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DEVELOPMENT OF LITHIUM INORGANIC ELECTROLYTE BATTERIES FOR NAVY APPLICATIONS

by

J. F. McCartney, W. H. Shipman, C. R. Gunderson,
C. W. Koehler

Fleet Engineering Department

February 1977

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ADMINISTRATIVE INFORMATION

The purpose of this report is to present pertinent test results, development accomplishments, and application experience, gained during the period of FY 75 to the present, with new lithium-inorganic electrolyte cells ($Li + SOCl_2$).

This work was sponsored by the Office of Naval Research (ONR), Vehicle Technology Department, the Naval Undersea Center (NUC), Independent Exploratory Development program, and more recently the Naval Sea (NAVSEA) Systems Command, Code 0331.

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The Naval Undersea Center (NUC) has completed an extensive test program of lithium-thionyl chloride ($SOCl_2$) cells of both the high-rate and low-rate configurations. Several deficiencies of earlier cells were corrected by modifying cell hardware design and the addition of chemical additives to the electrolyte for improved safety. As a result of this program, the improved cells are now being used, with complete success, in numerous ocean-oriented applications. Now that many of the problems and hazards of these cells are better

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understood, lithium-thionyl chloride cells and batteries can be developed for a variety of high- and low-rate applications involving both large- and small-size cells.

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SECTION 1
INTRODUCTION

A new lithium-inorganic electrolyte battery is now available that has valuable properties (1, 2, 3). It has high-energy density and the potential for a long shelf life; it can be configured for either low or high discharge rates and from very small to very large size cells. These characteristics are valuable to many ocean-oriented applications, including oceanographic instrumentation, sonar systems, biotelemetry devices, undersea weapons, small undersea vehicles, meteorological instrumentation, field communications, etc. However, only limited performance, safety and cost data have been available for this battery; these data were insufficient for a complete evaluation and selection for projected ocean-oriented applications.

The objective of the Lithium-Inorganic Electrolytic Battery Development Program was to determine the performance, safety, reliability and environmental limits of this battery, as configured for ocean systems, and to provide basic data for planners and designers of future military ocean systems. The major criteria investigated included energy-per-weight, volume and cost; power and endurance range; sensitivity to low temperature and depth; storage environments; operability and reliability; deployment factors; and cell emissions and hazards. Table 1-1 presents the types of data required by engineers in the development of reliable systems.

This program was implemented by first analyzing numerous possible applications to identify representative testing requirements. Three detailed test plans were prepared: (1) to determine the normal operating parameters to be expected from the cells; (2) to explore cell output characteristics during anticipated Navy use; and (3) to become aware of any possible hazards from mishandling large batteries made from these cells.

TABLE 1-1. POWER SOURCE CHARACTERISTICS.

Parameter	Data Format
Availability	Development status
Energy per weight	Watt-hours/kilogram
Energy per volume	Watt-hours/cubic centimeter
Energy per cost	Watt-hours/dollar
Power range	Watts
Endurance range	Hours
Rechargeability	Electrical, mechanical, none
Low-temperature performance	% capacity at 0°C
Expendability	Expendable, recovery desired, or essential
Critical materials used	Silver, platinum, etc.
Depth sensitivity	Surface, submerged – pressure equalized or hull
Shelf life	Years
Restart capability	Instantaneous, delayed, none
Emissions	Gases, heat, noise, etc.
Operability	Simple, specialized training, highly specialized
Reliability	Failure rate
Maintenance	None, periodic, after failure
Deployment	Drop, lower, position, etc.
Power conditioning	Input voltage, regulation, etc.
Start-up time	Predeployment, post-deployment
Hazard and safety	Explosives, toxic materials, etc.

Cells of various sizes and discharge rate designs were procured and tested. The tests identified numerous physical, material, engineering, and operational deficiencies. Experiments were initiated to discover ways to overcome these weaknesses. As a result, the corrections accomplished now provide a technology that is being used in multiple applications.

This report describes the types of cells tested, the test program, pertinent test results, cell improvements that have been made, application experience to date, and recommended development needed for wide applications of the technology.

SECTION 2
CELL DESCRIPTION

At the present time prototype lithium cells, with an inorganic liquid as the electrolyte, are available from several companies including GTE Laboratories, P.R. Mallory & Co., Inc., Honeywell, Inc., and Electrochimica Corp. The electrolyte is composed of inorganic salts (lithium aluminum chloride) in an organic solvent (thionyl chloride). Energy is produced by the electrochemical decomposition of the inorganic solvent material at the carbon electrode and oxidation of the lithium during discharge of the cell. The cathode is constructed of a high-porosity carbon which allows circulation of the catholyte and space for accumulation of reaction products. The inorganic solvent decomposes only when the load circuit is closed, thereby making it possible for the battery to operate effectively for several years. Figure 2-1 schematically illustrates the battery construction.

The inorganic lithium battery has an open-circuit voltage of > 3.6 volts. Unlike conventional solid cathodes, the distance between the reactive zones of the electrodes remains nearly constant upon discharge and the cells exhibit exceptional voltage stability, approaching 1 percent. Since the electrolytic solution is also the depolarizer, the weight of the cathode does not burden the cell and energy densities of 550 watt-hours/kg to 90% of the initial voltage are realized in simple cells.

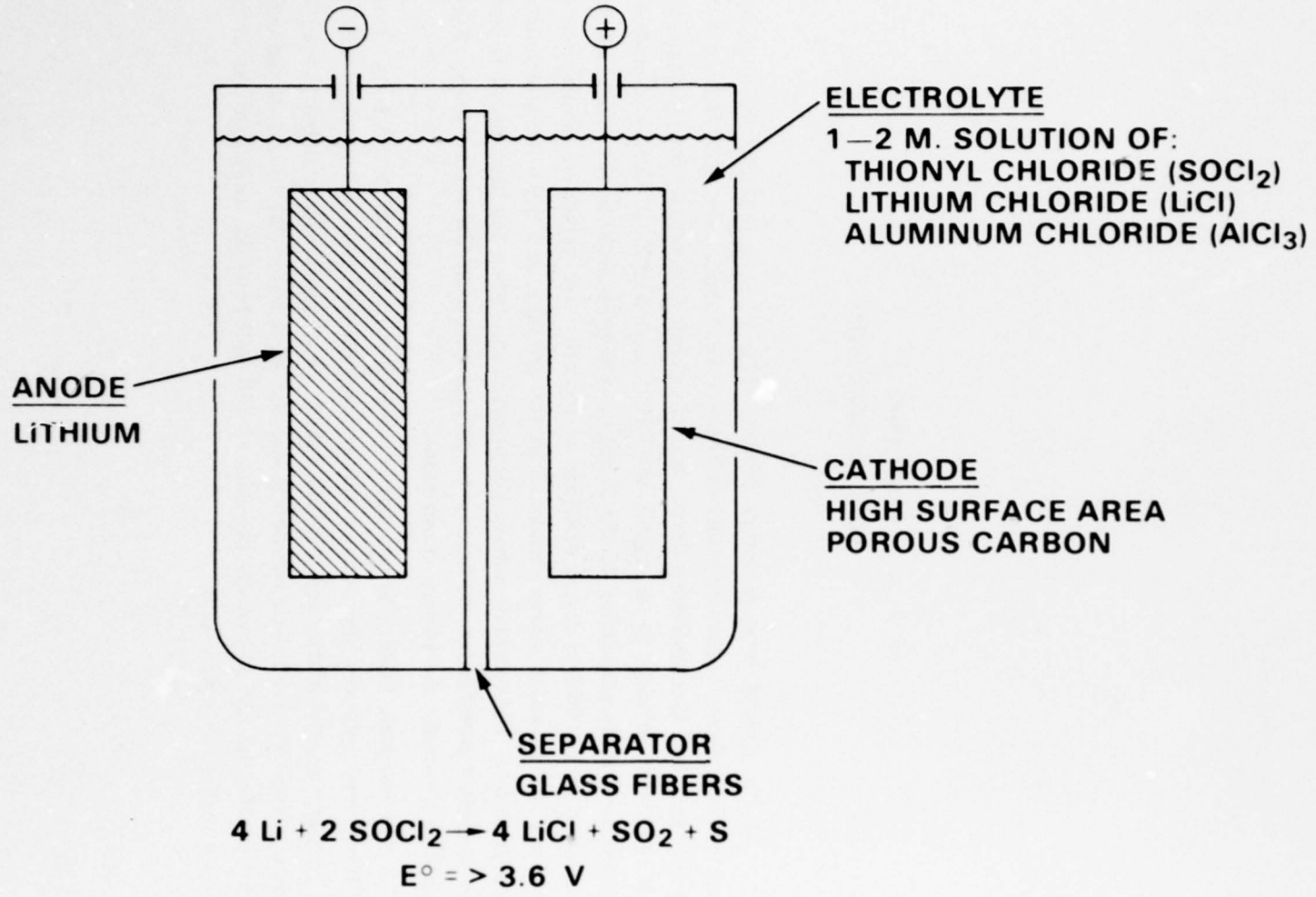


Figure 2-1. Battery Construction.

As described in Appendix A rechargeable alkali metal batteries, now being developed for electric vehicles for the 1985 time period, offer a potential improvement in energy density beyond that available with silver-zinc batteries (Figure 2-2). State-of-the-art or near-term batteries with performance better than that of silver-zinc batteries are limited to the primary type of zinc-air and lithium organic electrolyte batteries and the very high energy density now obtainable with lithium inorganic electrolyte batteries.

Beyond the weight and volume advantages, the lithium inorganic electrolyte cell has cost advantages that make it particularly attractive in large size cells of 100, 1000, or 10,000 ampere hours.

In spite of much work by many investigators the chemistry of the lithium inorganic battery is yet to be described. Workers at GTE (1) suggested the reaction

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

but the inadequate amounts of Li_2SO_3 and the incorrect LiCl to Li ratios observed per Faraday of charge indicate that it appears to be invalid. A second hypothesized reaction (2)

$$8\ Li + 4\ SOCl_2 = Li_2S_2O_4 + 6\ LiCl + S_2Cl_2$$

has also been considered invalid because S_2Cl_2 could not be shown to be a reaction product. EIC Corp. (2, 3, 4) has quantified the reaction products formed during discharge of this battery and found that at 25°C, 0.48 ± 0.07 mole of SO_2, 0.25 mole of elemental sulfur, and 1 mole LiCl are formed per Faraday of charge. These data are almost consistent with the following equation:

$$4\ Li + 2\ SOCl_2 = S + 4\ LiCl + SO_2$$

The measured amounts of sulfur and lithium chloride satisfy the equation but the quantity of sulfur dioxide is high by a factor of two. Thus it is clear that the cell chemistry cannot be described by a single simple equation.

The equilibria existing in the battery prior to current flow can be summarized as follows:

$$\begin{array}{lcccccl} & & & SOCl^+ & + AlCl_4^- & & \\ & & \text{Weak} & \uparrow\downarrow & \text{Strong} & & \\ SO^{+2} + 2\ Cl^- & \rightleftharpoons & SOCl_2 & \rightleftharpoons & SOCl^+ & + Cl^- \\ & & + & & + & & \\ LiAlCl_4 & & AlCl_3 & + & LiCl & & \\ & & & & \downarrow\uparrow & & \\ & & & & Li^- & + SOCl_2 & \end{array}$$

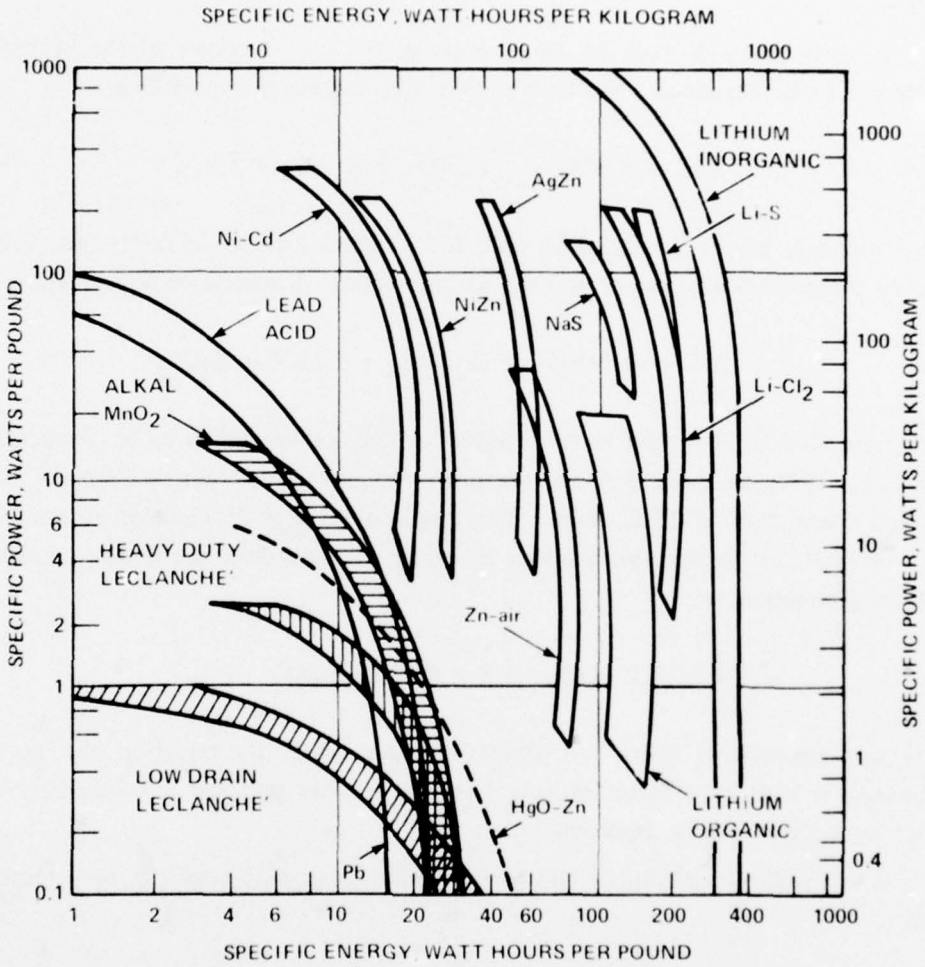


Figure 2-2. Performance Capabilities of Various Batteries.

From this diagram it can be seen that a very complex equilibrium exists between the following species:

$$SOCl_2,\ LiAlCl_4,\ LiCl,\ AlCl_3,\ SOCl^+,\ AlCl_4^-,\ Li^+,\ SO^{+2},\ Cl^-,\ SO_2$$

Sulfur dioxide was added because EIC (3) showed that thionyl chloride could not be separated from it by distillation and all thionyl chloride measured by them contained dissolved SO_2.

When current flows the following half cell reactions, and perhaps others, can take place:

$$Li \rightarrow Li^+ + e^- \qquad \text{I}$$

$$2\,SOCl_2 + 4\,e^- \rightarrow S^0 + SO_2 + 4\,Cl^- \qquad \text{II}$$

$$2\,SO_2 + 2\,e^- \rightarrow S_2O_4^{-2} \qquad \text{III}$$

Multiplying reaction I by 4 and adding it to reaction II yields the over all reaction

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

Reaction III must be considered since the sulfur dioxide is initially present at a low concentration but increases as the cell discharges and can act as a cathode depolarizer by this reaction. Possible presence of lithium dithionite must also be considered when the mass loading of the cathode is estimated.

It can be seen that the chemistry is not defined and may vary with temperature, state of discharge and, perhaps, with other as yet unidentified parameters.

Four sizes of cells have been tested in this program (AA, D, double-D, and 100 AH) and are depicted in Figure 2-3. Principal design characteristics of these cell types are shown schematically in Figure 2-4. A simple "bobbin" type of cell construction was preferred for low-rate applications. This consisted of a central "bobbin" cathode and a peripheral cylindrical anode attached to the cell container. This cell type was labeled "High Energy Cell" with a maximized capacity obtainable below a certain limiting discharge rate. The second "jelly roll" cell type is the "High Power Cell" shown in the same figure. It comprises high surface area electrodes assembled in a wound configuration for high-rate applications. Both cell types are built using commercial cell hardware wherever possible. A hermetic seal was designed specifically for use with the inorganic lithium battery system. A more conventional battery crimp seal was developed and tested. Cells were built with both types of seals using practical assembling procedures.

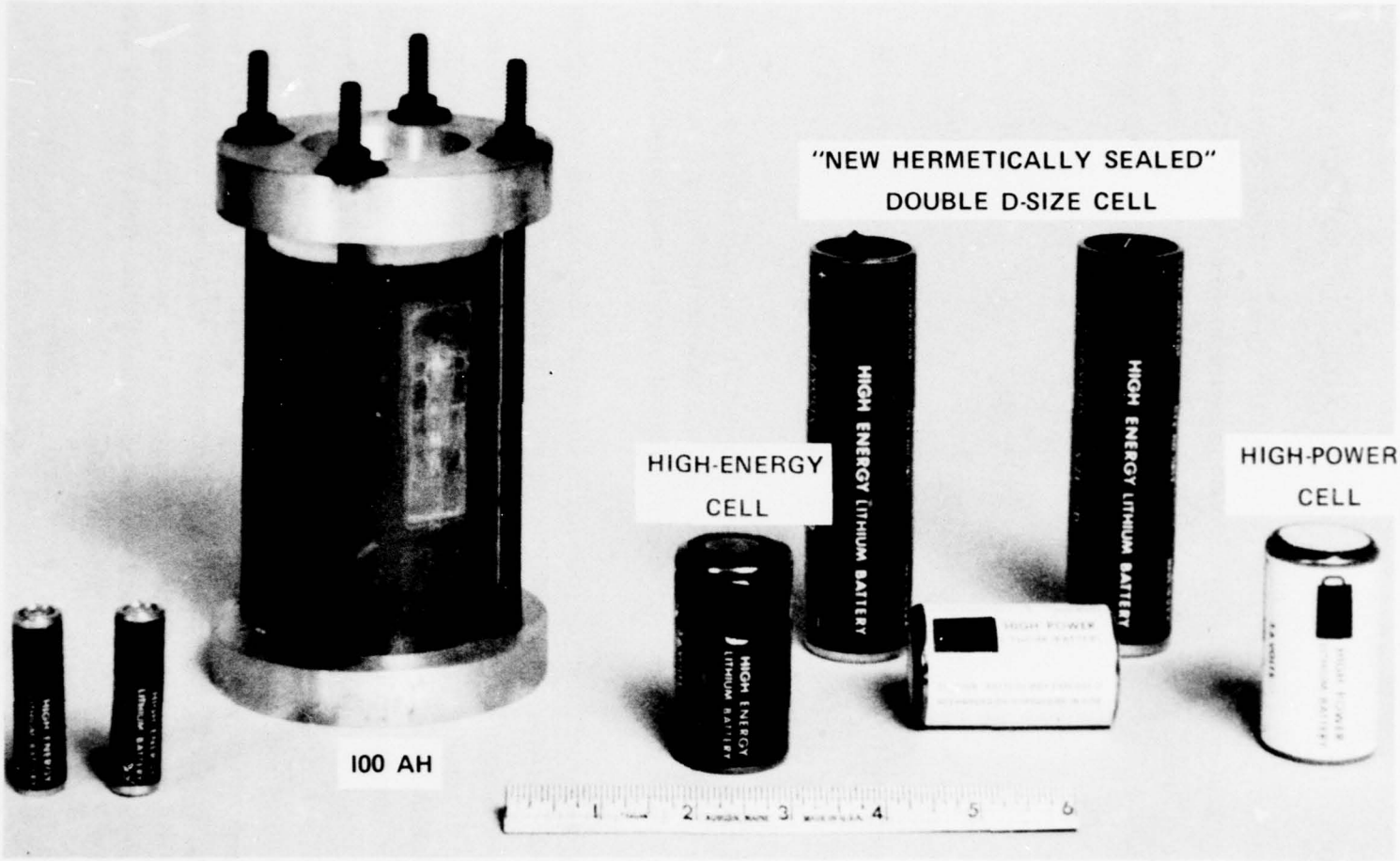


Figure 2-3. Four Types of Lithium Cells Tested.

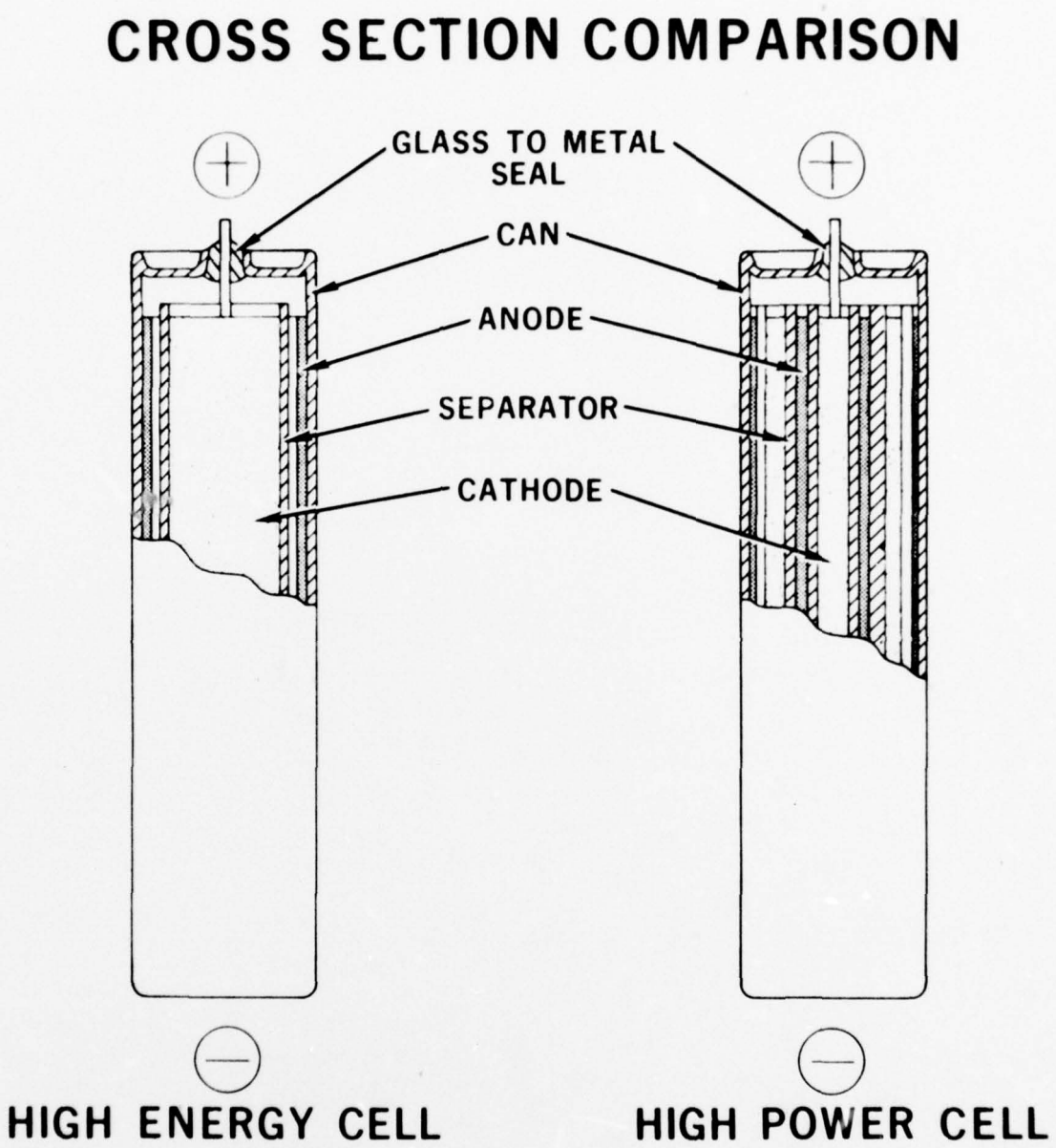


Figure 2-4. Cell Design Characteristics.

SECTION 3
CELL TESTS

Three detailed test plans were prepared to (1) determine the normal operating parameters to be expected from the lithium inorganic electrolyte cells, (2) explore cell output characteristics during anticipated Navy use, and (3) become aware of any possible hazards from mishandling large batteries made from these cells. A summary of the types of tests performed is shown in Table 3-1.

TABLE 3-1. TEST PLAN OF LITHIUM INORGANIC CELLS.

I. PERFORMANCE
- A. CONTINUOUS AND PULSE DISCHARGE
  - a. WITHOUT STORAGE
  - b. ROOM-TEMPERATURE STORAGE
  - c. HIGH-TEMPERATURE STORAGE
  - d. STORAGE IN HUMID ENVIRONMENT
- B. VOLTAGE DELAY/PASSIVATION
- C. ORIENTATION SENSITIVITY
- D. VOLT-AMPERE AT VARIOUS DISCHARGE STATES

II. ENVIRONMENT
- A. SHOCK
- B. VIBRATION
- C. HYDROSTATIC PRESSURE
- D. HIGH ALTITUDE

TABLE 3-1. TEST PLAN OF LITHIUM INORGANIC CELLS (Cont.).

III. SAFETY

- A. NAIL AND BULLET PENETRATION
  - a. FRESH CELL
  - b. DISCHARGED CELL
- B. SHORT CIRCUIT
- C. CHARGING CURRENT AND REVERSE POLARITY
- D. INCINERATION
- E. IMPACT

EARLY CELL TESTS

Reference 5 describes the test results with original D-size High Energy and High Power cells in FY 75. Numerous deficiencies in these cells were determined and corrected. As a result, an improved configuration has been evolved. Summarized in the following are the results of these tests:

The bulk of the testing effort utilized the D-size cell with a crimped seal. Fresh D-size high-energy cells provided the manufacturer's specified performance only at low current discharge rates of 100 milliamperes or less. Cell voltage prematurely decreased to below cutoff values when discharge rates were greater than 100 milliamperes on D-size cells. This means that D-size high-energy cells should not be used in applications having a continuous discharge life less than 5 days. Ideal applications should have discharge periods of weeks or months for maximum cell efficiency.

The performance tests were conducted at both room temperature and at 5°C with discharge rates varying from 5 to 100 milliamperes. Good performance and long life were achieved above 3 volts for a majority of the cells tested.

