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Lithium Batteries -- Where Are They Headed?

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 applications and lithium-thionyl chloride, lithium-sulfur dioxide, and lithium-vanadium pentoxide are the better known couples being developed for primary (nonrechargeable) battery applications. Comparisons of two representative examples of lithium battery electrochemistry, namely lithium sulfur dioxide ($LiSO_2$) and lithium thionyl chloride ($LiSOCl_2$) are made with other primary battery power sources in Table 1.

TABLE 1. PRIMARY BATTERY POWER COMPARISONS

	LECLANCHE'	ALKALINE	MERCURY	MAGNESIUM	Organic Electrolyte Li/SO_2 PC AN/C	$Li/SOCl_2$
NEGATIVE ELECTRODE	Zn	Zn	Zn	Mg	Li	Li
POSITIVE ELECTRODE	MnO_2	MnO_2	HgO	MnO_2	SO_2/C	$SOCl_2/C$
ELECTROLYTE	NH_4Cl/H_2O	KOH/H_2O	KOH/H_2O	$MgCl_2/H_2O$	SO_2 PC AN/LiBr	$LiAlCl_4SOCl_2$
ENERGY DENSITY (Wh/kg)	66	77	99	143	330	440-550
ENERGY DENSITY (Wh/cucm)	0 12	0 18	0 43	0 24	0 49	0 91-1 5
OPEN CIRCUIT VOLTAGE (V)	1.5	1.5	1.35	1.7	2 9	3 7
VOLTAGE STABILITY (0-90%)	1.5-0.7	1.5-0.8	1.3-1.1	1.7-0 9	2.7 2 0	3.6-3 2
POWER DENSITY (W/kg)	55	66	11	88	110	550-2200
POWER DENSITY (W/ cu cm)	0 09	0.09	0 04	0 18	0 16	0 3 - 2 7
TEMPERATURE RANGE (°C)	-6 - 54	-29 - 71	-8 - 71	5 - 71	-40 - 74	-40 - 100
OPERATING VOLTAGE (V) AT 1mA/cm^2	1 3	1.3	1.2	1 7	2.7	3 6
SHELF LIFE (YEARS) AT 21°C	1	2	>2	2	>2	>2

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

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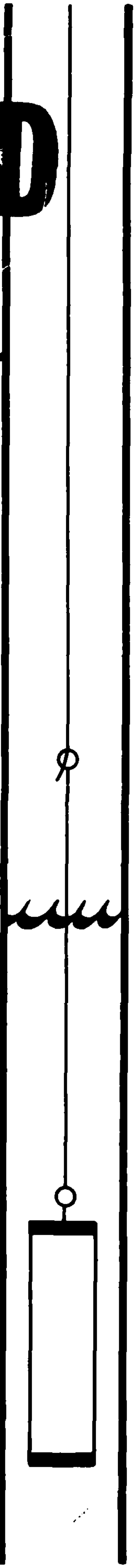


does not require an externally circulated electrolyte, as do several other high energy density batteries. It can be operated in any orientation, it has good shelf life in the activated condition, and it can be stored nearly indefinitely in a reserve configuration. The development status, performance, 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. It is particularly important to realize that sulfur dioxide was 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 cause violent explosions (and has).

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 presently being conducted by the Naval Ocean Systems Center, San Diego, CA, should further verify the safety of lithium-thionyl chloride cells.

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

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:

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

The theoretical capacity of $SOCl_2$ for this reaction is 0.45 Ah/g. Recent development has 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 V, and typical voltages under load are 3.2 to 3.4 V. For very high discharge rate applications, (current densities of more than one hundred mA per cm^2) the terminal voltage averages over 3.0 V at normal battery operating temperatures. The output voltage is nearly constant during discharge until 95 percent 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.

