Primary Battery Design and Safety Guidelines Handbook

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Preface

This handbook is for use by engineers and safety personnel as a guide to the safe design, selection, and use of the types of primary batteries used in National Aeronautics and Space Administration flight applications. The draft of the handbook was reviewed by members of the NASA Aerospace Flight Battery System Steering Committee and a number of Johnson Space Center Engineering, Quality, and Reliability offices. Most of the suggestions received have been incorporated into the final copy.

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First Aid for Exposure to Electrolytes

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<td>ABS</td>
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<td>ACRV</td>
<td>Assured Crew Return Vehicle</td>
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<tr>
<td>CDTR</td>
<td>cassette data tape recorder</td>
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<tr>
<td>CFES</td>
<td>continuous flow electrophoresis system</td>
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<tr>
<td>CFR</td>
<td>Code of Federal Regulations</td>
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<tr>
<td>CH₃CN</td>
<td>acetonitrile</td>
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<tr>
<td>(CH₃O)₂SO</td>
<td>dimethyl sulfite</td>
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<td>CIL</td>
<td>critical items list</td>
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<td>CMOS</td>
<td>complementary metal oxide silicon</td>
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<td>DOT</td>
<td>Department of Transportation</td>
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<td>EMF</td>
<td>electromotive force</td>
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<td>EMU</td>
<td>extravehicular mobility unit</td>
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<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
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<td>EVA</td>
<td>extravehicular activity</td>
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<td>FMEA</td>
<td>failure mode and effects analysis</td>
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<td>FS</td>
<td>fail-safe</td>
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<td>current</td>
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<td>IATA</td>
<td>International Air Transport Association</td>
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<td>ICAO</td>
<td>International Civil Aviation Organization</td>
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<td>IEC</td>
<td>International Electrotechnical Commission</td>
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<td>JSC</td>
<td>Lyndon B. Johnson Space Center</td>
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<td>KOH</td>
<td>potassium hydroxide</td>
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<td>LBB</td>
<td>leak-before-burst</td>
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<td>LDEF</td>
<td>Long Duration Experiment Facility</td>
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<td>Li-(CF)ₙ</td>
<td>lithium-polycarbon monofluoride</td>
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<td>Li-BCX</td>
<td>lithium-thionyl chloride/bromide chloride complex</td>
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<td>Li-FeS₂</td>
<td>lithium-iron disulfide</td>
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<tr>
<td>Li-I₂</td>
<td>lithium-iodine</td>
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<tr>
<td>Li-MnO₂</td>
<td>lithium-manganese dioxide</td>
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<td>Li-SO₂</td>
<td>lithium-sulfur dioxide</td>
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<td>Li-SOCl₂</td>
<td>lithium-thionyl chloride</td>
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<td>Li₂S₂O₄</td>
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<td>LiAsF₆</td>
<td>lithium hexafluoroarsenate</td>
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<td>LiI</td>
<td>lithium iodine</td>
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<td>lunar module</td>
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<td>maximum design pressure</td>
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MEOP  maximum expected operating pressure
MIL-STD  Military Standard
MSDS  Material Safety Data Sheet
MSFC  Marshall Space Flight Center
NASA  National Aeronautical Space Association
NDE  nondestructive evaluation
NEDA  National Electrical Distributors Association
NHB  NASA Handbook
NIOSH  National Institute for Occupational Safety and Health
NSTS  National Space Transportation System
ohms  resistance (load)
PDAP  Portable Data Acquisition Package
psi  pounds per square inch (static pressure)
psia  pounds per square inch absolute
psid  pounds per square inch differential
PTFE  polytetrafluoroethylene
PVA  polyvinyl alcohol
RAG  radioisotope thermoelectric generators
RAM  random access memory
RF  radio frequency
RT  room temperature
SARSAT  Search and Rescue Satellite Aided Tether
SCC  stress corrosion cracking
SCM  System Control Module
SPOC  Shuttle portable onboard computer
SRB  Solid Rocket Booster
TNT  trinitrotoluene
UL  Underwriter's Laboratory
ULP  ultrasonic limb plethysmograph
V  volts
WCCS  wireless crew communications system
Wsec  Watt-seconds
Introduction

1.1 Purpose

The purpose of this handbook is to present guidelines for the safe design and use of various types of primary batteries which will be used in NASA flight applications.

1.2 Definition of Primary Battery

A primary battery is one which cannot be recharged either for safety reasons or for reasons inherent in its design, or which is not designed for recharge whether or not limited recharging is possible. Primary batteries are often called "one-shot" batteries.

1.3 Approach

1.3.1 Battery Characteristics and Selection Criteria

Section 2 highlights specific design factors that should be considered in selection of battery type. Section 3 summarizes the characteristics of the types of primary batteries which have been used or are planned for use in NASA spaceflight programs. Section 5 describes in detail the individual primary battery types summarized in section 3. General background information may be found in references 1 and 2.

1.3.2 Safety

Areas known to have created safety problems in the past and previous successful hazard control provisions are cited in section 4. The higher the total energy of the battery, the greater is the safety concern. Individual safety factors and measures for each major battery type are given as part of the detailed descriptions in section 5.

1.3.3 Qualification/Certification

Broad requirements for qualification and certification of primary batteries are stated in section 6. Detailed requirements are determined by the specific NASA application.

1.3.4 Acceptance Testing

Tests are described in section 7 which should be performed by the battery manufacturer prior to shipment, by the user upon receipt of shipment, and/or by the user prior to installation in flight equipment.
1.3.5 Discharge Rate Conventions

In order to provide an idea of discharge rate intensity, the rate is expressed in either of two ways. In one convention, the rate is expressed as the 1-hr (or 10-hr, 100-hr, etc.) rate. This refers to the constant current which will deplete cell capacity in 1 hr (or 10 hr, 100 hr, etc.). For a 100 A-h cell, the 10-hr rate would thus be 10 amp, nominally. (Due to internal cell energy losses, the capacity may be reduced at higher rates, so that for a 100 A-h cell the 1/2-hr rate may be 160 amp (80 A-h) or less.)

In the other convention, the rate is expressed as the C rate. The C rate is the nominal capacity of the cell, although the rate is expressed in amperes as 2C (or C/5, C/10, etc.). Again, for a 100 A-h cell, the 2C rate would be 200 amp, nominally, and equate to the 1/2-hr rate. Likewise, the C/5 rate would be 20 amp. It should be understood that the "C/5" rate is C in A-h divided by 5 hours, thus yielding a rate in amps.

Unless noted otherwise, indicated EMFs are at room temperature.
Section 2
Design Considerations

The characteristics of the kinds of primary batteries which have been flown in prior NASA spaceflight programs, or are planned for imminent use, are summarized in section 3 so that designers seeking primary batteries for new applications can select the kind of battery most likely to meet their requirements. Specific design features aimed at enhancing both safety and reliability are given in section 4.

Designers should take cognizance of the potential internal shorting paths and incorporate appropriate controls.

Designers should incorporate sufficient strength in the cell/battery case to withstand internal gas pressure and electrode and separator expansion.

a. Do not allow cell cases to exceed their elastic limits.

b. Ensure that the selection of the cell/battery case relief valves does not allow the elastic limits to be exceeded.

c. Ensure that the activation procedure of a battery, e.g., silver-zinc, provides for the rapid filling of all cells to preclude pressure stress of an activated cell against one that is not activated.

d. Perform tests on a sample basis for each cell case lot because injection molded cell cases develop internal stresses if not annealed, making them susceptible to crazing and cracking, especially when contacted with certain fluids. For example, annealed acrylonitrile butadiene styrene (ABS) cell cases can be immersed in ethyl acetate without crazing, but will immediately craze if unannealed.

e. Avoid using a hard potting between two surfaces if both must move when in contact with another surface, e.g., a cell case and a battery case, due to different coefficients of expansion at temperature extremes.
Section 3
Primary Batteries Flown in Space Flight Programs

The following is a list of electrochemical couples used in primary batteries which have been or are being flown in NASA space vehicles. In this listing, the word alkaline almost invariably refers to the use of aqueous potassium hydroxide as the cell electrolyte, although sodium hydroxide has been used occasionally.

a. Silver oxide-zinc alkaline (silver-zinc)

b. Carbon-zinc (manganese dioxide-zinc-ammonium chloride, sometimes called Leclanche)

c. Zinc-air (oxygen) alkaline

d. Manganese dioxide-zinc alkaline (alkaline-manganese).

e. Mercuric oxide-zinc alkaline (mercury)

f. Cells having lithium metal anodes and one of the following materials as cathodes (electrolytes vary):
   1. Thionyl chloride (Li-SOCl₂)
   2. Thionyl chloride complexed with bromine chloride (Li-BCX)
   3. Sulfur dioxide (Li-SO₂)
   4. Polycarbon monofluoride (Li-(CF)ₙ)
   5. Manganese dioxide (Li-MnO₂)
   6. Iodine (Li-I₂)
   7. Lithium-iron disulfide (Li-FeS₂)

Table 3-1 shows the major characteristics of these types of primary batteries.

Two special cases are reserve silver-zinc batteries, which have the electrolyte stored separately in a reservoir and are activated by a squib; and thermal batteries, which do not use a conventional liquid electrolyte, but rather employ an inorganic salt electrolyte that is a nonconductive solid at ambient temperature together with an integral pyrotechnic mixture. When electrically activated, a primer ignites the pyrotechnic, the salt melts and becomes conductive, and the battery can deliver current. In both cases, the presence and premature firing of a squib is an added hazard. (These types of batteries have been suggested for inclusion in the Soyuz/ACRV system).
<table>
<thead>
<tr>
<th>Electrochemical type</th>
<th>Energy density*</th>
<th>Range of energy availability per cell (Wh)</th>
<th>Operating temperature range (deg C)</th>
<th>Rate capability</th>
<th>Shelf Life (NASA Recommended)</th>
<th>Nominal cell load voltage (V) at RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver oxide-zinc</td>
<td>65 to 215</td>
<td>135 to 450</td>
<td>0.02 to 615</td>
<td>-30 to 50</td>
<td>0.25 hr to tens of hours</td>
<td>1.5</td>
</tr>
<tr>
<td>Carbon-zinc</td>
<td>44 to 66</td>
<td>73 to 110</td>
<td>0.4 to 56</td>
<td>-5 to 55</td>
<td>Tens of hours to days</td>
<td>1.2</td>
</tr>
<tr>
<td>Zinc-air alkaline</td>
<td>330</td>
<td>650</td>
<td>0.06 to 10</td>
<td>0 to 45</td>
<td>Tens of hours to days</td>
<td>1.1</td>
</tr>
<tr>
<td>Manganese dioxide-zinc alkaline</td>
<td>44 to 100</td>
<td>105 to 240</td>
<td>0.04 to 22</td>
<td>-30 to 55</td>
<td>Tens of hours to months</td>
<td>1.2</td>
</tr>
<tr>
<td>Mercuric oxide-zinc alkaline</td>
<td>110</td>
<td>488</td>
<td>0.05 to 17</td>
<td>0 to 60</td>
<td>Tens of hours to months</td>
<td>1.3</td>
</tr>
<tr>
<td>Lithium-thionyl chloride</td>
<td>330</td>
<td>790</td>
<td>0.6 to 54</td>
<td>-40 to 70</td>
<td>Hours to months</td>
<td>3.3</td>
</tr>
<tr>
<td>Lithium-thionyl chloride/bromine complex</td>
<td>275 to 350</td>
<td>785 to 950</td>
<td>3.5 to 75</td>
<td>-40 to 70</td>
<td>Hours to months</td>
<td>3.2</td>
</tr>
<tr>
<td>Lithium-sulfur dioxide</td>
<td>180 to 355</td>
<td>320 to 585</td>
<td>1.5 to 100</td>
<td>-40 to 60</td>
<td>Hours to months</td>
<td>2.8</td>
</tr>
<tr>
<td>Lithium-polycarbonate monofluoride</td>
<td>125 to 205</td>
<td>370 to 1070</td>
<td>0.10 to 15</td>
<td>-50 to 70</td>
<td>Hours to months</td>
<td>2.7</td>
</tr>
<tr>
<td>Lithium-manganese dioxide</td>
<td>105 to 340</td>
<td>205 to 445</td>
<td>0.08 to 28</td>
<td>-20 to 55</td>
<td>Days to months</td>
<td>2.8</td>
</tr>
<tr>
<td>Lithium-iodine</td>
<td>110</td>
<td>510 to 570</td>
<td>0.33 to 1.9</td>
<td>0 to 50</td>
<td>Months to years</td>
<td>2.7</td>
</tr>
<tr>
<td>Lithium-iron disulfide**</td>
<td>128 to 173</td>
<td>24 to 33</td>
<td>1.9 to 2.6</td>
<td>-40 to 60</td>
<td>0.5 hr to year</td>
<td>1.5</td>
</tr>
</tbody>
</table>

