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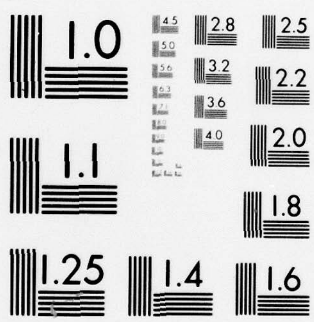

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SAFE, USEFUL LITHIUM BATTERIES FOR THE NAVY.

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BY F. M. BOWERS (Frederick)

RESEARCH AND TECHNOLOGY DEPARTMENT

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The Navy is the only military service in the United States presently using lithium anode batteries as a portable power source for certain tactical devices. The Navy also has at least 12 widely diverse additional applications for which lithium batteries are being developed. The technology that will permit the safe use, storage and disposal of the batteries, particularly those to be discharged at high rates is not being developed. Guidelines

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for the procurement, use, storage, and disposal have been prepared in order to keep potential users abreast of the latest developments and the safety of each application is being reviewed by the cognizant safety offices of each System Command in order to minimize potential hazards.

SUMMARY

This report presents the initial progress on the development of a technology base needed for the introduction of safe, useful lithium batteries into the Navy. The project was initiated after wide spread users of lithium batteries experienced safety incidents where cells exploded, vented toxic fumes, and caught fire. The report includes the results of an industry-government survey, verified safety incidents, present uses of lithium batteries in the Navy, applications for which they are proposed, a plan for the development of the required technology, and procedures for controlling the use of lithium batteries until the technology is developed.

J. R. Dixon

J. R. DIXON
By direction

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SAFE, USEFUL, LITHIUM BATTERIES FOR THE NAVY

INTRODUCTION

The high potential and light weight of lithium (Li) metal make it attractive as an anode for electrochemical power sources. "Practical" cells were first marketed in 1970 (Reference 1) and were composed of a lithium anode, an organic solvent containing a suitable salt and a sulfur dioxide (SO_2) cathode. These early cells had steel cans with crimped seals, and those that did not leak, demonstrated excellent low rate performance over a wide temperature range.

Concurrent with the Li/SO_2 development was the investigation of the lithium/carbon monofluoride (CF) and the lithium/oxyhalide electrochemical systems. Three oxyhalides, posphoryl chloride ($POCl_3$), sulfuryl chloride (SO_2Cl_2) and thionyl chloride ($SOCl_2$) were investigated (References 2, 3, and 4) as cathode materials. At present most of the lithium/oxyhalide cells being produced use thionyl chloride as the cathode active material. Thionyl chloride which is a liquid at room temperatures is both the cathode and the solvent for a suitable electrolyte usually lithium tetrachloroaluminate ($LiAlCl_4$). Lithium/oxyhalide cells and batteries are commonly called "lithium inorganic," because oxyhalides are inorganic chemicals; lithium sulfur dioxide cells and batteries are commonly called "lithium organic" because the commonly used electrolyte solvents, proplylene carbonate and acetonitrile, are organic chemicals; and lithium/monofluoride cells and batteries are commonly called lithium/monofluride even though the electrolyte solvent, methylacetate, is an organic chemical. In this report we will differentiate between the three systems by means of their cathodes.

Table 1 presents the characteristics of the three systems that are being developed in the United States for commercial, space and military applications (References 5, 6, 7, and 8). The reactions are still somewhat controversial but they do fit all of the known experimental facts. The energy density values are presented to show the relative capability of the systems. In practical cells the application might dictate performance limitations that would permit the use of only a small part of the theoretical energy.

BACKGROUND

ADVANTAGES. Lithium batteries offer three principal advantages over conventional "dry cells" (mercuric oxide/zinc, manganese dioxide/zinc, and manganese dioxide/magnesium). They are:

Table 1. CHARACTERISTICS OF COMMON LITHIUM ELECTROCHEMICAL SYSTEMS

System	Reaction	Theoretical Specific Energy Density WH/KG	Nominal Voltage	Voltage Plateaus	Ref.
$Li/PC,AN,LiBr/SO_2$	$2Li+2SO_2 \rightarrow Li_2S_2O_4$	1100	2.9	1	6
$Li/SOCl_2,LiAlCl_4/SOCl_2$	$4Li+2SOCl_2 \rightarrow 4LiCl+S+SO_2$	1144	3.6	1	5,8
$Li/MA,LiAsF_6/CF$	$Li+CF \rightarrow LiF+C$	1980	2.8	3	7

PC = Propylene Carbonate ($CH(CH_3)CH_2OCO_2$)

AN = Acetonitrile or methylcyanide (CH_3CN)

MA = Methylacetate ($CH_3CO_2C_{10}H_{19}$)

a. long shelf life (References 9 and 10)
b. excellent low temperature performance (References 1 and 11).
c. high gravimetric energy density.

