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Lithium/Sulfur Dioxide Cell and Battery Safety

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Purpose and Scope

This handbook is intended to acquaint the user with the characteristics of lithium/sulfur dioxide (Li/SO_2) primary electrochemical cells and batteries, and to promulgate policies for their safe use, handling, storage, transportation, and disposal. The highly energetic nature of these cells requires that safeguards be employed. It is recognized that these cells and batteries represent a significant advancement in the state of the art of primary electrochemical cells; therefore, it is not the intention of this document to discourage their use, rather to educate the user in the appropriate precautions to be taken.

This document covers all applications in which lithium/sulfur dioxide high-energy density cells are used. (Lithium/thionyl chloride cells and batteries have different safety considerations and, therefore, will not be addressed in this publication.

The applications covered by this handbook include the use of individual cells, batteries, and instruments containing Li/SO_2 cells or batteries. It is desirable that the user be aware of the safety precautions and prepare a safety plan prior to the purchase or delivery of the hardware containing these items. A safety plan guideline is provided in appendix A.

Appendix B contains DOT regulations pertaining to transportation of lithium/sulfur dioxide cells and batteries. A glossary of terms is included as appendix C.

Lithium/Sulfur Dioxide Electrochemical Cells

Electrochemical cells containing lithium metal anodes and several variations of cathode materials have recently been reported and are starting to appear in the marketplace. The system containing sulfur dioxide is the subject of this document.

Advantages and Disadvantages

The Li/SO_2 system offers the following advantages:

(1) High-energy density (275 W-h/kg)
(2) High operating voltage (2.9 V/cell)
(3) Low-temperature (−40° C) operation (40 to 60 percent of capacity delivered at 25° C)
(4) Potentially long shelf life (demonstrated 3 years' storage without refrigeration)
(5) Flat discharge voltage

The following disadvantages should be considered when selecting this system for use:

(1) The cells are pressurized with 2- to 4-atm SO_2 gas, which is toxic.
(2) A high-temperature excursion caused by a very-high-rate discharge (short) can cause gas venting.
(3) High-resistance shorts (bridging) across the glass-to-metal seal inside the case have occurred during high-temperature storage.
(4) A means must be provided for safe handling and storage.
(5) The cell configurations are similar to the Leclanché dry cell types available for home use and have been inadvertently used as a replacement.

Cell Construction

The Li/SO_2 cell uses lithium metal foil as the anode and sulfur dioxide as the cathode reactant or depolarizer. The cathode itself is a Teflon-bonded porous carbon matrix pressed into a metallic screen. The matrix provides the surface at which the SO_2 is electrochemically reduced to $S_2O_4^{2-}$. The metallic screen serves as the current collector. The nonaqueous electrolyte consists of acetonitrile in which SO_2 and usually lithium bromide are dissolved. The discharge reaction in its simplest form is most often written as

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

The cell components are hermetically sealed in a nickel-plated or stainless-steel case. A glass-to-metal seal

provides the separation of the negative electrode (lithium) attached to the case and the positive electrode (carbon matrix) attached to the center post.

The cell is fabricated as a "Jelly-Roll" construction in which alternate layers of the lithium ribbon and carbon mix separated by a polypropylene separator are spirally wrapped and inserted in the case. The electrolyte/depolarizer is added through a fill-port, which is then welded closed. The finished cell contains 2- to 4-atm pressure at room temperature.

A pressure-release device is integrally built into the cell case, which irreversibly opens only when the internal pressure exceeds the vent design, typically 400 to 450 psi. This would be caused by short circuit, overdischarge, or excessive temperature. In packaging, it is essential that the vent area not be covered or sealed to prevent gas expulsion.

Design Alternatives

Unbalanced Cell

Battery manufacturers have produced cells in which the ratio of Li to SO_2 has varied. To date the most experience has been gained using the SO_2-limited (lithium-excess) unbalanced cells. The Li to SO_2 ratio has been found to be as much as 1.8 (mostly early designs). The current ratio is 1.4. However, this design has been the subject of much concern because of undesirable discharge reactions causing accidents. When the SO_2 is consumed at the end of the normal discharge, cells in series can drive a depleted cell into reversal. The cell reaction results in the electrodeposition of finely divided lithium particles, which then produce the breakdown of the acetonitrile. The resultant products are cyanide and methane. If the methane pressure gets high enough, the cells will vent—sometimes with flame.

The problems described in the preceding paragraph are avoided in cells in which the ratio of Li to SO_2 is less than 1. This design is safer; however, the performance characteristics are below that of the balanced or lithium-excess cell designs.

Balanced Cell

In the balanced cell design (lithium to SO_2 ratio of 1.0 ± 0.1), the active materials should be depleted simultaneously, thus reducing but not eliminating the hazards. In one cell design of the balanced type there is the additional consideration that the Teflon-bonded carbon matrix may be limiting the reaction. The matrix becomes saturated with reaction product, thus retarding further reaction. In this situation there may be Li and SO_2 present when the cell reaches its cutoff voltage.