* With the exception of the silver oxide-zinc cell, the energy density is based on the smaller sizes (less than 40 Ah) normally used on Shuttle applications.

** AA cell only
For general safety in handling and storing batteries, the guidelines listed below should be observed. Specific procedures for individual types of batteries are included in section 5.

- Cells and batteries should not be handled roughly or dropped, because even ruggedly constructed cells can be damaged internally if handled this way.

- Until the cells are installed, terminals should be protected with tape or other non-conductive insulators to avoid shorting.

- If a cell is leaking, avoid contact with the electrolyte. If contact is made accidentally, immediately wash the affected area. (See appendix A.)

- Store cells in a cool dry place. Store silver-zinc cells/batteries upright at 0 to -5°C (activated) or 0 to -20°C (unactivated—warm to room temperature before activating). Store zinc-air cells on edge to prevent leakage, with the vents taped to prevent dryout.

- Personnel handling lithium cells should have prior training in the special hazards and controls associated with this type of cell.

The following subsections explain in detail major types of hazards and effective controls.

4.1 Short Circuits

4.1.1 Sources

Short circuits can occur in the loads served by the battery, through conductive electrolyte leaks between cells within a battery, or through careless contact with cell and battery terminals. Internal short circuits are rare in battery cells which have been prepared for flight by effective procedures.

4.1.2 Hazards

a. A sustained short circuit can result in extremely high temperature increases. Table 4-1 shows the effects of short circuiting relatively benign alkaline manganese cells and batteries through about 30 mΩ. Peak currents are reached in less than 1 sec.
Table 4-1. Alkaline Manganese Short Circuit Data

<table>
<thead>
<tr>
<th>Cell or battery size</th>
<th>Peak current (A)</th>
<th>Temperature rise (deg C)</th>
<th>Time to peak temperature (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>9 to 11</td>
<td>18 to 53</td>
<td>2.5 to 7.2</td>
</tr>
<tr>
<td>D</td>
<td>8 to 12</td>
<td>35 to 46</td>
<td>31.5 to 48.3</td>
</tr>
<tr>
<td>9 V (rectangular)</td>
<td>8 to 10</td>
<td>56 to 94</td>
<td>5.5 to 8.7</td>
</tr>
</tbody>
</table>

b. High temperatures can result in hot surfaces which bum crew members (45°C is the specification limit for touchable surfaces), meltdown of the protective plastic structure surrounding the battery, release of noxious or explosive substances (e.g., hydrogen), or initiation of a fire.

c. A short circuit through an electrolyte leak can decompose water in the electrolyte into hydrogen and oxygen and then provide the minuscule ignition energy (1 to 2 \(\mu J\)) to explode the hydrogen and oxygen mixture when the short circuit current terminates with a small arc at last contact. This type of failure is considered to have caused the lunar module (LM) descent battery explosion during the Earthward leg of the aborted Apollo 13 mission. Some obvious hazard controls had been omitted to save weight because such an event was considered unlikely. These controls were incorporated in the LM batteries for Apollo 14 and later missions.

4.1.3 Controls

a. Batteries should not be stored on metal shelves.

b. Batteries must have circuit interrupters which are physically and electrically close to the battery and are rated well below the battery's short circuit current capability. Interrupters may be fuses, circuit breakers, thermal switches, or any other effective device. The interrupter should be in the ground leg of batteries with metal cases so that battery grounds involving the battery case (usually grounded to the structure) may be sensed and interrupted. (A short to the case would complete the circuit without going through a fuse in the positive leg.)

c. All inner surfaces of metal battery cases must be coated with an insulating paint known to be resistant to the battery electrolyte. This aids in preventing battery grounds to the case through electrolyte leakage.

d. Cell terminals must be protected from contact with other conductive surfaces by potting or by a nonconductive barrier (e.g., a plastic sheet).

e. The parts of the battery terminals that extend inside the battery case must be insulated from unintentional contact with other conductors and from bridging by electrolyte leaks. Potting may be used.

f. Metallic components which pass through metal battery cases (terminals, connectors, relief valves, pressure plugs, structural screws) must be insulated from the case with an insulating collar or by other effective means, if they are
inside the volume of the case where leaking electrolyte may gain access to the case and cause shorts.

g. The parts of battery terminals on the outside of the battery case must be protected from accidental bridging. This may be accomplished by using a female connector, recessing stud-type terminals, or installing effective insulating barriers. Special attention should be paid that batteries are not accidentally discharged during handling.

h. Wire lengths inside the battery case must be insulated, restrained from contact with cell terminals, and physically constrained from movement due to vibration or bumping.

i. Personnel working with batteries having close exposed terminals must have finger rings removed or protected with tape.

4.2 Electrolyte Leakage

4.2.1 Sources

a. Excessive free electrolyte in vented cells

b. Inadequate design of electrolyte trapping or baffling provisions under covers of vented cells

c. Leakage through cracked cell containers

d. Faulty seals on sealed cells

e. Leakage of electrolyte forced through seals by cell overheating or overdischarge

f. Inadequate amalgamation of zinc electrodes, which can cause excessive hydrogen pressure that forces electrolyte out

4.2.2 Hazards

a. Conductive ground paths are provided between cells and to metal battery cases (see section 4.1).

b. The electrolyte is corrosive to materials and personnel.

c. The electrolyte may be toxic to personnel in either fluid form or vapor form.

d. Electrolyte grounds may decompose aqueous electrolytes into hydrogen and oxygen, providing an explosive gas mixture.
4.2.3 Controls

a. Sealed cells must provide proper design margins for the containment of gas products, electrolyte vapor pressure, thermal explosion of cell fluids (gaseous and/or liquid) over the temperature range of intended thermal environments and cell/battery operating capabilities.

b. Battery packaging design should accommodate the potential leakage or intentional release of the cell electrolyte into the battery case.

c. Excessive free electrolyte in vented cells should be corrected through cell tests, in which the quantity of free electrolyte is reduced until the cell capacity begins to decline. These tests must be conducted on cells whose ages are nearly identical to the proposed age for flight cells.

d. A cell cover can be designed with a cylindrical "standpipe" in the cell vent opening of the cover, extending downward from the underside of the cell cover toward the cell plates, as shown in figure 4-1. Then, when the cell is inverted in a gravity environment, the free electrolyte collecting on the inside of the cell cover does not rise above the opening of the standpipe. This represents the worst case. All other cell positions, including zero gravity, are better.

e. Cells having free electrolyte must be fitted with relief valves in their vent ports, not just with an opening and/or absorbent material. Relief valve opening pressures have ranged from 3 to 35 psid and are a function of the ability of the cell case to withstand internal pressure without cracking.

f. If inputs are feasible at the cell design level, microporous Teflon plugs may be installed on the vent opening on the underside of the cell cover. Such material, if not covered with electrolyte, will permit gas to escape while preventing the escape of electrolyte due to the material's small pores and nonwetting property.

g. If it is not feasible to use the controls mentioned previously, absorbent material (e.g., Furf or cotton wadding) can be used to fill the void spaces in a battery container or can be placed directly over the cell vents. This is a less satisfactory control since electrolyte may be trapped against conductive parts by the absorbent material, which may also be flammable.

h. Internal surfaces of metal battery cases must be coated with an electrolyte resistant paint. (See subsection 4.1.3c).

i. Prelaunch installation of batteries in the space vehicle should be in an upright orientation, relative to gravity, so that any free electrolyte is forced into the cell plates and separators and away from cell seals or vents by the Earth's gravity and launch acceleration. This decreases the chance of in-flight leakage.

j. If any input is possible during the initial design phase of vented cells with free electrolyte, a requirement should be made to extend the separator material as far as possible beyond the cell electrodes. This provides additional volume for capillary capture of the electrolyte, which then may require accelerative forces larger than 1 g for dislodgment. In-flight maneuvers nearly always provide significantly less accelerative force.
Figure 4-1. Spill-proof cell design.
k. Cell overheating due to internally generated heating on the load must be prevented with the use of adequate heat removal provisions, such as heat sinks or active cooling loops. As a rule of thumb, maximum allowable battery temperatures should not exceed 50°C. Incidence of higher temperatures will require evaluations on an individual basis. If the loss of battery power is tolerable, a heat-activated current interrupter should be used.

l. Heating of batteries from externally imposed heat must be prevented by insulating, shading, reflective paint, or installation away from heat sources. Batteries with electrical heaters should have redundant thermostats and/or thermal switches in the heater circuit.

m. Short circuits from any source must be prevented. (See subsection 4.1.3).

n. Cracked cell cases or seals may result from excessive internal pressure, failure to structurally support plastic cell cases which may be stressed by expansion as the battery is discharged, or wetting plastic cases with solvents which weaken them or cause crazing. Vented cell cases should be tested by application of internal pressure equal to 1.5 times their relief valve maximum vent pressure (proof pressure test). Cell cases should also be tested to determine their burst pressure. An adequate cell case support results from careful design. Contact with unevaluated solvents or known damaging solvents is a quality control problem; e.g., benzene on acrylonitrile butadiene styrene (ABS). Plastic cell cases should be annealed to eliminate stresses which will produce cracks. Surfaces of plastic cases which are sealed with potting, such as terminal feed-throughs, must be free of mold release. Stainless steel cell cases used for certain lithium cells (see subsection 5.6.4) shall be the L-grade to prevent corrosion of the weldment. Cracked seals on sealed cells that have no manufacturing defects may result from differential thermal expansion or internal overpressure caused by excessive temperatures. Thermal design and analysis are required.

o. Do not mix cells of different type, size, age, or manufacturer in a battery.