Short storage periods (less than three months) at room temperature (less than 25°C) do not adversely affect the performance of cells with crimped seals. However, longer periods (over eight months) have a very damaging affect on the cell by causing corrosion around the seal and reducing cell ampere-hour capacity. In addition, these cells severely passivate when stored for a long time, resulting in a significant voltage delay. The extreme case involves the nonhermetically sealed cells stored outside (in a metal chest) for one year. In this case corrosion was complete and cell capacity reduced to zero. The hermetically sealed cells are not expected to have this problem.

Another problem is that these cells seem to be sensitive to cell orientation during discharge. Maximum capacity is possible with the cell vertically upright, with minimum capacity resulting when the cell was vertically oriented with the positive terminal down. Any method that will allow the electrolyte to wet the electrodes will prolong the cell discharge life.

Another phenomenon, related to orientation sensitivity, is cell sleeping when discharging in a very quiet environment. This was observed in some tests and results in a premature decrease in cell voltage due to the clogging of the cathode or interelectrode region by products of the reaction which reduces electrolyte contact with the electrodes.

The high-power configuration (high rate) is more prone to explode than the high-energy configuration. These high-power cells will explode within 15 minutes if short circuited (discharging at a rate of about 20 amperes without cooling). They will also explode when exposed to a temperature slightly above 160°C (for about 1/2 hour) and when punctured rapidly by a sharp object. The explosion liberates a large quantity of white gas, probably vaporized thionyl chloride. This gas quickly hydrolizes because of the moisture in the atmosphere and forms acids of HCl and SO_2. Two methods that have been demonstrated to prevent the explosion are to keep the cell cool during high-rate discharge and to use an additive such as sulfur monochloride to dissolve the elemental sulfur produced during normal discharge.

High humidity has such a disastrous effect on steel-cased cells (complete case corrosion within a year) that submerging the cells in seawater has been shown as a rapid means of disposing of the cells.

Shock and vibration did not degrade the performance of the high-energy cells, at least not at the frequencies normally found on board ship.

Likewise, the effect of pressure on a pressure-compensated cell does not harm the cell (actually the performance improves because the electrolyte can more thoroughly wet the electrode surface area). Pressure equalization results in higher current densities from the cell electrodes.

Other methods that could be used to achieve higher current cells for propulsion and pulse power applications are to increase the electrode surface area by using large-area thin electrodes or possibly hermetically sealing the cell to prevent the escape of high-pressure gaseous discharge products from the cell.

Voltage delay, experienced with cells that have been stored for long periods of time, can be overcome by shocking the cell either physically or thermally (high temperature or very low temperature). Hydrostatic pressure ($\sim$200-ft. depth) also depassivates cells.

Cells of 100 ampere-hours have also been built and successfully tested. Cells with capacities up to 10,000 ampere-hours could be similarly designed that would be relatively economical for many military applications that require large amounts of energy.

The AA-size cell is designed for very low discharge rates lasting up to ten years. When discharging at 50°C at a rate of 1.6 milliamperes a cell capacity of 1.8 ampere hours (above 3 volts) was observed.

The DD-size cell can deliver higher currents. With this cell discharging at 160 milli-amperes (at 50°C), the capacity above 3 volts was observed to be 19.5 ampere hours.

The high-power cells have recently been tested to determine their performance during a 6-minute and a 2-hour discharge rate. The results are shown in Figures 3-1 and 3-2. These tests were conducted with the cell immersed in 150 milliliters of mineral oil to minimize temperature rise. The temperature increased from room temperature to a maximum of 120°F.

As a result of the FY 75 development effort the following conclusions have been reached:

a. The chemistry of the lithium-inorganic cell works and produces a battery with outstanding performance.

b. The advantages or fusing lithium-inorganic electrolyte cells are numerous:

1. High energy density (200-250 WH/LB)
2. High cell voltage (3.6 VDC)
3. Potentially long shelf life
4. Long operating life
5. Completely contained and no moving parts, fluids, or gases
6. Atmospheric pressure internally
7. Good low-temperature performance
8. Good voltage regulation
9. Potentially least expensive in larger size cells
10. Wide range of sizes possible
11. Can be pressure equalized for deep ocean applications
12. Good tolerance to high shock and vibration

The eleventh advantage has a tremendous value when larger batteries are to be used at deep ocean depths of 20,000 feet. Massive pressure hulls to house the batteries can be eliminated by pressure-equalizing cells.

c. There is a definite need for this cell in both high-rate applications (e.i., vehicle propulsion systems) and long-term, low-rate applications, as in surveillance system power sources.

d. The Fiscal Year 1975 effort has demonstrated the capabilities of the cell as well as uncovered some of its limitations. Basic work is still needed to understand the causes of these limitations and to suggest ways to minimize or eliminate them.

e. Future development work needs to concentrate on six of these problems:

1. High-power-cell hazards
2. The "sleeping" phenomenon
3. Voltage delay
4. Reverse polarity hazards

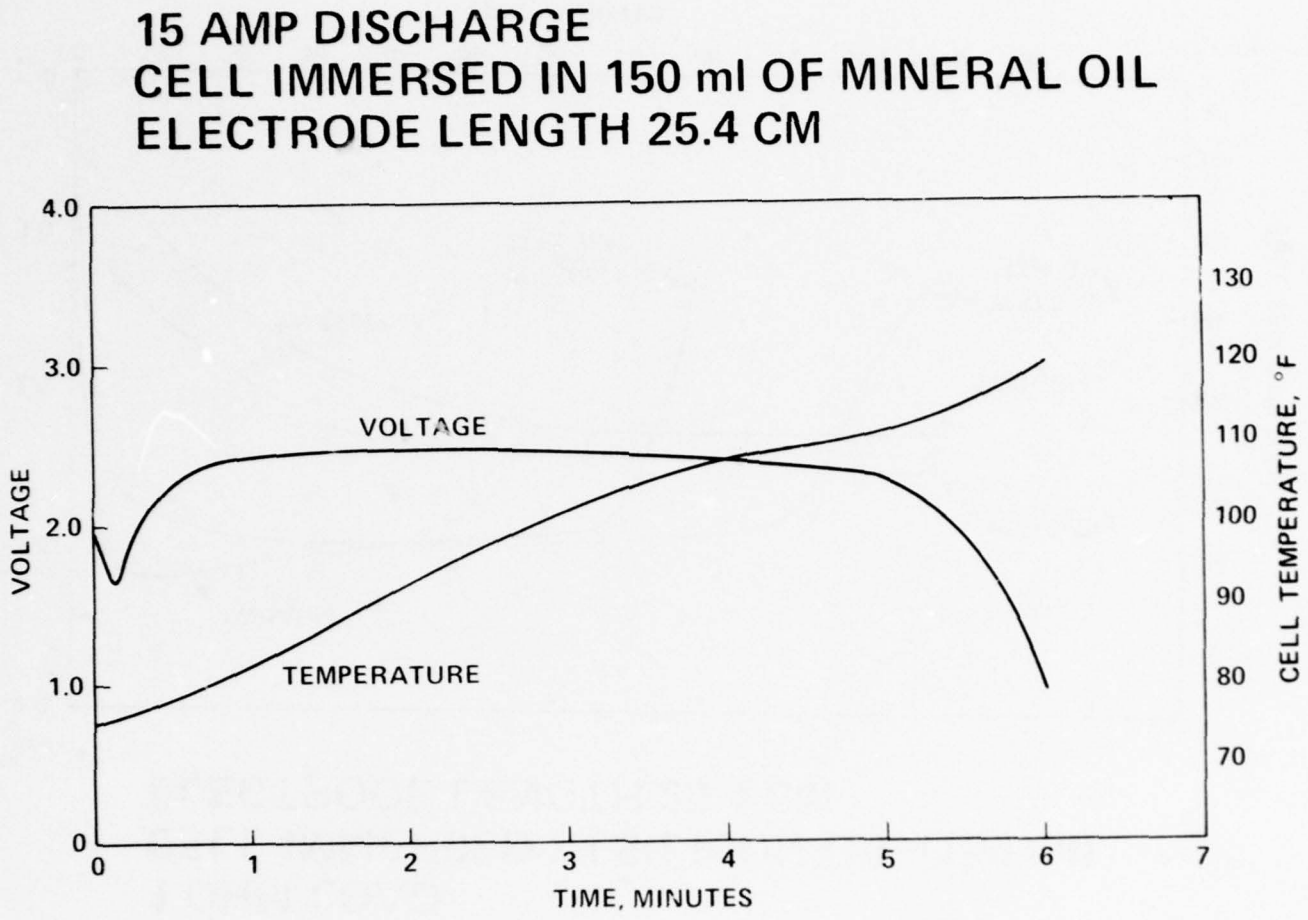


Figure 3-1. High Power D Size Cell.

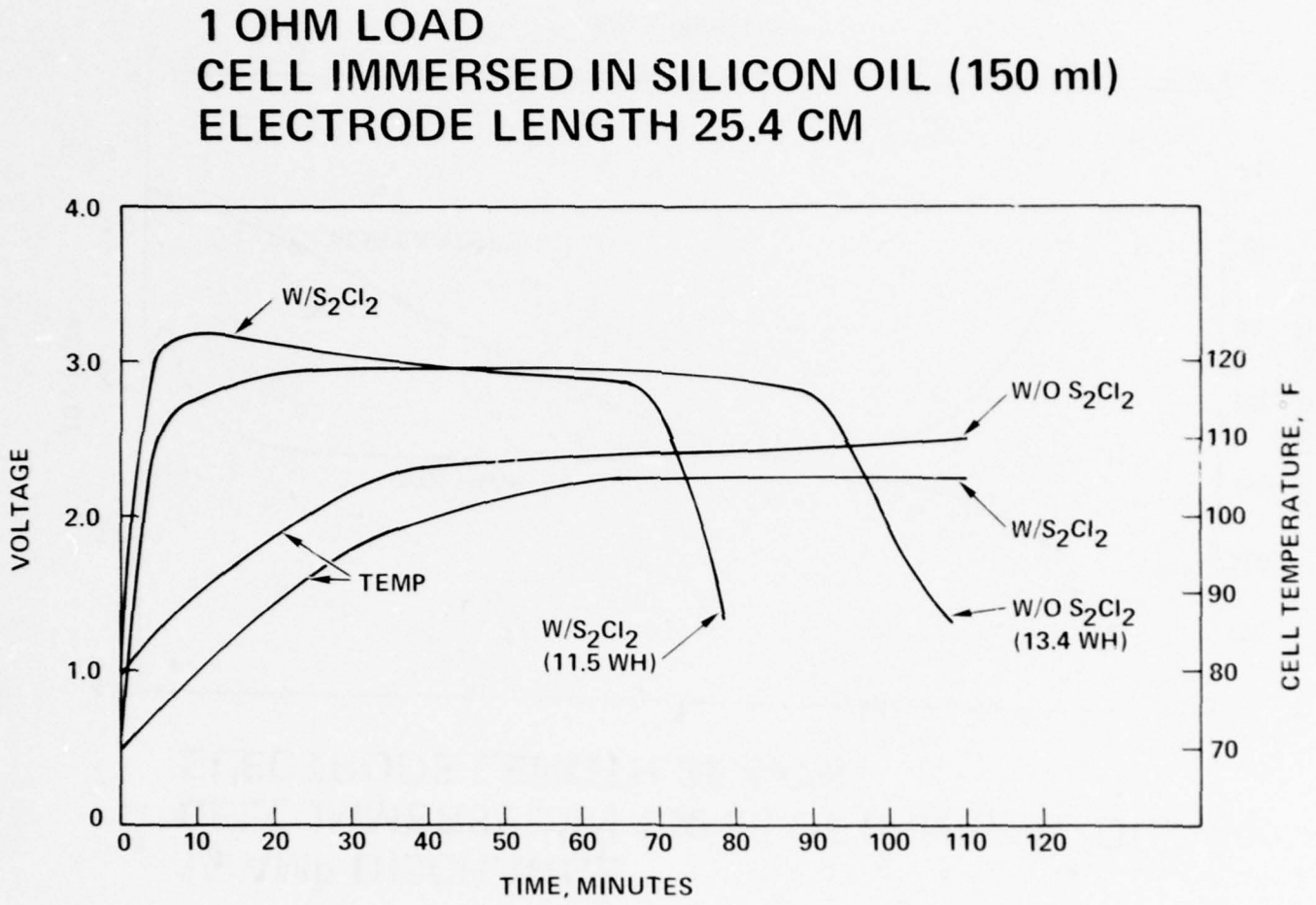


Figure 3-2. Comparison of High Power D Size Cells.

5. Pressure compensation and reserve activation
6. High-power-density applications
7. Large-size cells

SECTION 4

ACCOMPLISHMENTS OF FY 76

During FY 76 the test program was continued, addressing the shortcomings of earlier cell hardware. An improved configuration has evolved, solving the deficiencies observed in earlier cell hardware. This cell comprises a hybrid configuration with two (2) concentric anodes housed in a stainless steel, hermetically sealed case with purified electrolyte. The cell is a DD size, twice the length of the conventional D-size cell.

Recent test results on high-power, D-size cells and newly contructed DD and AA cells will be discussed in the following paragraphs.

HIGH-POWER-CELL-HAZARD TESTS

The high-power cells designed to provide high discharge rates are potentially dangerous when short circuited or penetrated. Table 4-1 summarizes the tests conducted to determine the causes of this problem. High-power cells will usually detonate when shorted or penetrated by a nail. Penetration by a bullet causes a thermite-like, nonexplosive, reaction. Possible reasons for this phenomenon are that the nail and the bullet will short out the cell internally, resulting in a heat build up. This electrical shorting will increase the sulfur content. The reason for different results is due to whether the cell is totally penetrated or not. The bullet diminishes the concentrations of reactants by ejecting thionyl chloride. But it does transfer enough kinetic energy to the lithium metal as it penetrates the cell to melt the lithium, resulting in a lithium-sulfur thermite-like reaction. The nail, though, stays in the cell, keeping the cell components intact, allowing a build up of heat and pressure to occur. This will result in a possible explosion.

TABLE 4-1 HIGH-POWER D-CELL HAZARD TESTS

TEST / CELL CONDITION	NAIL PENETRATION	BULLET PENETRATION	SHORT CIRCUIT
FRESH CELL (PASSIVATED)	ELECTROLYTE LEAK	ELECTROLYTE LEAK	EXPLOSION AFTER ~ 10 MINUTES
DEPASSIVATED CELL	EXPLOSION	FIRE OR EXPLOSION	EXPLOSION AFTER 10 MINUTES
DISCHARGED CELL	ELECTROLYTE LEAK	FIRE	NO HAZARD
DEPASSIVATED CELL WITH S_2Cl_2	FIRE AFTER ~ 10 MINUTES	FIRE AFTER ~ 10 MINUTES	GAS RELEASE AFTER ~ 10 MINUTES
DISCHARGED CELL WITH S_2Cl_2	ELECTROLYTE LEAK	ELECTROLYTE LEAK	NO HAZARD

One solution to the explosion problem was the addition of sulfur monochloride, S_2Cl_2. The purpose of the S_2Cl_2 is to keep the elemental sulfur in solution, thereby preventing it from reacting with the lithium. Similar penetration and short circuit tests were conducted on high power cells with S_2Cl_2. No explosion was detected.

A fully discharged cell may still be dangerous, unless it contains S_2Cl_2. When such a cell was penetrated by a nail, no explosion or fire resulted because of insufficient electrical energy to heat the lithium to its melting point. However the kinetic energy transferred by a bullet impact is sufficient to melt the lithium, thereby initiating the lithium-sulfur thermite-like reaction. By solubilizing the sulfur with S_2Cl_2 this reaction is precluded.

The addition of S_2Cl_2 to the battery adds to the number of possible chemical reactions. When heated, S_2Cl_2 will decompose and can potentially produce all or part of the following reactions. (Note that the following are not balanced equations but only show possible specified interrelationships.)

$$\begin{array}{ccc} & & S_2Cl_2 \\ & & \uparrow \\ S_2Cl_2 & \overset{\Delta}{\rightleftarrows} & SCl_2 + S \\ & \downarrow\uparrow\Delta & + \\ & S_2Cl_2 + Cl_2 & \end{array} \qquad \Delta = \text{Heat Addition}$$

Since boiling points of SCl_2 and $SOCl_2$ are 50^oC and 78^oC, respectively, the pressure in the battery will increase rapidly as the temperature rises. At high temperatures thionyl chloride will tend to decompose into sulfur monoxide and chlorine.

If the heat is derived from high current during the discharge, then the pressure in the battery case will be the sum of the vapor pressures of the thionyl chloride, and the three identified gases Cl_2, SO_2, and SO. At higher temperatures the vapor pressure of sulfur monochloride (B.P. 138^oC) must also be considered. If the temperature rise is high enough to produce sufficient pressure to rupture the battery case, the consequences will range from simple release of $SOCl_2$ to the atmosphere and hydrolysis according to reaction

$$SOCl_2 + H_2O \rightarrow 2\ HCl + SO_2$$

to fire and/or explosion. Our research strongly suggests that the reaction that initiates a fire or explosion is the thermite-like reaction

$$2\ Li + S \rightarrow Li_2S + \text{Heat}$$

The temperature reached by this exothermic reaction is of the order of 1500 to 1600 degrees Celsius (5). With the case open to the atmosphere at these temperatures, many possible reactions can produce hazardous gases. The probability of any or all of these reactions occurring is difficult to estimate because it is dependent on the extent of rupture of the case, the amount of discharge that has occurred prior to rupture, and the actual temperature

attained by the battery.

In the case of battery rupture and fire it is clear that the great bulk of gas will be sulfur dioxide and hydrogen chloride. Sulfur dioxide can be formed by three reactions:

$$SO + \tfrac{1}{2}O_2 \rightarrow SO_2$$

$$S + O_2 \rightarrow SO_2$$

$$SOCl_2 + H_2O \rightarrow SO_2 + 2\ HCl$$

and hydrogen chloride by hydrolysis of thionyl chloride.

Since there is an abundant supply of carbon in the cathode it is reasonable to expect both carbon monoxide and dioxide to be formed by the reactions

$$2\ C + O_2 \rightarrow 2\ CO$$

$$2\ C + 2\ O_2 \rightarrow 2CO_2$$

At high temperatures thionyl chloride will decompose to produce sulfur monoxide and chlorine gas as follows:

$$SOCl_2 \xrightarrow{Heat} SO + Cl_2$$

If sufficient CO is produced, the possibility of it reacting with the chlorine to produce phosgene must be recognized. The reaction would proceed as follows:

$$CO + Cl_2 \rightarrow COCl_2$$

If the battery is nearly fully discharged and a large amount of sulfur is present and the fire is oxygen starved, CO could react with the hot sulfur to produce a poison gas by the following reaction:

$$CO + S \rightarrow COS$$

While there is no evidence to show the formation of this gas, its potential presence must be considered in any safety evaluation.

The fire after container rupture can also be in part attributed to a direct reaction between hot lithium and atmospheric nitrogen:

$$3\ Li + N \rightarrow Li_3N$$

There is a small chance that at the high temperature of the fire some of the lithium will react with the cathode material to form lithium carbide by the following reaction:

$$2\ Li + 2C \rightarrow Li_2C_2$$

If water is applied to the fire, then the sulfur monochloride will react to produce additional hydrogen chloride and sulfur dioxide. Lithium nitride, if present, will form ammonia, and lithium carbide, if formed, will produce acetylene. The ammonia and acetylene, if at all present, will constitute a very small percentage of the total gas produced. Another

serious poison-gas-producing component is the teflon binder in the cathode. The thermal decomposition of the polytetrafluoroethylene can be hazardous. The fluorinated olefinic by-products, particularly the perfluoroisobutylene, are toxic when inhaled. In addition, the monomer at low temperatures can form with oxygen a polyperoxide which is very unstable and can detonate.

CELL SLEEPING

The phenomenon that is referred to as cell "sleeping" is illustrated in Figure 4-1. This phenomenon is a premature decrease in cell voltage when being discharged in a very quiet environment. When a cell is "sleeping," the cell voltage can be immediately restored to normal by gently tapping on the cell. Sleeping has been attributed to reaction products blocking catholyte circulation within the pores of the cathode structure and clogging the interelectrode region, reducing electrolyte contact with the electrodes. The amount of lithium chloride formed during discharge of a double-D-size cell is approximately 40 grams. The amount of thionyl chloride present at the end of the 25 ampere hours of discharge is only 14 grams. From these calculations it is clear that this small amount of solvent cannot hold the large amount of lithium chloride in solution. Thus, LiCl should crystallize throughout the cathode structure, thereby restricting the flow of the residual $SOCl_2$. There is no available solvent that could be initially incorporated in the battery in sufficient quantities to hold this large amount of LiCl in solution. Therefore, altering the cell chemistry is not the necessary approach to solving the sleeping problem. Instead, the cell has to be redesigned to include the following:

1. Purified electrolyte
2. Water- and gas-tight seal
3. Larger anode surface areas
4. Thinner cathodes
5. Slight increase in internal pressure due to the preservation of the gaseous products
6. All stainless case

Cells constructed in this manner were tested to see if the sleeping problem reoccurred, and as described above no sleeping was observed.

Both the AA-size and double-D-size cells show very stable voltage during their discharge and no premature voltage drop has been noticed. Several double-D-size cells were discharged in a very quiet environment at 5°C. All cells consistently delivered over 20 ampere hours (above 3 volts) when discharging at rates between 5 milliamperes and 200 milliamperes. It should be noted that the initial voltage delay (passivation) problem has also been reduced since the introduction of these redesigned cells.

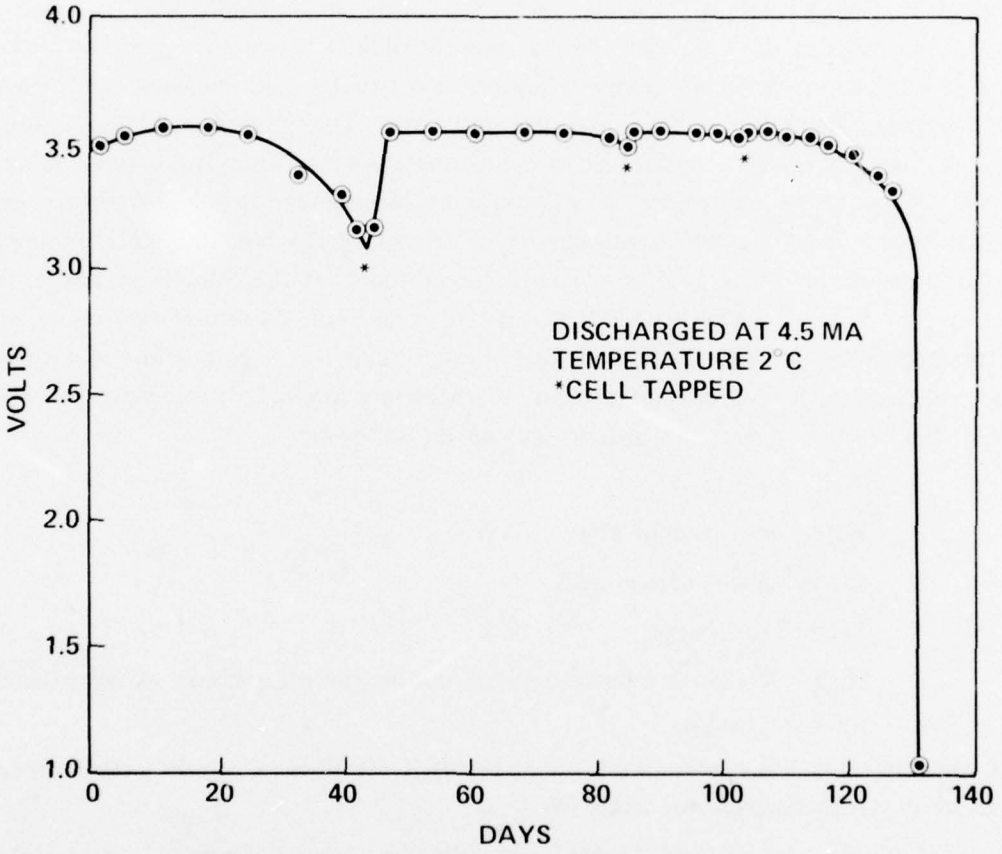


Figure 4-1. Premature Discharge of D-Cell Tested in a Quiet Environment.

INTERNAL RESISTANCE

As these cells discharge, their voltage-ampere characteristics change. Figure 4-2 shows a voltage-ampere curve for a double-D-size cell at various states of discharge. This declining voltage performance during cell discharge results from a depletion of the electrolyte, which results in a decrease in the wetted electrode surface area. In addition, the available surface area in the cathode structure is reduced due to the clogging of the cathode pores with reaction products. This effect may prove useful when it becomes necessary to determine the state of discharge of a cell. One simply compares the voltage-ampere curve of the cell against that of a "calibrated" cell (at the same rate and temperature).

ORIENTATION SENSITIVITY

The cells are sensitive to attitude during discharge. The cell capacity is reduced by 23% when placed horizontally and reduced by 66% when oriented vertically with the positive terminal downward, as shown in Figure 4-3. Maximum capacity results when the cell is oriented vertically upright. As previously mentioned, any method that will allow the electrolyte to wet the electrode will prolong the cell discharge life.

VOLTAGE DELAY

The performance of the lithium inorganic electrolyte cell is not adversely affected by high-temperature storage. However, a slight delay in reaching the operating voltage is noticed. One AA-size cell was stored for 29 days at 70°C without any noticeable voltage delay. The cell immediately delivered 9.6 milliamperes at 3.49 volts. (Total cell capacity above 3 volts was 2.1 ampere hours, at 5°C and 1.75 mA.) Another AA-size cell was stored for 77 days at 70°C. In this cell some voltage delay was noticed, as shown in Figure 4-4. It took 18 minutes to reach 3 volts while discharging at a rate of 8.5 milliamperes. When stored for 1 year at room temperature a longer voltage delay was observed in an AA-size cell. As shown in Figure 4-5, the cell took 4 1/2 minutes to reach 3 volts while delivering 8.5 milliamperes. The new double-D cells, stored about 1 month at room temperature, show very little voltage delay. They reach 3 volts within 20 seconds when discharging at 80 mA. (Total cell capacity above 3 volts is about 20 ampere-hours at 5°C; and at rates from 50 to 200 milliamperes).

Voltage delay, experienced with cells that have been stored for long periods of time, is overcome by shocking the cell either physically or thermally (high temperature or very low temperature). Hydrostatic pressure (~60 meters depth) also depassivates the cells.

