attention of industry and applicable government laboratories on these problems.

3. Provide the mechanism for a well defined, well managed procurement for development and test of the minimum family of batteries identified in (1) above.

A brief survey of typical naval requirements for primary batteries is given in Table 4. These requirements have been translated into a matrix defining a minimum set of lithium-thionyl chloride batteries which would satisfy current and projected DoD applications, and are shown in Table 5.

It appears that coordinated development of a family of 6 to 8 basic cells would satisfy the identified requirements and allow production to be concentrated on a few standard cells. This will reduce both the development cost and the unit cost of lithium-thionyl chloride batteries, and make safe, reliable high performance batteries available to the user community in the shortest time.

Table 4.

Typical Naval Systems Primary Cell Requirements

Application	Discharge Rate*	Capacity (Ah)
Remote Sensors	Low	50-100
Mines	Low	500
Aircraft Emergency Transponders	Low	5.5
Data Links	Low	100
Standby Power	Low	10-10K
Field Communications	Medium	20
Tactical Data Terminals	Medium	10
Portable Lighting	Medium	20
Countermeasures & Decoys	High	10-100
Vehicle Propulsion	High	1000-3000
Sonobuoys	High	10
Targets	High	1000
Torpedoes	Very High	50-300
Missiles	Very High	10
Ordnance Fuzing	Very High	1
Laser Designators	Very High	10

*Low - 100 hrs.
Medium - 10 hrs.
High - 1 hr.
Very High - 0.1 hr.

RATE \ SIZE	SMALL (~10 AH) A	MEDIUM (~100 AH) B	LARGE (~1000 AH) C	VERY LARGE (~10 000 AH) D
LOW (100 HRS) 1	EXPERIMENTAL EQUIPMENT ① A1		REMOTE SENSORS MINES AIDS TO NAVIGATION ② C1	STANDBY POWER ② D1
MEDIUM (10 HRS) 2			SUBMERSIBLES ③ C2	
HIGH (1 HR) 3	SONOBUOYS PORTABLE COMMUNICATIONS ② A3	COUNTERMEASURES & DECOYS ③ B3		
VERY HIGH RATE RESERVE (0 1 HR) 4	MISSILES COUNTERMEASURES ③ A4	TORPEDOES TARGETS ② B4		

① DEVELOPED
② IN DEVELOPMENT
③ DEVELOPMENT REQUIRED

Table 5. Matrix of Lithium Thionyl Chloride Batteries Required for Current & Projected Marine Applications.