4.3 Battery Gases

4.3.1 Source

One of the gases evolved by cells which causes safety concerns is hydrogen. Any battery containing vented cells and using an aqueous electrolyte will generate hydrogen even under a no-load status. Hydrogen will be vented from the cells, the amount depending on prior handling, the temperature, and the relief valve settings. See the information on the silver-zinc battery in subsection 5.1.7.2. Under unusual hard-short conditions, a silver-zinc battery may emit mercury vapor. Lithium cells, discussed in subsection 5.6, may release toxic gases if the sealed cells rupture.

4.3.2 Hazards

Hydrogen gas, mixed with air or oxygen, is flammable or explosive over a wide range of concentrations (i.e., 4 to 75 percent in air; 4 to 94 percent in oxygen). The accumulation of
hydrogen in enclosed spaces containing oxygen obviously must be prevented. Wherever a flammable and/or explosive mixture of hydrogen and oxygen exists, an ignition source is presumed to exist even though one may not be obviously identifiable. This is because the energy required for ignition is on the order of 1 or 2 \( \mu \text{J}(1 \times 10^{-6} \text{ Wsec}) \). Although mercury vapor is highly toxic, the amount available in most cells is low (a mercuric oxide-zinc cell is an exception; see subsection 5.5), and the necessary short very unlikely.

4.3.3 Controls

a. The traditional means of avoiding hydrogen accumulation is to provide continuous air ventilation at a rate sufficient to continuously dilute evolved hydrogen to a level below the 4 percent flammability level.

b. Low pressure (3 to 15 psid) relief valves can be provided on the cases rather than sealing the battery cases. It is preferable not to seal any secondary container in which the battery case is installed, unless a worst-case analysis shows flammable hydrogen and oxygen mixtures are not released into the container.

c. The volume of void spaces inside the battery case should be minimized through design or by adding electrolyte-resistant, nonflammable filler, such as potting. This limits the volume (and mass) of hydrogen which can accumulate prior to relief valve venting, thus limiting the force of any hydrogen explosion.

d. Any component inside the battery case which might provide an ignition source must be prohibited, such as arcing relay contacts. Threaded fasteners or connections which may otherwise come loose and provide short circuiting and arcing must be staked or locked. The battery must not be connected with the load applied, as arcing can result.

e. As late as possible before a battery is installed in the Orbiter, the battery case must be purged completely with dry nitrogen (or any other inert gas). Any secondary container in which the battery case is installed should also be purged, if at all feasible.

f. The provisions shown in subsections 5.1 and 5.2 for preventing electrolysis of electrolyte leaks must be followed in order to prevent hydrogen and oxygen generation.

g. Exposure of the battery to high temperatures should be minimized. (See subsection 4.4.)

4.4 High Temperature Exposure

For general purposes, high temperature is construed to mean temperatures higher than 50°C. However, surface temperatures exceeding 45°C are not permitted in places that may be touched by a crew member. It is agreed that some batteries and some battery designs can safely and successfully operate at temperatures well above 50°C. These batteries and battery designs are subject to review on the basis of individual circumstances surrounding each such battery application.
4.4.1 Sources

a. External heat sources are direct and indirect solar radiation, nearby hot surfaces, adjacent hot components, and circuitry or hot fluid and gas loops.

b. Internal heat is generated inside the cell and is due to electrical losses within discharging cells due to coulombic inefficiencies or parasitic chemical reactions. Figure 4-2 describes heat generation during discharge. During a short circuit, $\Delta V$ and $I$ (current) may both increase significantly.

\[
\frac{\Delta Q}{\Delta t} = \Delta V \times I
\]

where $I$ is the current flowing at each point $\Delta V$ is measured. For a constant resistance discharge, instantaneous heat is:

\[
\frac{\Delta Q}{\Delta t} = \Delta V \times \frac{V_L}{R}
\]

or

\[
\frac{\Delta Q}{\Delta t} = (V_0 - V_L) \frac{V_L}{R}
\]

Figure 4-2. Voltages used in heat evolution calculations.

4.4.2 Hazards

a. Excessive hydrogen gas generation is a potential hazard. Gas generation rates on open circuits are doubled for each 10°C temperature rise.

b. Electrolyte may be expelled along with vented gases at high gas generation rates or simply by thermal expansion of internal cell components, including the electrolyte itself.
c. Some cells, notably silver oxide-zinc, are subject to thermal runaway. At high
temperatures, silver oxide decomposes, yielding oxygen. The released oxygen
oxidizes zinc in the negative plates, resulting in heat evolution and an increase in
cell temperature which, in turn, increases the silver oxide decomposition rate.
This process cycle continues to accelerate and can finally result in melting and
charring of plastic cell cases and the extrusion of cell plate packs from cells.

d. Excessive temperature can increase the probability of internal short circuits in
silver-zinc batteries resulting from separator failure in over age cells caused by a
combination of silver oxide oxidization and zinc dendrite penetration. This can
result in very high temperatures which can fuse electrodes, char cell cases, and
ultimately release mercury vapor from the amalgamated zinc electrodes.

e. Charged zinc electrodes, wet with electrolyte, from a disassembled cell will get
hot if left out in the atmosphere and may cause a fire if in contact with paper or
other flammable material.

f. Lithium cells and batteries can vent, rupture, or explode if exposed to
temperatures above 180°C, the melting point of lithium metal.

4.4.3 Controls

a. Adequate short circuit protection must be provided (see subsection 4.1).

b. Cells should not be operated above the maximum current or temperature
specified by battery manufacturers.

c. A thermal analysis of the battery and its surroundings should be performed to
verify the probable battery temperatures under load and no-load conditions. This
is particularly necessary for high energy, high power batteries installed in
equipment stowed in the Orbiter payload bay.

d. If the battery thermal analysis shows that temperatures will become cold enough
to require heat inputs, electrical heaters must have redundant thermostatic
overtemperature controls.

e. If the thermal analysis shows that any combination of external and internal
heating may result in overtemperature, the following must be considered:

1. Provision of heat sinks, heat shunts, or active cooling

2. Provision of barriers against solar radiation or other convective, radiative, or
conductive heat sources

3. Provision of thermally actuated circuit breakers to interrupt load current near
hazardous temperatures

4. Provision of a thermally optimized onboard location (e.g., the battery is moved
to a cooler spot)
f. Batteries should not be used beyond the manufacturer's recommended wet life.

4.5 Circulating Currents

4.5.1 Sources

Circulating currents are unintended current flow, generally between cells or cell stacks connected in parallel. These currents can also occur between standby batteries and the prime power source they support or through electrolyte leakage paths between cells. They result in parasitic discharging and/or unintended charging of cells in the circulating current loop. Circulating currents between parallel, connected cell stacks can result from a lowered voltage in one or more of the stacks due to cell degradation, followed by a current flow from adjacent electrically sound stacks due to the resulting difference in stack potentials.

4.5.2 Hazards

a. Hazards associated with currents circulating through electrolyte leakage paths are described in subsection 4.2.2.

b. The hazard due to current flow between parallel stacks of cells or between a standby battery and a prime power source results from an unintended charge and/or discharge. In aqueous electrolyte batteries, charging can result in water electrolysis with consequent hydrogen generation. Charging of lithium primary batteries is hazardous and is covered in more detail in subsection 5.6. Unregulated discharging can result in overheating, the hazards of which are covered in subsection 4.4.

4.5.3 Controls

a. The prevention of electrolyte leakage paths is covered in subsection 4.2.

b. Circulating currents between parallel cells or cell stacks must be prevented by redundant blocking diodes located in each parallel leg. Small, low current Schottky barrier rectifiers have been used for this purpose to minimize the voltage drop. As a practical matter, it is a much better design practice to use fewer cells of larger capacity than many smaller cells in parallel.

c. Current circulation from a prime power source to its backup battery must also be prevented by redundant blocking diodes. Depending on the circuit power requirements, redundant controls may be installed, such as a high resistance or a fuse in series with the battery. Another option is to put a relay, which is held open by the prime power source, in series with the battery. The special case of lithium standby batteries is covered in subsection 5.6.
4.6 Structural

4.6.1 Sources

Structural sources include mechanical, chemical, and thermal stresses which reduce the integrity or functional capability of cell cases and battery cases.

4.6.2 Hazards

a. The breakage of mounting provisions permits unconstrained movement of the battery.

b. The breakage of cell cases permits the uncontrolled release of electrolyte and gases within the battery case.

c. Battery case breakage or other failure of battery case sealing provisions also permits the uncontrolled release of electrolyte and gases to the battery environment.

d. The fracture of internal current-carrying battery components results in arcing and explosion.

4.6.3 Controls

a. Materials should be selected using the guidelines of NHB 8060.1C, Materials and Processes Requirements for NASA Space Programs (ref. 3).

b. Proper vibration resistance of the battery assembly to the most severe type and level of vibration it will experience in service must be verified. In space applications, this often occurs during launch.

c. Proper shock resistance of the battery assembly to the most severe type and level of shock input it will experience in service or during transportation must be verified.

d. Battery cases are often made of lightweight materials such as aluminum alloy, magnesium alloy, and plastics. In such instances, a materials compatibility and stress analysis should be made to ensure proper maintenance of cell and battery case material strength and function after exposure to electrolyte, painted coatings, potting materials and the solvent solutions used on them, cell case sealing materials and their solvents, or any other material to which the battery may be exposed, within reasonable projections.

e. The primary batteries discussed here, with the exception of the lithium-sulfur dioxide battery, are not designed to operate as pressure vessels under normal circumstances. The lithium-sulfur dioxide cell has an initial pressure of approximately 45 psi at room temperature. However, it has a built-in pressure relief section which provides leak before burst capability in the range of 450 to 500 psi.
Alkaline-manganese, mercury, and Leclanche cells are manufactured with crimped seals. This minimizes any pressure buildup from hydrogen generation during normal operations. Some models also have a discrete resettable relief valve. Silver-zinc cells have a low pressure relief valve and can be pressure checked for leakage by restraining the broad sides of the case, removing the vent valve, and through this opening, pressurizing the cell case with nitrogen at 1.5 times the pressure setting of the relief valve.

During abnormal conditions, such as charging or short circuiting, pressures can build up in any cell. For these situations, external controls, such as diodes and fuses, are required.

The various lithium batteries are hermetically sealed with glass-to-metal seals. In addition to the lithium-sulfur dioxide battery, certain lithium-thionyl chloride batteries are manufactured with a venting capability. Since the electrolytes from these two types of batteries are highly toxic, the vented designs of these battery types cannot be used in the habitable areas of the Orbiter, but can be carried in the cargo bay.

The Li-BCX battery, which is used in the Orbiter cabin, is not provided with a vent, but is 100 percent pressure tested by exposure to 160°F for 2 hours; additionally, it is tested on a lot sample basis. Three percent of the lot at beginning of life and an equal number of discharged cells (from the lot sample capacity discharge test) are heated at 93°C (200°F) for two hours; and two additional cells, one fresh and one discharged, are heated at 149°C (300°F) for 15 minutes.

The other lithium batteries have organic electrolytes and operate at atmospheric pressure. They are hermetically sealed, but are manufactured only in small sizes. Hazard controls must rely on appropriate diodes and fuses in the circuit.