To study the nature of the *passivating* film, a badly passivated battery was opened and a small piece of the lithium anode was removed and placed in a Mark I Triga reactor at the University of California, Irvine. The sample was subjected to a neutron flux of 1.2 x 10^{12} n/sec/cm^2 for 3.5 hours. After allowing 16 hours for the induced activities to cool,

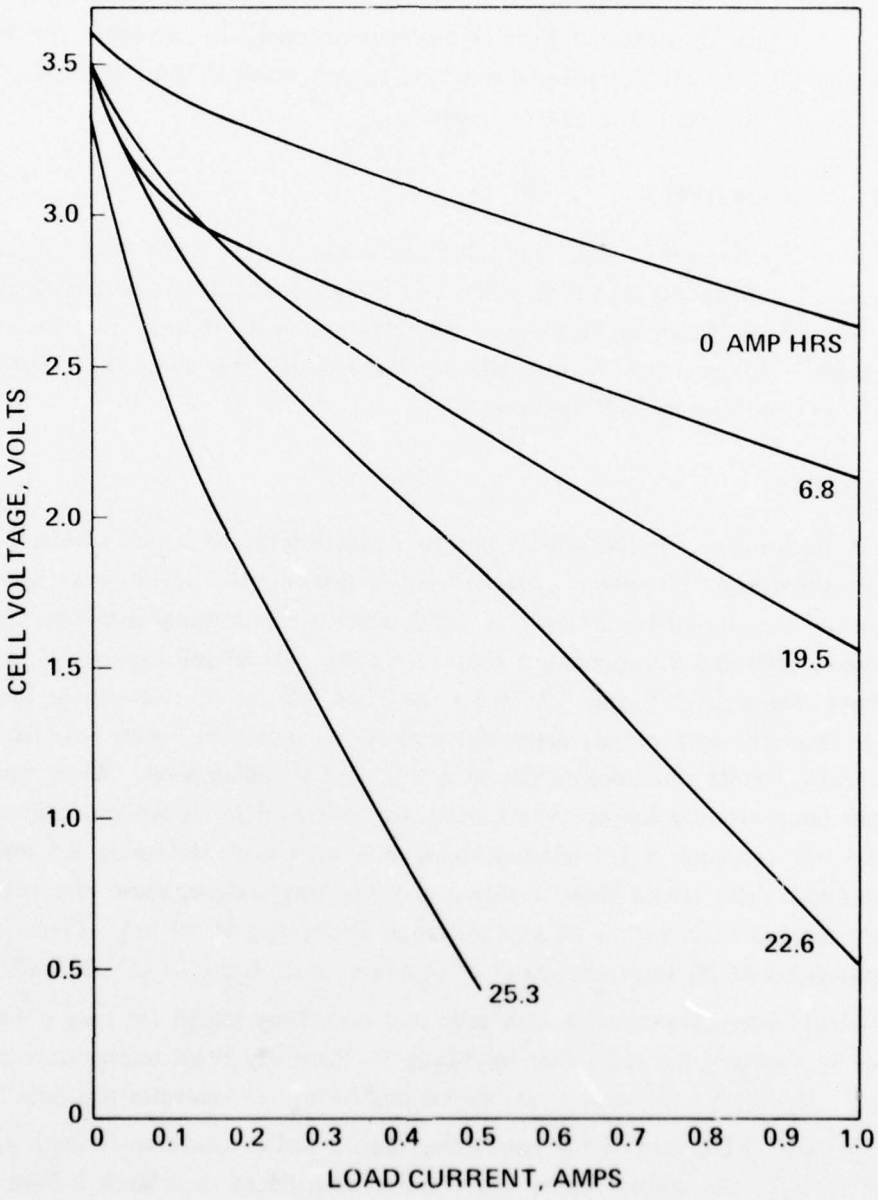


Figure 4-2. Internal Resistance vs State of Discharge.

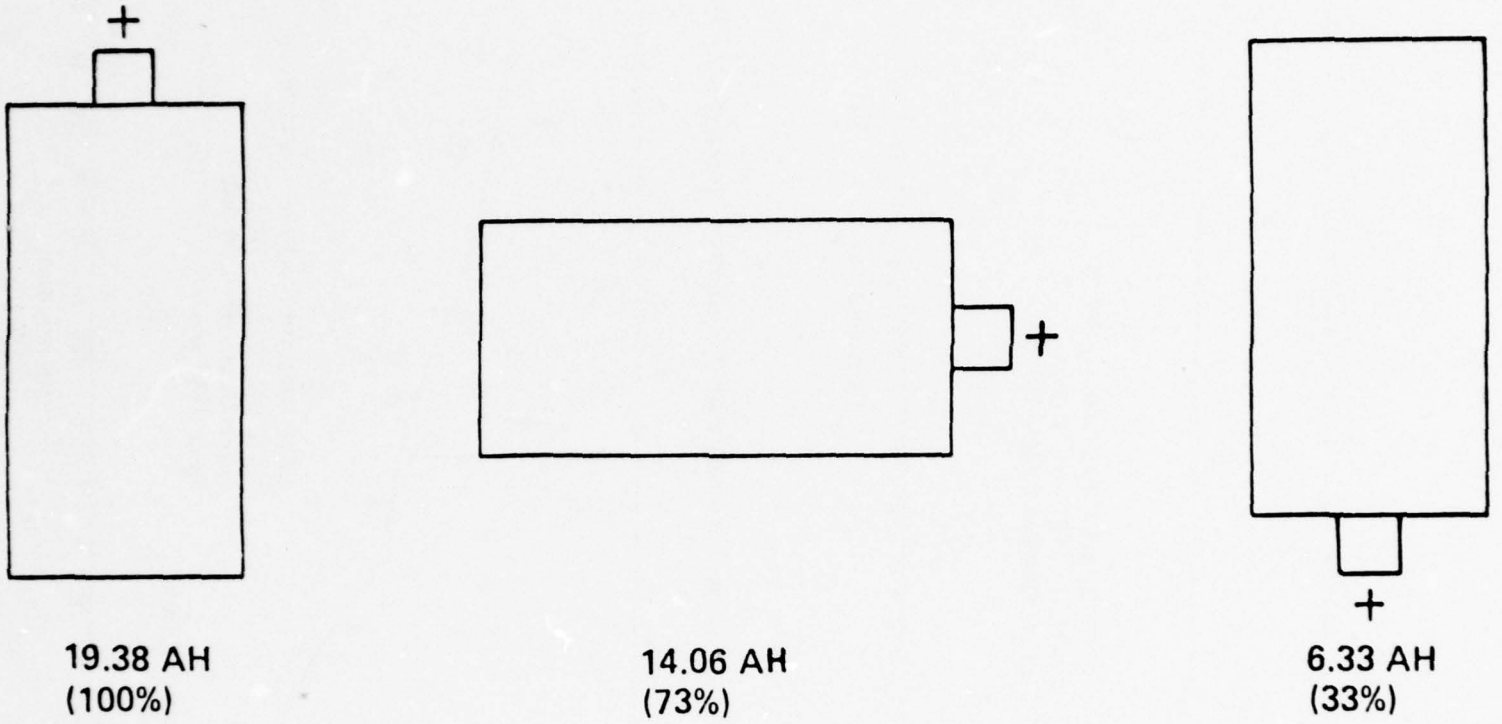


Figure 4-3. Orientation Sensitivity of DD Cells.

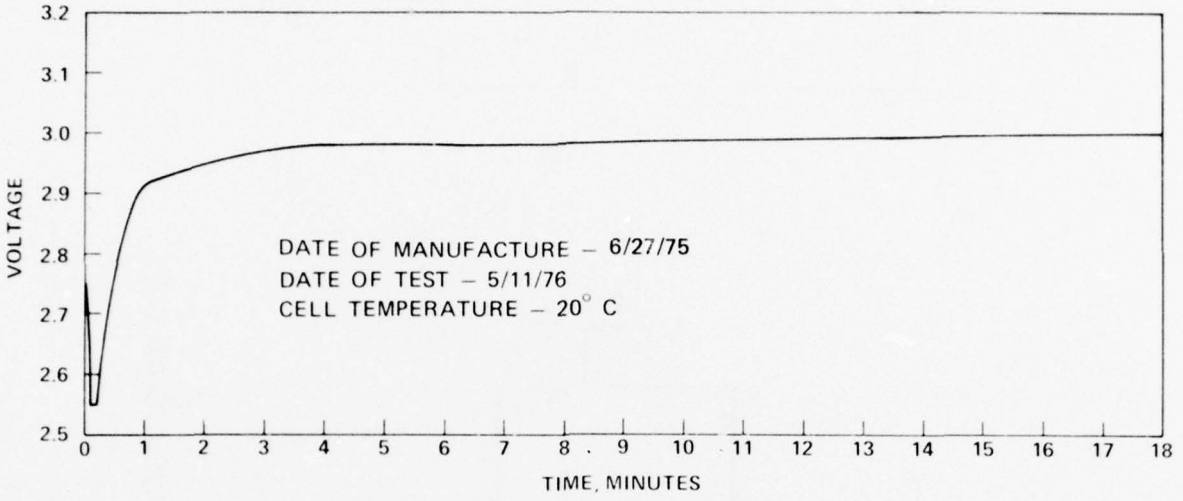


Figure 4-4. Voltage Delay Following High Temperature Storage for 77 Days at 71-75°C.

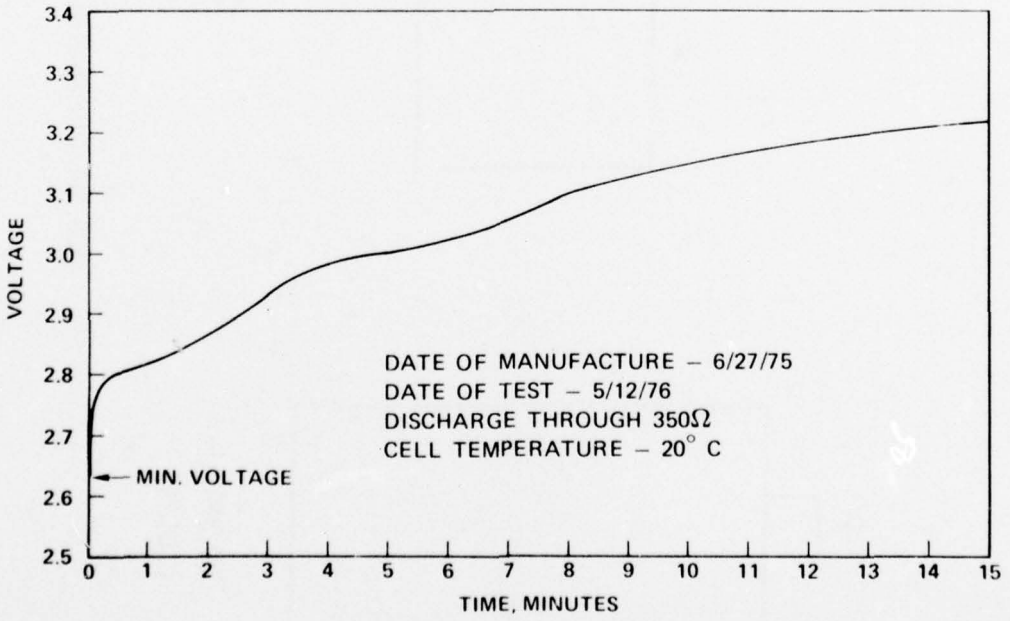


Figure 4-5. Voltage Delay of an AA Lithium Cell Stored at Room Temperature.

the sample was counted on a gamma spectrometer using a Ge(Li) detector. An analysis of the spectra indicated the following possible elements:

Cu, Br, Pt, or Ta, Mn, Fe, and Ni.

The surface of the lithium was also analyzed by X-ray fluorescence spectrometry; the amount of each observed element was estimated by standards addition. Table 4-2 shows estimated amounts of the observed elements.

TABLE 4-2

ANALYSIS OF THE LITHIUM ANODE SURFACE BY X-RAY FLUORESCENCE ANALYSIS

Element	Micrograms
Ca	54
Fe	77
Zn	13
Ni	3

The possibility that these metals are involved in the passivating mechanism must be considered.

REVERSE POLARITY HAZARD TESTS

Many battery applications require that several cells be connected in series. In a battery of this type it is possible for one of the cells to discharge more completely than the other cells. When this happens the cell will experience a reverse polarity and deprive the load of its normal operating voltage. The cell acts as a parasite, actually absorbing energy. A possible hazardous result of this is the formation of dendrites which would short out the cell internally if these bridge the gap between the anode and cathode structure. At this point there would be a danger of the cell overheating and venting $SOCl_2$ and/or cause lithium to react with other materials, such as free sulfur if S_2Cl_2 is not present.

As a test for this situation, a fully discharged double-D cell was connected in series with two fresh double-D cells. The voltage reached -0.2 volt at .5 amp after 39 minutes, and after 1 1/4 hour the voltage dropped to -0.05 volt at 15 amps. This indicated the presence of a lithium dendrite bridge. However, no otherheating or case rupture resulted, even when the current was increased to 3 amps.

In another test 10 high-power cells were connected in series and externally short circuited for 30 minutes. The cells were contained in an aluminum tube that was backfilled with mineral oil for improved heat transfer. The cells were initially passivated due to being stored for over 1 year. There was no explosion, case rupture, or fire, even with a current that eventually peaked at 25 amps.

PRESSURE COMPENSATION

When the internal components of the lithium cell are exposed to the ambient pressure (as in a deep ocean application), dramatic increase in cell performance results. Several cells of the low-rate configuration (in steel cases with conventional crimp seals) were pressure compensated and exposed to pressures reaching 5000 psi. To pressure compensate the cell a small hole was drilled in the top (through the positive terminal). A fluorocarbon fluid, Dow FC-75, surrounded the hole to prevent moisture in the air from entering the cell and reacting with the electrolyte and lithium. The cell with its bath of FC-75 was placed upside down in a glass jar and suspended from the lid of the oil-filled pressure tank. Wires were connected to the electrodes, soldered to connectors in the tank cover, and fastened to a voltmeter and ammeter. Figure 4-6 shows this test set up and the results of tests are shown in Figure 4-7. The first pressure reached was 2000 psi and curve B of Figure 4-7 shows the volt-ampere curve taken at that point. The cell was discharged about 1.5 ampere hours and curve C shows the volt-ampere curve at 2000 psi. It is slightly lower because it represents a greater state of discharge. Part of the difference between curve A and B can be attributed to the beneficial effect pressure has on voltage stability.

RESERVE ACTIVATION

The reasons for holding the electrolyte in reserve prior to activation are to make long-term storage possible, to provide for a safer assembly during handling and, to eliminate the passivation or voltage delay problem. The cells configured for high-rate applications are most suitable for reserve activation.

A survey of the literature on reserve activation techniques indicated that most designs placed the electrolyte in a frangible reservoir or one that had a frangible diaphragm. This was ruptured either manually, explosively with a primer, by a dissolvable link, by forced anodic dissolution of a hot wire, or by the pressure head of the sea. In some designs care was taken to ensure that the electrolyte thoroughly saturated the cathode structure and anode. This involved forcing the electrolyte into the cell structure by the action of a compressed gas. In most cases the reservoir was external to the cell assembly and a rather large battery resulted. However, in one design the expended reservoir could be removed.

A reserve-activated lithium battery for use in spacecraft is shown in Figure 4-8. The rated capacity is 160 ampere-hours at a current of 18 amperes. The circular section contains the electrolyte storage bellows, and pressurized freon gas is used to force the electrolyte into the cell.

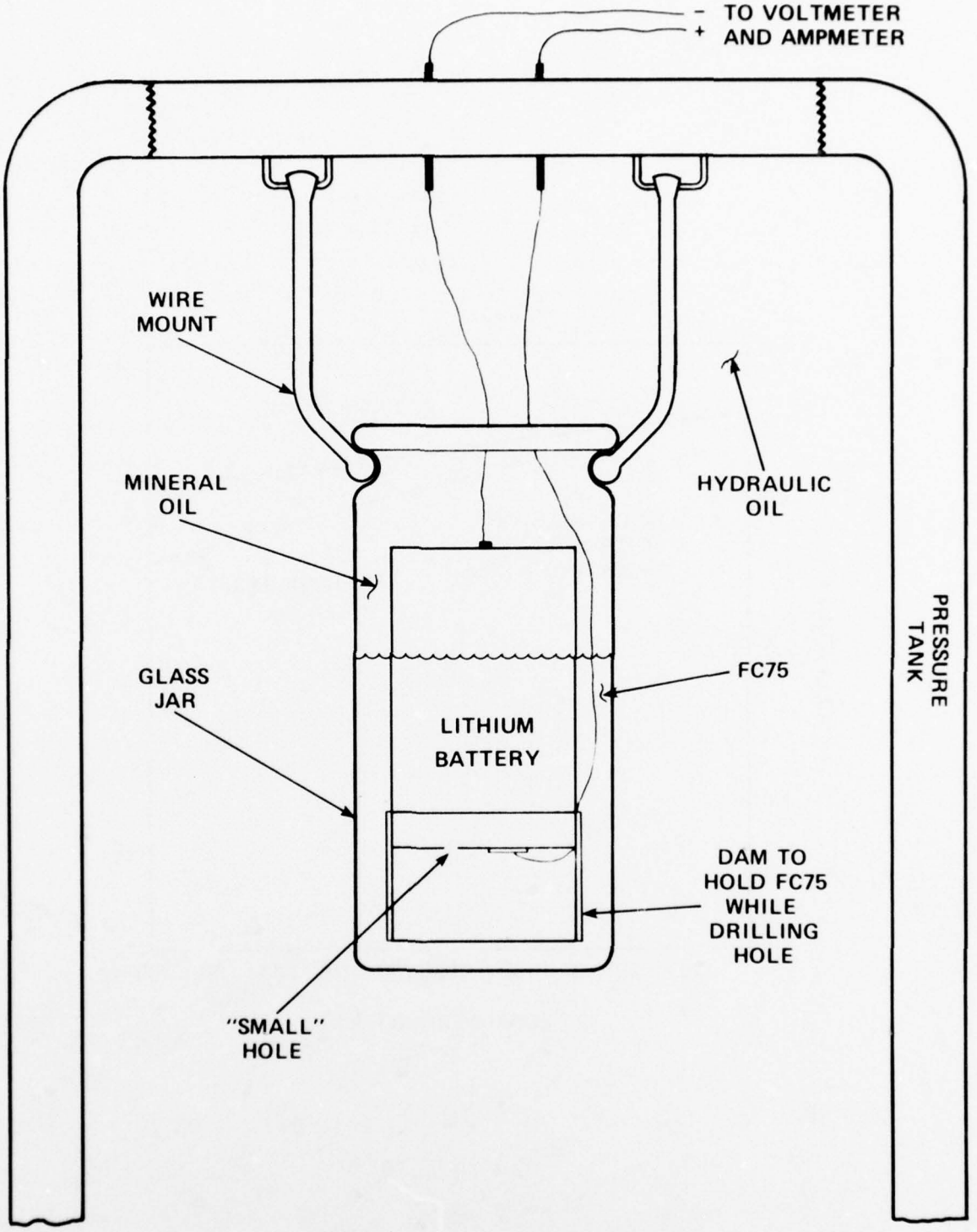


Figure 4-6. Lithium Battery Pressure Test Set-Up.

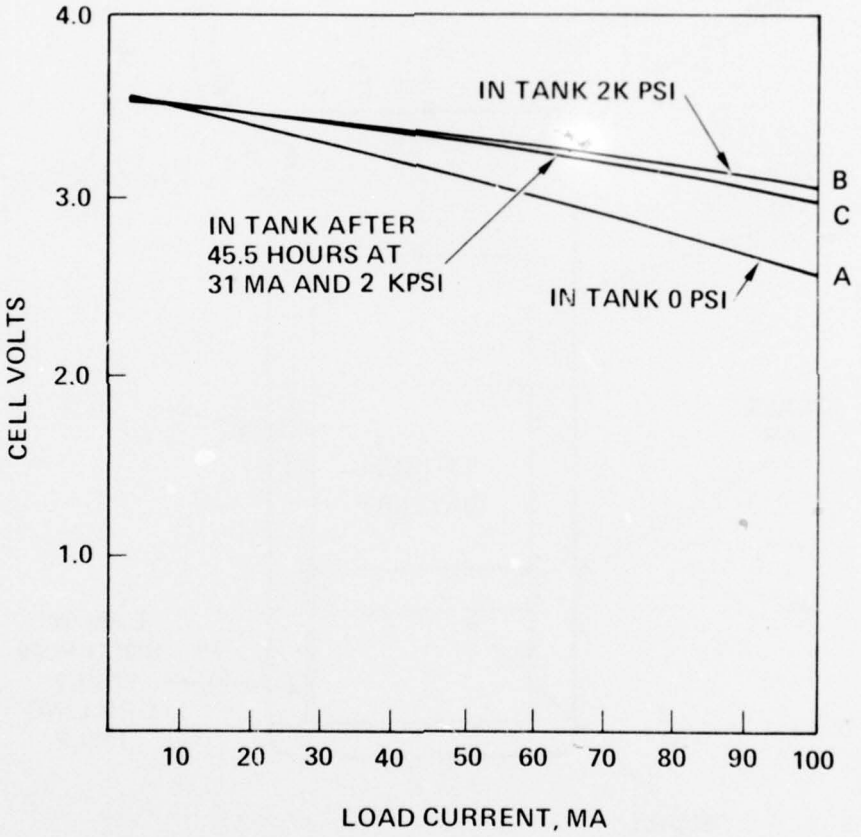


Figure 4-7. Pressure Improves Power Density.

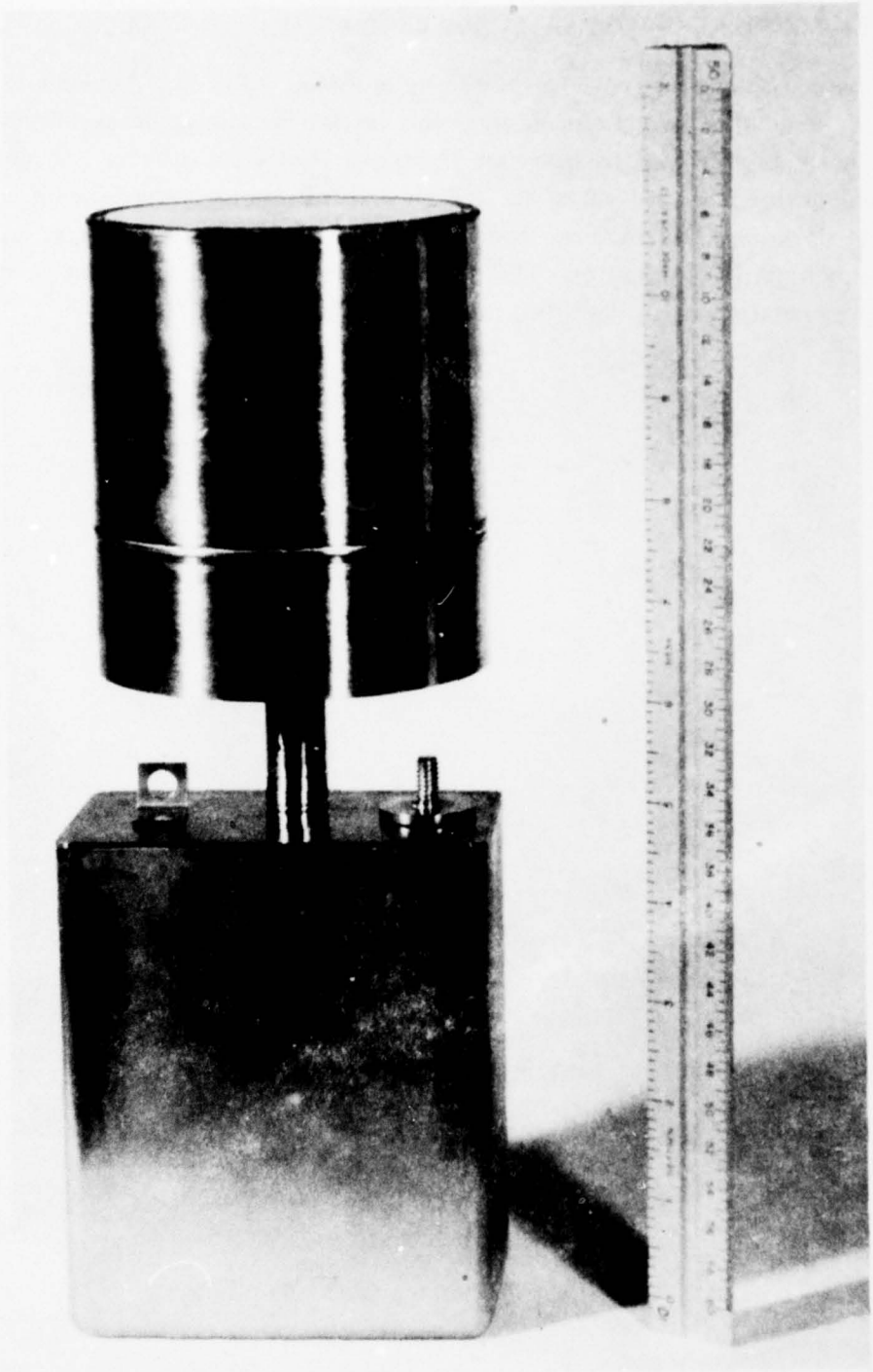


Figure 4-8. Reserve-Activated Lithium Battery.

COMBINED PRESSURE-COMPENSATED/RESERVE-ACTIVATED CELL

Several advantages could be realized by producing a cell that combines the two techniques. In addition to the advantages unique to each technique, the combination may provide a much safer cell. After activation the empty electrolyte chamber becomes a trap for any electrolyte that is ejected out of the cell, or boils off, during a short-circuit condition. This would slow down the reaction. The chamber will also trap any gases that may be produced during normal cell discharge. The flexible bellows would compress due to the external ambient pressure acting on it, providing pressure compensation for the cell.

SECTION 5

APPLICATION EXPERIENCE

Numerous possible applications of the lithium-inorganic cells have been investigated. These applications include moored surveillance buoys, directional command active sonobuoys, expendable sound source buoys, deep ocean acoustic navigation transponders, NavFac light-weight array cable test program, Marine Corps man-portable battlefield radar sets, laser designators, mobile sound simulators, geophysical monitoring balloons, submarine target location balloon transmitters, marine mammal implantable biotelemetry packages, arctic sensor buoys, torpedoes, and advanced untethered deep ocean search systems. Each of these applications could benefit from the use of lithium-inorganic batteries, but decisions to use these batteries have been dependent on the test results from this program.