Crimped Style Case

Li/SO_2 cells of early design (prior to 1979) featured the standard crimp style case, similar to that commonly used in the manufacture of dry (Leclanché) cells or alkaline cells available at many retail outlets. However, because of leakage problems with this design, its use is not recommended.

Hermetically Sealed Cell

Current cell designs include a borosilicate-glass-to-metal terminal that, together with the steel or stainless-steel welded case, provides a hermetically sealed cell safer and longer lasting than the early designs.

High Rate Cell

The internal cell design may vary with respect to the electrode surface area, which can affect discharge rate capability. The "high rate" design uses a larger number of thinner plates to provide greater surface, thus increasing the capability for a cell to be discharged at a higher rate. This design has been used for high-current-pulse applications.

Configurations

The cells are available in typical cylindrical sizes (e.g., "A," "B," "C," and "D") or fractional sizes (e.g., "¼C," "AA," and "DD"). The larger the cell the greater the capacity at the same voltage.

Potential Hazards

The following are the dangers associated with the indiscriminate handling, storage, use, and disposal of Li/SO_2 cells and batteries:

(1) Venting and expulsion of SO_2 gas and electrolyte, which is noxious to the eyes and mucous membranes of the nasal passages and mouth, and is a respiratory irritant. Venting may be caused by a high rate of discharge (shorting), overdischarge, or excessive temperature exposure.

(2) Violent explosion and fire of near fully discharged,

shorted, or overdischarged cells that were abused either thermally by external heating, electrically by charging, or mechanically by crushing or puncturing.

(3) Production of small quantities of cyanide and methane in an SO_2-limited cell (excess lithium) by the reaction of the acetonitrile solvent with lithium. Venting of a cell could expose workers to cyanide, which can evolve as an aerosol, and methane gas in limited quantities.

Safety Precautions Checklist

The hazards of Li/SO_2 cells and batteries can be prevented by observing the safety procedures described in this document. The following lists will aid in determining when appropriate precautions are necessary.

Cells—Nonoperational

(1) The balanced-cell or lithium-limited design is preferred except when specific requirements dictate an alternative, and then only with safety plan approval.

(2) Each cell shall be hermetically sealed and equipped with a venting device to relieve cell pressure if it exceeds design limits.

(3) To avoid catastrophic rupture, insure that the vent device is not encased and that gas products can be dissipated.

(4) Primary cells of the Li/SO_2 type shall not be charged.

(5) Positive steps must be taken to assure that there is no external mechanical or electrical bridging of positive and negative electrodes to avoid direct or high-resistance shorting.

(6) Dispose of cells that are leaking or deformed or the open circuit of which is less than 2.8 V when measured with a high-impedence voltmeter. (See last section of this handbook entitled "Disposal.")

(7) Avoid placing cells in storage environments (1 yr) where the temperature is greater than 45° C for extended periods. A 60° C limit shall not be exceeded in storage areas. Any significant increase in temperature will result in a capacity-loss and/or internal bridging of the glass-to-metal terminal or venting.

(8) Lithium cells and batteries shall not be discarded with general trash, or incinerated. (See last section entitled "Disposal.") Each cell must be protected against puncturing, crushing, denting, or any other physical deformation.

(9) Leaking cells shall be handled only when wearing rubber apron and gloves and a full faceshield, placed in plastic bags, and removed to a suitable storage or disposal area. (See section of this handbook entitled "Handling.")

(10) All cells must be electrically insulated from one another.

(11) Use first article buyoff, screening, selection, and acceptance-testing to minimize manufacturing inconsistency resulting in cell divergence.

(12) Insist that the manufacturer define and document the process used to improve the batch repeatability.

Cells—Operational

(1) Terminate discharge when cell voltage drops to 2.0 V (except for pulse or low-temperature operation when its use is approved).

(2) Minimize rate of discharge wherever possible. The maximum should not exceed the 10-h rate ($C/10$).

(3) To optimize cell use, maintain the operating temperature in the range of $-10°$ to 40° C.

(4) Avoid heat accumulation around cells by providing adequate heat transfer away from cells. Excessive heat can cause cell venting. The maximum surface temperature must not exceed 60° C.

Batteries

In addition to the measures previously listed for each cell, the following additional precautions are applicable to a battery of Li/SO_2 cells (an approved safety plan shall describe the intended design and use):

(1) To protect against an excessive or inadvertent high rate discharge, each battery shall be fused, preferably in the ground leg. For multivoltage designs each tap shall be fused in the positive leg in addition to fusing in the ground leg.

(2) In the battery where parallel strings are used, each string must contain a diode to avoid discharge if there is a short in another string.

(3) Bypass diodes have been considered for each cell to avoid overdischarge or reversal. Because the diodes draw current they will themselves discharge the cells. For this reason and because diodes are unreliable in general, they are not recommended for use except where absolutely necessary and then when reverse-leakage current is determined.

(4) To avoid venting, a thermal switch can be used in

such a way that it opens the electrical circuit and terminates discharge when the temperature exceeds 85° C. Switch closure is to occur at 60° C.

(5) Discharge of a battery of balanced cells without cell voltage monitoring or control capability shall be terminated when the average cell voltage drops to 2.0 V.