Battery containers (cases) that are used to enclose the assembly of individual cells must have redundant pressure relief valves or an alternate, non-hazardous method of relief in case of relief valve failed closed (such as an o-ring seal letting go at a non-hazardous pressure level). The BCX must be pressure tested to 1.5 times the pressure relief setting of the vent valves.

f. Some cells swell during discharge. Silver oxide-zinc cells swell in the direction normal to the plane of their plates (electrodes). Zinc-air button cells swell axially. Battery development testing must include determinations of such dimensional changes. The structural design of the battery cases must provide the strength necessary to withstand or negate the stress induced.

g. If it is known that significantly low or high temperatures will be experienced by the battery, whether from external or internal sources, attention must be given to the effects of differential thermal expansion and contraction between dissimilar materials (e.g., plastic cell cases and metal battery cases). In this example, plastic cell cases must not be "pinned" to a metal battery case by cement, hard potting, or mechanical means. Resilient filler may also be required in order to absorb dimensional changes due to large temperature changes.

h. When making intercell connections between terminals of several cells, the specified torque to avoid cracking plastic cell cases must not be exceeded.
i. The additional specifications in the following list are useful in addressing the applicable structural areas.

1. Fracture control (of pressurized vessels; e.g., battery case): MIL-STD-1522A

2. Materials and processes: NSTS 1700.7B, Jan. 1989 (ref. 4)

3. Allowable mechanical properties:
   - MIL-HDBK-5F, Metallic Materials and Elements for Aerospace Vehicle Structures
   - MIL-HDBK-17, Polymer Matrix Composites
   - MIL-HDBK-23, Structural Sandwich Composites

4. Screw threads:
   - MIL-S-7742D, Screw Threads, Standard, Optimum Selected Series: General Specifications for
   - MIL-S-8879C, Screw Threads, Controlled Radius Root with Increased Minor Diameter, General Specification for
5.1 Silver Oxide-Zinc Alkaline

5.1.1 Major Usage

This type of battery is used where any of the following characteristics are desired or permitted:

a. High power density (watts per unit weight or volume)

b. High energy density (watt-hours per unit weight or volume)

c. Long shelf life
   1. Moderately long: Several months to several years possible, depending on design and storage conditions
   2. Very long (years): Achievable only with reserve electrolyte design (i.e., the electrolyte is maintained separate from the cell electrodes until time of use, at which time it is admitted into the cells manually or by an automatic activation device actuated by gas, pyrotechnics, etc.)

d. Flat discharge curve, good regulation

e. Good low temperature performance (-30°C)

f. Expensive

5.1.2 Typical Applications

Small button cells have been used to power sequencer circuits and calculators. Large rectangular cells have been used in main vehicle batteries storing up to 18 kWh per battery at 165 Wh/kg. Smaller cells have been used in astronaut life support and mobility systems, space experiment power supplies, cameras, and other portable electronic equipment. (Secondary silver oxide-zinc batteries with an energy content in the tens of megawatt-hours have been constructed for Department of Defense nonspace applications.)

5.1.3 Electrochemistry

The cell reaction formula consists of two steps:

\[
\begin{align*}
\text{Ag}_2\text{O}_2 + \text{Zn} & \rightarrow \text{Ag}_2\text{O} + \text{ZnO}, \text{ emf} = 1.86 \text{ V} \\
\text{Ag}_2\text{O} + \text{Zn} & \rightarrow 2\text{Ag} + \text{ZnO}, \text{ emf} = 1.59 \text{ V} \\
\text{Ag}_2\text{O}_2 + 2\text{Zn} & \rightarrow 2\text{Ag} + 2\text{ZnO}
\end{align*}
\]

(peroxide step)  (monoxide step)  (overall)
In low rate discharges (e.g., 10-hr rate) the two steps may be observed, the first step lasting through about 20 percent of the discharge capacity (in ampere-hours). In medium to high rates of discharge (e.g., 0.5 to 1 hr) the voltage of the first step is overwhelmed by that of the second step. (See figure 5-1.)

![Figure 5-1. Silver oxide-zinc performance versus load.](image)

The electrolyte usually is a solution of 40 to 45 percent potassium hydroxide (KOH), by weight, in pure water (i.e., distilled water). Concentrations less than 30 percent result in rapid degradation of cellulosic separators. Although the electrolyte participates in chemical reactions at both the positive and negative plates, its overall composition has no net change. Therefore, it isn't shown in the cell reaction formula at the beginning of this subsection.

### 5.1.4 Electrodes and Separators

The descriptions in subsections 5.1.4.1 through 5.1.4.3 apply mainly to rectangular multiplate cells. They also apply in principle to smaller cylindrical and button cells.

#### 5.1.4.1 Positive Electrodes (Plates)

The positive plates consist of highly porous plaques of silver, supported by internal grids of silver or silver-plated copper mesh. The silver is electrolytically oxidized to the oxide and then to the peroxide during manufacturing.

#### 5.1.4.2 Negative Electrodes (Plates)

The negative plates are similar to positive plates except that they are made of a highly porous zinc metal. They are manufactured either by a direct plating of zinc from a zinc hydroxide slurry or by the electrolytic reduction of a zinc oxide paste applied to the supporting mesh.
5.1.4.3 Separators

Separators are placed between each positive/negative plate pair to prevent electrical short circuiting between the plates while permitting the ion transfer between the plates, which is necessary for the cell reaction to proceed. They are installed in a variety of configurations, from single sheets to multilayer wrappings around the positive or negative plates, depending on the wet shelf life desired. They may be absorbent or nonabsorbent, depending on the material from which they are made. Materials which have been used include cellulosic sausage casings, irradiated polymer films, polyvinyl alcohol films, and cellophane. The cellophane may or may not be pretreated with a silver solution to enhance resistance to oxidation by silver oxides. Additionally, a layer of porous, fibrous material is placed against the negative plate and a layer of woven or nonwoven, oxidation-resistant material (generally nylon) is placed against the positive plate. The function of both of these layers is to maintain a supply of electrolyte across the surfaces of the plates.

5.1.5 Capacities and Configurations

Cell capacities are available commercially from button cells yielding tens of milliampere-hours to a cylindrical cell yielding 12.5 A-h and rectangular cells yielding 650 A-h and greater.

5.1.6 Typical Characteristics

Figure 5-1 shows the room temperature characteristics of silver oxide-zinc cells at a high rate (1 hr) and a low rate (10 hr). Note the flat voltage and the fact that the useful capacity to an end voltage of 1.4 V at the 10-hr rate is obtained with a voltage regulation of approximately 30 percent. Regulation of less than 10 percent may be obtained by discharging about 15 to 20 percent of the cell's initial capacity so that subsequent discharges all occur at the lower discharge plateau.

Silver-zinc cells are charged to a cut off voltage of 2.00 to 2.10. At this point the positive electrode consists of a mixture of two active materials, monovalent silver oxide, Ag$_2$O, and divalent silver oxide, AgO. The resulting open circuit voltage is 1.86 V. The divalent oxide is predominant and with a resistivity of 10 ohm-cm is responsible for the peak open circuit voltage. The open circuit voltage of a monovalent silver oxide cell is 1.62 V. Monovalent silver oxide has a resistivity of $10^8$ ohm-cm (ref.5). During the discharge of a cell, a two step voltage curve is seen, the nature of which is dependent upon the rate of discharge. At very high rates, the hump in the curve is essentially washed out. For applications which require close voltage regulation with low current pulses, however, the hump can present a serious initial problem. To solve this problem, electroformed plates can be reduced to the monovalent form during the electrode fabrication process by heat treatment or partial discharge.

Another result of having mixed oxides present is a delay in reaching the operating voltage when the circuit is closed. This voltage delay may only be a millisecond, but will vary with the time the battery has been on wet stand. After extended wet stand, some of the divalent oxide converts to the monovalent oxide which then forms a coat on the divalent particles. This creates a high impedance, low voltage transient. While this may only be a millisecond with the voltage quickly stabilizing, it can be avoided by a conditioning
discharge of about one second at a medium discharge rate. As the discharge proceeds, the cell impedance drops due to the formation of increasing amounts of the highly conductive silver oxide.

Figure 5-2 shows the effect of low temperatures on the energy output (watt-hours) of a silver oxide-zinc cell at high and low rates. The effect of higher temperatures (up to about 70°C) during discharge is to slightly elevate the energy output.

![Figure 5-2 Silver oxide-zinc performance versus load and temperature.](image)

5.1.7 Safety

5.1.7.1 General

All of the provisions of section 4 apply to silver oxide-zinc primary batteries. Particular attention must be paid to the very high short circuit currents they will deliver. For example, a battery of 20 cells in series having a 400 A-h capacity will deliver peak currents of 1,500 to 1,800 amp. Internal short circuits resulting from separator failure in over age cells by a combination of silver oxide oxidation and zinc dendrite penetration can result in very high temperatures which can fuse electrodes, char cell cases, and ultimately release mercury vapor from the amalgamated zinc electrodes. For batteries with different voltage taps, seen most often with reserve batteries, each tap shall have a fuse in addition to the ground leg fuse. Certain conformed coatings which are used to insulate the inside surface of metallic battery cases, and which are resistant to KOH, may be rapidly attacked when zincate is also present.

5.1.7.2 Hydrogen Gas

An additional significant factor of silver oxide-zinc primary batteries is hydrogen evolution. The silver oxide-zinc alkaline battery, in normal operation and with sound interelectrode dielectric insulation, will evolve two gases, hydrogen and oxygen.
Oxygen is evolved while secondary cells are being charged when individual cell charge voltages exceed the decomposition potential for water in the electrolyte (approximately 2 V). Oxygen may also be present in newly activated primary cells due to the initial presence of air in the cell and the release of loosely held oxygen from the positive plates.

Hydrogen is evolved during open circuit stand, during discharge, and when the gassing voltage is exceeded during charging. The cell or battery will continue to emit hydrogen even after it is discharged. The amount of hydrogen evolved on stand is higher after charging and then decreases to a steady state rate which is logarithmically proportional to the battery temperature and directly proportional to the quantity of zinc in the cell. The source of hydrogen on stand is the reaction of the electrolyte with the zinc negatives according to this equation:

$$2\text{KOH} + \text{Zn} \rightarrow \text{K}_2\text{ZnO}_2 + \text{H}_2 \text{ (gas)}$$

During discharge, the amount of hydrogen evolved is reduced due to the increasing nonavailability of elemental zinc at the electrode-electrolyte interface. This occurs because the zinc is oxidized to zinc oxides and hydroxides by the discharge. The reaction of the electrolyte with oxidized zinc discharge products does not produce gas, as demonstrated in the following equations:

$$\text{ZnO} + 2\text{KOH} \rightarrow \text{K}_2\text{ZnO}_2 + \text{H}_2\text{O}$$

$$\text{Zn(OH)}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$$

However, since there is normally excess zinc in the negative electrode, some hydrogen can still be emitted from a discharged cell.

If a battery is heated during discharge, either by internal resistance losses or from an external source, there are two effects:

a. The rate of hydrogen evolution is increased due to the temperature dependence of the hydrogen evolving reaction.

b. Occluded bubbles of hydrogen within the plates and separators increase in volume and escape from the cell.

Thus, the amount of hydrogen generated from the cell will temporarily exceed the equilibrium values for the applicable instantaneous temperatures.