As a result of test experience with these cells and the resulting design improvements that have been accomplished to date, multicell batteries are being introduced to the Fleet for certain applications.

At the present time cell capabilities and limitations must be carefully compared to determine if the limited cell technology can be adapted to a specific application of interest. NUC has provided this type of assistance to each of the activities listed below. Follow-up on the performance obtained from lithium-thionyl chloride batteries has revealed 100% success with all applications described in the following discussion.

MARINE MAMMAL RESEARCH

The Naval Undersea Center is using AA-size hermetically sealed lithium cells (similar to the heart pacemaker battery) with marine mammals to power sensors and RF transmitters that telemeter brain waves along with eye and muscle movement. The required life of the battery is 1800 hours of "on" time and the battery consists of two cells, one AA-size, delivering a positive 3 volts and one half-sized AA cell, delivering a negative 3 volts. Lithium inorganic cells, as compared with previously used mercury batteries, are advantageous for this application because of their high available power and long life in a compact form, their lighter weight, and their lack of a need for gas venting. The instrumentation is shown in Figure 5-1.

BALLOON INSTRUMENTATION PACKAGE

The Naval Undersea Center is using 25 double-D size hermetically sealed cells for each balloon-supported radio package. Two power levels are required from the battery, 16 volts at 150 milliamperes and 13 volts at 800 milliamperes. The total operating time is 120 hours. The main advantage of lithium batteries for this application is their high energy and light weight, since the battery weight is not to exceed 10 pounds. This could not be accomplished by any other type of battery. Twenty instrumentation packages will be built. The balloon to be instrumented is shown in Figure 5-2. Figure 5-3 shows the battery case and cells.

LASER DESIGNATOR POWER SOURCE

The Naval Weapons Center, China Lake, California, and NUC have used high-rate cells to energize a laser in a target desingation system, as shown in Figure 5-4. The requirement for the tests was to deliver 6 to 10 amperes in a pulsed mode (1 minute on and 1 minute off) at a voltage greater than 20 volts. A test was made to compare the number of pulses available from a series circuit of ten high-power lithium inorganic cells against the standard NiCd battery pack. The lithium battery pack delivered 50 satisfactory cycles, whereas the NiCd pack delivered 10 cycles. Additional development is planned for FY 76 to optimize high-rate cell design for this application.

DEEP OCEAN TRANSPONDERS

Several transponders (shown in Figure 5-5) developed by Sonatech, Inc., Goleta, California, will be installed in the ocean with lithium inorganic electrolyte batteries. The battery pack has two requirements, a low-level receiver and a high-level transmitter. The low-level receiver requires 8 volts and a continuous 1 milliampere for a period between 6 months and 5 years. The high-level 200-watt transmitter produces 10-millisecond pulses at 24 volts for 2-million pulses over a 5-year period. The battery pack consists of 40 D-size cells; however, the double-D-size cell is being evaluated for this application.

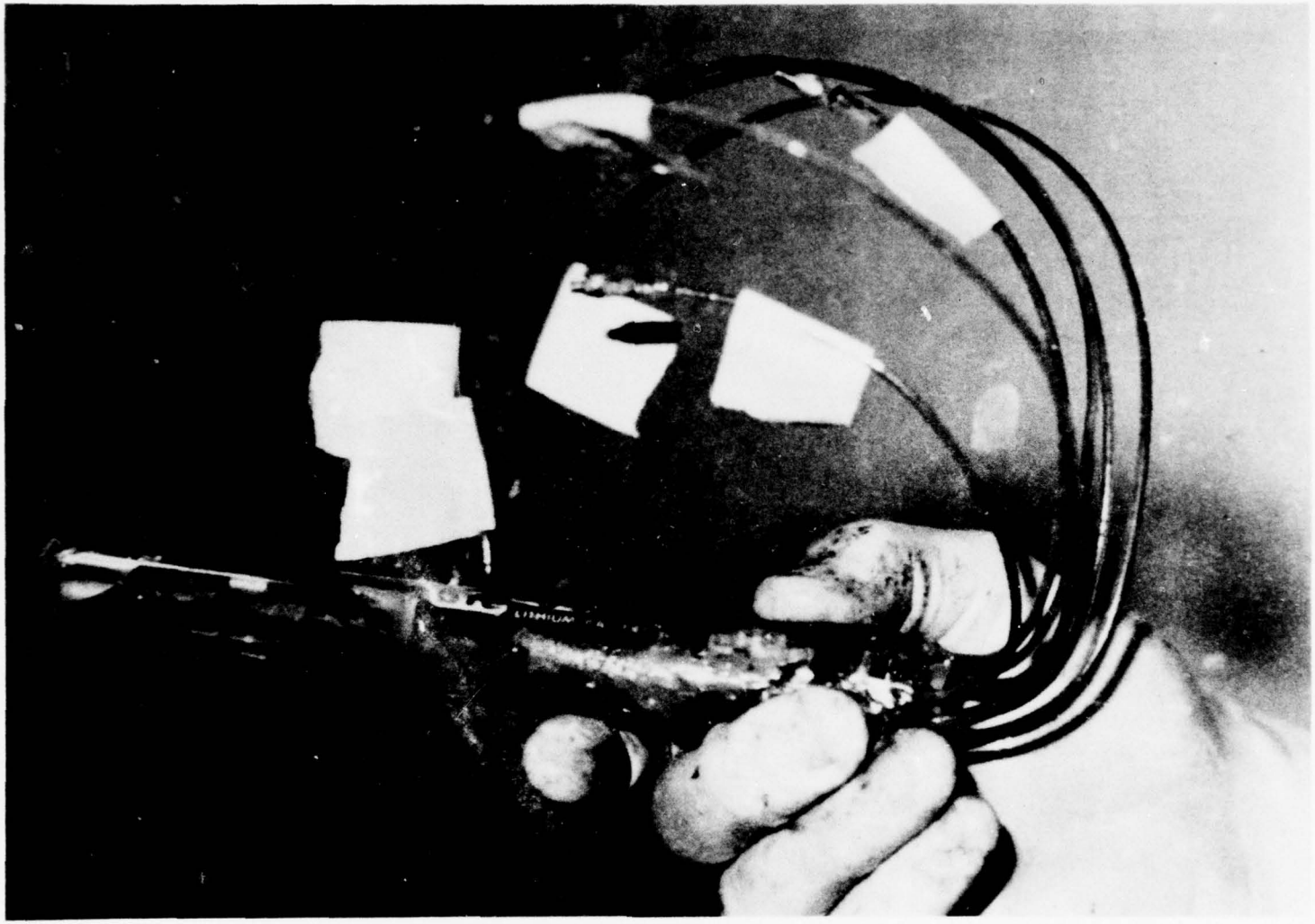


Figure 5-1. Biotelemetry Package Using AA-Size Lithium Cells.



Figure 5-2. Tethered Balloon System Using 25 DD-Size Lithium Cells.

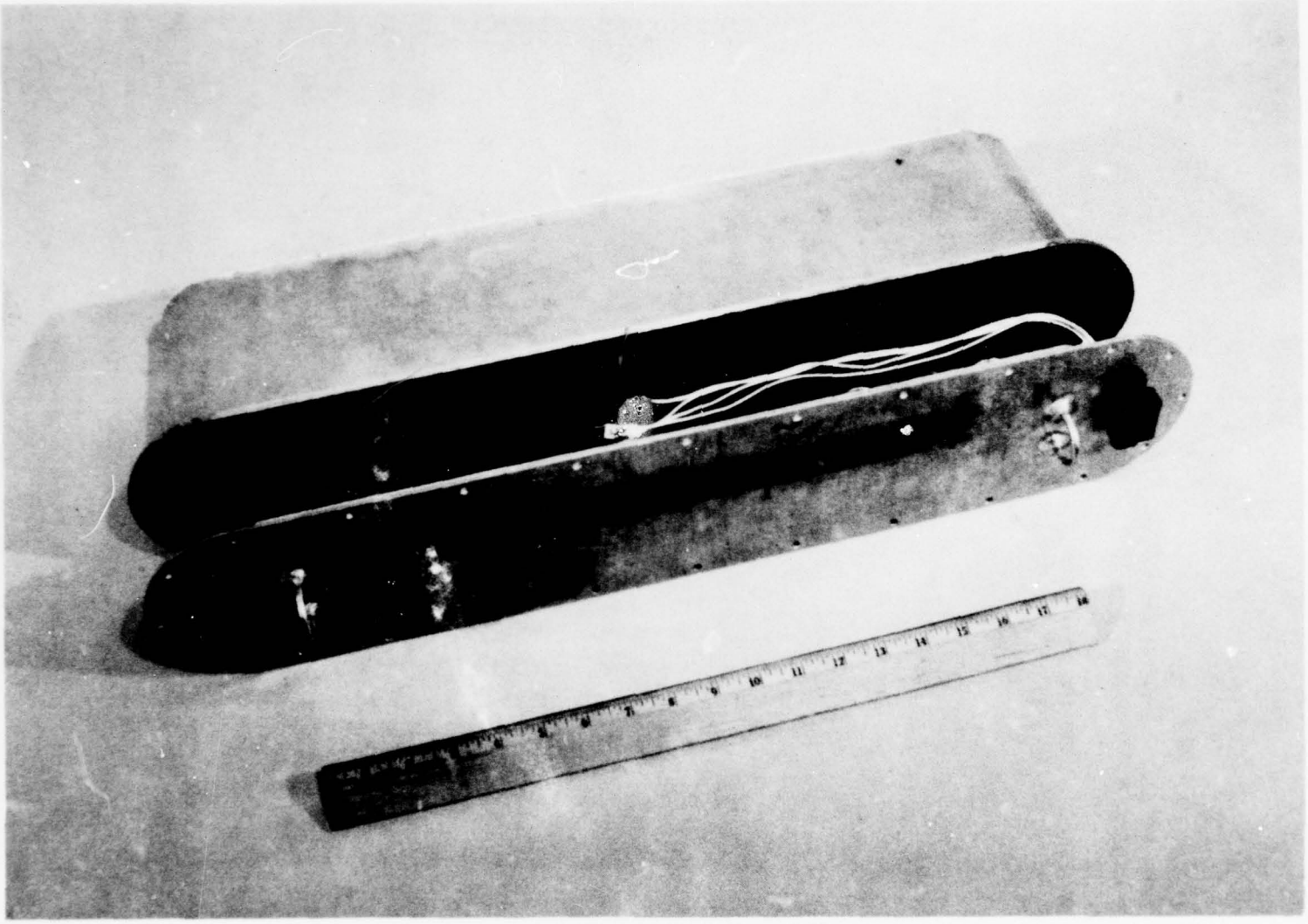


Figure 5-3. Battery Container for Tethered Balloon Systems.



Figure 5-4. Modular Universal Laser Equipment Using 10 D-Size Cells.



Figure 5-5. Deep Ocean Transponder Using 40 D-Size Cells.

GEOPHYSICAL MONITORING BALLOON

A lightweight, expendable command receiver has been developed at UCSD for ONR for terminating scientific balloon flights (Figure 5-6). The receiver operates at 138.54 MHz and the command is actuated by a sliding tone from 300 Hz to 400 Hz. A phase locked loop detector circuit operates an SCR firing circuit to actuate a guillotine-type explosive cutter. Experience with the command receiver has shown that most high energy density batteries freeze-up at high altitudes and provide insufficient current to fire the squib. It is believed that the lithium inorganic electrolyte battery will be less likely to freeze at the high altitudes anticipated in most balloon flights (freezing point for thionyl chloride is -104.5^{o}C). Test flights were planned in FY 76 to determine the command receivers performance with a 15-volt lithium inorganic electrolyte battery. These flights have not been conducted yet; however, laboratory tests have been conducted that verify the suitability of the lithium batteries for this application.

NAVFAC LIGHTWEIGHT CABLE EXPERIMENT

The NUC Hawaii Laboratory is constructing an underwater cable system experiment. Five battery packs are needed for a central electronics bottle, two sound velocimeters, and two current meters. The system will be deployed for a year in the deep ocean with an ambient temperature near 0°C. The system, except for the acoustic receiver, will be off until it is interrogated by an acoustic command. The acoustic receiver will be energized for the entire 1-year system life. The system will be interrogated every hour for a year and will be on for 3 minutes for each interrogation.

Since power source space, weight, and reliability are critical in this application 50 size DD and 25 size AA lithium inorganic electrolyte cells will be used.

The batteries are to be in a sealed container for a year with the electronic circuitry they are powering. Therefore, they should not leak any gasses or liquids that will cause corrosion or short circuiting of the electronics. For this reason only hermetically sealed cells will be used.



Figure 5-6. Geophysical Research Balloon Using 5 D-Size Cells.

ARTIC DATA BUOYS

Polar Research Laboratory, Inc., (PRL), Santa Barbara, California, is developing, under NOAA contract, an air droppable (ADRAMS) data buoy for use with the NIMBUS F satellite. This is similar to the NIMBUS F data buoy work performed for ONR. PRL is also developing a different type of arctic data buoy for the Sensor Technology Program (ONR) that could well utilize lithium inorganic batteries.

The first application at PRL will be the ADRAMS (shown in Figure 5-7) because the inorganic lithium battery appears to solve several of the problems that have been experienced with other power sources. The requirement is 175 amp-hours at 12 volts with peak loads of 250 ma for 1 second each minute. Hermetically sealed DD-size cells are being used for this application.

The experience gained from this initial arctic application will provide engineering data for the other similar applications that need an advanced power source. Laboratory tests conducted by PRL have shown an ability to pulse discharge double D-size cells for 1 second per minute. The following data has been obtained at 66 ma:

Temp (^{O}C)	Starting Voltage	Voltage at End of 1 Sec
-40	3.6 volts	not measured
-62	3.6 volts	3.2
-68	3.53 volts	3.0

The same cell has provided 20 AH above the cutoff voltage of 3.0 volts at a discharge rate of $\sim$28 ma and at -13.7^{O}C.

SEISMIC SENSORS

The U.S. Geological Survey will be installing several sensors in the Santa Barbara Channel this year to monitor seismic activity around the Dosquadros Oil Field. These sensors requires a 5-year, reliable power source with a highly regulated output (1%) since they will be supplying power to voltage controlled oscillator (VCO) circuits.

Hermetically sealed DD-size cells will be used for this application.

All of these applications are now using lithium-inorganic electrolyte cells, but with technology improvements accomplished during FY 75. These accomplishments include hermetic seals, larger cell sizes, depassivation techniques, shock and vibration limit information, disposal methods, causes of explosions, and methods of eliminating explosions.



Figure 5-7. Arctic Data Buoy.

In summary the chemistry of the lithium-inorganic cell works and produces a battery with outstanding performance. There is a definite need for this cell in both high-rate applications (i.e., vehicle propulsion systems) and long-term, low-rate applications as in surveillance system power sources.

There are many additional applications that require an advanced power source that could be satisfied by lithium-inorganic cells if development for these applications was carried out. A partial list of known applications is given in Table 5-1.

APPLICATIONS CURRENTLY BEING PURSUED

Several applications are being pursued at this time. These applications require large-size cells or very high rate cells that require additional development.

High-Rate Torpedo Battery

The Navy has specific requirements for high-energy-density, high-rate, safe, reliable, and low-cost power sources for underwater weapon propulsion applications.

In addition to the development projects discussed in the preceding sections, the Naval Undersea Center has been particularly active in the development of high-rate lithium propulsion batteries for torpedoes.

The development of high-rate lithium propulsion batteries is based on many design considerations. These include the physical configuration of the cells, the size and number of cells in the battery, the use of reserve-type cells as compared with active cells, the design electrode current density, the cell operating efficiency, and methods of rejecting waste heat and controlling cell temperature rise (see Appendix B).

A conceptual design of a reserve-type high-rate lithium/SO Cl_2 propulsion battery has been completed. It has been determined that this type of battery is feasible and would be very competitive in size and weight with other propulsion systems being developed. Other significant advantages include low noise, low cost, versatility in power level and run time, and design simplicity.

The lithium torpedo battery module developed at NUC contains 20 sets of bi-polar electrodes that provide 57 amperes at 50 volts. Each module is 12.25 inches in diameter and is 0.725 inch thick. The 50-volt modules are grouped in parallel (7 modules per group) to provide 400 amperes at 50 volts, or by connecting in series with other paralleled groups (total of 6) would provide 300 volts at 400 amperes. Figure 5-8 shows a model of one of these modules. The battery would be 26-30 inches in length, depending on the achievable practical electrode density. This determination is presently under study. A report providing details on this torpedo propulsion battery has been prepared (Reference 6).

TABLE 5-1. TYPICAL CELL APPLICATIONS

LOW RATE	HIGH RATE
MOORED SURVEILLANCE BUOYS	SONOBUOYS
ACOUSTIC TRANSPONDERS*	EXPENDABLE SOUND SOURCES
ARRAY & CABLE SYSTEMS*	ACOUSTIC DECEPTION DEVICES
MARINE MAMMAL BIOTELEMETRY*	MARINE CORP FIELD RADARS
MINES	LASER DESIGNATORS*
SUBMERSIBLE TENDED ARRAY SYSTEM**	TORPEDOES**
ARCTIC BUOYS*	MARINE CORP RADIOS
SEA FLOOR SEISMIC SENSORS*	UNDERSEA SEARCH SYSTEMS
GEOPHYSICAL BALLOONS*	MANNED SUBMERSIBLES**
NAVIGATION BALLOONS	

* THESE APPLICATIONS ARE NOW USING LI-$SOCl_2$ CELLS

**THESE APPLICATIONS ARE ACTIVELY BEING PURSUED

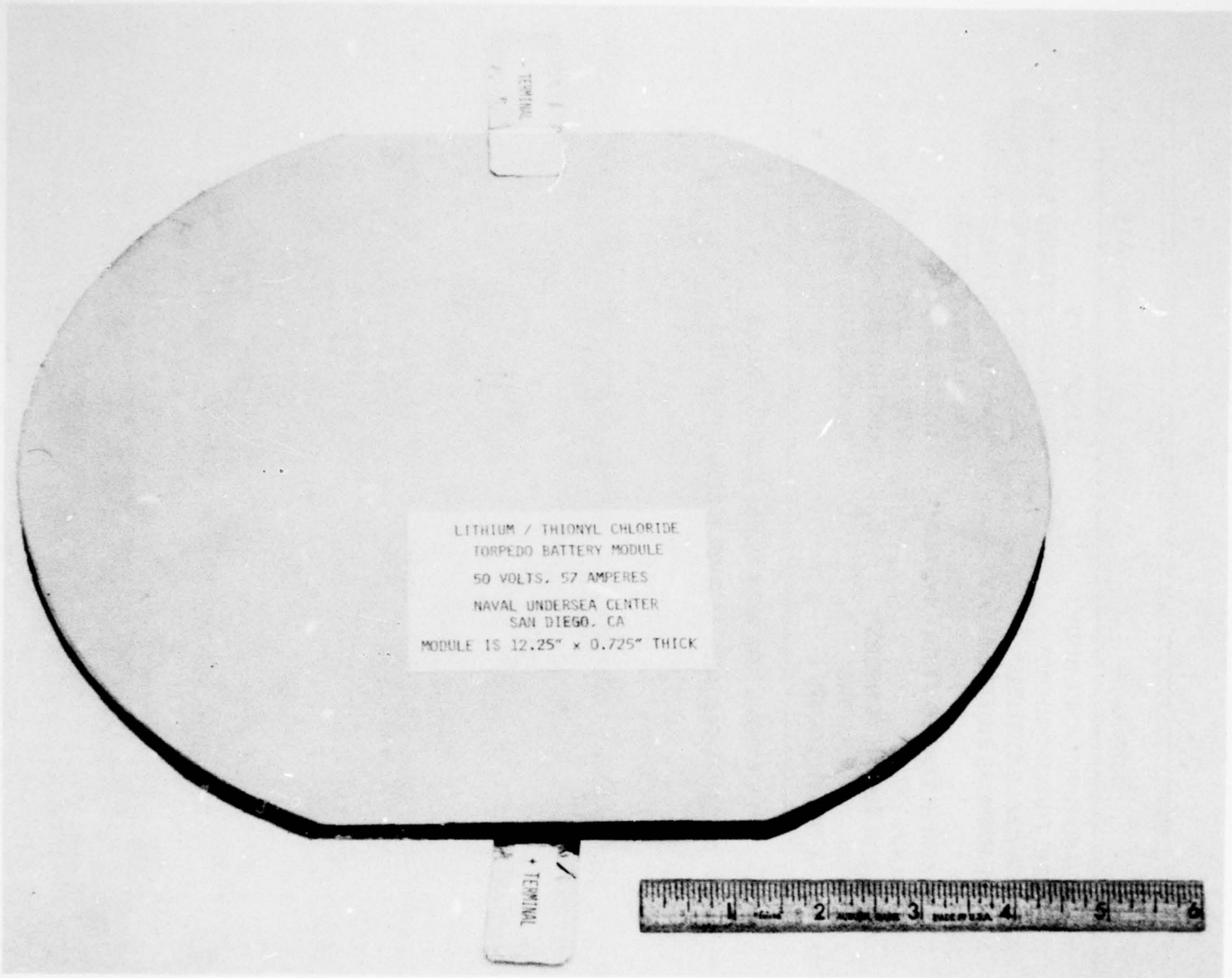


Figure 5-8. Torpedo Battery Module.

The most important consideration for this application of a lithium thionyl chloride battery for torpedo propulsion has been safety.

Almost all batteries have safety problems unique to their chemistry. In general the more energetic the battery chemistry, the greater the hazard. Thionyl chloride chemistry is no exception to this rule. It is clear that both lithium and thionyl chloride are highly reactive substances. This battery contains design features that minimize the potential hazards.

The design features take into consideration that during military applications there is a chance of bullet penetration. Previous experience with non-reserve-electrolyte cells indicate that if the bullet is of small caliber and fails to penetrate the battery completely and is captured inside the battery, a fire is the result. If a bullet of small caliber completely passes through the battery, then there is no fire and the only result is the leaking of the thionyl chloride from the battery. Such a release of electrolyte will constitute a problem in poorly ventilated areas because thionyl chloride reacts with water to form sulfur dioxide and hydrogen chloride gas.

These batteries are free from shorting hazards because of their reserve electrolyte configuration. Personnel handling a device powered by these cells are in no danger of electrocution or fire resulting from a short since the batteries have no available power prior to activation by the pressure of the water.

There will be few hazards encountered during storage and transportation. Accidents such as nail penetration, crushing, exposure to explosion, or fire will only result in electrolyte release and the associated gas formation. Under some of these conditions a limited activation of the cell can result from electrolyte leaking into the battery compartment, making electrical energy available. It must be understood that the application of water post case rupture will result in the formation of hydrogen gas.

Disposal of used batteries after a test run of a device using these batteries as a power source has been made safe by including sulfur monochloride in the electrolyte. Once these batteries are discharged, there is a significant amount of lithium unreacted, and the large amounts of sulfur formed during discharge are now available to form an explosion. The inclusion of sulfur monochloride solubilizes the sulfur and precludes a reaction with lithium, thus making the battery safe. Inadvertent case rupture during handling and transportation must still be guarded against.

Submersible Tended Array System (STARS)

The Naval Undersea Center, San Diego, California, has completed a conceptual design of a towed undersea surveillance array system that employs a remotely controlled submerged vehicle. The Submersible Tended Array System (STARS) is designed to provide a rapidly deployed underwater surveillance asset capable of being monitored for long periods of time.

STARS is intended for use in remote ocean basins not presently monitored by existing fixed systems, and to provide a "backup" or "area enhancement" capability for ocean basins presently under surveillance. STARS can be deployed from surface ships and could also be deployed by high-performance surface units, submarines, or tactical aircraft in support of local Anti-Submarine Warfare (ASW) or Special Warfare (SW) operations.

The STARS vehicle is powered by lithium inorganic electrolyte batteries, driving a 16 inch ducted propeller by means of a 2-horsepower AC induction motor.

Lithium inorganic electrolyte batteries were selected for this application because of their ability to provide 5 to 6 times the energy per unit size and weight of silver battery systems. These cells can be configured to provide 500 – 600 WH/Kg when large low-rate cells are required for systems such as STARS. This is by far superior performance relative to other battery and most engine systems presently used for underwater propulsion.

Figure 5-9 illustrates the general arrangement of the STARS vehicle, while Figure 5-10 depicts the battery characteristics.

Deep Submergence Rescue Vehicle (DSRV)

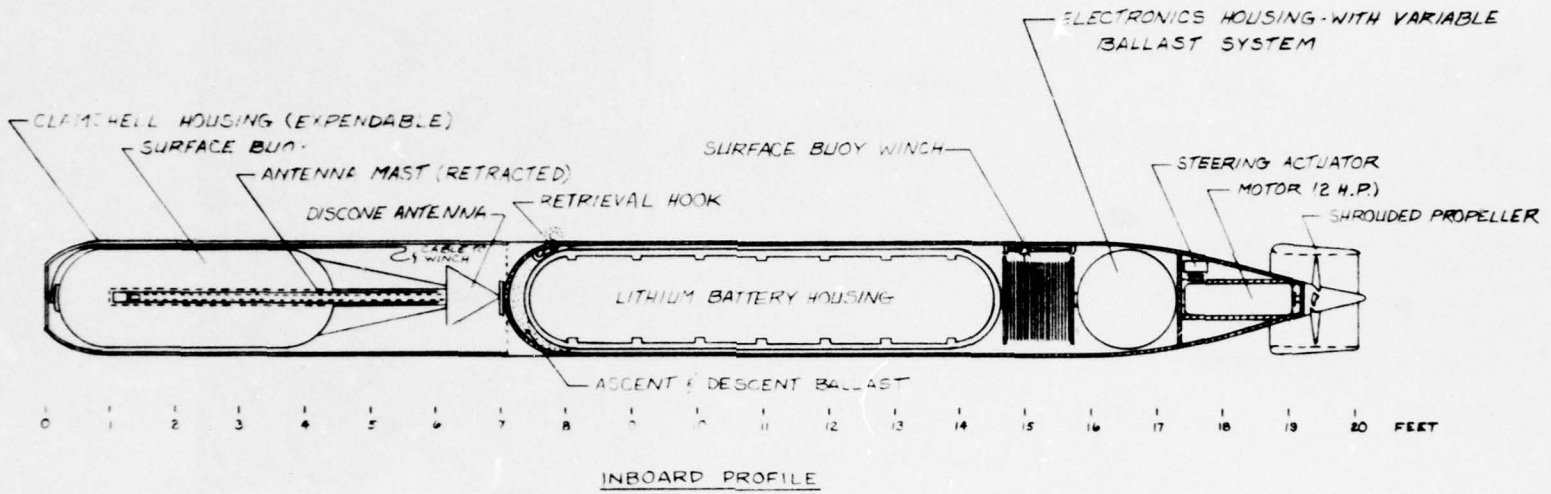
The Navy's deep submergence vehicles and swimmer support vehicles in fulfilling their missions are highly dependent upon the performance characteristics of their power source. Due to space and weight limitations, silver-zinc battery systems have commonly been used. These batteries have often failed to provide the safe, reliable power that is required to permit these assets to effectively carry out assigned missions, and have been more expensive than was necessary. The Deep Submergence Rescue Vehicle (DSRV) is shown in Figure 5-11.