(6) Batteries shall be packaged so that there is sufficient and proper insulation between cells and leads to avoid cell-to-cell contact and shorting.

(7) The application shall dictate whether the battery case must be designed to contain vent products if cell venting occurs.

(8) Backfilling of pressurized sealed battery packs shall be accomplished with dry argon or dry air.

Purchasing Requirements

Safety Plan

A safety plan (app. A) shall be prepared that describes the specific item and details of the intended use, handling, storage, transportation, and disposal of Li/SO_2 cells and batteries. It is desirable that the plan accompany the procurement documents and be approved prior to contract award. Implementation of the plan can best be accomplished if it is approved prior to approval of purchase.

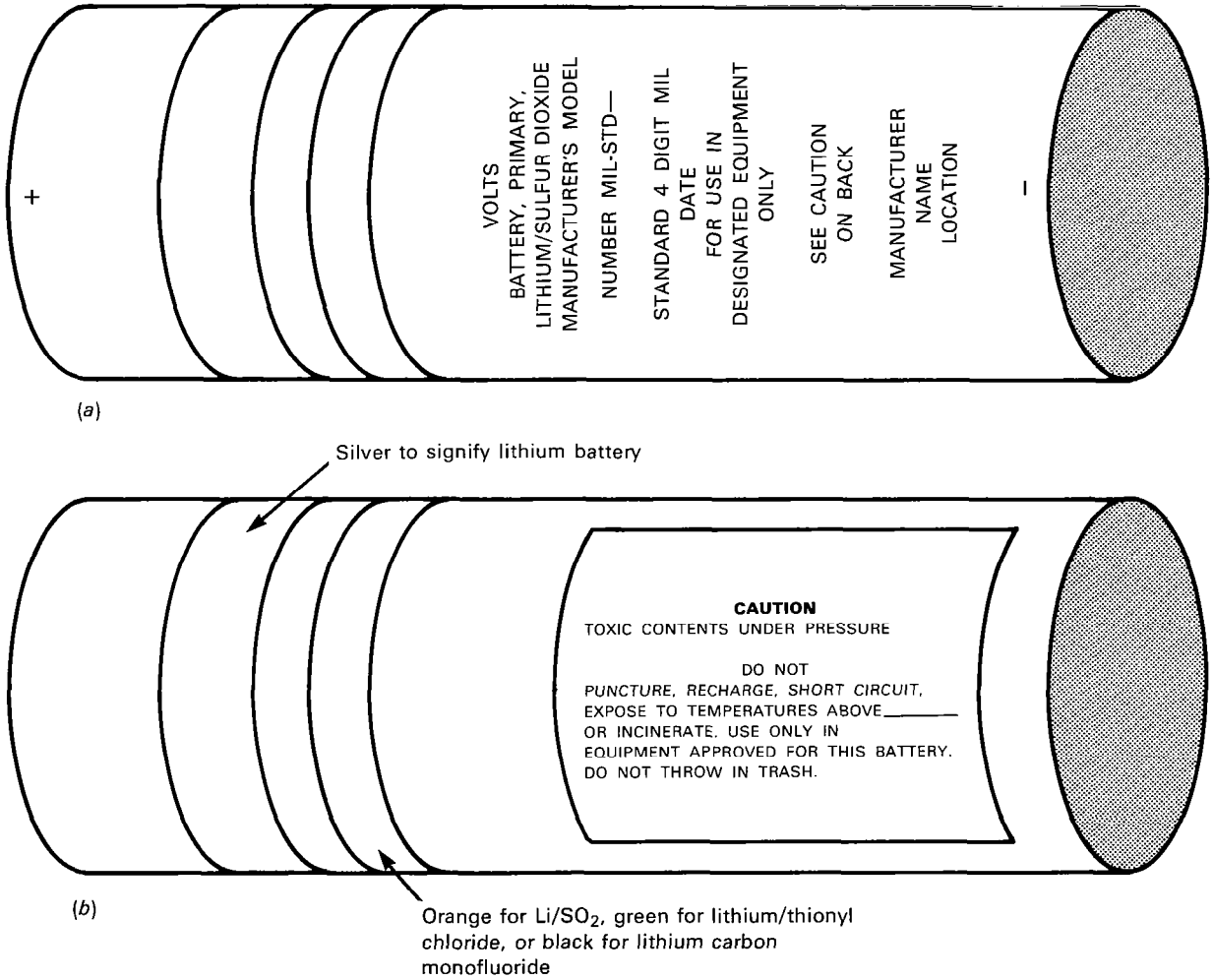

Figure 1. Battery labeling. (*a*) Front. (*b*) Back.

Labeling

All packages containing lithium cells or batteries shall be marked per Department of Transportation requirement DOT-E 7052 (app. B). This involves a "FLAMMABLE SOLIDS" label (red and white).

Each container shall be clearly marked with the statement "Batteries [or cells] containing lithium metal." Each cell shall be marked as given in figure 1. Batteries and balloon payload packages shall be marked with similar appropriate information.