Shelf Life. Taylor (Reference 10) reports that crimped sealed Li/SO_2 cells stored at room temperature lost 25 percent of the initial capacity in five years. Nineteen percent of this loss was due to the leakage of SO_2 through the crimped seals. Hermetic seals have replaced the crimped seals and eliminated SO_2 leakage with the attendant possibility that the capacity loss on storage will be reduced to perhaps six percent over a five year period. Excellent shelf life is also claimed for $Li/SOCl_2$ (Reference 11), however, this reference does not provide substantiating experimental data.

Low Temperature Performance. Figure 1 of Reference 12 compares the performance of Battery BA584N made with Li/SO_2 cells with similar batteries containing the conventional types of "dry cells". The results show that Li/SO_2 batteries are capable of delivering a substantial part of their capacity at $-40^{\circ}C$ whereas other "dry cell" batteries are not.

The development of the $Li/SOCl_2$ system has not progressed as far as the Li/SO_2, however, there are strong indications (Reference 13) that its low temperature performance may at least equal that of the Li/SO_2.

Energy Density. Lithium/sulfur dioxide cells and batteries have demonstrated energy densities in excess of 100 Wh/lb and 9 Wh/in^3 (References 1, 9, 14, and 15) when discharged at low rates. Gilman (Reference 16) estimates that developed $Li/SOCl_2$ cells will have about a 50 percent improvement in performance over Li/SO_2.

DISADVANTAGES. Lithium batteries have two major disadvantages. They are:

a. materials limitations
b. safety

Materials Limitations. Lithium is a highly active alkaline metal that reacts with most of the gases found in the atmosphere such as oxygen, hydrogen, nitrogen, carbon dioxide, sulfur dioxide and moisture (Reference 17). It also reacts with many plastics, glasses and organic solvents. These characteristics of lithium affect cell design, the electrolyte solvents that can be used, and the selection of structural materials. In the Li/SO_2 cell, acetonitrile, which is the solvent for the electrolyte, reacts with lithium in the absence of SO_2 to release methane gas (Reference 18). However, when SO_2 is present the following reaction

$$2\ Li + 2\ SO_2 \rightarrow Li_2S_2O_4$$

takes place and forms a lithium dithionite film which prevents the lithium and acetonitrile from reacting. The $Li_2S_2O_4$ film is responsible for the excellent shelf life of the Li/SO_2 cells but it may cause slight voltage delays under some discharge conditions.

In $Li/SOCl_2$ cells the formation of a lithium chloride passivating film over the surface of the lithium has resulted in operational delays of up to several seconds when cells are first used (Reference 19 and 20). The delay varies depending upon how the cell has been designed, manufactured and stored and how it is being discharged.

The chemical activity of lithium has also forced the use of electrolytes that have low conductivity. This restricts the rate at which lithium cells may be discharged. Table 2 lists the conductivity values at 20°C for some of the common electrolytes used in lithium cells. The value for 42 percent aqueous potassium hydroxide solution, which is the electrolyte commonly used in both high and low rate silver oxide/zinc cells has been included for comparison.

Table 2. SPECIFIC CONDUCTIVITY OF SOME COMMON LITHIUM CELL ELECTROLYTES AT 20°C

Electrolyte	Specific Conductivity $(ohm/cm)^{-1}$
$SOCl_2$, $LiAlCl_4$	0.1
CH_3CN, SO_2, $LiAsF_6$	0.4
CH_3CN, SO_2, LiBr	0.5
KOH (42%)	0.4

Cell Designs. There are three basic cell designs under development at present:

a. coiled electrode-cylindrical
b. bobbin-cylindrical
c. parallel plate - prismatic

Virtually all of the cells currently being produced employ the "so-called" coiled electrode-cylindrical type design. In this design, the electrodes are long thin strips to provide as much surface area as possible and offset the low conductivity of the electrolyte. Cells are assembled by covering a strip of lithium with a strip of separator material which in turn is covered by a strip of teflon bonded porous carbon. The three strips are wound into a coil and inserted into a cylindrical can. The cans are either mild steel, nickel plated mild steel, or nickel depending on the cathode material. The carbon-teflon current collector strip is made by expanded metal screen. The cathode active material is reduced at the carbon electrolyte interface and the product of the reaction, either $Li_2S_2O_4$, LiCl or LiF as the case may be, is formed in the pores of the carbon current collector.

Cells are always constructed with excess active materials and the capacity of the cells are limited by the amount of reaction product that the porous carbon can accept. Thus, a discharged lithium cell differs from the more conventional types in that it still contains highly reactive and corrosive materials when it is ready to be disgarded.