During this study the DSRV power requirements (present and future) were reviewed. Specifications for advanced lead acid and lithium batteries were prepared. Preliminary designs were prepared for the battery installations. The advantages and disadvantages of these power source candidates were compared with the existing silver-zinc batteries. Acquisition and operating costs were estimated. Problem areas were identified and development requirements, plans and schedules, and cost estimates were prepared.

Discussions with DSRV personnel have indicated a minimum requirement of 300 AH per 120-volt battery at a 5-hour rate is required for training missions. A 9-trip rescue mission would require a minimum of 3250 AH per 120 volt battery, with each trip averaging 6 hours.

For short missions and operator training, 60 advanced lead acid cells could be designed to fit within each of the existing silver-zinc battery boxes to provide 300 AH at the 5-hour rate. The cost of these cells is less than $100 per cell and it should be possible to provide a 120-volt battery box capable of at least 100 charge cycles for $10,000.

For actual rescue missions an advanced lithium organic or inorganic electrolyte battery could be developed to fit within the existing battery space that would provide 3250-4000 AH.



INBOARD PROFILE

Figure 5-9. Submersible Tended Array System (STARS) Tow Vehicle.



SIZE	3.625" x 4.250" x 6.180"
WEIGHT	6.2 lbs
ELECTRODE AREA	2877 cm^2
DESIGN CAPACITY	518 Ahr
RATED LOADS	4.89 A
CURRENT DENSITIES	1.7 mA/cm^2
ENERGY DENSITIES	
Whr/in^3 (achieved/goal)	18.6/25
Whr/lb	286/350
AVERAGE VOLTAGE	3.43V

Figure 5-10. Large Cell for STARS Battery.

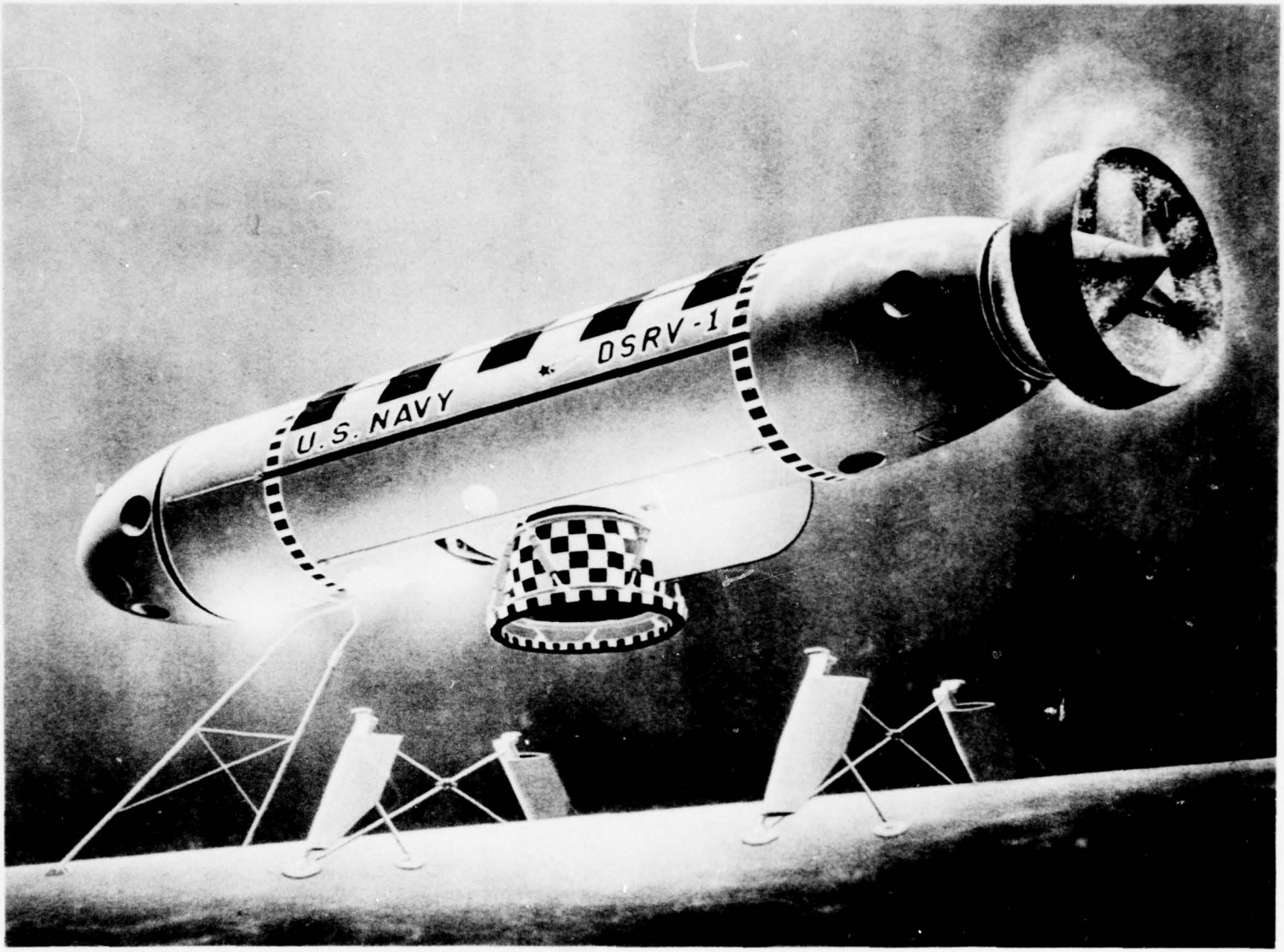


Figure 5-11. Deep Submergence Rescue Vehicle (DSRV).

This would allow a 9-trip rescue mission to be carried out without interruption for recharging batteries. Either of these technologies could be developed to provide safe, reliable, economical batteries within a 2-year period. It is estimated that each 120-V battery box would cost $25k - $40k or a total of $50k - $80k for a complete rescue mission.

A comparison of battery candidates for DSRV is shown in Figure 5-12.

CONCLUSIONS

The following major conclusions have been derived from this program:

- $Li/SOCl_2$ batteries can now be used for selected low-rate applications.
- High-reliability, low-rate cells should be applied within 12 months of manufacture. They should incorporate purified electrolytes, stainless-steel enclosures, and hermetic seals and operate at electrode current densities below 1 MA/cm^2.
- Maximum cell capacity is obtained when the electrolyte is allowed to wet the full electrodes, i.e., oriented vertically upright.
- Lithium cells become unsafe when heated above 75°C or when punctured.
- Future high-rate batteries for propulsion should be reserve-type cells activated underwater, with the cell in imminent contact with the surrounding water for adequate cooling.

A future development program should fully explore the major problem areas that currently bar general Fleet use of the lithium inorganic cells. The goal of this program should be to solve these major problems and assist in the initial application of engineering work needed for projecting the technology toward wide-scale use in the Navy.

The major areas that should be addressed under a continuing development program are:

1. Pressure equalization of cells
2. Reserve cell development
3. Hazards caused by external or internal short circuits, changing currents, seal failure, or rapid case rupture
4. Packaging of cells to provide safe, reliable batteries
5. Cooling of high-discharge-rate batteries
6. System optimization for propulsion batteries and motors

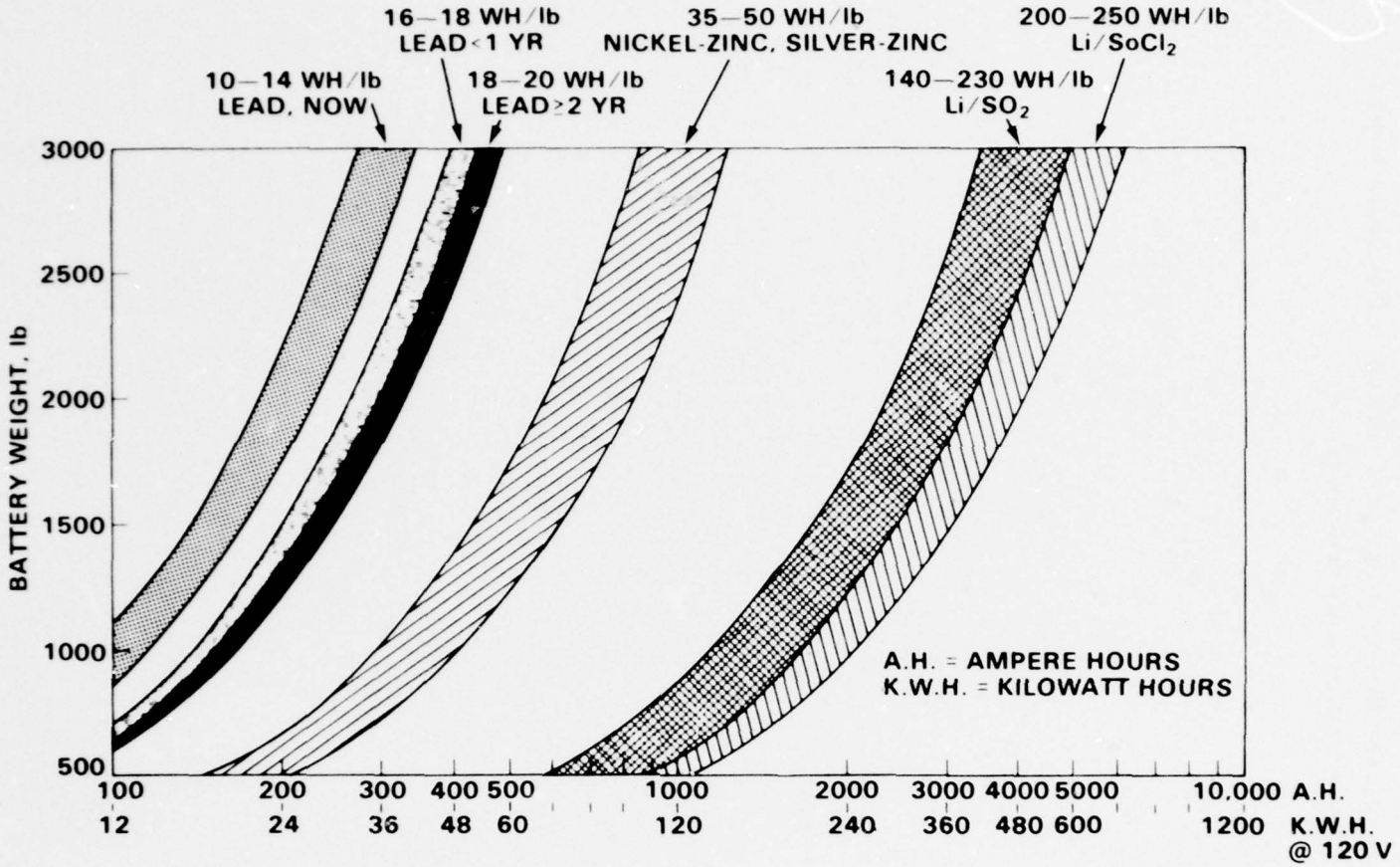


Figure 5-12. Underwater Vehicle Power Source Candidates.

7. High-power-density cells, configured specifically for high rates of discharge.
8. Large-size cells with capacities of 1000 to 20,000 ampere-hours for discharge rates of between 1 day and 1 year.

Table of References

1. Auborn, J. A., *et al., J. Electrochem Soc 120* (12), 1613-19 (1973).
2. Holleck, G.L., Turchan, M.J., Cogley, D.R., ECOM-74-0030-4, Jan 1975.
3. Holleck, G.L., Driscoll, J.R., Toland, D.E., ECOM-74-0030-6, Jul 1975.
4. Holleck, G.L., Turchan, M.J., Toland, D.E., ECOM-74-0030-5, Apr 1975.
5. McCartney, J.F., Shipman, W.H., Gundersen, C.R., NUC TN 1618, Oct 1975.
6. Conceptual Design of an Advanced Lithium Torpedo Battery, McCartney, J.F. and Shipman, W.H., Naval Undersea Center, NUC TN (In progress).

APPENDIX A

MARINE BATTERIES – AN OVERVIEW

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Marine Batteries–An Overview

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ABSTRACT

The requirements for rapid advancement in the development of marine propulsion batteries are numerous. These include a variety of manned and unmanned vehicle systems that operate on or below the surface to depths of 6000 meters. This paper provides a historical overview, a summary of state-of-the-art developments, and present research and development requirements for marine batteries. Future trends and potential applications including vehicles with drag reduction are discussed.

INTRODUCTION

The navies of the world, oceanographic organizations, and ocean-interested industries continuously seek improved energy sources for the vehicles and equipment that they employ (reference 1). Their goal is to obtain advances in speed, range, depth, silence, and other attributes needed for better job performance. Deep diving submarines, swimmer support vehicles, electric torpedoes, countermeasure vehicles, and untethered work systems are presenting major challenges to designers. A particular challenge is in the area of power plant development, where the goal is nearly always higher energy and power density and often quieter and more reliable performance under adverse environmental conditions.

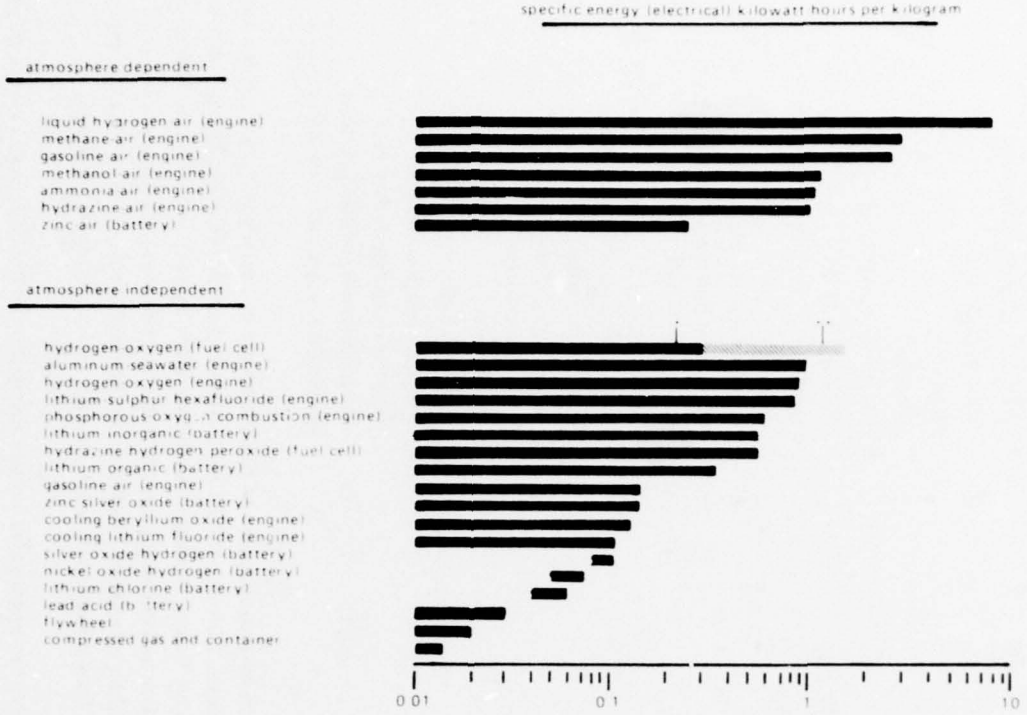
A listing of the selection criteria for major power sources is in table 1. It is necessary to consider all these criteria when evaluating sources for underwater projects.

Table 1. Criteria for selecting candidate power sources.

Parameter	Data Format
Availability	Development status
Energy per weight	Watt-hours/kilogram
Energy per volume	Watt-hours/cubic centimeter
Energy per cost	Watt-hours/dollar
Power range	Watts
Endurance range	Hours
Rechargeability	Electrical, mechanical, none
Low-temperature performance	% capacity at 0 C
Expendability	Expendable, recovery desired or essential
Critical materials used	Silver, platinum, etc.
Depth sensitivity	Surface, submerged – pressure equalized or hull
Shelf life	Years
Restart capability	Instantaneous, delayed, none
Emissions	Gases, heat, noise, etc.
Operability	Simple, specialized training, highly specialized
Reliability	Failure rate
Maintenance	None, periodic, after failure
Deployment	Drop, lower, position, etc.
Power conditioning	Input voltage, regulation, etc.
Start-up time	Predeployment, postdeployment
Hazard and safety	Explosives, toxic materials, etc.

Some programs which have contributed to the knowledge of ocean vehicle technology are the developments of the Trieste, Dolphin AGSS (555), Alvin and similar vehicles, Moray Deep Jeep, Deep Submergence Rescue Vessel, Remote Underwater Work System, and NR-1 (a nuclear-powered deep-submergence research and ocean engineering vehicle). Lead-acid or silver-zinc batteries power most of these vehicles when submerged. However, as the need arises for more auxiliary power and operating times greater than a few hours, more compact power sources are required.

In past years, the Navy has investigated several alternatives to the battery as a source of submerged power to replace the conventional diesel-electric submarine plant (figure 1). Projects DECCA (semiclosed-cycle diesel engine), Alton (Walter-cycle turbine plant), Wolverine (semiclosed-cycle gas turbine), and Ellis (ambient pressure combustor and steam boiler plant) all achieved some measure of success before they were terminated in favor of the nuclear plant. However, none was installed on board ship. A good review of these projects was published in reference 2.



* high pressure gas storage tankage included

** gas storage system not included

Figure 1. Mass energy storage capability of various systems. Weight includes only stored reactants or material in which energy is stored. Weight for structure, tankage, or conversion system is not included; battery systems are complete as shown.

Since this work was done, the state of technology has advanced in several areas to the point where new plants show promise of better characteristics. The lithium battery is a prime example. Thermodynamically, the maximum energy obtainable from a galvanic cell is fixed by the equivalent weights of the two electrode materials involved and the reversible voltage of the cell. The latter depends upon the relative positions of the two materials in the electromotive series. As shown in figure 2, high energy cells would have lithium anodes.

To reduce the constraints imposed on marine systems, new power sources are needed that are nonnuclear, do not use expensive and critical materials such as silver and platinum, and are less expensive and more mobile than cable-powered systems. It is the purpose of this paper to explore available and future power sources that meet these criteria as well as to present a historical overview of the development of power sources.

HISTORICAL OVERVIEW

Archeologists have found batteries made by the Parthians who dominated the Baghdad region between 250 B.C. and 224 A.D. The copper-iron combination in these ancient batteries is the same as that which Luigi Galvani used in 1786, when he "discovered" the galvanic cell.

The battery chronology in table 2 shows that many significant developments are more than a century old, and developments are now occurring at a rapid rate. Lithium anode battery developments that are capable of very high energy density dominate the more recent literature.

The battery was the first practical source of electrical energy developed for portable power and is still the most widely used source where portability is the prime requisite. Military and space programs demand power sources which are compact, dimensionally adaptable, capable of operation over a wide temperature range, and highly dependable after long storage periods. These requirements are only marginally satisfied with existing batteries, and for this reason several development programs are now underway.

The workhorses are still the carbon-zinc dry cells and the rechargeable lead-sulfuric acid cells. These are followed by the alkaline and mercury dry cells and the nickel-cadmium rechargeable batteries.

In the past 3 years, a tremendous interest in lithium anode batteries has been shown as more companies have become involved in their development. Their benefits have been realized in practical hardware and some of the previous claims for this new energy source have been realized. Benefits include high energy density, superior cold temperature performance, long active shelf life, and improved cost effectiveness for the total system.

Table 2. Battery Chronology.

1800	Volta	Unlike metals and electrolyte in contact – "voltaic piles," first power source
1800	Nicholson and Carlisle	Electrolysis of water into hydrogen and oxygen
1807	Humphry Davy	Electrolysis of caustic-sodium, potassium, etc., using voltaic "batteries"
1827	Georg Simon Ohm	Ohm's Law
1830	Michael Faraday	Electrochemical laws
1836	Daniell	$Cu\|CuSO_4\|ZnSO_4\|Zn$ chemical battery
1836	Elkington	Electroplating of silver
1846	Bottger	Electrodeposition of iron
1849	Russell and Woolrich	Cadmium plating
1860	Plante'	Lead storage cell or battery
1866	Leclanche'	$Zn\|NH_4Cl\|C$ battery
1872	Clark	Zinc-mercury standard cell

Table 2. Continued

1881	Lalande and Chaperon	Zinc-copper oxide cell
1882	Gladstone and Tribe	Double sulfate theory
1886	Gassner	"Dry" cell
1892	Weston	Cadmium-mercury standard cell
1894	Walker, Wilkins, Lones	Air depolarized cell
1899	Junger	Nickel and silver alkaline batteries
1901	T. A. Edison	Nickel storage battery
1910	T. A. Edison	Commercial nickel-iron alkaline cell
1910		Flashlight cell D size
1910		Telephone dry cell
1939	Andre'	Silver-zinc battery
1941		Batteries for rockets and missiles
1943	Adams	Cuprous chloride battery
1945	Ruben	Mercury cell
1945	Otto	Thermal cell
1955	Ruben	Alkaline cell commercial development
1965	Booth	Maintenance free lead-acid battery

STATE OF THE ART

The most efficient known method for converting one form of energy into usable electrical energy is the electrochemical process. Batteries, of which many different types have been commercially produced, are examples of devices that directly convert stored chemical energy into electrical energy. They are generally classified into two groups: primary and secondary. The distinction is based on the nature of the chemical reaction. Primary batteries are discarded when sufficient electrical energy can no longer be obtained, e.g., LeClanche' flashlight batteries. Secondary batteries convert chemical energy by reactions that are essentially reversible; by passing the current in a reverse direction to that during discharge, the chemicals are restored to their original state, e.g., lead-acid secondary battery.

Table 3 is a summary comparison of various types of primary and secondary battery systems. These data represent optimum performance for each battery type, and the limitations expressed in the table are the most critical. There are many application conditions where the combined effect of shelf life, self discharge, low temperature, etc, could degrade the estimated performance characteristics by 25 percent or more. Each candidate is discussed in the following sections.

LeClanche'

The LeClanche' dry cell is the most popular type of primary cell; it is ideal for simple applications where an inexpensive and noncritical source of electricity is all that is needed. It is not normally considered a propulsion battery, but advanced versions could be constructed for that purpose.

The basic zinc-carbon cell has a carbon cathode, an electrolyte (a paste of an ammonium chloride solution with moisture-retaining agents added), and a depolarizer (a mixture of manganese dioxide and carbon) held between the electrolyte and the cathode (in primary battery technology, the positive terminal). The zinc anode, which is also the outer casing of the cell, is the negative terminal. Since the zinc case is a chemical constituent of the LeClanche' system, it is consumed during the process of discharge; this deterioration may lead to leakage and, consequently, to corrosion of the equipment in which the cell is housed. To mitigate this weakness, leak-resistant LeClanche' cells are also produced. These have an additional tube that is wrapped around the anode casing and is fixed to a steel plate at the bottom and a plastic cover at the top.

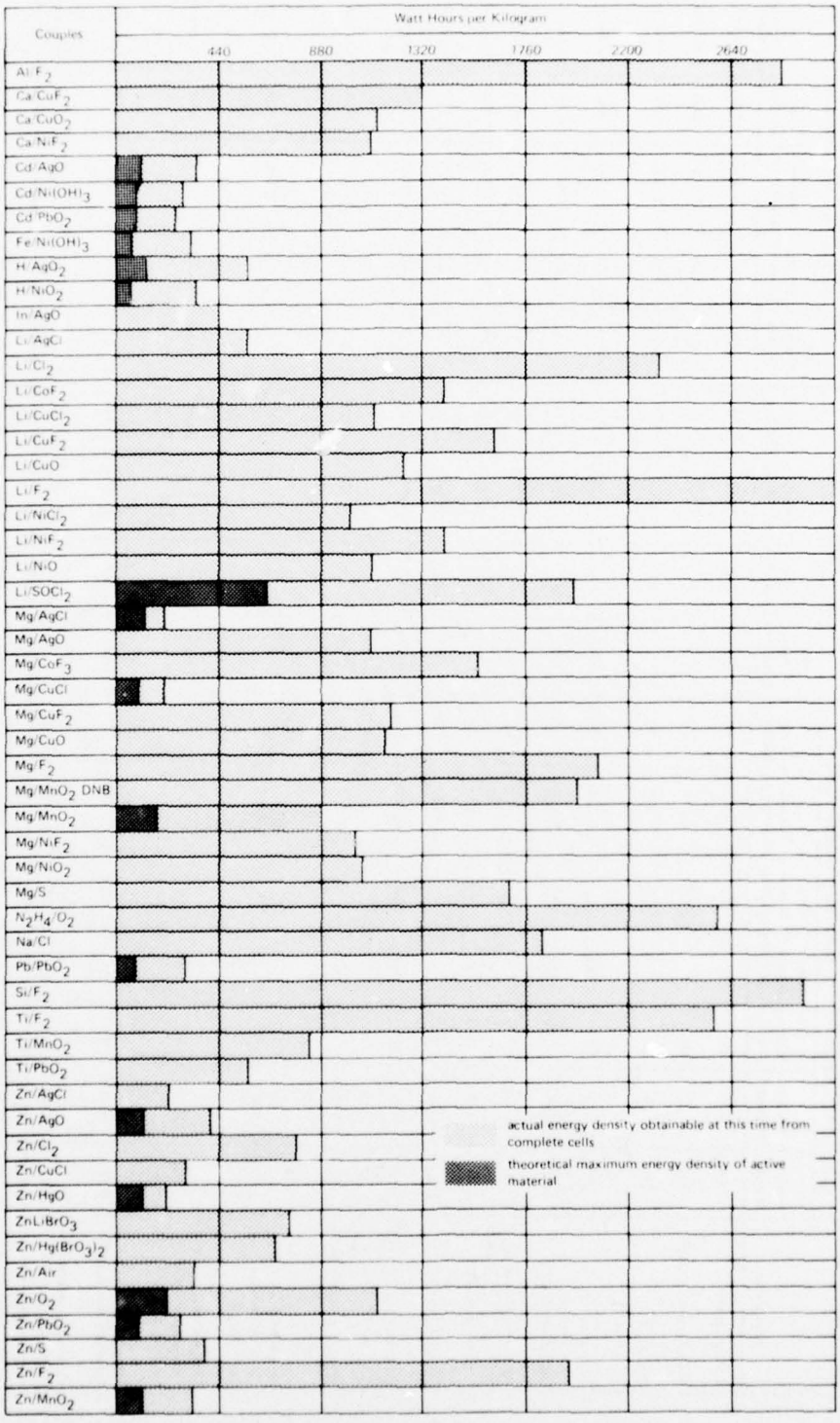


Figure 2. Theoretical and actual energy density of various coupled electrode materials.