A silver oxide-zinc battery cell which has a severe internal short circuit can evolve oxygen, hydrogen, caustic vapor, mercury vapor, and the oxidation products of the organic materials in the separators and plastic cell containers. The rate and volume of each evolved material depends on the severity of the short circuit (amount of heat evolved), state of charge, the temperature and amount of material available to vaporize, oxidize, and/or decompose thermally.

Mixtures of hydrogen and oxygen are combustible in the composition range of 4 to 94 percent hydrogen at 25°C and 1 atm. In the composition range of 18 to 94 percent hydrogen, the combustion rate attains the explosive level, reaching a maximum explosive force when the hydrogen and oxygen concentrations are at their approximate
stoichiometric values (67 percent hydrogen and 33 percent oxygen). The energy required to initiate the combustion is infinitesimal, on the order of 1 or 2 μJ. A static or electric spark is sufficient to ignite a combustible mixture. This amount of energy is considered always present by people working with hydrogen (e.g., submarine battery personnel).

In view of the foregoing, particular attention must be paid to the hazard control provisions in subsection 4.3.3.

5.1.8 Activation

5.1.8.1 Requirements

Primary silver oxide-zinc batteries are supplied with their electrodes fully charged and with no electrolyte in the cells. Electrolyte must be added by the user. A small amount of charging to "top off" the cells may be required, but generally that is not necessary. The battery manufacturer must be required to develop and supply any special activation equipment and instructions for activation, as well as supplying electrolyte in premeasured plastic bottles, one for each cell plus one or two spares.

5.1.8.2 Activation Instruction Requirements

These should include the following, as a minimum:

a. Instructions for operating, cleaning, and maintaining the special activation equipment, if any

b. Procedure for performing a proof pressure test (1.5 times the maximum operating pressure) or a leak test to assure each cell is sound structurally

c. Instructions for safe handling of the electrolyte including emergency first aid and medical care for personnel coming in contact with the electrolyte, which is generally a 40-percent solution of potassium hydroxide in water

d. Instructions for adding the electrolyte into the cells, including vacuum applications (if any), soak periods, and preliminary cell case leak checks. A vacuum activation is recommended to assure more complete wetting of the cell pack

e. Instructions for cleaning up electrolyte spills on and in the battery

f. Acceptance checks for an activated battery, including

1. Open circuit voltage checks of cells and battery

2. Load checks on battery

3. Megger checks between battery terminals and metal battery cases to verify absence of grounds, including ground-chasing techniques. (If a megger check is performed between terminals of unactivated cells, it should be done in an area of low humidity.)
4. Battery sealing and purging, including verification of battery case relief valve function

5. Safing of battery terminals after filling

6. Other factors which may be based on problems experienced during battery development

5.2 Carbon-Zinc

5.2.1 Major Usage

This type of battery is used where any of the following characteristics are desired or permissible:

a. Low discharge rate (tens of hours to days)

b. Good shelf life (up to 2 years at room temperature)

c. Low cost (relative to other cell types herein)

d. Weight and volume not critical (see table 3-1)

e. Voltage regulation not critical (sloping discharge curve at higher rates)

f. Low temperature performance not critical

5.2.2 Typical Applications

The number of present-day applications for the carbon-zinc cell is very large. These applications include use in flashlights, portable radios, hand-held calculators, toys, and many other portable electric and electronic devices. It is noteworthy that designers of almost all dry-cell, battery-operated devices used aboard the Shuttle Orbiter have selected the alkaline manganese type of dry cell in lieu of the carbon-zinc type. This is probably due to the better high rate performance, flatter discharge curve, and somewhat better low temperature performance of the alkaline manganese type.

5.2.3 Electrochemistry

The reactions occurring during the carbon-zinc cell discharge are not precisely known. They vary with the rate of discharge, electrolyte composition, discharge temperature, prior conditions, and duration of storage. Generally, the following models are used as the most typical representations:

\[ \text{Zn} + 2\text{MnO}_2 + 2\text{NH}_4\text{Cl} \rightarrow \text{ZnCl}_2 \cdot 2\text{NH}_3 + \text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O} \]

or

\[ \text{Zn} + 2\text{MnO}_2 \rightarrow \text{ZnO} \cdot \text{Mn}_2\text{O}_3 \]
Reference 1 provides a learned discussion of the variety of possible reactions. Cell EMF varies between 1.56 to 1.62 V, depending on active material content.

5.2.4 Construction

5.2.4.1 Positive Active Material

The positive material is a thick paste of finely ground manganese dioxide and carbon powders mixed with water, ammonium chloride (sal ammoniac), and zinc chloride. The latter three components constitute the electrolyte, occurring in the rough proportions of 65:25:10, respectively. Manganese dioxide and carbon are in the rough proportions of 3:1, respectively. The carbon is added for conductivity. In cylindrical cells, the positive paste is extruded in a cylindrical bobbin of the length and diameter appropriate to the size of cell being made. A carbon rod current collector is inserted along the axis of the bobbin.

5.2.4.2 Negative Active Material

The negative active material is zinc alloy, typically drawn into a can of the required diameter. It serves as both a container and an anode. The alloy is essentially pure zinc with fractional percentages of cadmium and lead added to improve strength and drawing qualities, respectively. The presence of other metallic impurities is strictly avoided, since almost any other metal impacts performance adversely.

5.2.4.3 Separator

The classical carbon-zinc dry cell battery separator is a thin wall of gelatinized paste between the bobbin and the can, which is typically poured in while runny and allowed to gel in place. The paste contains additional electrolyte within the gel for conductivity. The paste consists mainly of cornstarch and flour. The separator may also be gel-impregnated paper, which is available in a variety of types.

5.2.4.4 Closure

Precise details of dry cell closures vary according to manufacturer, and are beyond the scope of this document. It will suffice to say that the assembled zinc can and bobbin receive a primary seal of potting material, through which the carbon rod current collector protrudes. The carbon rod is sufficiently porous to permit the escape of hydrogen evolved within the cell without concurrent seepage of electrolyte. A variety of secondary closures of sheet steel and absorbent material are installed around this assembly to further prevent electrolyte leakage from damaging equipment and personnel.

5.2.4.5 Variations

Subsections 5.2.4.1 through 5.2.4.4 relate to the Leclanche version of the cylindrical carbon-zinc battery. If lower temperature or higher rate performance is required, the zinc chloride variation may be used. It has a slightly different internal construction, and the
ammonium chloride in its electrolyte is largely or totally replaced with zinc chloride. The zinc chloride cell is more expensive than the Leclanche cell, but does not outperform the alkaline manganese cell (described later in this document) in energy content, high rate, or low temperature performance. Hence, there are trade-offs to consider in selecting the zinc chloride version rather than the alkaline manganese version.

A further variation of the Leclanche version is to make flat, rectangular cells which are stacked. The stacks are coated with wax before being placed in their container. This configuration provides a better energy-to-volume ratio than the cylindrical cells by avoiding the wasted space occurring in the multicell batteries of cylindrical cells. Flat cells are generally used in higher voltage (multicell), low capacity applications.

5.2.5 Capacities and Configurations

The cylindrical cells are commercially available incapacities from 0.38 A-h (N-size) to 40 A-h (no. 6 size). Batteries containing flat cells are available with the cells having capacities from 0.14 to 4.0 A-h. A listing of common carbon-zinc cylindrical cell sizes is given in table 5-1.

<table>
<thead>
<tr>
<th>Cell designation</th>
<th>Nominal diameter (cm)</th>
<th>Nominal height (cm)</th>
<th>Nominal volume (cm³)</th>
<th>Approximate weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 6</td>
<td>6.3</td>
<td>15.2</td>
<td>483.0</td>
<td>1000</td>
</tr>
<tr>
<td>F</td>
<td>3.2</td>
<td>8.7</td>
<td>69.0</td>
<td>150</td>
</tr>
<tr>
<td>D</td>
<td>3.2</td>
<td>5.7</td>
<td>4.6</td>
<td>96</td>
</tr>
<tr>
<td>C</td>
<td>2.4</td>
<td>4.6</td>
<td>20.0</td>
<td>42</td>
</tr>
<tr>
<td>B</td>
<td>1.9</td>
<td>5.4</td>
<td>15.0</td>
<td>34</td>
</tr>
<tr>
<td>A</td>
<td>1.6</td>
<td>4.8</td>
<td>9.4</td>
<td>22</td>
</tr>
<tr>
<td>AA</td>
<td>1.3</td>
<td>4.8</td>
<td>6.9</td>
<td>15</td>
</tr>
<tr>
<td>N</td>
<td>1.1</td>
<td>2.7</td>
<td>2.6</td>
<td>6</td>
</tr>
</tbody>
</table>

5.2.6 Typical Characteristics

Due to the high internal impedance of carbon-zinc cells (approximately 1/4 ohm for a D-size cell), the available energy is significantly decreased by using them in high rate applications. Due to the increased internal impedance at low temperatures (up to six times the room temperature value at -20°C), the available energy is also reduced by use in low temperature applications. The total energy output of the cells is increased by use in intermittent service, as compared to continuous drain. This is because the buildup of reaction products at the reaction interface during discharge (which raises internal impedance) is permitted to diffuse from the interface during periods when no discharge is occurring. These factors are depicted in figures 5-3 through 5-5.
5.2.7 Safety

There are no unusual safety hazards with the carbon-zinc battery. The general hazards and controls given in section 4 provide adequate coverage for this battery type. (It must be reiterated, however, that they must not be placed in series with alkaline manganese cells.)

Figure 5-3. Leclanche D cell at room temperature—effect of load on capacity to 0.9-V end voltage.

Figure 5-4. Leclanche F cell discharged through 83.3 ohm to 1.0 V—effect of temperature on capacity.
5.3 Zinc-Air Alkaline Cells

5.3.1 Major Usage

This type of battery is used where the following characteristics are desired or permissible:

a. Low discharge rate (tens of hours to days)

b. Good shelf life (1-2 years, if sealed against air access and water loss)

c. Low cost

d. High energy density on basis of both weight and volume

e. Good voltage regulation

f. Low temperature performance not critical

5.3.2 Typical Applications

Although commercial zinc-air cells have been available in flooded electrolyte, large cell configurations since before 1935, the small, limited electrolyte cells suitable for powering portable electronic devices have been available only since about 1975. Hence, applications are limited at this time. Commercial use of these cells is usually in devices
such as hearing aids. Applications in the Shuttle Orbiter have included wireless crew communications units, a miniature oscilloscope, and various experiments. At the Lyndon B. Johnson Space Center (JSC), they are used where possible for in-cabin applications instead of lithium cells because they are inherently less hazardous and are capable of equivalent energy densities.

5.3.3 Electrochemistry

The zinc-air cell involves a discharge of oxygen from the air against a zinc anode according to the following reaction:

\[ \text{O}_2 + 2\text{Zn} \rightarrow 2\text{ZnO} \]

Cell EMF varies between 1.38 to 1.56 V and remains essentially unchanged, even in a discharged cell.