Safety. The early users of lithium cells encountered safety problems which have continued up to the present. In 1972, Wilburn (Reference 1) reported that lithium batteries might be unsafe under some conditions. He found that when Li/SO_2 cells were short circuited, the internal pressure and temperature increased to a point where the cells ruptured and caught on fire. By 1974 several investigations had been started to determine the causes of the safety incidents encountered by potential users of Li/SO_2 cells and batteries. References 9 and 21 report the results of two of these investigations. Brooks (Reference 21) devised seven tests for cells, (a) short circuit (b) increasing load, (c) hot plate, (d) cell deformation, (e) dynamic environment, (f) case rupture, (g) incineration, and five tests for batteries, (a) short circuit, (b) increasing load, (c) hot plate, (d) fresh and salt water immersion, (e) reverse discharge. All cells in his experiments contained vents and all batteries contained 10 ampere fuses. Cells and batteries malfunctioned, i.e., vented or fuse opened, on all of his tests with the exception of the case rupture and the water immersion. There was some loss of capacity in the samples discharged after the water immersion tests. Warburton, (Reference 9) found during the discharge of "C" size cells at approximately the 30 minute rate that the internal cell temperature rose to approximately the melting point of lithium (186^{o}C) and those with vents vented and those without vents exploded. He estimated that the internal pressure of the test cells reached 30 atmospheres.

Safety Incidents. On 6 October 1974, the first of five accidents related to aircraft equipment occurred with Li/SO_2 batteries:

a. 6 October 1974 - Fire on an aircraft life raft in a warehouse in Miami, Florida traced to the batteries used to power the Emergency Locator Transmitter (ELT). This device transmits a signal after an aircraft has been forced down or crashed to assist the search planes in locating the downed aircraft.

b. Twenty-five days later, on 31 October 1974, there was a fire on a Cessna 182 in flight near Chicago, Illinois which was traced to the batteries in the ELT.

c. 6 November 1974, there was an explosion on board a Bonanza in a hanger in Chicago, Illinois, traced to the batteries in the ELT.

d. 15 November 1974, during the inspection of slide raft equipment on a Northwest Airlines aircraft, a fire broke out that was traced to the batteries in the ELT.

In December 1974, the FAA started an investigation of lithium battery safety. Reference 22 is the report of their findings. The report recommended that only cells with hermetic seals and vents be used in the construction of batteries. It also recommended that groups of cells connected in series be appropriately fused.

In August 1976, during a test of the slide raft equipment on a Delta Airlines Lockheed L1011 aircraft, a lithium battery exploded. The light which is part of the slide raft equipment had been turned on for approximately three hours when the center cell of the battery exploded with sufficient force to propell an adjacent cell into a concrete wall and crack it*.

Other users of lithium batteries have experienced safety incidents.

a. In August 1976, a 10,000 Ah size $Li/SOCl_2$, discharged cell exploded killing one and injuring at least two others at Hill AFB. A number of cells had been tested and were being prepared for shipment back to the manufacturer when the accident occurred. The cells were subsequently destroyed at Hill AFB (Reference 23).

b. On 23 February 1977 at the Brunswick Corporation, Costa Mesa, CA, a battery consisting of eleven "C" size cells connected in series was being discharged at about the 30 minute rate and was over discharged. One or more cells vented and the battery caught on fire (Reference 24).

c. On 24 February 1977 an engineer was opening a discharged experimental cell prior to post mortem examination in the Honeywell Laboratory, Plymouth Meeting, PA. The cell exploded and his hand was lacerated by the metal cell can cover (Reference 25).

d. On 11 March 1977, the battery in a Target MK38 was being discharged at about the one hour rate in the Hazeltine Laboratory, Braintree, MA. The test was stopped when the battery voltage reached 24 volts ($\sim$1.85 volts/cell). At this time the skin temperature of the target had reached an estimated 40°-$50^{\circ}C$. Shortly after the

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*Telecon between Paul Neuman, FAA Systems and Equipment Branch AFS-130, and F. M. Bowers, Code CR-33 of this Center on 2 August 1977 test was terminated the battery exploded and caught fire. The explosion was contained by the 0.105 inch thick aluminum body of the Target. The fire burned for several minutes and then went out (Reference 26).

e. During 1976 winter field tests, three Norwegian soldiers became seriously ill from inhaling the fumes after a Li/SO_2 cell vented to release internal pressure. A subsequent analysis of the cell did not disclose the cause of the malfunction (Reference 27).

f. On 21 June 1977, *Mr. J. Bene (NASA) Langley, described the results of a series of experiments on Li/SO_2 cells. "D" size cells were discharged in a -20°C constant temperature bath into reversal to simulate a weak cell in a series connected string. The discharge current was about two amperes. The voltage on reversal was a -0.4 volts with the exception of a -1.0 volt spike that occurred a short time after the cell was forced into reversal. Cells removed from the circuit and the bath after the spike, exploded within 16-30 minutes. Ten to 12 cells were tested in this way. Cells removed from the circuit and the bath before the spike, became warm but did not explode.

g. On 3 June 1977 eleven discharged experimental Li/SO_2 cells chilled to -65°F were drop tested from a height of 16 feet onto a concrete pad. Three exploded on impact with a flash of light similar to the incident reported in (c) above (Reference 28).

h. Reference 29 reports that the Canadian Transport Ministry has ordered the removal of all lithium battery powered ELT's from Canadian aircraft as a result of the explosion and venting of these batteries. The order affects about 16,000 aircraft.