TABLE 3. COMPARISON OF STATE OF THE ART BATTERY SYSTEM CHARACTERISTICS

Type of Cell	Basic Cell Characteristics			Battery for 0- to 2000-ft Depth*				Battery for 10,000-ft Depth				Battery for 20,000-ft Depth*				Limitations
	Weight W-hr/kg	Volume W-hr/cm^3	Cost W-hr/$	Dry Weight kg/kW-hr	Wet Weight kg/kW-hr	Volume cm^3/kW-hr	Cost $/kW-hr	Dry Weight kg/kW-hr	Wet Weight kg/kW-hr	Volume cm^3/kW-hr	Cost $/kW-hr	Dry Weight kg/kW-hr	Wet Weight kg/kW-hr	Volume cm^3/kW-hr	Cost $/kW-hr	
LeClanche (P)	74.8	0.17	25	15	6.8	7,757	54	17.7	8.64	8,512	232	23.6	13.2	9,889	486	Low rate
Mecuric oxide zinc (P)	10.3	0.37	6.25	10	6.4	3,542	170	11.3	7.7	3,805	246	14.1	9.5	4,428	360	Low rate
Alkaline (P)	50.6	0.23	25	13.2	7.7	5,314	50	15	9.1	5,937	174	19.1	11.8	6,822	348	Low or medium rate
Magnesium (P)	13.2	0.23	12.5	8.6	2.7	5,756	90	10.9	4.6	6,380	224	15	7.7	7,232	406	Hydrogen
Nickel cadmium (S)	20.2	0.04	.90	55.5	25.9	28,580	1200	20.4	32.7	32,259	1839	8.6	49.5	3,657	2760	None
Lithium inorganic (P)	550	0.92	6.25	2.3	0.9	1,328	160	2.7	0.9	1,591	196	3.6	1.8	1,771	240	Early development
Lithium organic (P)	209	0.38	6.75	5.4	2.3	3,329	160	6.8	2.7	3,723	244	9.1	5	4,215	350	Early production
Silver zinc (S)	110	0.26	1.33	7.7	4.1	4,297	750	7.7	4.1	4,297	750	7.7	4.1	4,297	750	None
Lead acid, stationary (S)	21.3	0.05	11.11	46.8	31.8	21,484	110	46.8	31.8	21,484	110	46.8	31.8	21,484	110	Low and medium rate
Lead acid, automatic (S)	48.0	0.10	83.3	20.9	11.4	11,267	21	20.9	11.4	11,267	21	20.9	11.3	11,267	21	Medium and high rate
Magnesium-silver chloride, seawater activated (P)	154	0.31	1.4	7.3	4.55	3,608	718	7.3	4.6	3,608	718	7.3	4.5	3,608	718	High rate
Magnesium-cuprous chloride, seawater activated (P)	90.2	0.18	5.0	12.3	7.7	6,019	205	12.3	7.7	6,019	205	12.3	7.7	6,012	205	High rate
Magnesium-iron, seawater activated (P)	220	0.11	5.0	5	2.3	10,020	202	5	2.3	10,020	202	5	2.3	10,020	202	Low rate
Lithium, seawater activated (P)	458	0.38	12	2.3	0	2,903	94	2.3	0	2,903	94	2.3	0	2,903	94	High rate, early development

*Includes encapsulations.
P, primary type battery
S, secondary type battery

High performance zinc-carbon cells are relatively new and give an improved performance over the basic type; this improvement is derived both from constructional modifications and changes in the materials used. These cells have the zinc can, separator, electrolyte, depolarizing mix, and carbon cathode of the conventional LeClanche' battery, but the thick-paste separator is replaced with a specially developed low-resistance electrolyte-wetted paper. This allows for a greater weight of active materials to be included.

The general characteristics of the zinc-carbon cell are as follows: a nominal voltage per cell of 1.5 volts; a steady fall of voltage on discharge, although voltage will "recover" to a certain degree under intermittent use; limited shelf life; and a limited acceptable temperature range in storage and operation.

Mercuric Oxide Zinc

The mercuric-oxide primary cell system was developed by Samuel Ruben during World War II to meet military needs for a primary cell with a better capacity-volume ratio and better storage performance, particularly under poor environmental conditions, than the LeClanche' battery. In achieving this objective, the Ruben cell produced another important asset: a very stable output voltage.

The basic construction of the mercury cell can be either cylindrical or flat pellet. The zinc anode is isolated from the plated steel outer case with an additional inner top, and, as in the alkaline-manganese type, the self-venting casing plays no part in the chemical reaction. The electrolyte is a solution of potassium hydroxide containing zinc oxide. The electrolyte takes no part in the chemical processes, but acts only as a vehicle for the movement of ions.

The open-circuit voltage of the mercury cell is 1.35 volts in the available industrial range, but in the commercial market a 1.4-volt cell is more common. This higher voltage is achieved by adding a small percentage of manganese dioxide to the cathode. The constant-voltage discharge at normal temperatures is a particularly important characteristic of the mercury system and is of benefit to designers requiring good voltage regulation in their power supply without the use of additional control circuitry.

A special cell structure with a large anode surface area has been developed that will function satisfactorily down to -20C. The basic design difference from the standard cell is the assembly of the anode in the form of corrugated zinc foil wound into a roll instead of a pressed-powder pellet.

Mercury cells offer exceptionally stable output voltage, environmental stability, long life in use and storage, and miniaturization.

Manganese Dioxide Alkaline Zinc

The manganese-alkaline cell has been developed during the last decade. Its chemical construction is similar to that of the zinc-carbon cell, except that it uses potassium hydroxide as the electrolyte. Mechanically, however, it is rather different. Although the polarity of the cell is the same as that of the LeClanche' cells the outer case of nickel-plated steel is positive and plays no part in the chemical reaction. The positive terminal is in contact with the cathode through the nickel-plated case and is formed externally as a stud. The potassium hydroxide electrolyte is suspended in the electrodes and is absorbent so that there is no free liquid. The potassium hydroxide does not participate in the chemical reaction but acts only as an ion-transfer agent. The depolarizer is a mixture of manganese dioxide and carbon particles.

This system offers better voltage stability than the zinc-carbon type and a life span which is about three times greater. Its performance is notable under continuous current drain, and it does not require "rest" periods to sustain its life. It can be stored for 2-1/2 years or more without serious loss of power. Performance is satisfactory over an environmental temperature range of -20 to +70C.

Manganese-alkaline cells have a nominal voltage of 1.5 volts and are available in a wide range of sizes, including the five main international sizes for conventional batteries.

In their application, manganese-alkaline cells are indicated when the zinc-carbon types may lack the desired characteristics, particularly where current demands are heavy and superior performance is required.

Magnesium Manganese Dioxide

Theoretically, magnesium is a more attractive anode material for primary cells than is zinc, since it has a considerably higher electrode potential and more than twice the ampere hour capacity per unit of weight. The open-circuit voltage of a magnesium cell is approximately 2.0 volts. The magnesium battery will last about twice as long as a LeClanche' battery of equal size and weight. The high temperature storage characteristics are very good because of the formation of a self-protecting layer of magnesium hydroxide on the anode. However, this feature leads to the disadvantage of time delay in voltage stabilization. The delay time is defined as the time required after the circuit is closed for a cell or battery to reach a specified voltage, usually the minimum voltage necessary to operate the device. Another disadvantage is the production of hydrogen during discharge; this is particularly a problem in sealed compartments. This hydrogen is formed by a side reaction of magnesium with water that produces magnesium hydroxide and hydrogen. The rate of hydrogen generation is 0.25 liter per ampere-hour per cell at 21°C and 1 atmosphere.

Nickel-Cadmium Cells

The nickel-cadmium cell is mechanically rugged and will withstand electrochemical abuse, i.e., it can be overcharged, overdischarged, or stand idle in a discharged condition.

Although the nickel-cadmium cell operates at a slightly lower voltage than the lead-acid cell, it shows little self discharge. It can be trickle charged, and when standing idle it evolves practically no gas, so that for some purposes it can be hermetically sealed. It can be operated over a temperature range of −45°C to +82°C, and it is characterized by an excellent service life under both cycle and float operations. Initially it is more expensive than the comparable lead-acid cell, which is limited for many applications. The two nickel-cadmium constructions in use are the pocket type and the sintered-plate construction. The sintered-plate construction differs from the pocket type in the method of support. Plates are made from nickel powder that is molded into shape and heated at high temperature. This gives a strong, porous plate that contains about 80 percent pore volume. The active material is impregnated in the pores of these plates by soaking them in a solution of nickel salts to make positive plates or in a solution of cadmium salts to make negative plates.

The sintered-plate design, because of the thinner plate construction and larger electrode surface area, offers advantages over the pocket type in that the cells operate at higher current drains and are more efficient at low temperatures. On light drain applications, the pocket and sintered-plate batteries have similar characteristics.

Lithium Organic

Many companies are presently developing a new line of high energy density batteries that employ a lithium anode. Many have already exhibited an energy density that is four times greater than mercury-zinc cells. They are lighter, have greater power output, can operate over far greater temperature ranges (−54°C to +74°C),and have a remarkably long projected shelf life of up to 20 years.

The lithium organic battery contains a lithium anode, a carbon cathode, and an organic electrolyte of liquid sulphur dioxide. The liquid sulphur dioxide is the depolarizer. The cells are constructed by winding rectangular strips of anode-separator cathode-separator stacks into a cylindrical roll, which is then placed in a nickel-plated steel can. This method increases the surface area of the electrodes and gives the cells a high current capability.

There are several cathodes which have been previously used. The most stable is V_2O_5, followed by the (CX) series, then 502. Various electrolytes are used with added salts for stability and conductivity.

The main advantages of the lithium organic cells are very high power densities, operation at extremely low and high temperatures, long shelf life, high working voltage, high current capabilities, and flexible design.

Lithium Inorganic

The lithium inorganic cell differs from the lithium organic or sulphur dioxide cell in that the cathode reactant (liquid oxyhalides, such as thionyl chloride or sulfuryl chloride) also serves as the sole solvent for the electrolyte (usually lithium tetrachloroaluminate).

As in the sulphur dioxide cell, a low weight, high surface area, carbon positive electrode acts as a catalyst for the reduction of the cathode reactants, thus permitting the cell reaction to proceed. Since the solvent serves as the cathode depolarizer for the cell, there is no need for a separate supply of cathode reactants, and the attendant results are greatly reduced cell weight and increased specific energy.

Current versions of the lithium-thionyl chloride cell exhibit specific energies of approximately 500 watt-hours per kilogram, more than 50 percent higher than previous lithium-sulphur dioxide cells and more than eight times higher than the common flashlight battery. Other features include improved low temperature operation (down to –45 C) and voltage stability.

Large cell technology is advancing and this is discussed in the section "Near-Term Battery Development."

Lithium Water

The lithium-water cell has unique features which make it especially practical for marine use. Its electrolyte can be predominantly seawater, and the system is in principle insensitive to deep ocean pressures. Some preliminary experiments have confirmed that operating the battery under a hydrostatic head should not significantly alter its characteristics.

Systems have already been developed specifically for marine use. An 8-kilowatt, 20-volt bipolar module for torpedo application with a discharge time of 10 minutes has been constructed and successfully tested. For longer duration (12 to 20 hours, continuous or intermittent), an 800-watt, 12-volt battery with monopolar cell has been built. In both of these designs, unalloyed lithium is coupled to nickel or iron cathode structures. Power control at desired levels is automatically attained by adjusting the electrolyte composition.

The lithium-water battery is inherently applicable to the marine environment, particularly because of the following attributes: the solubility of lithium hydroxide in seawater prevents scaling problems; the free flooding of the battery eliminates pressure compensation requirements; and the battery is neither cathode nor electrolyte limited.

Silver-Zinc Cells

Until recent developments in lithium high energy density cells, the silver-zinc battery offered the highest energy density for any primary system commercially available. It has been used as a storage battery for a limited number of cycles. The cell essentially consists of porous silver-oxide positive plates, zinc negative plates, and a potassium hydroxide electrolyte. Porous separators physically separate the plates and are saturated with electrolyte. Cell cases are plastic, e.g., nylon, bakelite, and for lightweight applications a pressurized rectangular magnesium battery case is used. For applications where long storage is required, automatic activation mechanisms have been constructed, consisting essentially of a storage container and a pressurization mechanism for transferring the electrolyte to the battery.

The active wet life of the cells ranges from 2 to 18 months, depending on the model and temperatures of operation. Dry shelf life estimates are more than 10 years at 27°C, 2-1/2 years at 52°C, and 2 months at 74°C for 50 percent capacity retention.

The energy output (per unit weight or volume) of the base system is usually much higher than that of the final packaged unit. The extent of energy output reduction is dependent upon the ruggedness required, and low-rate types generally offer the highest energy density. The high energy density is achieved only with the larger batteries, e.g., 200 ampere-hours with density generally decreasing in small sizes. Secondary batteries offer about 88 to 110 watt-hours per kilogram and 0.27 watt-hour per cubic centimeter in certain models, but they generally fall in the category 88 to 110 watt-hours per kilogram and 0.15 to 0.20 watt-hour per cubic centimeter.

Silver-zinc cells are being used as a source of main power in deep-ocean submersibles. This cell type is selected because it offers high energy density, tolerance to high rates of discharge, and long dry storage life. Its disadvantages are high cost, short cycle life for deep discharge cycles, short wet storage life, and difficulty in determining state of charge.

Submersible installations include batteries mounted within the pressure-resisting hull and those in the free-flooding area outside the pressure hull. There are several problems associated with pressure-compensated silver-zinc cells, including electrolyte carryover, spill angle, heat transfer, battery shorts, etc.

Silver-Cadmium Cells

The silver-cadmium battery has several advantages in a storage application, and it offers a compromise between the long cycle life, low capacity of the nickel-cadmium cell and the high capacity, low cycle life of the silver-zinc battery. Lives of 3000 cycles at shallow discharge and weights of 72.6 watt-hours per kilogram have been reported.

The positive plate is a porous structure that contains graded sintered silver, whereas the negative electrode contains compacted cadmium compounds. A semipermeable membrane separator is used between the two electrodes. In the zinc-silver-oxide battery, the dendritic electroplating of zinc onto the separators may cause damage during the overcharged period. Because of their relative insolubility, cadmium negatives cause no similar separator damage under overcharge or other severe operating conditions. They are not subject to the negative corrosion that is evident on zinc electrodes. Consequently, the silver-cadmium cell system is more durable than the silver-zinc system, principally because of the difference in negative solubility. The electrolyte is a potassium hydroxide solution held within the absorbing separator.

The silver-cadmium battery exhibits a long flat plateau voltage range. Under given discharge rates and temperatures, the plateau voltage regulation will be about ±5 percent at a fixed load. The plateau voltage will drop with a decrease in operating temperature. Open circuit voltage is about 1.25 volts, and load voltage is about 1.15 volts at a 1-hour discharge rate.

Under most conditions of service, the maximum value for watt-hours per kilogram varies from 52.8 to 72.6 and the value for watt-hour per cubic centimeter from 0.12 to 0.16. With a discharge depth of less than 10 percent, cycle lives on the order of 2000 to 3000 might be expected. For deep discharges, approximately 50 percent, a cycle life of 300 to 500 might be anticipated.

The battery has an excellent dry storage life. After activation, the discharge retention is also high, with as much at 85 percent of the original capacity remaining after 1 year's charged wet stand at approximately 21°C. The time for 50 percent capacity retention is about 2 years at 27°C, 115 days at 52°, and 58 days at 71°C. Dry shelf life is over 3 years with negligible capacity loss.

The cost per cell is close to that of the silver-zinc cell, but more cells are required because the nominal cell voltage is lower.

Lead-Acid Cells

The active material of the positive electrode is lead dioxide and that of the negative is a highly reactive spongy lead. The electrodes are electrically insulated from each other by separators. Many different types of separators are used, such as resin-impregnated cellulose materials, microporous rubber, and fiberglass mat. The electrolyte in fully charged batteries is a solution of sulfuric acid with specific gravities ranging from 1.215 to 1.300, depending on the intended service.

In the fully charged state, the negative electrode exists as lead, the positive as lead dioxide, and the concentration of sulfuric acid at its maximum level. As the cell is discharged, the positive electrode is converted to lead sulfate. The overall reaction results in the consumption of sulfuric acid and an equivalent production of water. The consumption of sulfuric acid during the discharge of a lead-acid battery provides a convenient method by which the state of charge can be measured. When the cell is charged, the lead sulfate is converted to lead dioxide at the positive plate and lead at the negative plate and the sulfuric acid is again concentrated.

The major types of batteries produced are Automotive, motive, and stationary. Automotive batteries are designed to furnish high currents (200 to 300 amperes for a 6-volt system) for a few seconds or minutes over a wide range of temperatures. Motive power batteries are required to supply power for 3 to 10 hours, and are designed to withstand frequent discharges instead of remaining almost fully charged as in the case of automotive batteries. Stationary batteries, unlike the automotive and motive types, are designed for longlife applications that do not require the mechanical ruggedness of highcurrent output. Low selfdischarge, stability, and high efficiency are the important features. The stationary batteries must have a long life under continuous float conditions. A fourth class of lead-acid batteries are those which have been designed with an electrolyte-retaining separator to prevent loss of the electrolyte when the batteries are inverted. These batteries are generally smaller in size than the other types and are designed for portable high rate power applications for which the conventional dry cells would not be suitable.

Somewhat similar in purpose of the electrolyte retaining cell described above is the recently introduced gel-type cell. The gel-type cell has most of the advantages of the conventional lead-acid cell without many of the drawbacks. Since the electrolyte is immobilized, the battery can be operated on its sides and no maintenance, such as monitoring of liquid levels, is required. Its discharge and cycle life characteristics are similar to other lead-acid batteries.

Lead-acid cells have been used in many deep-ocean systems, including deep submergence vehicles, where the batteries are pressure equalized and located externally to the pressure hull. Unless low energy density rules out the lead-acid battery, it will probably be extensively used for a long time. It is a proven, inexpensive, rugged, reliable, and relatively easy-to-service source of power. It also has a high cell voltage (2.0 volts), a relatively long life cycle, and a trouble-free service life. There are off-the-shelf units designed specifically for pressure-balanced use external to pressure hulls.

Magnesium-Water Activated Cells

These cells are stored dry in an inactive condition in hermetically sealed containers and are activated by adding water. They have the advantage over other reserve cell systems in that the electrolyte does not need to be transported with the battery. One disadvantage is slow activation time, requiring several seconds to minutes. They are used in powering airborne equipment, signal lights, air-sea rescue equipment, etc.

The magnesium-silver chloride and magnesium-cuprous chloride are two types of water-activated cells that are available commercially. The silver chloride cells operate at higher voltages and have higher capacities than the cuprous chloride cells. The cuprous chloride cells, however, are less expensive. Both of these cell systems have a constant voltage-time discharge curve and the characteristic of evolving heat during cell discharge that make them applicable for operation in low temperature environments. The heat evolved during cell discharge is mainly caused by the corrosion of the magnesium; the energy of this reaction is liberated as heat instead of electrical energy.

Magnesium Inert Cathode Seawater Cell

Improved versions of the magnesium anode, inert cathode seawater cell have demonstrated the capability to furnish power, generally in conjunction with an electronic converter, for a variety of ocean-based devices. The silverless, magnesium anode, inert cathode seawater cell is particularly attractive for underwater electronic devices that are characterized by their use in large numbers or in an expendable manner. This battery provides a low cost power supply in the practical watt-to-tens-of-watts power range. It also has merit, with respect to initial cost, simplicity, and safety, for mechanically rechargeable use, i.e., replacement of the magnesium electrodes to restore battery energy in contrast to conventional applied current charging.

This battery has two main drawbacks: (1) the cell voltage is low, approximately 0.5 volt and (2) in operation it produces a flocculent reaction product and scale which tends to accumulate on the electrodes and reduce the electrochemical activity. Transistor converters are used to raise the battery voltage to useful levels without having to use a large number of cells in series. The clogging problem is more difficult to treat, and the current density of the cell must be limited so that for a given rate of electrolyte circulation through the cell clogging does not occur within the desired operating life.

Magnesium inert cathode seawater battery systems have provided design power output for uninterrupted tests in excess of 3-1/2 years. The Naval Research Laboratory has successfully deployed this type of battery system in the Gulf of Mexico (1 year) and in the Arctic (test is now in progress with more than 6 months of performance). A line of marker beacons (pingers) is presently being manufactured that employs the basic magnesium inert cathode seawater cell.

Zinc-Air Cells

The zinc-air cell is comprised of a caustic alkali electrolyte, an anode of amalgamated zinc, and a carbon cathode capable of utilizing atmospheric oxygen. The operating voltage is 1.1 to 1.2 volts under load and 1.4 to 1.5 volts at open circuit. The carbon cathode is porous and gas permeable to "breath air," but close-grained enough to resist electrolyte penetration. The electrolyte is usually a 20 percent sodium hydroxide solution for low-temperature service. Lime is added to react with the sodium zincate formed and to provide continuous regeneration of the sodium hydroxide electrolyte. The cell is shipped dry, with the caustic cast around the anode and cathode and with the lime in dry form at the bottom of the container. The lime is "activated" by the addition of water.

The intrinsic simplicity of its design, the ruggedness of its construction, and the reliability of the electrochemical reaction make it ideal for numerous applications, including navigational buoys, lighthouses, and railroad signal systems.

The cells can be assembled into large battery systems with a capacity of thousands of ampere-hours. These cells can provide continuous service in many critical applications (such as navigational buoys) for periods in excess of 2 years without maintenance. There are several types of zinc-air and zinc-oxygen batteries being produced at this time. Many are designed for high rate applications on the order of a day. Portable zinc-air batteries are being used in man-packed transceivers, night vision devices, etc.

The zinc-air system is recommended where very high energy density 220 to 330 watt-hours per kilogram is required and air can be supplied to the battery.

Investigations have been made of supplying oxygen from compressed gas tanks for applications where air is not available, e.g., underground, undersea, and in space. The energy density is greatly reduced (about 50 percent) when oxygen is furnished in this manner.

Metal Hydrogen Batteries

Recent developments of nickel-oxide hydroxide and silver-oxide hydroxide cells have resulted in usable cell systems. The first system has been developed into cell sizes with a capacity of about 50

ampere hours for use in satellites. These consist of multiplate cathodes of sintered nickel-oxide electrodes and Platinum catalized anodes with gas-separating separators and a potassium hydroxide electrolyte. These are assembled in pressurized cases and the water produced on charge is stored for use on discharge. There are both low and high pressure systems which have given several thousand cycles at about 60 percent depth of discharge.

NEAR TERM BATTERY DEVELOPMENT (1980)

The prime component needed for widespread electric vehicle usage is a high energy density, high power density, low cost, and long life propulsion battery. Although much effort is being devoted to the development of improved batteries, progress is slow because of technological problems. It is obvious that electric vehicles must be developed to save oil resources for more efficient uses. The resulting near term battery developments should have a significant impact on future marine battery capabilities.

The battery systems that have been identified for near term electric vehicle consideration (therefore also candidates for marine applications) are improved lead acid, nickel zinc, nickel iron, zinc air, and lithium chlorine.

Large primary type lithium batteries could also be used for special marine applications requiring very high energy and densities.

The comparative energy densities of these batteries are in figure 3.

Lead-Acid Batteries

Improvements in energy density and cycle life can be realized by reduction of container weights, improvement in efficiency of active materials (now $\leq$ 60 percent utilization), and reduction of grid weight. It is unfortunate that weight reductions of grid and active materials usually cause a decrease in cycle life. However, an improved understanding of how lead-acid cells actually work and of novel electrode construction does promise significant improvements. For example, the French and German battery companies are testing trucks and buses powered by lead-acid batteries with specific energies of 40 watt-hours per kilogram. The Japanese have reported lead-acid batteries with specific energy densities of 60 watt-hours per kilogram. The cycle life expectancy of these very high performance lead-acid batteries is expected to be greatly reduced. While this would be detrimental to practical electric vehicle propulsion it would be tolerable for special purpose marine vehicles now tolerating the poor cycle life and very high cost of silver-zinc batteries.

From this point of view, it is very likely that significant battery improvement could be realized for marine vehicle applications by using the advanced high performance lead-acid battery technology that now exists in laboratories for limited cycle life marine applications.

Nickel-Iron Batteries

Industrial nickel-iron batteries that are marketed today were invented by Thomas Edison. These batteries are noted for their ruggedness, long cycle life, and high energy density (between lead acid and nickel iron it has very high discharge rates). Problems with hydrogen gas production and self discharge have restricted their use for many applications.

There have been recent developments that indicate that significant improvements in nickel-iron batteries are now possible. Projections of this technology suggest the following nickel-iron battery capabilities: an energy density greater than 60 watt-hours per kilogram; tens of years of life with thousands of deep cycles; exceptionally rugged; low cost; a power capability greater than 100 watts per kilogram; and good voltage regulation with good charge and discharge efficiency.