Recommended Manufacturer Requirements

Cells, Batteries, and Instruments

The manufacturer must provide a complete description of the cell and battery design including type of cell and coulombic ratio of active materials. The manufacturer shall be required to meet all safety, labeling, handling, and transportation requirements described in this document.

Cells and Batteries for Balloon and Flight Experiments

A qualification plan to assure quality and uniformity of the product must be developed. The specific items to be addressed depend on end use. Suggested tests include the following:

(1) First article inspection
(2) Cell lot inspection/sampling plan
(3) Capacity tests
(4) Storage tests
(5) Drop test
(6) Pulse test
(7) 160° F storage test
(8) Criteria for acceptance
(9) Incineration
(10) Short circuit
(11) Reverse discharge
(12) Environmental

Use

Inappropriate or careless application of lithium cells or multicell batteries has resulted in venting of internal gases, explosions, and fires. For this reason, use of lithium cells or batteries shall be limited to appropriate engineering applications. Prior to acquisition of lithium cells, the physical, chemical, and thermal environment anticipated in service life shall be defined. This definition shall include system design data including current drain, spatial configuration, safety features to be employed, and a synopsis of cell-routing from initial procurement to final disposition. The safety plan guideline (app. A) shall be completed and approved prior to procurement.

Manufacturers of lithium cells are cognizant of the potential hazard under certain conditions and have, therefore, incorporated various safety features into both individual cells and multicell batteries. Under no circumstances should these safety devices be bypassed or compromised by spatial configuration in any service packages. To insure the integrity of the safety devices, it is recommended that, whenever possible, completely assembled batteries be obtained from a battery manufacturer. In instances where battery procurement from a manufacturer is not possible, assembly shall be performed by personnel who have been fully briefed on the hazards of lithium cells. If this is done, the battery must be tested in accordance with DOT-E 7052, paragraphs 7*g* and 7*h*. (See app. B.)

It is desirable for the appropriate safety office to review and approve all uses of lithium cells and batteries, their storage, and related equipment as well as their disposal and waste products. If preassembled battery packs using lithium cells are obtained, review of the design and verification of the use of appropriate safety devices (vents, fuses, and diodes) shall be ascertained.

The certification of each cell and battery for each application testing and use shall accompany the cell and battery at all times throughout all phases of testing and use.

Handling

New Cells or Batteries

Four major cautions must be emphasized in handling a usable lithium cell or battery:

(1) The cell casing must be protected from fracture, puncture, or shearing. Liberation of internal components of the lithium cell poses the threat of fire, explosion, and toxic or physical effects to personnel in close proximity to the damaged cell or battery.

(2) Excessive temperature excursions caused by discharge of the cells at high rate ($>C/10$) must be avoided. Operating under conditions of high ambient temperature or in situations where thermal dissipation is minimized can result in excessive heat in cell(s). Sulfur dioxide can reach significant pressures quickly. The result is a venting of the SO_2 and electrolyte.

(3) Under no circumstances shall lithium cells or batteries be handled, placed, or transported with flammable liquids or gases or a significant concentration of flammable fumes.

(4) Bridging (shorting) the case (anode) to the center post (cathode) with either a metal tool, equipment chassis, or another cell casing must be avoided. Arcing at the anode can generate sufficient instantaneous heat to initiate battery venting, or, at the least, cause reduced service life of the cell. This situation can be avoided by keeping individual cells separated to avoid cell-to-cell contact.

Testing benches shall be constructed or covered with nonconductive materials. Cells shall also be kept clear of random, stray, or waste wiring and cable or nonessential tools. Multicell batteries shall be equipped with nonconductive terminal caps until they are installed or placed in service. Batteries shall contain cells the cases of which are electrically isolated from one another and that have leads placed so that they cannot work their way through the insulation during handling and vibration.

Discharged or Inoperative Cells and Batteries

Cells and batteries that have been used or stored for significant periods of time must be disposed of in the appropriate manner. Caution shall be a chief consideration in all handling operations. To prepare for disposal and shipment, disconnect all electrical leads and allow cells to stand in a well-ventilated area for a minimum of 24 h to reduce activity of materials. Refer to the last section of this document entitled "Disposal" for more detailed requirements and procedures.

Storage

The requirements set forth in this section are intended for designated user storage areas; however, it is important that temperature be controlled under 50° C and ventilation be provided in any area where batteries are handled or used.

Lithium cells and batteries shall be stored in their original shipping containers in a cool, dry location away from personnel or vehicular trafficways. If original shipping containers are not available, storage containers should be obtained. These containers should be of strong fiberboard, wood, plastic, metal drums, or other approved material. Individual cells and batteries shall be sealed in plastic and these inner containers shall be surrounded with a minimum of 1 in. of vermiculite on all sides. Containers shall also be equipped with nonconductive dividers to prevent cell-to-cell or battery-to-battery contact.

The storage area shall have adequate ventilation to prevent buildup of sulfur dioxide fumes in excess of 5 ppm.

Storage areas shall be temperature controlled; temperatures above 50° C shall be avoided. No other materials commodity shall be stored in the same area with cells or batteries. Smoking shall be strictly prohibited in cell and battery storage locations with "No Smoking" signs posted in all prohibited areas.