With the exception of the fatality at Hill AFB, all of the preceding safety incidents involve Li/SO_2 cells and batteries. In most cases the conditions leading up to the safety incident are known but the cause is not. In no case were the tests abusive although some occurred at marginally high rates of discharge. Usually the purpose of the tests was to determine if lithium batteries could be used to power a piece of equipment. The fact that more incidents have incurred with Li/SO_2 cell and batteries is probably because they are more widely used.

The safety incidents fall in five categories:

a. cell design

b. too high a rate of discharge and/or discharge at too high a temperature.

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*Meeting between Army, Air Force, Navy and NASA on lithium battery safety at Goddard Space Flight Center on 21 June 1977.

c. reversal (weak cell in a battery)

d. incomplete development

e. miscellaneous

This report deals primarily with the safety of Li/SO_2 cells and batteries, however, several experiments on $Li/SOCl_2$ batteries merit particular attention. Reference 30 reports the results of Dey's studies on the thermal runaway encountered when $Li/SOCl_2$ "D" cells were short circuited. As a part of this work he was examining the efficiency of a low pressure vent to prevent explosions induced by cell reversal. Figure 1 shows the results of the experiment. Of particular importance are the facts that the cell was reversed a relatively short period of time; the reversal current was small; the internal pressure did not increase sufficiently to open the low pressure vent; and the cell did not get hot. In Reference 31, McCartney reports that an explosion can be prevented by the addition of sulfur monochloride (S_2Cl_2) which will dissolve the elemental sulfur (See Table 1) formed during discharge. In Reference 32, Dey reports on the results of a preliminary investigation of the system $Li/S/SOCl_2/S_2Cl_2$ using differential thermal analysis. A mixture consisting of .126gms of equal volumes of $SOCl_2$ and S_2Cl_2, 0.012gms of Li and 0.033gms of S, exploded when the temperature was raised to 256°C; and a second mixture with 0.91gms of equal volumes of $SOCl_2$ and S_2Cl_2, 0.012gms of Li and 0.031gms of S exploded at 234°C. A mixture of 0.013gms of Li, 0.045gms of S, and 0.161gms of $SOCl_2$ exploded at 204°C. Dey tentatively concluded that the S_2Cl_2 did not have a beneficial effect as a quenching agent, but is continuing his investigation using various proportions of reactants. It would be of interest to determine if the temperature difference at which the explosions occurred was due to the S_2Cl_2 reducing the activity of the sulfur or whether the S_2Cl_2 acts as a diluent.

VERIFIED USES OF LITHIUM BATTERIES BY THE FLEET. At present the Fleet use of lithium batteries is limited to those containing SO_2 cathodes, as follows:

a. ANPRC Life Raft Radio. Two "D" size cells in series.*

b. MQM-74C Target Drone. Size and number of cells is unknown (Reference 33).

c. Interactive Display Terminal (IDT) (Reference 34). Three, series connected, "D" size cells. The battery is discharged within a range of 0.16 to 6.0 watts.

d. Sonatech Transponder (Reference 34). The size and number of cells in the battery is proprietary.

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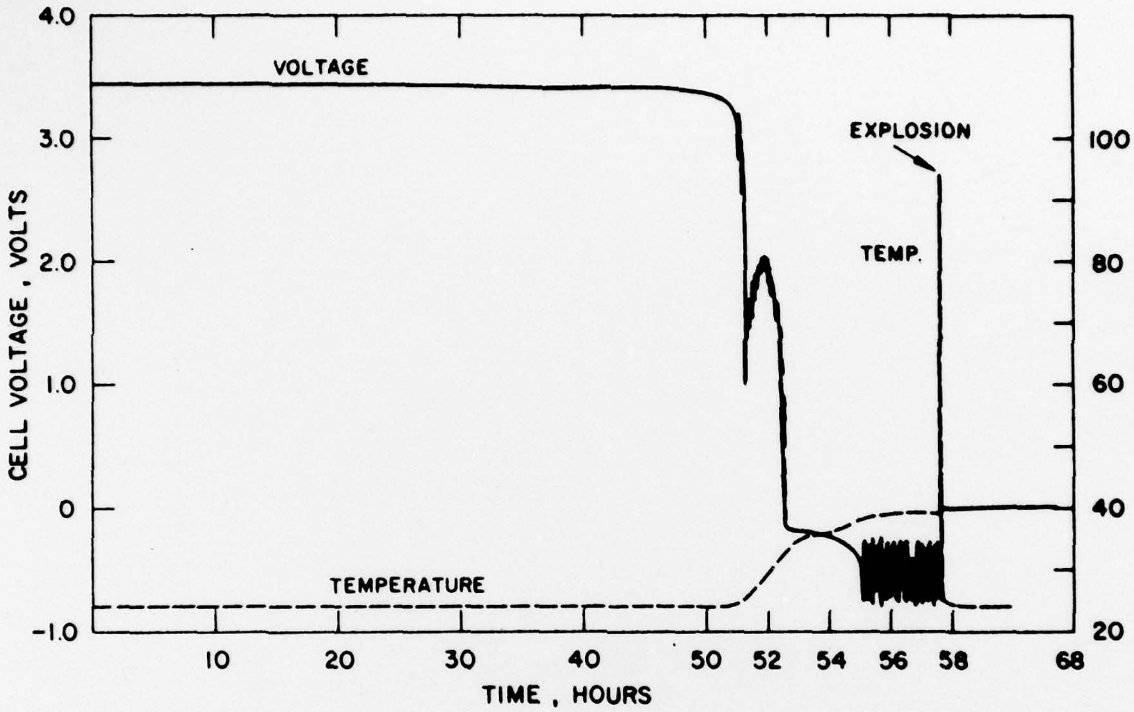
*Meeting on Lithium Battery Safety held at NAVSURFWPNCEN, 28 February 1977.