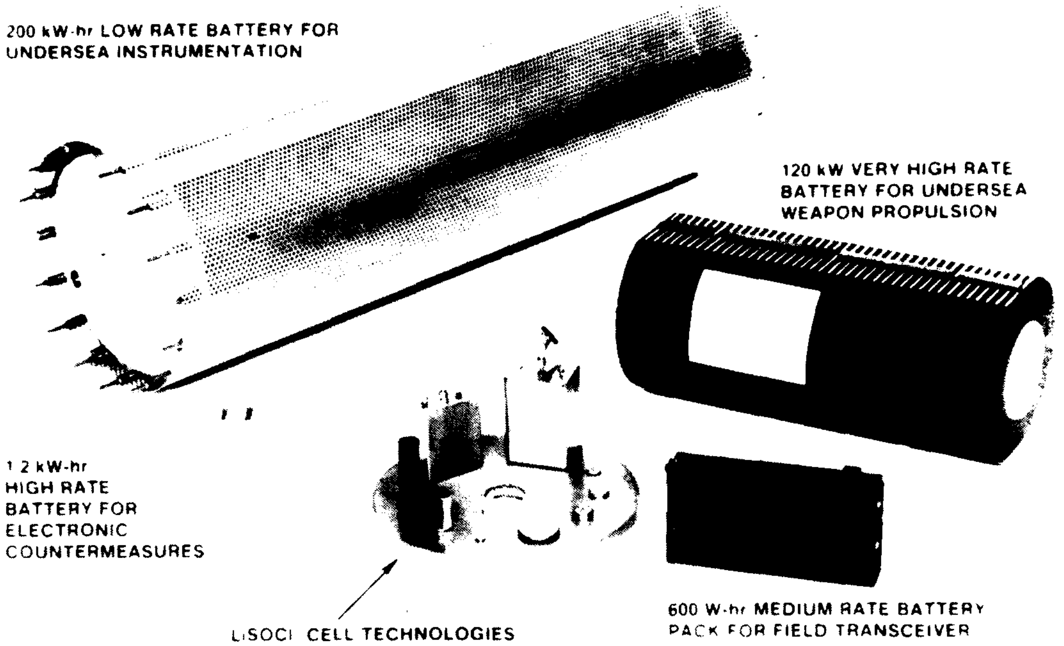
Cell Construction

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 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 Sylvania produces rectangular cells up to 10,000 Ah capacity and 44 x 31 x 25 cm (17.3 x 12.2 x 9.8 in) 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 in) in size. Disc-like cell forms are being produced by Altus in sizes from 2.26 cm (0.89 in) diameter to 43.2 cm (17 in) 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 Ah, are shown in Figure 1.

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

FIGURE 1. LITHIUM THIONYL CHLORIDE BATTERY DEVELOPMENT PROGRAMS



a case, support structure, current collectors, and losses reduce the available specific energy to a fraction of this value.

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 percent per year.

Development 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

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[1] GTE Sylvania Data Sheets

[2] Tadiran (Israel Electronics Industries) Data Sheets

[3] Honeywell Data Sheets

TABLE 2. SAFETY SITUATION

Problem	Solution
Explosions occur when lithium melts	Prevent lithium from melting
	Release reactive materials from cell before lithium melts
	Control the lithium when it melts
Explosions occur when cells are deeply discharged	Provide electrical controls to prevent voltage reversal at end of life
Hazardous materials are expelled from cells during adverse conditions	Contain or dilute expelled products
	Minimize quantity of hazardous materials
	Increase the tolerance of cells to adverse conditions

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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 Ah/lb) and 950 Wh/liter (15.5 Wh/in^3) at a current of 40 A for 250 hours.[1] The 10,000 Ah GTE cell weighs 78.8 kg (173.7 lb) 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 in) diameter disc cells built by Altus. The cells are stacked to form a battery system with overall external dimensions of 0.53 m (21 in) diameter and 1.52 m (60 in) long. The projected weight of the overall battery system is about 523 kg (1150 lb). Results of cell testing indicate that at least 180 kWh will be delivered by the battery system where the specific energy 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 in) in diameter and 3.5 cm (1.4 in) thick. Each cell weighs 13.3 kg (29.3 lb).

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 and their solutions are briefly presented in Table 2. Additives have been found to be effective in preventing certain reactions.

FUTURE DEVELOPMENT

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 an orderly array of standard sizes and discharge rates.

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[4] Altus Model 1700-1400 Data Sheet

TABLE 3.

MATRIX OF LITHIUM-THIONYL CHLORIDE BATTERIES REQUIRED FOR CURRENT AND PROJECTED MARINE APPLICATIONS

SIZE / RATE	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

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.

Typical naval requirements for primary batteries have been translated into a matrix defining a minimum set of lithium-thionyl chloride batteries which would satisfy current and projected Department of Defense applications, and are shown in Table 3.

It appears that coordinated development of a family of six to eight 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 to the user community in the shortest time.

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