It is desirable that the storage facilities and firefighting provisions be reviewed and approved prior to placement of lithium cells in any area. Once the storage area is approved and established, the quantity of cells and batteries that are added to or removed from storage must be monitored. Significant (more than 10 percent) increases in the volume of stored cells shall be noted so that any necessary additional provisions or alterations to the storage area or its firefighting equipment can be made.

Fire Protection

A graphite-type compound or extinguisher such as Lith–X–type (class D) will extinguish burning lithium. Carbon dioxide and dry chemical extinguishers have been found to be ineffective in such fires and may, in fact, tend to compound the problem of extinguishing the fire. Special instructions on the use of class D extinguishers should be issued as the operating techniques differ from those associated with other types of extinguishers. "Hands on" instruction is necessary for a reliable safety program.

Although lithium reacts when water is applied, sprinkler systems are approved for areas where lithium batteries are stored and used. Should a fire involving lithium batteries generate sufficient heat to activate a sprinkler system, it is considered the best course of action to let the lithium expend itself and allow the sprinklers to "flood" the surrounding area. This will cool the batteries and surrounding combustibles, thereby minimizing further cell venting and propagation of the fire to other areas.

All areas where lithium batteries are stored or used shall be equipped with a class "D" extinguisher. In the event that a class "D" is not available for any reason, a water extinguisher may be used, but efforts should be aimed at preventing the spread of fire to other combustibles and not directed on the burning lithium cells.

Transportation

Transportation of lithium cells or batteries by motor vehicle, rail freight, cargo vessel, and "cargo only" aircraft has been authorized by the Department of Transportation under DOT Exemption DOT-E 7052 (app. B). Cells or batteries will not be shipped or transported as part of an experiment or in other instruments or equipment unless approved in the safety plan. Cells and batteries must be packaged in compliance with DOT-E 7052. Future revisions shall be adopted as they become approved. Inspection and transportation shall be accomplished by the appropriate review and approval authority.

Disposal

Potentially Hazardous Cells and Batteries

If any potentially hazardous cell or battery (see app. C) is discovered, the individual shall clear the area, contact the appropriate safety office, and furnish the following information:

(1) Type of cell:
   (*a*) Lithium/sulfur dioxide
   (*b*) Lithium/thionyl chloride
   (*c*) Other lithium type
(2) Manufacturer, model number, lot number, or other pertinent identification on battery
(3) Number of cells and batteries
(4) Physical dimensions of cell or battery
(5) Ampere-hour capacity of cell or battery and nominal voltage of the item
(6) Case style:
   (*a*) Crimped jacket
   (*b*) Hermetically sealed
   (*c*) Other
(7) Specific condition of cell or battery; e.g., charged, partially discharged, or fully discharged

The safety office should come to the scene and assess the degree of hazard and arrange for and monitor the packing, crating, and transportation operations to the waste storage facility.

The safety office shall then arrange for the battery or cell to be transported to the waste disposal contractor.

Other Cells and Batteries

Cells and batteries that are judged to be in good condition but are no longer required shall be handled in the following manner:

(1) The cells and batteries shall be packed in accordance with DOT-E 7052 (app. B).

(2) The user shall furnish the information outlined in the preceding subsection entitled "Potentially Hazardous Cells and Batteries."

(3) The user shall call the transportation office to schedule a pickup time and date.

(4) The transportation office will coordinate delivery of the packaged cells and batteries to the waste storage area to await transportation to the waste disposal contractor.

APPENDIX A

Safety Plan Guideline

SOURCE

Submitted by _____ Phone _____

Division _____ Building _____ Room _____

ITEM (*check appropriate entries*) _____ Cells _____ Batteries

Delivered: _____ As a component _____ In an instrument

DESCRIPTION

Manufacturer _____

Location _____

Model/designation _____ Cell _____ Battery

Total number _____ Cell _____ Battery

Capacity (A-h) at _____ rate _____ Cell _____ Battery

Voltage _____ Cell _____ Battery

Size _____ Cell _____ Battery

Weight _____ Cell _____ Battery

Weight of lithium, grams per cell or battery _____

Additional information to be provided:

(1) Physical design (sketch or diagram including cell design)

(2) Description of use (include operating procedures and contingency plans for safe use and handling)

(3) Description of transportation procedures

(4) Description of storage area

(5) Planned storage time and intended use date

(6) Disposal procedures

(7) A list of manufacturer tests and criteria for acceptance

APPENDIX B

*DOT-E 7052 (9th Revision)**

DEPARTMENT OF TRANSPORTATION
RESEARCH AND SPECIAL PROGRAMS ADMINISTRATION
WASHINGTON, D.C. 20590

1. Power Conversion, Inc., Mount Vernon, New York, is hereby granted an exemption from those provisions of this Department's Hazardous Materials Regulations specified in paragraph 5 below to offer packages prescribed herein of a certain flammable solid for transportation in commerce subject to the limitations and special requirements specified herein. This exemption authorizes the shipment of lithium batteries and provides no relief from any regulation other than as specifically stated. Each of the following is hereby granted the status of a party to this exemption:

Honeywell Incorporated, Horsham, Pennsylvania - PTE-1.
Duracell International Inc., Elmsford, N.Y. (formerly Mallory Battery Co., Tarrytown, N.Y.) - PTE-2.
Eagle-Picher Industries, Inc., Joplin, Missouri - PTE-3.
GTE Products Corp., Needham Heights, Massachusetts - PTE-4.
U.S. Department of Defense, Washington, D.C. - PTE-5.
Ray-O-Vac Corporation, Madision, Wisconsin - PTE-6.
Department of Energy, Washington, D.C. (including its contractor Sandia Laboratories, Albuquerque, New Mexico) - PTE-7.
National Aeronautics and Space Administration, Washington, D.C. - PTE-8.
The Boeing Company, Seattle, Washington - PTE-9.
Battery Engineering, Inc., Newton, Massachusetts - PTE-10.
Jet Propulsion Laboratory, Pasadena, California - PTE-11.
Texas Instruments Inc., Dallas, Texas - PTE-12.
Ocean Research Equipment, Inc., Falmouth, Massachusetts - PTE-13.
Bunker Ramo Corporation, Westlake Village, California - PTE-14.
Environmental Device Corporation, Marion, Massachusetts - PTE-15.
Gould Inc., Andover, Massachusetts - PTE-16.
Panasonic Company, Secaucus, N.J. - PTE-17.
Matsusita Battery Industries Co., LTD., Osaka, Japan - PTE-18.
Electrochem Industries, Inc., Clarence, N.Y. - PTE-19.
Reach Electronics, Inc., Lexington, NE - PTE-20.
Tadiran, Israel Electronics Industries, Ltd., Rehovot, Israel (U.S. Agent: Plainview Electronics Corp., Plainview, N.Y.) - PTE-21.
EG&G Environmental Equipment, Herndon, Va. - PTE-22.
Sonatech, Inc., Goleta, Ca. - PTE-23.

*The 10th Revision is now in effect. Text is the same as the 9th Revision. Expiration date of 10th Revision is April 1984.

Hercules Incorporated, Wilmington, Delaware - PTE-24.
Altus Corporation, Palo Alto, Ca. - PTE-25.
Raytek Incorporated, Mountain View, Ca. - PTE-26.
Wilson Greatbatch Ltd., Clarence, N.Y. - PTE-27.
General Electric Company, Gainesville, Fl. - PTE-28.
Rockwell International Corporation, Anaheim, Ca. - PTE-29.

2. BASIS. This exemption is based on Power Conversion's application dated March 31, 1980, submitted in accordance with 49 CFR 107.103 and Department of the Army's application dated January 10, 1978, submitted in accordance with 49 CFR 107.103. The granting of party status is based on the following applications submitted in accordance with 49 CFR 107.111 and the public proceeding thereon:

Honeywell Inc.'s application dated March 7, 1980.
Duracell International Inc.. (formerly Mallory Battery Company's) application dated October 16, 1978, June 7, 1979 and January 31, 1980, and July 22, 1980.
Eagle-Picher Industries, Inc.'s application dated September 28, November 4, and April 24, 1980.
GTE Products Corporation's application dated April 7, 1980.
U.S. Department of Defense's application dated March 24, 1980.
Ray-O-Vac Corporation's application dated February 7, 1980, and July 23, 1980.
Department of Energy's application dated March 26, 1980.
National Aeronautics and Space Administration's application dated February 27, 1980.
The Boeing Company's application dated February 29, 1980.
Battery Engineering, Inc's application dated March 18, 1980.
Jet Propulsion Laboratory's application dated February 12, 1980.
Texas Instruments, Incorporated's application dated April 17, 1980.
Ocean Research Equipment, Incorporated's application dated September 10, 1979
Bunker Ramo Corporation's application dated October 15, 1979.
Environmental Devices Corporation's application dated November 29, 1979.
Gould, Incorporated's application dated March 27, 1980.
Panasonic Company's application dated May 15, 1980.
Matsusita Battery Industries Company Limited's application dated May 15, 1980.
Electrochem Industries, Incorporated's application dated May 19, 1980.
Reach Electronics, Incorporated's application dated January 28, 1980.
Tardiran, Israel Electronics Industries, Ltd's application dated May 14, 1980
EG&G Environmental Equipment's application dated May 28, 1980
Sonatech, Incorporated's application dated June 4, 1980
Hercules Incorporated's application dated June 10, 1980
Altus Corporation's application dated June 25, 1980
Raytek Incorporated's application dated June 25, 1980
Wilson Greatbatch Limited's application dated June 25, 1980
General Electric Company's application dated June 25, 1980
Rockwell International Corporation's application dated June 18, 1980

3. HAZARDOUS MATERIALS (Descriptor and class). Lithium batteries and cells containing metallic lithium, vanadium pentoxide, monofluorographite, sulfur dioxide, lithium bromide salts, acetonitrile, or mixtures of acetonitrile and propylene carbonate; also lithium batteries and cells containing lithium metal, a depolarizer such as thionyl chloride or sulphuryl chloride and a lithium salt such as lithium tetrachloroaluminate or lithium perchlorate - classed as flammable solid; devices containing

lithium batteries specifically identified to, and acknowledged in writing by, the Office of Hazardous Materials Regulation (OHMR), prior to the first shipment.