REFERENCE:
A.N. DEY, P.R. MALLORY & CO., INC.,
27th POWER SOURCES SYMPOSIUM, JUNE 1976.

FIGURE 1. *VOLTAGE AND WALL TEMPERATURE-TIME PROFILES OF* $Li/SOCl_2$ D CELLS WITH 20" ELECTRODE AND A LOW PRESSURE (120 PSIG) VENT ON OVER DISCHARGING AT A CONSTANT CURRENT OF 0.25 A.

DEVICES UNDER DEVELOPMENT. The following devices are committed to the use of lithium batteries as the power source:

a. Target MK 38. The battery consists of thirteen 7.5 ampere hour series connected cells. The battery will be discharged at about the one hour rate. This device will only be used in water and has experienced at least one safety incident when tested out of the water (Reference 26).

b. Sonobuoys*. There are at least five different sonobuoys under development that will use lithium batteries. Their operational lives will range from one to eight hours. Several will contain batteries made up of "D" size cells.

c. ASH 20 - Flight Recorder. A program is underway to replace rechargeable sealed nickel oxide/cadmium batteries with lithium/sulfur dioxide batteries.

d. Trident Buoy**. Number, size of cells and discharge requirements have not been disclosed.

e. Multi-Frequency Spot Jammer (Reference 35). This device contains a multi-section lithium battery made up of 27 "D" size cells. The major drain is 17 ampere pulses with an 80 percent duty cycle. The device is intended only for in-water use.

f. Propelled Rocket Ascent Mine (PRAM). The main battery is lithium/sulfur dioxide with a capacity of seven to eight kilowatt hours.

g. CAPTOR Mine. This mine has a special device that will use six "C" size lithium/sulfur dioxide series connected cells.

h. Underwater Device. A lithium thionyl chloride battery with capacity of 180 kilowatt hours is under development (Reference 36).

i. Underwater Propulsion Battery. The objective is to develop critical perfomance data to determine the feasibility of a design concept for a lithium/thionylchloride 16 kilowatt hour water-cooled battery to be discharged at the 10-15 minute rate. (Reference 37).

SAFE, USEFUL BATTERIES FOR THE NAVY

In fiscal 1976 NAVSEA 03 recognized that the use of lithium batteries by the Fleet was imminent; that there might be associated safety problems with their use; that a strong technology base would

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*Telecon F. M. Bowers, NAVSURFWPNCEN and W. Leupold, NAVAIRDEVCEN on 5 August 1977.

**Telecon F. M. Bowers, NAVSURFWPNCEN and P. Solarz, NUSC 23 May 1977.

be needed to provide safe lithium batteries for a wide variety of applications; that because of the complexity of the problems, the time limitations of weapons development would not permit the development of the technology during such development; and that developing the technology in one Center would eliminate time consuming and costly duplication of effort. Accordingly, the NAVSURFWPNCEN was assigned the task to develop the technology upon which the safe use of lithium batteries by the Fleet could be based. The program consists of three principal parts:

a. State of the Art

b. Experimental

c. Implementation

STATE OF THE ART. A survey has been made of the kinds of lithium batteries commercially available at present and their uses. Lithium cells are available for heart pacers, electric watches, flashlights and special instruments such as memory circuits and ELT's. Lithium/thionyl chloride, and lithium/lead sulfide cells are being used for heart pacers; lithium/sulfur dioxide cells are being used for watches; lithium/lead sulfide and lithium/sulfur dioxide batteries are being used for memory circuits; lithium/sulfur dioxide cells are being used for flashlights; lithium/manganese dioxide cells are being used for pocket calculators; and lithium/sulfur dioxide batteries are being used for ELT's. With the exception of the ELT batteries and flashlight cells which usually consist of "C" and "D" sizes, the commercial requirements are limited to small cells of the button type. The high voltage, approximately three volts per cell, and the long shelf life, are two features that are commercially attractive. The cells presently used for heart pacers, hearing aids and watches are either mercuric oxide/zinc, silver oxide/zinc or manganese dioxide zinc which have nominal cell voltage of 1.35, 1.56 and 1.50 volts respectively. Thus one lithium cell will replace two conventional cells. Lithium cells have demonstrated less of a tendency to self discharge (References 10 and 20) than conventional cells. This characteristic is extremely important in low rate discharge applications such as heart pacers where self discharge plays an important part in the performance life. When a heart pacer is powered by a lithium battery, the user will have to submit to the minor medical operation of battery replacement every five to ten years whereas mercuric oxide/zine batteries must be replaced every two years.