5.3.4 Construction

Figure 5-6 is a simplified schematic of a coin-size zinc-air cell. Its essential features are given in the following list:

a. A steel container which is the positive terminal and is perforated on its flat surface to permit air to diffuse into the cell (new cells are received with an adhesive-backed film seal covering the holes to minimize capacity loss from admission of air and loss of water)

b. Microporous, nonwetting film which retains the small amount of free electrolyte within the cell while permitting air to diffuse through to the cathode screen (see appendix B)

c. A small void for expansion of zinc to zinc oxide as the discharge progresses

d. A fine-mesh metal cathode screen loaded with a thin coating of catalytic material (generally a mixture of manganese dioxide and carbon), which promotes the reaction of oxygen with the electrolyte during discharge

e. A separator

f. A highly porous, granular slug of zinc anode saturated with the 30 to 40 percent aqueous solution of potassium hydroxide electrolyte

9. A steel lid, which is the negative terminal, coated internally with copper and externally with nickel

h. A plastic sealing grommet which is crimped between the lid and container
5.3.5 Capacities and Configurations

Virtually all zinc-air cell configurations available today are the button and coin types with capacities that range from 0.05 to 7 A-h. Some development work has been done with rectangular cells of up to 200 A-h; but this development is continuing. In present applications requiring higher capacities, cells are connected in parallel to achieve the desired capacity. Table 5-2 lists the dimensions of some of the higher capacity cells.

### Table 5-2. Typical Zinc-Air Cells

<table>
<thead>
<tr>
<th>Cell model</th>
<th>Capacity (A-h)</th>
<th>Diameter (mm)</th>
<th>Height (mm)</th>
<th>Weight* (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>630</td>
<td>0.9</td>
<td>15.5</td>
<td>5.8</td>
<td>4.0</td>
</tr>
<tr>
<td><strong>796</strong></td>
<td>1.2</td>
<td>20.3</td>
<td>4.8</td>
<td>5.0</td>
</tr>
<tr>
<td>635</td>
<td>1.5</td>
<td>15.5</td>
<td>8.9</td>
<td>6.0</td>
</tr>
<tr>
<td><strong>1200</strong></td>
<td>2.6</td>
<td>30.5</td>
<td>5.1</td>
<td>10.3</td>
</tr>
<tr>
<td><strong>1204</strong></td>
<td>7.0</td>
<td>30.5</td>
<td>10.2</td>
<td>18.8</td>
</tr>
</tbody>
</table>

*This is the weight prior to discharge. The weight increases during discharge due to oxygen combining with the zinc anode. The theoretical weight increase is 0.2985 g O\textsubscript{2}/A-h.

**No longer available. This information is supplied to give an appreciation of the energy density of this cell type.
5.3.6 Typical Characteristics

Figure 5-7 shows the effects on performance of model 630, 0.9 A-h cells discharged to 0.9 V when load (ohms), temperature, and ambient gas composition are varied. Predictably, low temperatures and high rates reduce cell capacity. The effect of varying the partial pressure of oxygen is noteworthy. At 21°C there is very little difference in performance. At -1°C, the capacity performance is proportional to the oxygen partial pressure. At 43°C, there is also little difference in performance at higher rates. The 50 percent reduction in capacity at 120 ohm, 43°C, and 5-psia oxygen is due to the cells drying out. The 5-psia oxygen was bone dry, the partial pressure of water in the electrolyte was quadrupled by increasing the temperature from 21° to 43°C, and the 120-ohm load provided the 100-hr rate, allowing maximized conditions for cells to dry out. Had the 5-psia oxygen been humidified sufficiently (approximately 0.7 psia of partial pressure of water), there is little doubt that performance would have been similar to that for 21°C. This demonstrates the importance of preventing the loss of water from zinc-air cells, both during storage and low rate discharges.

![Figure 5-7. Effects of gas composition and temperature.]

Figure 5-8 shows shelf life test results on model 796,1.2 A-h cells. Four different storage conditions were used:

a. Air holes untaped, cells in sealed bag, 4°C
b. Air holes untaped, cells in sealed bag, room temperature
c. Air holes taped, cells in sealed bag, 4°C
d. Air holes taped, cells in sealed bag, room temperature
An unintended variable was added on samples stored for 18 months with air holes untaped at 4°C storage; the sealed bag in which the cells were stored was found to be slit when removed from storage. The slit had permitted the cells to dry out. Discharge voltages were below 0.9 V initially and did not recover. Using the remaining data, it can be concluded that capacities exceeding 85 percent of the initial values are maintained for up to 18 months under the following storage conditions:

a. A 4°C (commercial refrigerator) storage environment

b. All air holes on cells, or batteries containing cells, taped over with tape that is impermeable to oxygen and water vapor

c. Taped cells or batteries stored in sealed bags

A sealing tape that has been used is 3M type 92 adhesive-backed, 0.07-mm-thick tape. The equivalent DuPont tape is called Kapton. The heat sealed bags used are made of 0.15-mm-thick polyethylene film. Spare multicell batteries packaged for immediate flight storage do not have sealed air holes, but rather are sealed in an inner bag of Film-Pak 1177, manufactured by Ludlow in Holyoke, Massachusetts, per specification MIL-B-22191C.
5.3.7 Safety

5.3.7.1 Cell Leakage

Zinc-air cells are frequently observed to leak caustic electrolyte. Leakage may range from a potassium carbonate encrustation at the cell seals, due to seepage, to the release of significant quantities of electrolyte. Leakage can vary from lot to lot and may not occur for several months after manufacture. In order to minimize ground currents, battery cases made of caustic-resistant plastic are preferred. Metal cases treated as required in subsection 4.1.3. b may be used. In order to preclude damage to adjacent equipment or flight personnel, air holes in the battery cases must be lined internally with an air-permeable, nonwetting film (such as GORE-TEX®) which is sealed around its edges.

5.3.7.2 Overdischarging and Charging

NASA/JSC tests have shown that cells may be made to leak and/or burst (nonexplosively) by subjecting to either overdischarging (forcing to negative voltage) or charging. Partial protection for equipment and personnel is achieved by using strong battery cases with a nonwetting lining such as the GORE-TEX® material described previously. Further protection against overdischarge in multicell batteries is achieved through the selection of a suitably high cutoff voltage and the use of a low voltage warning or cutoff in the using device. For example, in figure 5-9, there is little further usage to be gained by discharging cells beyond 1.0 to 1.1 V per cell at the lower discharge rates. Use of a high-end voltage means that weaker cells will see less overdischarging. Protection against charging is accomplished by preventing the parallel connection of a zinc-air battery with any external power source, or by using blocking diodes in series with the battery.

![Figure 5-9. Model 796 zinc-air cell performance at various loads at room temperature.](image)
5.3.7.3 Series-Paralleling Zinc-Air Cells in Batteries

Battery capacities are often required which exceed the capacity of available single cells many times. In such cases, multiple cells must be connected in parallel to provide the required capability. That is, if 1.0 A-h cells are used and 6 A-h are required, six parallel strings of cells are required. Each string must contain \( n \), the number of series-connected cells necessary to meet the required battery voltage level. Note the basic principle that paralleling cells increases capacity but not nominal voltage and connecting cells in series increases voltage but not nominal capacity.

In a battery of series-parallel connected cells, the voltage of one or more parallel strings containing a weak or failed cell or cells may be lowered sufficiently for parallel strings of normal cells to supply a circulating current which may charge the weak string (or strings). Even if the current is very low, it can dissipate the capacity of the strong strings and charge the weak strings. This condition must be prevented by using a blocking diode in each parallel string. (Note: This possibility primarily relates to performance issues; thus, the necessity of diode use may be determined by performance criteria.) Another source of circulating currents can be caused by high impedance in the cell-to-cell contacts due to dirty cell surfaces. It is highly desirable to clean mating surfaces with a cotton swab moistened (but not dripping wet) with a solvent cleaner and then to dry the surface with a dry swab. Intercell contact is further enhanced by applying a thin film of a suitable grease to the negative surface of each cell prior to stacking them.

5.3.7.4 Zinc-Air Cell Growth

Even though cells are designed with an internal expansion volume (see subsection 5.3.4 and figure 5-6), zinc-air coin cells grow axially during discharge. Height increases of 0.25 to 0.5 mm per cell may be expected during complete discharge of the cells, as shown in table 5-2. The design of multicell batteries must accommodate this fact, since a six-cell stack may grow 3 mm (nearly 1/8 in.). Present designs have used leaf-type springs which apply a preload of 1 to 1.5 kg on each stack for good cell-to-cell contact and for resistance to vibration. The springs must be freely compressible for the distance expected from axial cell growth.

5.3.7.5 Hydrogen Evolution

Controls for the hydrogen gas hazard with such cells as silver-zinc and alkaline manganese were given in subsection 4.3.3. For zinc-air cells, however, there are added considerations. The battery case cannot be sealed, as oxygen is necessary for its operation. For that reason, it also cannot be purged with nitrogen. As described below, hydrogen evolution can also affect electrolyte leakage. The most applicable control is adequate ventilation. The rate of hydrogen evolution by zinc-air cells standing open circuit at 21°C (70°F) is 0.01 cc of hydrogen per hour per gram of zinc. Therefore, a battery containing ten cells, each containing ten grams of zinc, would evolve one cc of hydrogen per hour. The hydrogen evolution rate will be approximately doubled or halved for each 10°C (18°F) the temperature is raised or lowered, respectively. When the cell is being discharged, the hydrogen evolution is less.
5.3.7.6 Storage Position

Refer to the zinc-air coin cell schematic shown in figure 5-6. Assume the pull of gravity runs from the top to the bottom of this figure. In cells stored in this position over a period of time, free electrolyte runs down onto the air diffusion membrane from the saturated porous zinc anode and can form a pool all the way across the cell, blocking the air access holes. Hydrogen continues to be generated in the cell due to zinc corrosion caused by the electrolyte:

\[ \text{Zn} + 2\text{KOH} \rightarrow \text{K}_2\text{ZnO}_2 + \text{H}_2 \]

As hydrogen continues to evolve, pressure builds up inside the cell until, finally, liquid electrolyte is forced through the membrane and leaks out of the positive terminal perforations. Hence, cells should not be stored with their holes facing down. In some batteries, cells are installed so that some cell stacks have holes facing down and some have holes facing up. In that case, the batteries should be stored so that all cells are on their edge (visualize the gravity vector running from left to right in figure 5-6). In this position, it is doubtful that electrolyte would ever fill the expansion volume. Hence, some of the perforations will always be open to allow hydrogen to escape, preventing an increase in pressure within the cell and reducing the likelihood of leakage.

5.4 Manganese Dioxide-Zinc Alkaline Batteries

5.4.1 Major Usage

This type of battery is used where any of the following characteristics are desired or permitted:

a. Low power density (watts per unit weight or volume)

b. Low energy density (watt-hours per unit weight or volume) but better than carbon-zinc

c. Good shelf life (2 years at room temperature)

d. Moderate cost

e. Better voltage regulation and low temperature performance than carbon-zinc

5.4.2 Typical Applications

The alkaline manganese battery has myriad commercial applications in portable electric and electronic devices. A sampling of applications in the Shuttle Orbiter includes

a. Digital multimeter
b. Kneeboard light
c. Mission clock
d. Gas sampler
e. 35-mm camera
f. Mini centrifuge
g. Treadmill exerciser
h. Penlights
i. Radiation monitor
j. Gyroscopic optical device
k. Spotmeter
l. Tape recorder
m. Temperature recorder
n. Mass spectrograph
5.4.3 Electrochemistry

The discharge reaction of the alkaline manganese cell is considered to follow the following formula:

\[ \text{Zn} + 2\text{MnO}_2 \rightarrow \text{ZnO} + \text{Mn}_2\text{O}_3 \]

The typical EMF is 1.58 V.