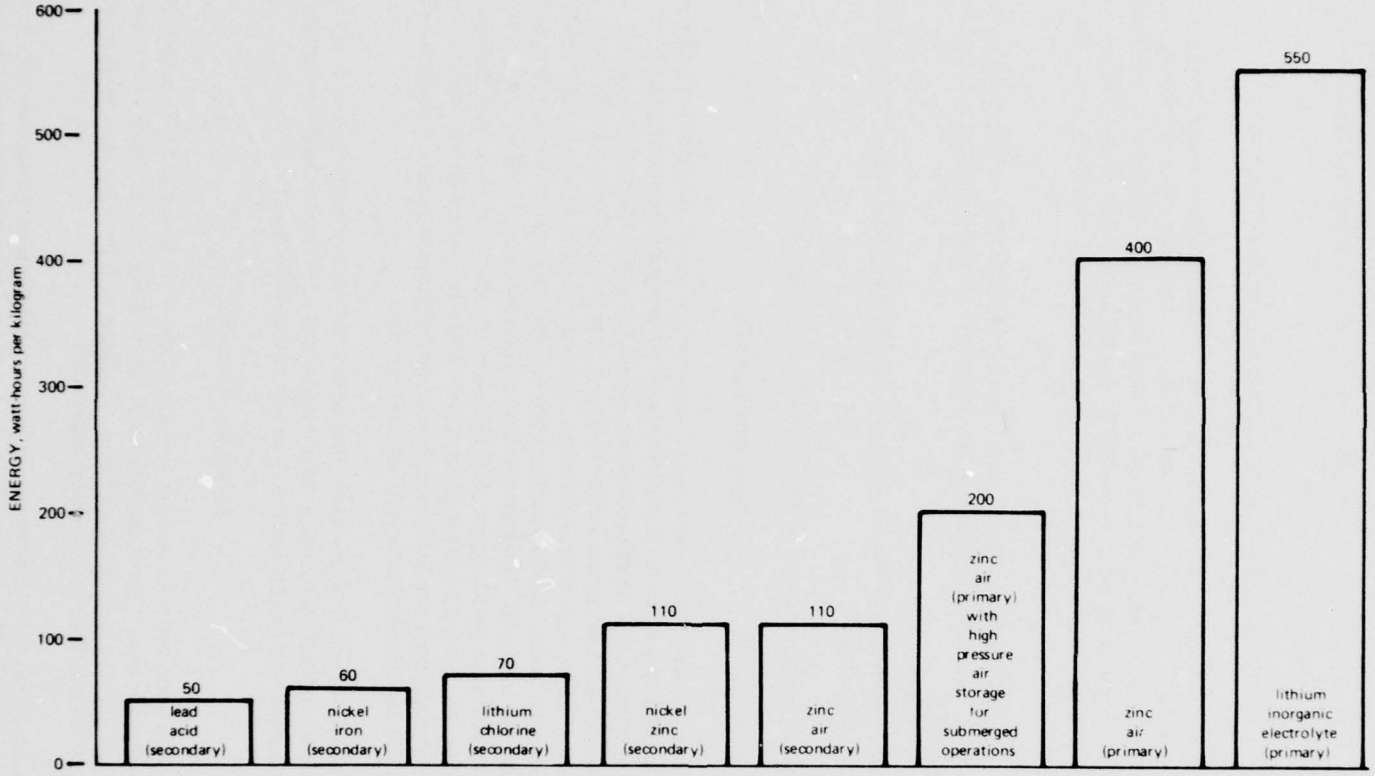


Figure 3. Near term battery candidates (~ 1980).

Zinc-Air Batteries

The zinc-air system, like the nickel-zinc system, has also been under development for a number of years. This development has resulted in primary zinc-air batteries with energy densities of approximately 200 to 400 watt-hours per kilogram. Such primary zinc-air batteries are now being marketed. A considerable amount of work has also been directed toward developing a rechargeable zinc-air system required for battery-powered vehicles. Reasonable success has been attained in terms of mechanically recharging the battery. This involves replacing the zinc anodes and electrolyte with new zinc anodes as they become depleted. Any electric vehicle battery would require replacement of a large number of anodes each time the battery was recharged, which would mean exposure to a caustic electrolyte during replacement. Consequently, mechanically recharging the zinc-air system does not appear to be suitable from an application standpoint. Electrically recharging the zinc-air system is a much more difficult technical problem, and only limited success has been attained. The problem is largely one of attaining a reasonable cycle life. However, a large amount of development work is continuing in this area, and a useful zinc-air system may be developed in the future.

Developers in France have described a new rechargeable system with 110 watt-hours per kilogram and an acquisition cost of $40 per kilowatt-hour. For submerged applications the requirements for air or make up oxygen storage would reduce the energy density up to 50 percent.

Lithium-Chlorine Battery

A nongas lithium-chlorine molten salt battery has been developed that is capable of several hundred cycles (reference 2). These cells consist of a lithium-aluminum alloy pressed on a steel grid anode, a thick porous carbon cathode, a boron nitride separator, and a potassium-chlorine, lithium-chlorine electrolyte. Operating temperature is 450C. The unit is enclosed in a steel case with the anode connected to the case and the cathode brought out through a boron nitride terminal stud.

This system is now being developed for producing prototype batteries for evaluation in lift trucks. The capacity is 720 ampere-hours at 36 volts. The total battery is insulated to maintain the operating temperature for periods up to 72 hours between discharges. The heat involved during discharge maintains the temperature. At present the finished battery gives 70 watt-hours per kilogram and 0.31 watt-hour per cubic centimeter. It can be rapidly recharged in 20 minutes or longer, depending upon the current-carring capacity of the terminal. This is a 20 percent saving in volume and approximately a 3-to-1 weight advantage over the lead-acid cell.

Lithium Inorganic Electrolyte Batteries

A number of corporations are currently developing the lithium inorganic electrolyte battery for government and industrial use.

This development effort has emphasized the thionyl chloride reaction, since it produces the most energy density of the sealed cells. Cells can be configured for low rates of 1 month (550 watt-hours per kilogram and 0.92 watt-hour per cubic centimeter) to very high rates of 10 minutes (220 watt-hours per kilogram and 0.37 watt-hour per cubic centimeter). This is by far superior performance when compared with other battery and engine systems for marine propulsion applications. The cell sizes manufactured range from 1 ampere-hour to 15,000 ampere-hours. During 1975 and 1976, the Naval Undersea Center performed an extensive test program with ten different types of lithium-thionyl chloride cells (reference 3). Based on these tests, NUC and other activities are applying reliable low-rate type cells with capacities of up to 25 ampere-hours. The test program has aided in the identification of many deficiencies with the present large size, high-rate cells. Many of the deficiencies can be readily corrected, but others are less understood and additional development is required. Cells up to the 500 ampere-hour size have been designed for spacecraft use, and very large cells have been developed and tested for submarine propulsion. NUC is studying the use of this technology for applications in the Deep Submarine Rescue Vehicle and Swimmer Support Vehicle. It is believed that this cell technology will produce an excellent high energy density, underwater power source.

To produce a reliable lithium cell several design features are important: use of a hermetic seal and use clean chemicals (thionyl chloride in particular); provision for adequate cooling; case material of stainless steel; methods to prevent case puncture or seal rupture; and use of a reserve type cell (when high rate cells must be stored prior to use).

High rate lithium propulsion batteries require a special development effort because of possible thermal excursions. These batteries should be of the reserve type for a long shelf life and safe handling during extreme environments. Large, medium rate cells with a reserve electrolyte are now being considered, but further design development is needed. NUC is testing a 160 ampere-hour cell at the 2 hour rate for underwater vehicle propulsion.

Techniques required to handle waste heat rejection and the problems of short circuits and reverse polarity are currently being considered.

The lithium cell offers the following advantages:

1. Three to six times the energy density of silver-zinc batteries
2. Completely sealed, no moving parts, no fluid circulation required
3. No noise
4. High reliability
5. No critical materials
6. No sensitivity to shock or vibration
7. Pressure compensated
8. Variable power source for low and high speed propulsion
9. Good low temperature performance
10. High cell performance (3.6 volts open circuit and flat voltage discharge curve).
11. Low cost

Although these are primary cells, it would take 10 to 100 recharge cycles from a silver-zinc battery for it to be more economical than a lithium inorganic electrolyte battery.

Under burst vehicle speed conditions the lithium battery may be designed to provide as much rejected heat as electrical power. This heat may then be used for boundary layer control purposes. The lithium battery also provides a widely variable speed power source. It will operate most efficiently at low speeds and provide very high power for burst speeds.

FAR TERM BATTERY DEVELOPMENT (1985)

There is a potential for very advanced batteries that would compete with gasoline engines for automobiles and gas turbines or pumped hydroelectric storage for load leveling of utility systems. Such batteries would have to provide an energy density of 220 watt-hours per kilogram and 3 to 5 years of life at an acquisition cost of $20 per kilowatt-hour (reference 4).

For these goals the sodium-sulfur, lithium-metal-sulfide, zinc-chlorine, and lithium-chlorine batteries are being developed by various laboratories and companies. The energy densities of these candidates are in figure 4. Except for the zinc-chlorine battery, these are nonaqueous systems and generally have operating temperatures of 300 to 500C. An ambient temperature lithium-metal-sulphide battery has recently been reported (reference 5). All of these rechargeable batteries have the potential for very high energy and power densities. However, they are in early laboratory stages and will require much development before becoming a useful battery system for marine applications. These batteries do offer the hope of eventually being able to power a great variety of marine vehicles and equipment.

SUMMARY

Figure 5 shows the performance capabilities of state-of-the-art batteries and selected advanced concepts. Rechargeable alkali metal batteries, now being developed for electric vehicles for the 1985 time period, offer a potential improvement in performance beyond that available with silver-zinc

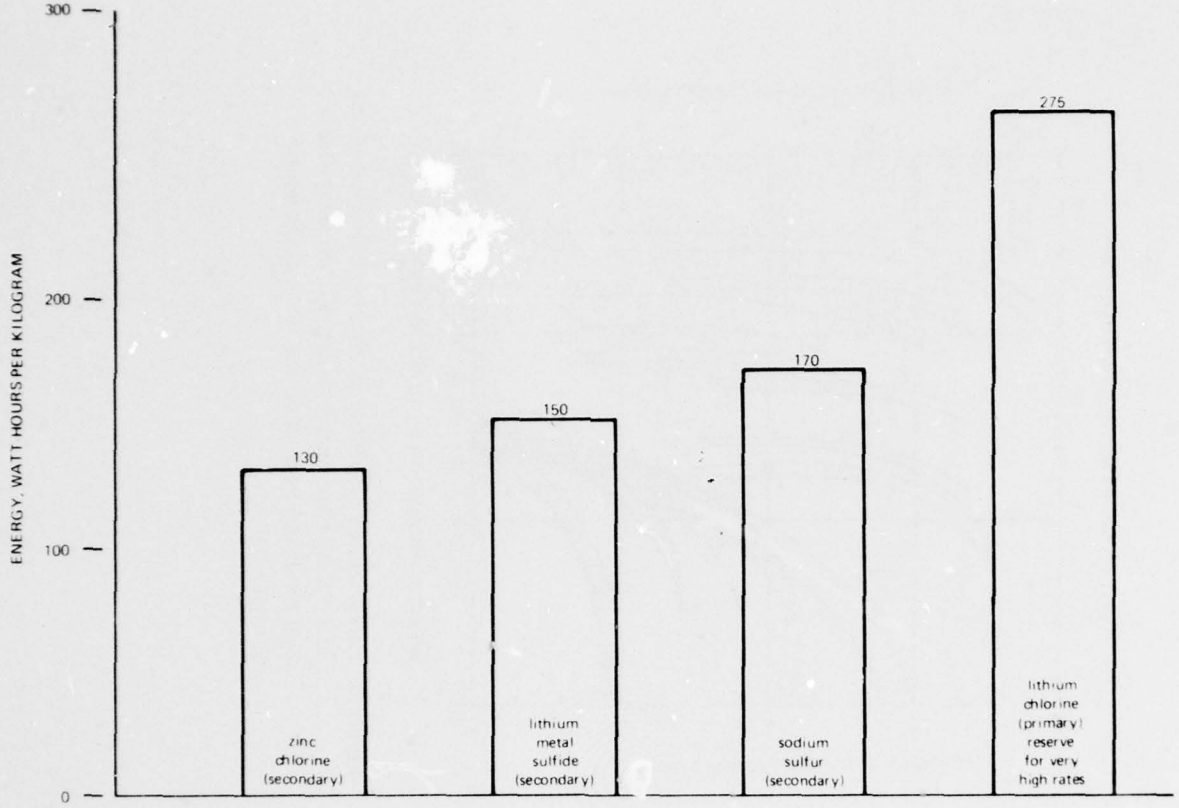


Figure 4. Far term battery candidates (1985).

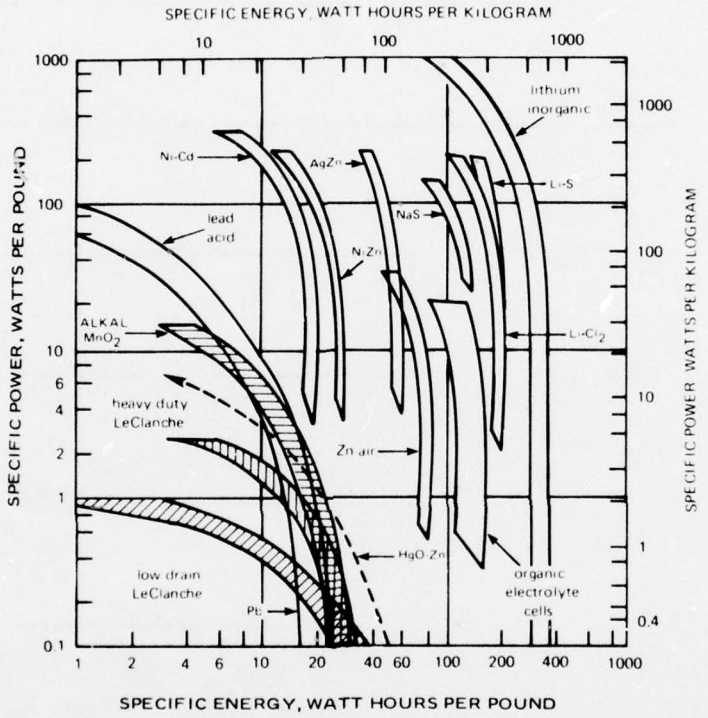


Figure 5. Performance capability of various battery systems These data have been extracted from reference 6 and modified to include the lithium inorganic primary battery.

batteries. State-of-the-art or near term batteries with performance better than that of silver-zinc batteries are limited to the primary type of zinc-air and lithium organic electrolyte batteries and the very high performance, lithium inorganic electrolyte battery.

New opportunities to use advanced battery technology are immediately available in many marine applications. These include the use of data now available for electric vehicle propulsion or off-peak utility storage. (This technology is not yet adequate for its intended application because of low cycle life and high manufacturing costs.) Another opportunity is use of state-of-the-art, low cost, rechargeable batteries for exercise or crew training purposes and the more expensive, very high performance, lithium primary type battery for missions that demand very high energy density. Recent developments have been made in lead-acid batteries and lithium battery technology. Lead-acid batteries now provide 50 percent more capacity than previously possible, and lithium batteries supply very high energy density (six times greater than silver-zinc batteries) with the large size cells now being made. This combination could replace silver-zinc batteries where a primary "one shot" operation is practical and economical.

Until now, the development of batteries for equipment has been done without adequate redesign of the equipment, a procedure which does not fully use the battery's energy since the equipment is not redesigned for greater efficiency. Reduction in drag and other inefficiencies must be included in the future as part of the overall system design. If this is done there will be much more efficient use of battery energy and some of the present batteries will serve as interim power sources.

Advanced battery and vehicle drag reduction technologies could provide an effective improvement in energy utilization, up to 48 times that obtainable from silver-zinc batteries for future high performance marine vehicle applications.

REFERENCES

1. McCartney, J. F., "Expendable Power Sources for Undersea Applications," Technical Note 1931, May 1975, Civil Engineering Laboratory, Naval Construction Battalion Center, Port Hueneme, California

2. Reinertson, J. H., Naval Engineers Journal, May 1963

3. Schaefer, J. C., "The ESB-SOHIO CARB TEK^{R} Molten Salt Cell," Record of the Tenth Intersociety Energy Conversion Engineering Conference, August 1975

4. McCartney, J. F., Shipman, W. H., and Gundersen, C. R., "Investigation of Lithium-Thionyl Chloride Batteries for Navy Applications," Eleventh Inter-Society Energy Conversion Engineering Conference, 1976

5. Robinson, A. L., "Advanced Storage Batteries: Progress, but Not Electrifying," Science, Vol. 192, 7 May 1976

6. Whittingham, M. S., "Electrical Energy Storage and Intercalation Chemistry," Science, Vol. 192, 11 June 1976

7. Yao, N. P. and Birk, J. R., "Battery Energy Storage for Utility Load Leveling and Electric Vehicles: A Review of Advanced Secondary Batteries," IECEC 1975 Record, IEEE Catalog No. 75CHO 983-7 TAB, pp. 1107-1119

APPENDIX B

HEAT TRANSFER ANALYSIS FOR HIGH-RATE CELLS

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HEAT TRANSFER ANALYSIS FOR HIGH-RATE CELLS

Heat transfer analysis was made for a system of lithium inorganic cells packaged as a power source for a torpedo. The system consisted of 114 cells, each with a 2.5-inch diameter and a 6.42-inch length. The cells were arranged in a hexagonal close-pack in a 12.5-inch-diameter cross section, 6 cells deep. The system was sized to deliver 120 kw of usable power. Waste heat was predicted to be 44 kw.

As shown in Figure B-1, the cell active region was annular in configuration. The region interior to the active region was to contain the electrolyte which would be displaced by seawater subsequent to water entry. The anode-cathode structure consisted of a jelly roll which resulted in 17 layers of electrode pairs.

When activated, the electrolyte (consisting primarily of thionyl chloride) saturated the porous layers of the jelly roll.

A steady-state and a transient solution were made, the results of which are shown as Figure B-2. The steady-state solution predicted a temperature difference between the interior hot spot and the bulk cooling water of 192°F. The transient solution resulted in a temperature difference of 174°F for an 8-minute torpedo run at full power. The maximum rise in temperature of the cooling water was found to be 19.8°F at a volume flow rate of 21.6 gpm.

The details of the model for the equivalent thermal diffusivity of a cell are described in the following section.

Assumptions made in the development of the model for equivalent thermal conductivity are the greatest potential source of error in the solution. To test the model, an experiment should be conducted on an available cylindrical cell, monitoring internal temperature during a high discharge rate. However, based on the analysis, the heat transfer problem can be handled effectively.

The details of the model for the equivalent thermal diffusivity of a cell are described in the following section.

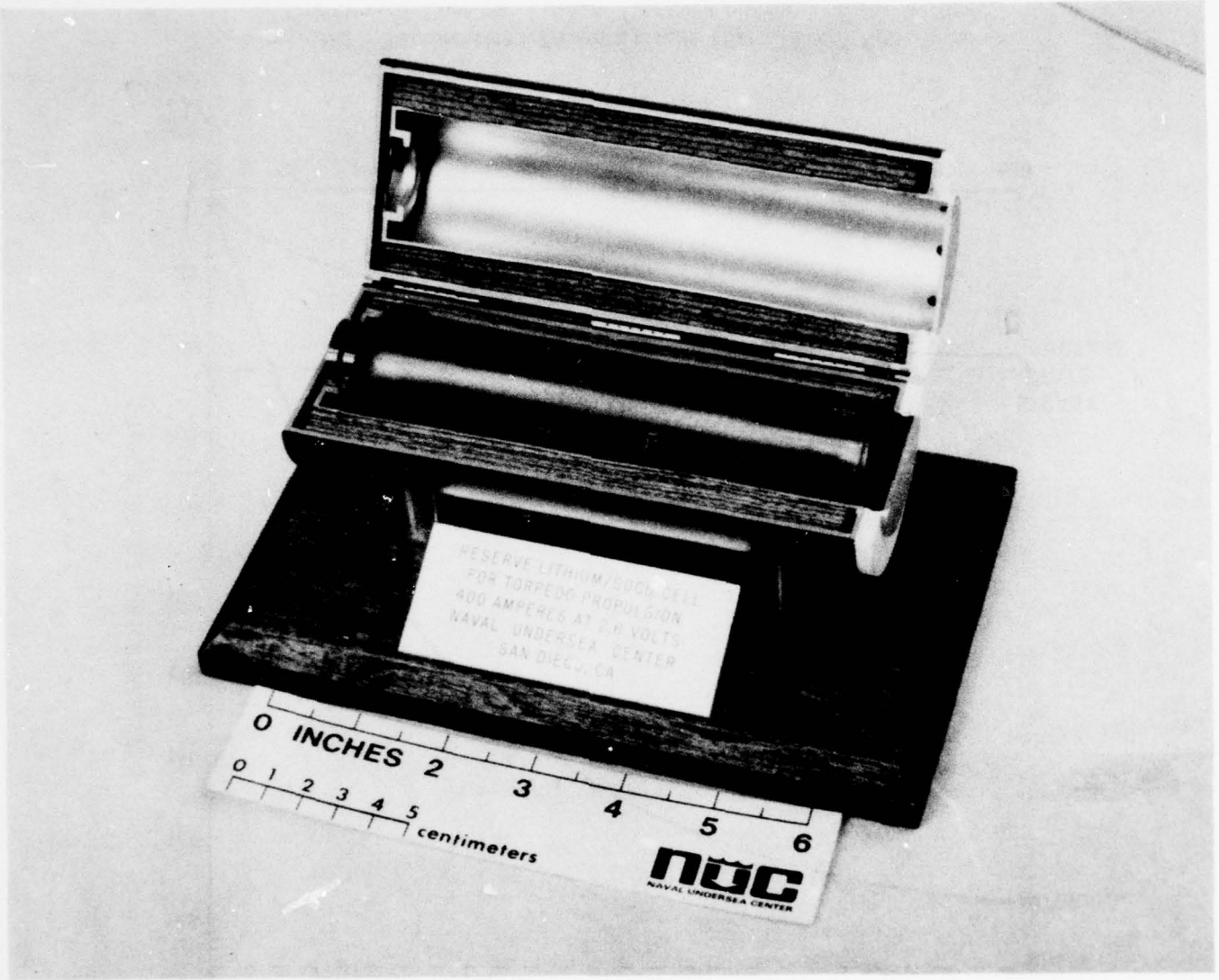


Figure B-1. Reserve Lithium/$SOCl_2$ Cell for Torpedo Propulsion.

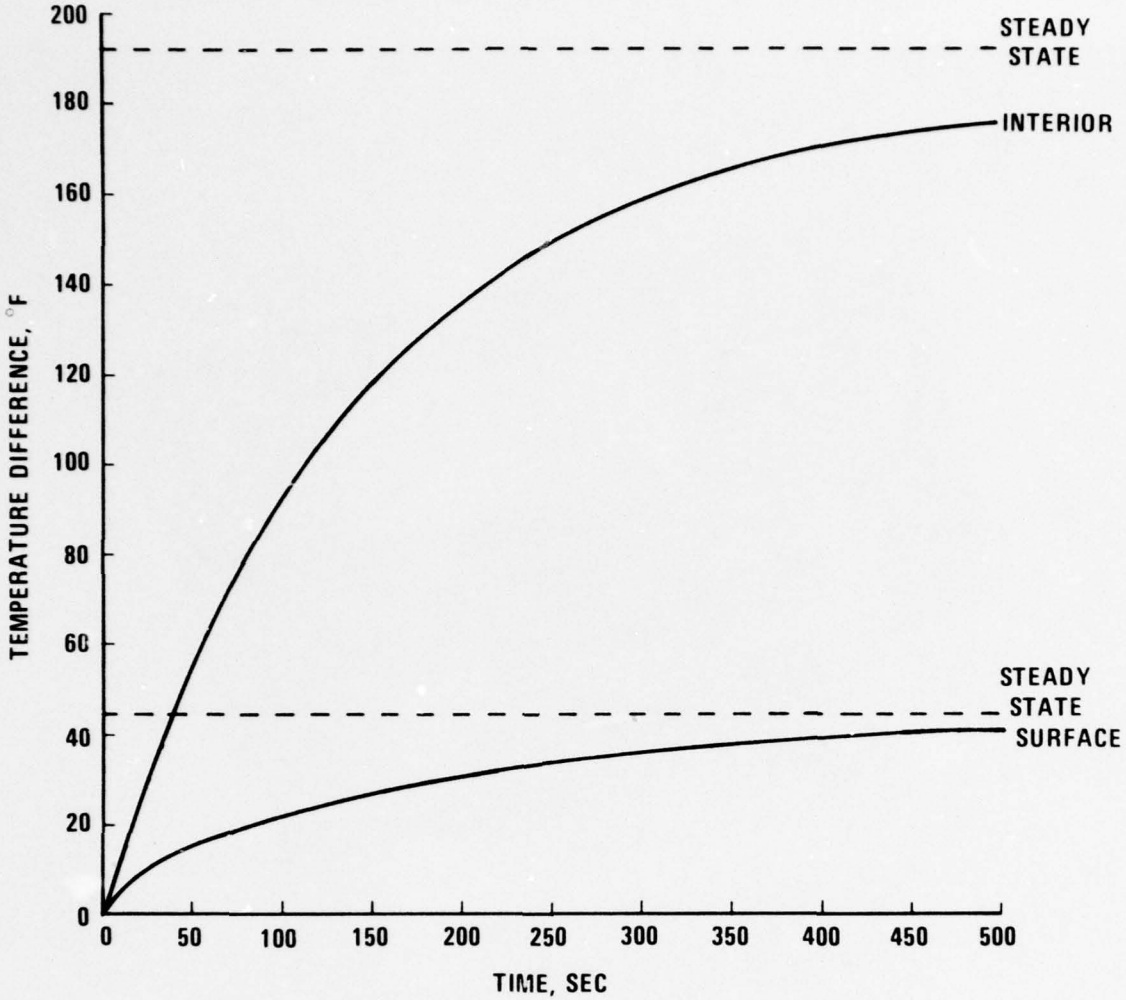


Figure B-2. Temperature Difference From That of Local Bulk Value as a Function of Time for Lithium-Thionyl Chloride Torpedo-Battery.

TRANSPORT PROPERTY MODELS

Each cell is constructed from 17 layers of anode-cathode pairs (shown at the right). Each pair consists of:



a. 5-mil-thick fiberglass, 56% porous
b. 2.5-mil-thick lithium
c. 4-mil- thick aluminum
d. 2.5-mil-thick lithium
e. 5-mil-thick fiberglass, 56% porous
f. 4-mil-thick aluminum
g. 5-mil-thick carbon/teflon, 10% teflon, 77% porous

The porous materials are saturated with thionyl chloride electrolyte when the cell is activated.