The survey did not reveal any safety incidents with the small cells and batteries used commercially, probably because they are discharged at low rates and the batteries contain only a few cells.

During the survey the Headquarters of the U.S. Army Electronic Command (ECOM) and Wright Patterson Air Force Base (WPAFB) were visited. ECOM is the center of all army development of batteries for communication gear. WPAFB develops most of the batteries used by the Air Force. ECOM plans to use Li/SO_2 batteries for all communication gear, but none of the lithium batteries they have developed have yet been released for general field use. The first will be the BA-5598( )/U which will be released for use in Alaska during the winter of 1977-78. ECOM is preparing a safety statement for each battery that describes to the user how and with what equipment the battery may be safely used. It also describes safe storage, handling, and disposal procedures. Batteries with cell sizes of "C", "D" and double "D" are being developed. All cells contain hermetic seals and vents. All batteries have appropriate fuses and in some cases diodes. The highest rate of discharge at present is the ten hour rate. There are some applications that require a five hour rate but whether ECOM will develop lithium batteries for them is not known.

WPAFB is developing lithium batteries for a wide range of applications. Most of these are low rate, i.e., ten hours to several months. The survey did not disclose when the batteries that are being developed will be ready for tactical use.

Practically everyone who has experimented with lithium batteries has experienced safety incidents. The fundamental causes are not known. Four methods have been used to circumvent the problems associated with safety incidents:

a. hermetic seals and vents

b. fuses

c. diodes

d. excess active materials

The early cells had crimped seals and did not have provisions for relieving the rapid rise in pressure that occurred during high rated discharges and malfunctions such as short circuits. Accordingly the various manufacturers devised vents that opened at predetermined temperatures and pressures and spewed out gases consisting of acetonitrile and sulfur dioxide. Under some conditions methane and cyanide gases may also be present (Reference 38). Venting reduces explosion hazards but the gases have caused illness when venting occurred indoors (Reference 27). Similar effects could be expected if venting occurred within the confines of a ship or submarine. In some cases venting has been accompanied by fire (Reference 22, 24, 26) which seems to be short lived but may be sufficient to ignite other flamable materials. Thus a vent has only limited value as a safety device for many Navy applications.

Fuses are used in both cells and batteries to keep them from being discharged at rates too high for safety. In batteries it is usually the practice to connect a fuse into a series connected group of cells but this does not keep a single cell in a group from overheating and venting if it develops a short circuit. Sometimes electronic equipments produce transients that place momentary high drains on the battery. Thus fuses must be selected with care so that they do not burn out and render the battery inoperable as a result of a slight malfunction of the electronic circuitry.

Diodes are sometimes used to keep a weak cell in a group from being charged by the rest of the cells. Diodes reduce the voltage and may require that additional cells be added to compensate for the drop in voltage.

The sulfur dioxide in Li/SO_2 cells prevents the lithium from reacting with acetonitrile to produce methane gas. Since the cells contain excess lithium, they also contain excess sulfur dioxide to prevent the generation of methane which in turn could build up sufficient pressure to open the vent, if the cell becomes overheated.

The industry-government survey disclosed that safety devices generally reduce the frequency of some kinds of safety incidents, but they will not be effective in all cases. The Li/SO_2 cells that exploded at NASA Langley* had vents. The $Li/SOCl_2$ cell that exploded during the reversal experiments described in Reference 30 had a vent. Although the cell that ruptured (Reference 25) did not have a vent, a small hole had been drilled through the cell case prior to the explosion, and Reference 28 indicates that such cells may be shock sensitive.

The survey also indicated that the lithium battery manufacturers have not yet come to grips with the storage of cells and batteries and disposal of scrap. Li/SO_2 and $Li/SOCl_2$ cells and batteries are generally made to order. Development of these types has not reached a point where the product is considered a commercial item and widely sold on the open market. Since production has not reached the point where large numbers of cells and batteries are being manufactured, the vendor is able to keep lot sizes small, use reactive materials rapidly, exercise close quality control, keep scrap to a minimum and ship finished work immediately after it is manufactured. The small numbers of defective cells and the small amount of scrap that cannot be reworked is disposed of by a licensed hazardous material disposal agent or by dumping into a water filled tank under controlled conditions.