5.4.4 Construction

A good discussion of the construction of alkaline manganese cell is given by Kordesch in reference 2. This subsection contains a less detailed discussion. Note that the alkaline manganese cells are constructed "inside-out" compared to the carbon-zinc cell (i.e., the zinc anode forms the central core of the cell and is surrounded by a thick-walled annulus of manganese dioxide cathode material, all contained in a steel can).

5.4.4.1 Positive Active Material

Manganese dioxide and carbon powders in the rough ratio of 6:1 are thoroughly mixed and inserted in a cylindrical steel can of the desired cell size. A cylindrical cavity is formed for the length of the center of the cathode, which is then lined with a macroporous woven or felted separator material inert in the potassium hydroxide electrolyte.

5.4.4.2 Negative Active Material

A highly porous zinc anode core, which can be made by several methods, is inserted into the cavity (see subsection 5.4.4.1) and a brass, spike-like, negative current collector is inserted axially into the zinc. The zinc anode may be amalgamated with 0.1 to 7 percent of mercury to suppress corrosion and hydrogen gas evolution. Considerable effort is currently being made to totally delete the mercury from these cells. The cathode and anode are both saturated with electrolyte, an aqueous solution of 25 to 50 percent potassium hydroxide.

5.4.4.3 Closure

Cell closure varies between manufacturers and provides cell terminals, sealing against electrolyte loss, and permeability for the release of evolved hydrogen.

5.4.5 Capacities and Configurations

Coin, button, and cylindrical cell configurations are available; capacities range from 0.03 to 20 A-h.
5.4.6 Typical Characteristics

As with other primary batteries, energy output is reduced by high rates or low temperatures (but to a lesser degree than carbon-zinc cells). A notable difference from the carbon-zinc cells is that a continuous discharge does not decrease the total energy output significantly. Figure 5-10 shows the effect of load versus capacity and may be compared with figure 5-3, which shows the effects for carbon-zinc cells. The typical effect of temperature on the alkaline manganese cell capacity is shown in figure 5-11 for high (~10-hr) and low (~100-hr) rates. Table 4-1 shows the typical heating effects for short-circuited alkaline manganese cells and their peak currents during short circuiting. The peak current is also referred to as the flash current (see references 6 and 7).

![Figure 5-10. Alkaline manganese D cell at room temperature—effect of load on capacity](image)

![Figure 5-11. Effect of load and temperature on alkaline manganese D cell capacity.](image)

5.4.7 Safety

As shown in table 4-1, short circuit effects are significant. The provisions for controls given in section 4 cover short circuits adequately, as well as other factors.
5.5 Mercuric Oxide-Zinc Alkaline

5.5.1 Major Usage

This type of battery is used where any of the following characteristics are permissible:

a. Very flat voltage characteristic in cells using nonhybrid cathode (see subsection 5.5.4.1) at low rates
b. Good energy density on weight and volume bases
c. Good shelf life (up to 2 years at room temperature)
d. Good high temperature performance (up to 95°C for short times)
e. More expensive than carbon-zinc or alkaline manganese
f. Poor performance at low temperature

5.5.2 Typical Applications

Some typical applications of the mercuric oxide-zinc alkaline battery include

a. Voltage references due to the very stable open circuit voltage of a nonhybrid cathode cell
b. Hearing aids (now mostly supplanted by zinc-air cells)
c. Watches
d. "Down-hole" applications in logging oil well drilling
e. Military radio batteries
f. Instrumentation
g. Aerospace penlights

5.5.3 Electrochemistry

The accepted reaction for the mercuric oxide-zinc alkaline is

\[ \text{HgO} + \text{Zn} \rightarrow \text{Hg} + \text{ZnO} \]

The EMF for nonhybrid cathode cells is 1.35 V. The EMF for hybrids is up to 1.40 V. (Hybrid cells contain a quantity of cadmium oxide in the cathode).
5.5.4 Construction

5.5.4.1 Positive Active Material

The cathode material for nonhybrid cells is a pelletized mix of finely ground mercuric oxide and graphite in the weight ratio of approximately 10:1, wet with electrolyte. The electrolyte is an aqueous solution of up to 50 percent potassium hydroxide, by weight. The electrolyte contains dissolved zinc oxide to limit anode corrosion. In hybrid cells, up to 30 percent of manganese dioxide, by weight, may be added to the powder mix to prevent agglomeration of liquid metallic mercury into globules during discharge. The pellets may be coin-shaped as in shorter cylindrical cells or arc shaped as in longer cells (described in subsection 5.5.4.2).

5.5.4.2 Negative Active Material

The anode is zinc and may be in one of several forms, depending on the application. Smaller (shorter) cylindrical cells may contain a wound spiral of thin, corrugated, zinc ribbon, wound together with a fibrous, absorbent material between the windings. It may also be a pressed, powdered zinc pellet, saturated with electrolyte. In longer cells, the anode may consist of long, pressed, powdered zinc pellets, bent into arc sections along their narrow dimensions. These are nested in the container in circles. The anode may also be perforated zinc sheets formed into a tube within the cell. In all cases, the zinc is amalgamated with up to 15 percent mercury, by weight, to reduce anode corrosion by the electrolyte.

5.5.4.3 Separators

The separator system consists of a layer of ion-permeable, barrier membrane polymer, such as polyvinyl alcohol (PVA), next to the cathode. A second layer, or set of layers, of electrolyte absorbent cellulosic material is next to the anode.

5.5.4.4 Closure

The container consists of a steel can, in contact with the cathode and separators, surmounted with a copper lid that is nickel plated externally. A polymer grommet seal is crimped between the can and the lid. Details of the closure and internal construction are shown in cutaway figures in references 2, 6, and 7.

5.5.5 Capacities and Configurations

Cells are available with capacities in the range of 0.05 to 14.0 A-h and in configurations from button cells to large, cylindrical cells. Table 5-3 lists several cell sizes available.
Table 5-3. Mercuric Oxide-Zinc Alkaline Cell Sizes

<table>
<thead>
<tr>
<th>IEC designation</th>
<th>Approximate diameter (mm)</th>
<th>Approximate height (mm)</th>
<th>Approximate weight (g)</th>
<th>Approximate capacity (mA-h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>11.0</td>
<td>30.0</td>
<td>12.0</td>
<td>800</td>
</tr>
<tr>
<td>R6</td>
<td>13.5</td>
<td>50.0</td>
<td>30.0</td>
<td>2,400</td>
</tr>
<tr>
<td>R9</td>
<td>16.0</td>
<td>8.0</td>
<td>4.0</td>
<td>350</td>
</tr>
<tr>
<td>R41</td>
<td>8.0</td>
<td>3.5</td>
<td>0.5</td>
<td>45</td>
</tr>
<tr>
<td>R42</td>
<td>11.6</td>
<td>3.5</td>
<td>1.5</td>
<td>100</td>
</tr>
<tr>
<td>R43</td>
<td>11.6</td>
<td>4.0</td>
<td>2.0</td>
<td>150</td>
</tr>
<tr>
<td>R44</td>
<td>11.6</td>
<td>5.2</td>
<td>2.5</td>
<td>210</td>
</tr>
<tr>
<td>1115M(NEDA)</td>
<td>30.0</td>
<td>60.0</td>
<td>166.0</td>
<td>14,000</td>
</tr>
<tr>
<td>R48</td>
<td>8.0</td>
<td>5.2</td>
<td>1.0</td>
<td>95</td>
</tr>
<tr>
<td>R50</td>
<td>16.0</td>
<td>16.5</td>
<td>12.0</td>
<td>1,000</td>
</tr>
<tr>
<td>R51</td>
<td>16.0</td>
<td>50.0</td>
<td>40.0</td>
<td>3,600</td>
</tr>
<tr>
<td>R52</td>
<td>16.0</td>
<td>11.0</td>
<td>8.0</td>
<td>500</td>
</tr>
</tbody>
</table>

Definitions:
IEC-International Electrotechnical Commission
NEDA-National Electrical Distributors Association

5.5.6 Typical Characteristics

The influence of load on capacity is small at moderate rates (e.g., the estimated room temperature capacity to 0.9 V end voltage for an R51 cell (penlight size) ranges between 3.98 ± 0.1 A-h from the 30-hr rate to the 100-hr rate). Higher rates reduce the available capacity. Performance at low temperatures is a function of anode construction (ref. 2); for example, the full capacity of a cell is available at 21°C. At -10°C, cells with pressed pellet anodes yield less than 10 percent of their full capacity, whereas wound anode cells yield 50 percent. At -20°C, neither construction yields useful energy.

5.5.7 Safety

The unique hazard of mercuric oxide-zinc alkaline cells is the mercury. Each cell contains at least 3.74 g of mercury per ampere-hour of rated capacity. Thus, an R51 cell (AA penlight size) contains at least 13.4 g of mercury. Mercury vapor is toxic to the human central nervous system when there is continuous exposure to 0.01 mg mercury per cubic meter of air, or 8.3 parts per billion by weight. This equates to a toxic level of 0.69 mg of mercury in the 2450 cu ft void volume of the Orbiter cabin. Additionally, metallic mercury readily amalgamates with many metals, including those used in the vehicle structure, causing embrittlement and failure. Under certain failure conditions (e.g., overheating, shorting, and charging), cells may open, vent, or burst, releasing mercury simultaneously. Mercuric oxide-zinc batteries for use in the Shuttle Orbiter are subject to Standard M/P 15 of JHB-8080.5, JSC Design and Procedural Standards Manual (appendix C). Thus, the mercuric oxide-zinc battery user must be able to show that no mercury can escape or provide a decontamination plan for the prompt recovery of all escaped mercury (or prove that no decontamination plan is necessary). An application to waive all or part of Standard M/P 15 can be presented to the Space Shuttle Program Requirements Control Board (NASA Level II), which decides whether the waiver is permissible. This involves completing a JSC form 281A, "Space Shuttle Program Level II Change Request." The form must be accompanied by justification data including the analysis and results of abuse tests—such as short circuit, exposure to high temperature (e.g., 180°C), overdischarge, and shock tests—involving the presumptive failure of cell seals. From the
foregoing information, it should be clear that, for Orbiter use, a significant savings in time and expense may result from the selection of a cell type that has a significantly smaller or no mercury content, such as alkaline manganese or silver oxide-zinc cells. Note that almost all cells which use zinc negatives contain small amounts of mercury amalgamated with the zinc to reduce hydrogen gassing. This is generally not considered hazardous. Again, even this amount of mercury utilization in commercial alkaline cells is being reduced or eliminated.

5.6 Lithium Anode Cells

For the purpose of this document, a lithium cell is any cell using elemental lithium as its anode whether its electrolyte and cathode consist of organic or inorganic chemicals; regardless of cell size, battery configuration, and number of cells in a battery; and regardless of location, in or on the vehicle. Lithium batteries have very high energy densities relative to other practical batteries. Table 5-4 gives a comparison of lithium-thionyl chloride/bromide chloride complex (Li-BCX) D-size cells with other familiar battery systems. Zinc-air cells are omitted from this chart due to the lack of availability of a commercial cell in a comparable size; however, zinc-air energy densities are competitive with the lithium systems.