This exemption does not authorize the transportation of cells containing lithium metal which have been discharged to the extent that the open circuit voltage is less than two volts, or batteries containing one or more such cells.

4. PROPER SHIPPING NAME (49 CFR 172.101). Lithium batteries.

5. REGULATION AFFECTED. 49 CFR 172.101, 175.3.

6. MODES OF TRANSPORTATION AUTHORIZED. Motor vehicle, rail freight, cargo vessel and cargo-only aircraft.

7. SAFETY CONTROL MEASURES. Packaging prescribed is as follows:

a. Cells and batteries must be packed in strong inner fiberboard containers limited to a maximum of 500 grams of lithium in one inner container. No cell containing more than 12 grams of lithium may be shipped under this exemption.

b. When drums are used, the inner containers must be separated from each other and all inner surfaces of the drum by at least one inch thickness of vermiculite or other equivalent noncombustible cushioning materials.

c. Inside boxes must be further overpacked as specified in paragraphs (8c) or (8d).

d. Packages must be marked as prescribed in subpart "D" of 49 CFR Part 172. Packages must be labeled with the FLAMMABLE SOLID label shown in 49 CFR 172.420.

e. Each cell and battery must be equipped with an effective means of preventing external short circuits.

f. Each cell and battery must incorporate a safety venting device or be designed in such a manner that will preclude a violent rupture under any condition incident to transportation such as a "dead short" or involvement in a fire. The design of cells and batteries not equipped with a safety venting device must be specifically identified to this office prior to the first shipment of package. Batteries containing cells or series of cells connected in parallel must be equipped with diodes to prevent reverse current flow.

g. Three representative cells must be taken from each week's production of each cell type and be subjected to the test prescribed in section 3.2.1(l) of Appendix B, Report ECOM730242F on file with the OHMR.

h. One representative battery must be taken from each week's production of each battery type and must be subjected to the test prescribed in Section 3.3.2(l) of the above referenced report.

i. At least 10 cells and one battery of each type of each week's production must be subjected to a thermal stability test at 75°C. for 48 hours and show no evidence of distortion, leakage or internal heating.

8. SPECIAL PROVISIONS.

a. Persons who receive cell and batteries covered by this exemption may reship them pursuant to the provisions of 49 CFR 173.22a in any of the packagings authorized in this exemption including those in which they were received.

b. A copy of this exemption must be carried aboard each vessel and aircraft used to transport packages covered by this exemption.

c. For shipment by cargo-only aircraft, the outside container must be a removable head drum of the DOT Specification 17H or 17C series (or equivalent) and be equipped with a gastight gasket.

d. For shipment by water, motor vehicle, rail freight, the outside container must be either (1) strong wooden box, (2) DOT Specification 12B fiberboard box (or equivalent), (3) DOT Specification 21C fiber drum, or equivalent, or (4) metal drum as authorized in paragraph (c) above.

e. Cells containing no more than 12 grams of lithium metal and also containing acetonitrile and sulfur dioxide, and which are hermetically sealed, and batteries constructed of such cells, are excepted from the requirements of 7.g., 7.h., 7.i. and 8.c., of this exemption when in compliance with the following:

Prior to the first shipment, 10 cells or 4 batteries of each type to be offered for transportation must be tested as follows, without showing any evidence of out-gassing, leakage, loss of weight, or distortion:

i. The cells or batteries shall be stored for 6 hours at a pressure corresponding to an altitude of 50,000 feet at 24°C ± 4°C.

ii. The cells or batteries shall then be subjected to the thermal stability test at 75°C for 48 hours as required in paragraph 7.i.

iii. The cells or batteries shall be rigidly clamped to the platform of a vibration machine. A simple harmonic motion having an amplitude of 0.03 inch (0.06 inch maximum total excursion) shall be applied. The frequency shall be varied at the rate of 1 cycle per second per minute between the limits of 10 and 55 cycles per second. The entire range of frequencies and return shall be traversed in 95 ± 5 minutes for each of three mutually perpendicular mounting positions of the battery and two perpendicular positions of the cells. One of the directions of vibration shall be perpendicular to the terminal face of the battery or cell. Open circuit voltage shall be observed for 30 seconds during the last quarter of each vibration period. Periodic retesting is not required.

iv. The batteries (not cells) must be subjected to a shock test as follows:

The battery shall be secured to the testing machine by means of a rigid mount which will support all mounting surfaces of the battery. Each battery shall be subjected

to a total of three shocks of equal magnitude. The shocks shall be applied in each of three mutually perpendicular directions. Each shock shall be applied in a direction normal to a face of the battery. For each shock, the battery shall be accelerated in such a manner that during the first 3 milliseconds the minimum average acceleration is 75 gravity units (G). The peak acceleration shall be between 125 and 175 G. Cells and batteries meeting the requirements of this paragraph must be packaged in accordance with 7.a., and 8.d. of this exemption.

f. Packagings or shipping paper bearing the former proper shipping name "Lithium metal in cartridges" or "Batteries containing lithium metal" prior to the issue date of the sixth revision may be used until stocks are depleted.