EXPERIMENTAL. Figure 2 is the general experimental program that is being followed to develop the technology base that will provide safe lithium batteries for the Navy. The program is being coordinated through the Joint Logistic Chiefs Sub-Panel for Batteries and Fuel Cells to prevent any duplication of effort within the Department of Defense. Regular meetings are held with representatives from the Army, Air Force, NASA and other government agencies to keep

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*Meeting between Army, Air Force, Navy and NASA on lithium battery safety at Goddard Space Flight Center, 21 June 1977.

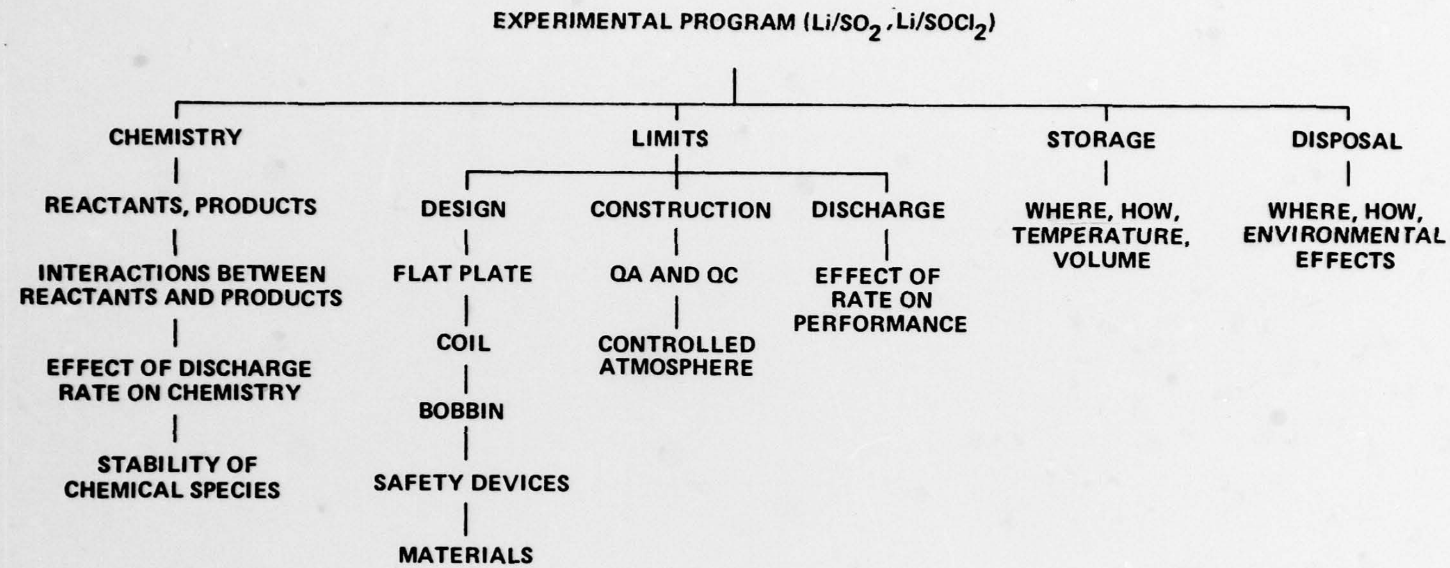

FIGURE 2. GENERAL EXPERIMENTAL PROGRAM FOR THE DEVELOPMENT OF THE TECHNOLOGY BASE NEEDED TO PROVIDE SAFE LITHIUM BATTERIES FOR THE NAVY.

abreast of the latest developments. The inter-service cooperation and pooling of ideas with other government agencies should result in solutions to common problems in the shortest period of time. Periodic contacts are also made with industry to keep abreast of their developments. They have not attended government meetings because of their restrictions on the disclosure of proprietary information.

The Navy is already using Li/SO_2 batteries in the Fleet and most of the lithium batteries that are being proposed for new applications are of that type. For that reason and also because of funding restrictions, our investigations have been limited to the Li/SO_2 electrochemical system.

Chemistry. Since a battery is a device that transforms chemical energy into electrical energy, the mechanism of energy transformation, including intermediate steps, must be known to determine if unstable products are formed and trigger the violent reactions that have been observed. At present little is known about the transformation process. Accordingly a group of exploratory experiments are being conducted on "D" size cells containing four thermocouples to determine the heat distribution within a cell during low rate and high rate discharges. One thermocouple is positioned inside the cell as close as possible to the terminal connection with the carbon electrode; the second is positioned midway between the top and bottom of the cell and also midway between the center post and the can; the third is positioned on the outside of the can immediately opposite the connection of the lithium anode to the can; and the fourth is a control thermocouple in contact with the can and positioned 180 degrees from the third thermocouple. These cells are being discharged at various rates and the temperatures recorded. Since many of the safety incidents have been accompanied by increases in temperature these experiments will indicate the location of the heat and whether it is of chemical, electrical or mechanical origin. If it is either electrical or mechanical, corrective action may lie in design modifications. If the origin is in the chemical reactions it may be necessary to limit the way the batteries are used. In any event the completion of these experiments will contribute important information on how the Navy can safely use lithium/sulfur dioxide batteries. A second group of experiments has been planned to determine what products are formed when a cell is forced discharged, and whether these products are unstable. Forced discharge happens during the deep discharge of a series connected group cells that contain a weak cell. The stronger cells force the potential of the weak cell through zero volts to some negative value. The second group of experiments will provide information on whether deep discharges can result in the formation of toxic and explosive reaction products.