Thermal Conductivity of Thionyl Chloride

No experimental data are available on the thermal conductivity of thionyl chloride. However, data are available on vapor pressure, thermal expansion coefficient, viscosity, density, and heat capacity. An empirical formula which uses speed of sound and density is the Bridgeman equation (ref. 1, p. 260):

$$k = 2.80 \left(\frac{N\rho}{M}\right)^{2/3} \kappa a$$

where: k = thermal conductivity, cal/cm-s-°C

N = Avagadro's Number

ρ = density, g/cm^3

M = molecular weight

κ = Boltzman constant, 1.3805×10^{-16}

a = velocity of sound

The velocity of low frequency sound is:

$$a = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_T}$$

for liquids where $C_p/C_v = 1$ (ratio heat capacities). Here, p is pressure and T is temperature. To obtain $\left(\frac{\partial p}{\partial p}\right)_T$, vapor pressure and thermal expansion coefficient can be used:

$$\left(\frac{\partial p}{\partial v}\right)_T = - \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \quad , \quad v = \frac{1}{\rho}$$

$$= - \left(\frac{\partial p}{\partial T}\right)_v \frac{\rho}{\left(\frac{\partial v}{\partial T}\right)_p \frac{1}{v}}$$

But,

$$\left(\frac{\partial p}{\partial v}\right)_T = -\left(\frac{\partial p}{\partial v}\right)_T \frac{1}{\rho^2}$$

So:

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \left(\frac{\partial p}{\partial v}\right)_v \frac{1}{\left(\frac{\partial v}{\partial T}\right)_p \frac{1}{v} \rho}$$

Data determined at Hooker Laboratories are:

Specific gravity @ 15.5°C:	1.640
Coefficient thermal expansion:	1. x 10^{-6}°C^{-1}
Vapor pressure:	96. mm of hg @ 20°C
	147.9 @ 30°C
	221.3 @ 40°C
	321.6 @ 50°C
	458.1 @ 60°C
	637.9 @ 70°C
	746.0 @ 75°C

viscosity: 0.801 cp @ 0°C
0.545 cp @ 37.8°C

Heat Capacity: 0.24 cal/gm-°C

$(\partial p/\partial T)_v$ can be obtained from a plot of vapor pressure vs. temperature, as shown on the following page (Figure B-3).

Then,

$$\left(\frac{\partial p}{\partial \rho}\right)_T = (0.2)\ (144) \quad \frac{1}{(10^{-6})\ (1.64)\ (62.4)/32.2}$$

$$= 9.06 \times 10^6 \text{ ft}^2/\text{sec}^2$$

And,

$$a = 3.01 \times 10^3 \text{ ft/sec}$$

$$= 91.75 \times 10^3 \text{ cm/sec}$$

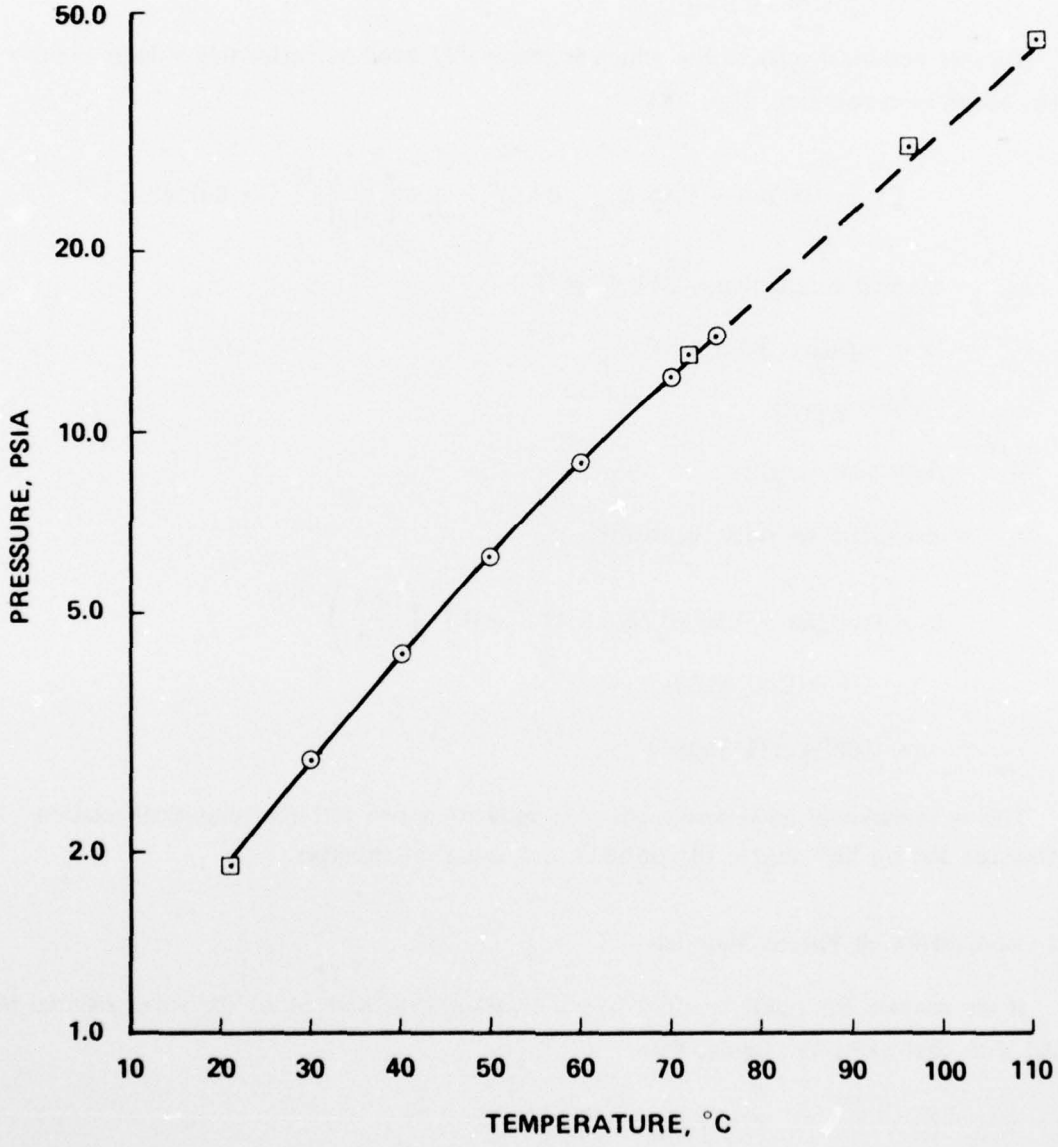


Figure B-3. Vapor Pressure of $SOCl_2$ as a Function of Temperature.

Thus, substituting into the Bridgman equation:

$$k = 2.80 \left(\frac{6.023 \times 10^{23} (1.64)}{119} \right)^{2/3} (1.3805 \times 10^{-16}) (91750)$$

$$= 1.4539 \times 10^{4} \text{ erg/cm-s-}^{\circ}\text{C}$$

$$= 0.0838 \text{ BTU/ft-hr-}^{\circ}\text{F}$$

Another empirical relationship which is reasonably good at correlating a large number of data is the Smith equation (ref. 2, p. 78).

$$k = 0.00266 + 1.56 (C_p - 0.45)^3 + 0.3 \left(\frac{\eta}{M} \right)^{1/3} + 0.0242 \ \nu^{1/9}$$

where: k = thermal conductivity, BTU/hr-ft-°F

C_p = heat capacity, BTU/lb-°F

η = specific gravity

M = molecular weight

ν = kinematic viscosity, centistokes

Then:

$$k = 0.00266 + 1.56 (0.24 - 0.45)^3 + 0.3 \left(\frac{1.64}{119} \right)^{1/3} + 0.0242 (0.545/1.64)^{1/9}$$

$$= 0.0824 \text{ BTU/ft-hr-}^{\circ}\text{F}$$

This is remarkably good agreement of results from two different empirical relationships. One can have a high degree of confidence in using this number.

Thermal Conductivity of Porous Materials

If we assume, for tightly packed layers, that the heat path along the solid material is in parallel with that along the liquid, then:

$$k = k_s n_s + k_\ell n_\ell$$

where: k = equivalent thermal conductivity

k_s = thermal conductivity of solid

k_ℓ = thermal conductivity of liquid

n_s = volume fraction of solid

n_ℓ = volume fraction of liquid

The thermal conductivities of the materials of interest are:

carbon: 3.0 BTU/ft-hr-°F

teflon: 0.14 BTU/ft-hr-°F

glass: 0.605 BTU/ft-hr-°F

Since the carbon/teflon solid is constructed by pressing the teflon and carbon together, again one may assume parallel heat paths along each constituent. Thus, for the solid carbon/teflon layer:

$$k = (3.0)\ (0.9) + (0.14)\ (0.1)$$
$$= 2.714 \text{ BTU/ft-hr-°F}$$

In the saturated condition, the carbon/teflon layer has a thermal conductivity:

$$k_{ct} = (2.714)\ (0.23) + (0.083)\ (0.77)$$
$$= 0.6881 \text{ BTU/ft-hr-°F}$$

The fiberglass layer, in the saturated condition, has a thermal conductivity:

$$k_{fg} = (0.605)\ (0.44) + (0.083)\ (0.56)$$
$$= 0.3127 \text{ BTU/hr-ft-°F}$$

Thermal Conductivity Model for Cell Active Region

Since the heat path is perpendicular to the layers of each anode-cathode pair, a series model for the overall thermal conductivity of the entire active region may be assumed:

$$\frac{t}{k} = \frac{t_{fg}}{k_{fg}} + \frac{t_{\ell i}}{k_{\ell i}} + \frac{t_{a\ell}}{k_{a\ell}} + \frac{t_{\ell i}}{k_{\ell i}} + \frac{t_{fg}}{k_{fg}} + \frac{t_{a\ell}}{k_{a\ell}} + \frac{t_{ct}}{k_{ct}}$$

where: t = thickness of one anode-cathode pair

k = apparent thermal conductivity of active region

t_{fg} = thickness of one fiberglass layer

k_{fg} = thermal conductivity of saturated fiberglass layer

$t_{\ell i}$ = thickness of one lithium layer

$k_{\ell i}$ = thermal conductivity of lithium

$t_{a\ell}$ = thickness of one aluminum layer

$k_{a\ell}$ = thermal conductivity of aluminum

t_{ct} = thickness of one carbon/teflon layer

k_{ct} = thermal conductivity of saturated carbon/teflon layer

$$\frac{t}{k} = \frac{5}{0.3127} + \frac{2.5}{41.2} + \frac{4}{118} + \frac{2.5}{41.2} + \frac{5}{0.3127} + \frac{4}{118} + \frac{5}{0.6881}$$

$$= 39.435$$

$$k = \frac{28}{39.435}$$

$$= 0.7100 \text{ BTU/ft-hr-°F}$$

Heat Capacity Model for Cell Active Region

The total amount of heat any system of n constituents can store is simply:

$$q = \sum_{i=1}^{n} m_i \, c_{vi}$$

where:

m_i = mass of *ith* constituent, gm

c_{vi} = heat capacity for *ith* constituent, cal/gm-°C

Then, an apparent heat capacity for the entire system may be defined as:

$$C_v = \frac{\sum_{i=1}^{n} m_i \, C_{vi}}{\sum_{i=1}^{n} m_i}$$

For the present cell with the core filled with seawater:

constituent	mass, gm	heat capacity, Cal/gm°C
seawater	60.4	1.0
aluminum	291.78	0.216
lithium	17.7	0.960
carbon	27.6	0.173
teflon	3.0	0.25
glass	78.1	0.20
thionyl chloride	248.25	0.24

Substituting these data into the equation, the apparent heat capacity for the cell is:

$$C_v = 0.305 \text{ BTU/lb-}^\circ\text{F}$$

An apparent density may be defined:

$$\rho = \frac{\sum_{i=1}^{n} m_i}{\text{volume}}$$

$$= \frac{726.83}{440}$$

$$= 1.652 \text{ g/cc}$$

Finally, an apparent thermal diffusivity for the cell may be defined:

$$\alpha = \left(\frac{k}{\rho c}\right)_{\text{apparent}}$$

$$= \frac{0.7100}{(1.652)\ (62.4)\ (0.305)}$$

$$= 0.0226 \text{ ft}^2/\text{hr}$$

All properties have been evaluated at 100°F.

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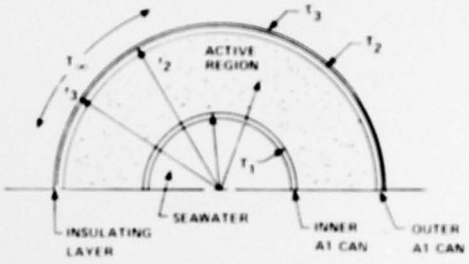
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Section References:

1. Bird, R. B; W. E. Stewart; and E. N. Lightfoot; Transport Phenomena; John Wiley; New York (1960).

2. Jacob, M, Heat Transfer, Volume I, John Wiley, New York (1955).

STEADY-STATE SOLUTION



The model for the steady-state heat transfer in a cell uses the geometry at the right and the following assumptions:

1. Steady State has been reached.
2. No thermal gradient in the inner and outer aluminum shells.
3. One-dimensional (radial) heat transfer.
4. Uniform heat generation in the active region.

Start with the heat conduction equation,

$$\nabla^2 T = \frac{-\dot{q}}{k} \qquad (1)$$

where: T = temperature

$\dot{q}$ = heat generation per unit volume

k = thermal conductivity.

Integrating once with respect to r:

$$\frac{\dot{q}r^2}{2} = -kr\frac{dT}{dr} + C_1 \qquad (2)$$

where: C_1 = integration constant

Boundary conditions are:

$$k\frac{dT}{dr} = 0 \ @ \ r=r_1 \qquad (2a)$$

$$T = T_2 \ @ \ r=r_2 \qquad (2b)$$

Therefore:

$$C_1 = \frac{\dot{q} r_1^2}{2} \tag{3}$$

The local heat flux at any point is:

$$q'' = -k \frac{dT}{dr} \tag{4}$$

Using equation (2):

$$q'' = \frac{\dot{q}}{2r} \quad (r^2 - r_1^2) \tag{5}$$

Integrating equation (2) and using boundary condition (2b):

$$T - T_2 = - \frac{\dot{q}}{2k} \left[\frac{(r-r_2)^2}{2} \quad - \quad r_1^2 \quad \ln (r/r_2) \right] \tag{6}$$

For a thin outer insulating layer:

$$q'' = \frac{k_o}{t_o} \quad (T_2 - T_3) \tag{7}$$

where: k_o = thermal conductivity of outer layer

t_o = thickness of outer layer

At the outer surface, the heat flux is:

$$q'' = h_x \quad (T_3 - T_\infty) \tag{8}$$

where: h_x = local surface conductance

T_∞ = local bulk temperature of the cooling water

Making a heat balance:

$$h_x A_o \ (T_3 - T_\infty) = \frac{k_o}{t_o} \ \pi r_3^2 \ \ (T_2 - T_3) = \frac{\dot{q}}{2r} \pi r_2^2 \ (r_2^2 - r_1^2) \tag{9}$$

where: A_o = outer area exposed to the cooling water

Assuming that 80% of the outside area is wetted,

$$A_o = 0.8\ \pi r_3^2 \tag{10}$$

From equations (9) and (10):

$$T_2 - T_\infty = \frac{\dot{q}}{2r_2}\left(\frac{r_2}{r_3}\right)^2 \quad (r_2^2 - r_1^2) \quad \left[\frac{1.25}{h_x} + \frac{t_o}{k_o}\right] \tag{11}$$

Combining equations (6) and (11):

$$T-T_\infty = \frac{\dot{q}}{2r_2}\left(\frac{r_2}{r_3}\right)^2 \quad (r_2^2 - r_1^2) \left[\frac{1.25}{h_x} + \frac{t_o}{k_o}\right] - \frac{\dot{q}}{2k} \tag{12}$$

$$\left[\frac{(r-r_2)^2}{2} - r_1^2 \ln \frac{r}{r_2}\right]$$

TRANSIENT SOLUTION

For transient heat conduction, the proper starting point is:

$$\rho C_p \frac{\partial T}{\partial t} = k \nabla^2 T - \dot{q} \qquad (1)$$

For radial direction variation only:

$$\rho C_p \frac{\partial T}{\partial t} = \frac{k}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) - \dot{q} \qquad (2)$$

Although the problem can be handled quite well with finite-element or finite-difference computer codes, a closed-form solution with the present boundary conditions is not possible (such a code was not available at the time this analysis was needed). It is necessary, therefore, to construct a solution from various available solutions with different boundary conditions and/or geometry.

Slab Model for Transient Heat Conduction -

From reference 1, page 132, the solution for transient heat conduction in a slab with uniform heat generation, one boundary at constant temperature T_o, the other boundary subject to convection, and the initial temperature throughout at T_o:

$$T - T_o = \frac{\dot{q}}{2k} \left[\frac{2 + \frac{bh}{k}}{1 + \frac{bh}{k}} - x^2 \right] + 4 \frac{\dot{q}\, h}{k^2} \sum_{n=1}^{\infty} A_n (x,t) \qquad (3)$$

where:

$$A_n (x,t) = \frac{\sin (\beta_n x) \; (1 - \cos \beta_n b) \; e^{-\alpha \beta_n^2 t}}{\beta_n^2 \sin (2\beta_n b) \left[\frac{h}{k} \left(1 + \frac{bh}{k} \right) + b \beta_n^2 \right]} \qquad (4)$$

$$\beta_n = \text{positive roots of } \beta \cot (\beta b) + \frac{h}{k} = 0 \qquad (5)$$

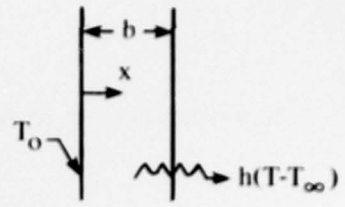
b = slab thickness

x = coordinate measured from face where $T=T_o$

h = surface conductance

α = thermal diffusivity

t = time



Solid Cylinder Model for Transient Heat Conduction -

From reference 1, page 205, the solution for uniform heat generation, the boundary at T_o, and the initial temperature throughout at T_o:

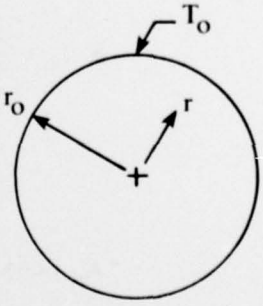
$$T-T_o = \frac{\dot{q} r_o^2}{4k}\left[1 - \frac{r^2}{r_o^2} + \frac{2k}{r_o h}\right] - \frac{2h\dot{q}}{r_o k^2} \sum_{n=1}^{\infty} B_n\,(r,t) \qquad (6)$$

where:

$$(B_n\, r,t) = \frac{J_o\,(r\beta_n)\; e^{-\alpha\beta_n^2 t}}{\beta_n^2\left(\frac{h^2}{k^2} + \beta_n^2\right)\; J_o\,(r_o\beta_n)} \qquad (7)$$

β_n = positive zeros of

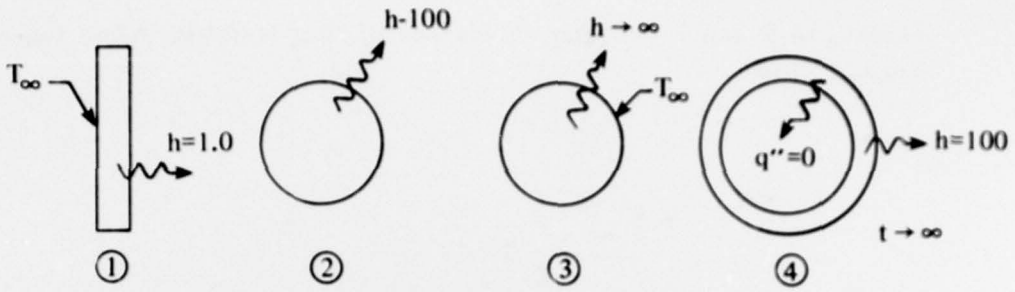
$$\beta\, J_1\,(\beta\, r_o) - \frac{h}{k}\, J_o\,(\beta\, r_o) = 0 \qquad (8)$$



r_o = radius of cylinder

Cell Model for Transient Heat Conduction -

An *approximate* solution to the cell heat transfer problem can be constructed from the solutions for the slab and solid cylinder.



At the interior critical point (hot spot), the temperature difference between the point and the local bulk flow is, approximately:

$$\Delta T_{max} = \Delta T_{①} \frac{\Delta T_{②}}{\Delta T_{③}} \qquad (9)$$

where $\Delta T_{①}$ is the solution for a slab of thickness, r_2-r_1, outside surface temperature equal to the local bulk temperature, and inside boundary condition of natural convection with surface conductance of 1.0 BTU/hr-ft^2-°F. Temperature difference $\Delta T_{②}$ is the solution for a solid cylinder of the same volume as the cell active region with outside surface conductance of 100 BTU/hr-ft^2-°F (a value which can reasonably be obtained with proper design). Finally, $\Delta T_{③}$ is the temperature difference for a solid cylinder with an infinite outside surface conductance (same as a surface temperature of T_∞) and a volume equal to the cell active region volume.

The difference between the surface temperature of the cell and the local bulk temperature can be approximated with:

$$\Delta T_{surf} = \frac{\Delta T_{④}}{\Delta T_{②}'} \Delta T_{②} \qquad (10)$$

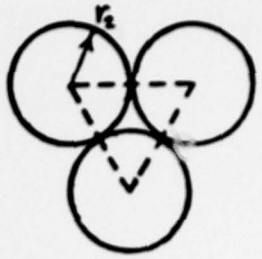
where $\Delta T_{④}$ is the steady-state solution for the cell, and $\Delta T_{②}'$ is the solution for $\Delta T_{②}$ as $t \rightarrow \infty$.

These solutions were handled with the aid of the 1110 computer. The loss per cell is 385.965 watts, which, when allocated uniformly to the active region, is 130757.2 BTU/hr-ft^3 for a cell active region volume of 17.409 in^3.

Section References:

1. Carslaw, H. S. and J. C. Jaeger, *Conduction of Heat in Solids,* Oxford University Press, London, 1959.

BULK FLOW SOLUTION



The cross section of a single flow passage between cells have a curvilinear triangle shape.

The area is:

$$A = \text{area triangle - 3 area sector}$$

$$= \frac{1}{2}(2r_2)(2r_2) \sin(60°) - 3(1/3\ \pi r_2^2) \quad (1)$$

The wetted perimeter is:

$$P = 3(2\ \pi r_2/6)$$

$$= \pi r_2 \quad (2)$$

The hydraulic diameter is:

$$D_h = \frac{4A}{P} \quad (3)$$

In the thermal entry region an *approximate solution for the Nusselt number* can be obtained from:

$$Nu = \frac{(Nu_\infty)_\Delta}{(Nu_\infty)_o} (Nu)_o \quad (4)$$

where

Nu = Nusselt number, hD/k

h = surface conductance

D = duct diameter (actual or hydraulic)

k = fluid thermal conductivity

$(Nu_\infty)_\Delta$ = Nu for thermally developed laminar flow in a triangular duct

$(Nu_\infty)_o$ = Nu for thermally developed laminar flow in a circular duct

$(Nu)_o$ = Nu in the thermal entry region for laminar flow in a circular duct

The boundary condition which most closely fits the present situation is that of uniform heat flux to the flow from the cell walls.

From reference 1, page 117,

$$(Nu_\infty)_\Delta = 3.00 \tag{5}$$

$$(Nu_\infty)_o = 4.364 \tag{6}$$

Also from reference 1, page 127,

$$(Nu)_o = \left[\frac{1}{(Nu_\infty)_o} - \frac{1}{2} \sum_{m=1}^{\infty} \frac{e^{-\Upsilon_m{}^2 x^+}}{A_m \Upsilon_m{}^4} \right]^{-1} \tag{7}$$

where:

x^+ = $2x/D\ Re\ Pr$

x = flow direction coordinate measured from duct entrance

D = duct diameter

Re = Reynolds number, VD/υ

Pr = Prandtl number, υ/α

V = average velocity of flow

υ = kinematic viscosity of fluid

α = thermal diffusivity of fluid

Υ_m = constant (see reference)

A_m = constant (see reference)

Usually, the series converges within 3 or 4 terms. Assuming h_x = 100 BTU/ft^2-hr-°F is a reasonable value at the downstream end of each cell (upstream it would be higher), the mass flow rate, $\dot{m} = \rho VA$, can be obtained from equation 7 by iteration. Then,

$$T_\infty(x) - T_\infty(0) = q/\dot{m}\, C_p \tag{8}$$

where:

$T_\infty(x)$ = local bulk temperature at x

$T_\infty(0)$ = bulk temperature at upstream end of cell

q = heat transfer into the flow passage, BTU/hr

$\dot{m}$ = ρVA, mass flow rate in a passage

C_p = heat capacity of fluid

If it is assumed that the flow is swirled by some means between cells, then a mixed flow will enter the flow passage at each cell location. Using equation 8, the maximum bulk temperature will be:

$$(T_\infty)_{max} - (T_\infty)_{amb} = 6 \left[T_\infty (x) - T_\infty (0) \right] \quad (9)$$

where $(T_\infty)_{max}$ = maximum bulk temperature (at the downstream end of the battery section)

$(T_\infty)_{amb}$ = ambient bulk temperature (at entrance to the battery section)

The heat transferred to the flow per cell location at steady state is:

$$q = \dot{q} \ (3) \ (\frac{1}{6} \ V_a)$$

$$= \dot{q} \ V_a/2 \quad (10)$$

where: V_a = volume of active region in single cell

Using equations 4, 5, 6, and 7, fixing h_x = 100 BTU/hr-ft^2-°F, and evaluating properties at the film temperature (assumed to be 100°F), the necessary mass flow rate is found to be 0.400 gpm per flow channel or 21.6 gpm for the entire battery. The Reynolds number for the flow is 1482, well within the laminar region assumed.

Using equations 8, 9, and 10, substituting values V_a = 17.409 in^3 and $\dot{q}$ = 130,757 BTU/hr-ft^3, the steady-state temperature difference across the battery for the bulk flow is found to be 19.76°F.

Section References:

1. Kays, W. M., Convective Heat and Mass Transfer, McGraw-Hill, New York, 1966.

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