9. REPORTING REQUIREMENTS.

a. Any incident involving loss of contents of the packages must be reported to the OHMR as soon as practicable.

b. Application for renewal of this exemption must include test data obtained under 7.g., 7.h., and 8.e. This data must also be made available upon request by the OHMR.

10. EXPIRATION DATE. May 15, 1982.

Issued at Washington, D.C.:

J. R. Grothe for

29 AUG 1980
(DATE)

Alan I. Roberts
Associate Director for
Hazardous Materials Regulation
Materials Transportation Bureau

Address all inquiries to: Associate Director for Hazardous Materials Regulation, Materials Transportation Bureau, Research and Special Programs Administration, U.S. Department of Transportation, Washington, D.C. 20590. Attention: Exemptions Branch.

Dist: USCG, FAA, FHWA, FRA

APPENDIX C

Glossary

Battery components or constituents—All internal and external parts of a lithium battery including lithium cells, fuses, diodes, and accessory wiring or circuiting contained in a battery pack.

Cell components or constituents—All internal and external parts of a lithium cell including the anode, cathode, and outer jacket.

Discharge rate—The current associated with the number of hours required to discharge a cell to the **end-of-discharge voltage.** For example, the 100-h rate for a 10-A cell would be a current of 0.1 A. The equation $C/n = I$ (where C is the **rated cell capacity,** n is the number of hours required, and I the rate) can also be used to designate rate. The term $C/100$ has the same meaning as the 100-h rate.

Disposal—Removal of cells or batteries from the area of use in an approved and safe manner.

End-of-discharge or cutoff voltage—The voltage at which the anode or cathode active material is near depletion. The minimum discharge voltage shall be 2.0-V/cell average except in high-current-pulse or low-temperature applications where it can be lower.

Fully discharged cell or battery—A cell or battery having a voltage equal to or less than the **end-of-discharge voltage** as established by testing or less than the **open-circuit voltage** when disconnected from a load.

Handling—The actual physical transfer or movement of batteries including such activities as loading and unloading of batteries from transport vehicles, installation or removal from service packages, and activities relating to segregation and placement in storage.

Lithium anode—Elemental lithium (Li) in pure form attached internally to the cell case. During discharge it produces lithium ions (Li^+), thus releasing electrons to support the load. In so doing it performs as the negative electrode.

Lithium/SO_2 battery—A group of one or more cells electrically connected in series or parallel combinations. These cells constituting a battery may, depending on application, be installed in an outer casing having its own electrical connectors to prevent SO_2 venting into manned compartments. It is desirable for safety purposes to restrict battery size to 10 cells. The design and intended use of any battery in which the number of cells is 10 or greater in series or parallel circuits shall be reviewed prior to use.

Open-circuit voltage (OCV)—The voltage of a cell or battery when disconnected from a load. Any cell the OCV of which is less than 2.8 V at ambient conditions when measured with a high impedance voltmeter shall be submitted for disposal.

Potentially hazardous cells and batteries—Cells or batteries in one of the following conditions:

(1) Are of nonvented case style construction
(2) Are of an unapproved design
(3) Are of crimp-style case construction
(4) Are of an unidentifiable type
(5) Are of unidentifiable construction (e.g., corroded or encapsulated to hide construction features)
(6) Have been physically abused (e.g., dropped, crushed, sheared, or punctured)
(7) Have seen operational abuse (e.g., high rate of discharge, shorted, or anomaly during testing)
(8) Are leaking, corroded, or bulged

Rated capacity—The number of ampere-hours the manufacturer has designated that a cell can produce to the **end-of-discharge voltage,** usually at the 100-h ($C/100$) rate.

SO_2/carbon cathode—A Teflon-bonded carbon structure at which the sulfur dioxide (SO_2) reacts with the electrons from the anode to produce dithionite ion ($S_2O_4^{2-}$). As such it is the positive electrode attached to the center post of the unit.

Storage containers—Boxes, drums, or other cartons used to hold cells or batteries (either prior to use or disposal), that isolate batteries from environmental stress and maintain cells and batteries in a safe and orderly fashion.

Transport—Shipment to or from an installation, not including movement of cells or batteries at a particular site.

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15. Supplementary Notes

16. Abstract

The new high-energy lithium/sulfur dioxide primary electrochemical cell, having a number of advantages, has received considerable attention as a power source in the past few years. With greater experience and improved designs by the manufacturers, this system can be used in a safe manner provided the guidelines for use and safety precautions described herein are followed. In addition to a description of cell design and appropriate definitions, there is a safety precautions checklist provided to guide the user. Specific safety procedures for marking, handling, transportation, and disposal are also given, as is a suggested series of tests, to assure manufacturer conformance to requirements.

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