Limitations. (Figure 2) The purpose of this part of the Experimental Program is to evaluate the effects of cell and battery design and construction on performance, shelf life and safety. Part of this effort will be to evaluate the stability of materials, quality assurance methods, quality control and the effectivity of safety devices.

Storage. A literature survey provided nothing on the storage of lithium batteries. Perhaps their use has been so limited that safety considerations with respect to storage have not been necessary. But the batteries are now in the Fleet and it has been established that they can explode, catch fire and release toxic gases so safe storage procedures must be developed. Considerations are:

a. Can cells and batteries be safely stored in their associated device?

b. How large a stockpile can be permitted?

c. What specific instructions should be promulgated with respect to warehouse fires? and;

d. What environmental controls are needed during storage?

Disposal. The safe, environmentally acceptable disposal of lithium batteries poses a difficult problem. As previously stated the discharged batteries contain energetic, potentially hazardous materials. Therefore, casually discarding discharged batteries in common trash containers must be avoided. The only known investigation on lithium battery disposal is reported in Reference 38. This report recommends that lithium battery disposal be limited to (1) secured landfills and (2) disposal ponds with provisions for leachate monitoring and control. The recommended disposal procedures are not suitable for many of the Navy uses, therefore, other methods are being investigated.

PROGRESS

As stated before, the Navy is the only service that is now using devices powered by lithium batteries. Although these batteries are being discharged at rates lower than the ten hour rate (generally considered safe), there are some developments where a 15 minute rate of discharge is proposed. Other investigators have reported that Li/SO_2 and $Li/SOCl_2$ batteries may be unsafe when discharged at such high rates (References 1, 9, 22, 26, 32, and 39). At present the cause of the instability is not known.

Early in this investigation it was found that the Navy lacked procedures for controlling the use of lithium batteries and as a result lithium batteries could be introduced into the Fleet without adequate safeguards. Accordingly a meeting was convened at the Naval Surface Weapons Center on 28 February 1977 to appraise cognizant safety representatives from the Naval Material Command and the Air, Sea, and Electronic System Commands of the problem. An action item from this meeting was the preparation of guidelines for the procurement, use, storage and disposal of lithium batteries (Reference 40). These will be distributed as an enclosure to a NAVSEA instruction that is now being circulated through channels for approval. The instruction designates NAVSEA 04H-3 as the focal point for lithium battery safety and requires that potential users of lithium batteries submit through their appropriate chains of command, a description of the battery and its intended application for a safety analysis. The results of the analysis together with safety recommendations will then be sent to the user. It is hoped that this procedure will minimize safety incidents in the Navy. However, the strong technology base needed to make firm recommendations has not been developed and cannot be without adequate funding.

A survey of industry and government on uses, manufacture, storage and disposal of lithium batteries has been completed. A literature search has been completed. Both surveys show that little is being done to strengthen the technology base needed by the Navy to take maximum advantage of the improved performance that can be realized from lithium batteries.

A subcommittee on lithium battery safety has been formed as a part of the Joint Logistic Chiefs Sub-Panel on Batteries and Fuel Cells. This subcommittee meets every two months to discuss safety programs and coordinate formal programs within DOD and NASA in order to avoid duplication of effort.

CONCLUSIONS & RECOMMENDATIONS

1. The Navy lacks the technology needed to insure the safe use of lithium batteries in the many, diverse proposed applications.

2. Lithium/sulfur dioxide batteries with unit cells containing vents and hermetic seals, and groups of cells containing appropriate fuses are safe when discharged at low rates under conditions that will keep the batteries cool.

3. The commercial applications such as watches, hearing aids, heart pacers and small calculators, usually use small individual cells. In some cases batteries of two or three small cells are used. The author was unable to find any safety incidents involving the cells and batteries used in these applications.

4. The military intends to use batteries containing large size cells. The maximum size presently being considered by the army is 20 ampere hours. The Navy and Air Force have battery applications that will require large cells of several thousand ampere hours.

5. The Navy has several in-water applications with high discharge rates of 15 minutes to one hour. The recovery and postmortem examination of these batteries should be avoided.

6. Storage and disposal procedures have not been developed. It might be necessary to establish accountability procedures to insure safe disposal.

7. It is strongly recommended that the Navy establish a central location to develop the necessary technology for the safe use of

lithium batteries. To attempt to develop this technology as a part of weapon developments will result in duplication of efforts, schedule slippages, and cost overruns.

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