Table 5-4. Energy Density of D-Size Cells (Manufacturer's Data)

<table>
<thead>
<tr>
<th>Cell type</th>
<th>Maximum watt-hours / kilogram</th>
<th>Maximum watt-hours / liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-zinc</td>
<td>66</td>
<td>110</td>
</tr>
<tr>
<td>Alkaline manganese</td>
<td>100</td>
<td>240</td>
</tr>
<tr>
<td>Mercuric oxide</td>
<td>110</td>
<td>488</td>
</tr>
<tr>
<td>Silver oxide-zinc (larger rectangular cell sizes)</td>
<td>215</td>
<td>450</td>
</tr>
<tr>
<td>Li-BCX</td>
<td>350</td>
<td>950</td>
</tr>
</tbody>
</table>

Under unique and abusive conditions, lithium cells can be forced to yield their contained energy suddenly and explosively. For example:

a. Any condition which causes the lithium anode to reach its melting point, 180.5°C. Heating conditions include the application of external heat, externally applied short circuits, and physical abuse such as crushing or penetration by a sharp object, which result in internal shorting, or failure to provide for the removal of heat generated by internal losses while discharging at high rates.

b. Overdischarge: Any cell which is discharged until its voltage falls to 0 V and is then forced to continue discharging into negative voltage, whether by cells in series with it or by another power supply undergoing overdischarge, or by forced discharge.

c. Charging long enough at a high rate, however low or high that may be for a particular lithium cell chemistry.

d. The design of some lithium cells, such as lithium-sulfur dioxide, and some lithium-thionyl chloride cells, include a burst disc in the cell case to relieve internal
overpressure under certain abusive use conditions. A cell which by design releases toxic sulfur dioxide gas into a sealed habitable volume is clearly not acceptable for such an application.

It must be noted that lithium-based cells are subject to extremely close review and are required to have seemingly excessive hazard controls incorporated in and on them. They can yield extremely high energies per unit weight and volume relative to other cell types. They have uniquely hazardous failure modes. The chemicals contained in them are usually either highly flammable (e.g., lithium), corrosive, and/or toxic (e.g., sulfur dioxide, hydrogen chloride, and cyanide derivatives). In their various failure modes, they are subject to leakage, venting (spewed leaks), or violent explosions accompanied by scattered shrapnel and toxic materials. Hence, every effort is made to provide utmost assurance that every known or suspected failure mode is prevented by effective hazard controls. The use of other types of cells is strongly encouraged wherever feasible. Weight and volume differences alone are not necessarily sufficient justification for the use of lithium-based cells.

5.6.1 Major Usage

This type of battery is used where any of the following characteristics are desired or permitted:

a. Generally low power density (watts per kilogram or liter)
b. High energy density (watt-hours per kilogram or liter)
c. Good shelf life (see table 3-1)
d. Moderate cost
e. Good voltage regulation
f. Hazardous behavior under off-nominal usage controllable with appropriate diodes and fuses
g. Good temperature range of operation (see table 3-1)

5.6.2 Typical Applications

NASA applications have included the following (chemical formulas are defined in subsection 5.6.3):

a. Li-SO₂ and Li(CF)ₙ used in the Long Duration Experiment Facility (LDEF)
b. Li-BCX used in the wireless crew communications system (WCCS)
c. Li-SOCl₂ used in the Shuttle portable onboard computer (SPOC)
d. Li-MnO₂ used in the temperature recorder, SARSAT and portable data acquisition package (PDAP)
e. Li-(CF)$_n$ used in the Shuttle Solid Rocket Booster (SRB) and External Tank (ET) range safety systems
f. Li-BCX used in the extravehicular mobility unit (EMU) TV and helmet lights
g. Li-BCX used in the AN/PRC-96 survival radio
h. Li-BCX used in the cassette data tape recorder (CDTR)
i. Li-I used in the system control module (SCM)
j. Li-I used in the large format camera
k. Li-(CF)$_n$ and Li-I used in the continuous flow electrophoresis system (CFES)
l. Li-BCX used in the ultrasonic limb plethysmograph (ULP)
m. Li-SO$_2$ used in the ORFEUS-SPAS, CRISTA-SPAS, and ASTRO-SPAS payloads, Galileo satellite, and LDEF

5.6.3 Electrochemistry

Several lithium anode battery chemistries are described in the following subsections. The format used is

a. Name and formula (or abbreviated designation)

b. Reaction formula (best present estimate)

c. Electrolyte content

d. EMF

e. Typical current drain rates

Extensive details of lithium cell chemistry are given in references 2 and 8.

5.6.3.1 Lithium-Thionyl Chloride (Li-SOCl$_2$)

a. 4 Li + 2 SOCl$_2$ $\rightarrow$ 4 LiCl + S + SO$_2$

b. Electrolyte: LiAlCl$_4$ dissolved in the SOCl$_2$ catholyte

c. EMF: 3.6 V

d. 10-hr rate and lower currents
5.6.3.2 Lithium-Thionyl Chloride/Bromide Chloride Complex (Li-BCX)

a. $8 \text{Li} + 2\text{SOCl}_2 \cdot \text{BrCl} \rightarrow 6 \text{LiCl} + \text{S} + \text{SO}_2 + 2 \text{LiBr}$

b. Electrolyte: LiAlCl$_4$ and BrCl dissolved in the SOCl$_2$ catholyte

c. EMF: 3.9 V (higher than the Li-SOCl$_2$ EMF due to BrCl complexing)

d. 10-hr rate and lower currents

5.6.3.3 Lithium-Sulfur Dioxide (Li-SO$_2$)

a. $2 \text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$ (lithium dithionite)

b. Electrolyte: SO$_2$ + LiBr dissolved in an organic solvent such as CH$_3$CN (acetonitrile)

c. EMF: 3.1 V

d. 10-hr rate and lower currents

5.6.3.4 Lithium-Polycarbon Monofluoride (Li-(CF)$_n$)

a. $n\text{Li} + (\text{CF})_n \rightarrow n\text{LiF} + n\text{C}$

b. Electrolyte: LiAsF$_6$ (lithium hexafluoroarsenate) dissolved in (CH$_3$O)$_2$SO (dimethyl sulfite)

c. Alternate electrolyte: LiBF$_4$ (lithium tetrafluoroborate) dissolved in butyrolactone and tetrahydrofuran or propylene carbonate and dioxolane

d. EMF: 3.1 V

e. 2-hr rate and lower currents

5.6.3.5 Lithium-Manganese Dioxide (Li-MnO$_2$)

a. Li + MnO$_2$ → LiMnO$_2$

b. Electrolyte: LiClO$_4$ (lithium perchlorate) dissolved in propylene carbonate and dimethoxyethane (alternative electrolyte used by Panasonic is a combination of dimethylformamide, tetrahydrofuran and acetonitrile. Also, an electrolyte developed by Duracell, lithium-trifluoromethanesulfonate salt in propylene carbonate, ethylene carbonate, and dimethoxyethane, is preferred due to its lower level of toxicity.)

c. EMF: 3.2 V
d. 2-hr rate and lower currents

5.6.3.6 Lithium-Iodine (Li-I₂)

a. 2 Li + I₂ → 2 Lil

b. Electrolyte: Lil, formed at the solid interface between the anode and cathode when first assembled into contact with one another

c. EMF: 2.8 V

d. Days and lower currents

Note: The iodine cathode consists of poly-2-vinylpyridine containing dissolved iodine.

5.6.4 Construction

A detailed discussion of the internal construction of each of the six types of lithium batteries just summarized is considered beyond the scope of this document, particularly in view of the accurate and detailed presentations given in references 2 and 8. Therefore, the following material is purposely general. It can be stated, however, that larger lithium cells are hermetically sealed with a glass-to-metal feed-through. Closures are made by welding Li-BCX and Li-SOCI₂ cells use a 304L stainless steel case to prevent corrosion at the weldment. Li-SO₂ cells generally use nickel-plated steel for cases.

5.6.4.1 Cathodes

Cathodes are generally of three types, as described in the following subsections.

5.6.4.1.1 Soluble Cathodes. These cells have liquid solvent cathode material, which contains various ionic solutes. They include Li-SO₂, Li-SOCI₂, and Li-BCX. The soluble cathodic material is often referred to as catholyte, since it is a combination of electrolyte solution and cathode. The catholyte discharge reaction takes place at a positive, inert electrode consisting of porous carbon mixed with a binder and spread on a metal screen current collector.

5.6.4.1.2 Solid Cathodes. In these cells, the cathode material is a solid mixed with conductive material such as carbon and a binder, which is spread on a metal screen current collector. A fluid electrolyte provides for ion movement between the cathode and lithium anode. These cells include Li-(CF)n and Li-MnO₂.

5.6.4.1.3 Solid Electrolyte. The cathode, anode, and electrolyte in these cells are all solids. One example, Li-I₂, is contained herein. In the Li-I₂ cell, the Lil solid electrolyte is formed when the lithium anode and iodine cathode pellets are first placed in contact with each other during construction. This forms a thin, high impedance, ionically conductive film which thickens by formation of the Lil discharge product as discharge progresses.
5.6.4.2 Anode

The anode material is almost invariably a lithium foil sheet which may be pressed into a conductive metal screen.

5.6.5 Capacities and Configurations

Coin, button, and cylindrical cells having capacities from 0.03 to 35 A-h are available. Large, rectangular cells having capacities in the range of 20,000 A-h have been made for Department of Defense applications.

5.6.6 Typical Characteristics

No attempt will be made herein to show complete sets of performance characteristics for each of the six previously mentioned cell types. The figures in this subsection depict Li-BCX D-size cells that are demonstrative of behavior trends.

Figure 5-12 shows the effect of temperature on capacity, with load as a third variable. Performance at high and low temperatures is reduced, being optimized in the range of 10°C to 30°C. Performance is also reduced by increased current drain. The reduction of capacity at high temperatures (70°C) does not occur for all lithium batteries. Figure 5-13 is a cross-plot of data used in figure 5-12.

![Figure 5-12](image)

*Figure 5-12. Li-BCX D cell capacity versus load at various temperatures (using fresh cells).*
Figure 5-13. Li-BCX D cell—effect of load and temperature on capacity.

Figure 5-14 shows the shape of the discharge curve for a 20-ohm load at various temperatures. The 20-ohm load results in the 80-hr rate at room temperature. The initial bump is not present on other lithium cell types. It is due to the preferential discharge of the bromine complex agent relative to the lithium/thionyl chloride reaction. Figure 5-15 shows capacity at various loads as affected by storage time and temperature.

Figure 5-14. Li-BCX D cell—typical discharge curves.
Figure 5-15. Li-BCX cell—effect of storage time and conditions on capacity.

The performance of thionyl chloride cells would be similar to that of Li-BCX cells, except voltages would be slightly lower and there would be no initial bump.

The lithium anode develops a passivating layer of lithium chloride on exposure to thionyl chloride. The thickness increases at a decreasing rate with time. It is responsible for the "voltage delay," that is, slow voltage rise, e.g., 60 seconds to operating voltage, which is characteristic of these cells. Without this passivating layer, however, as happens when lithium melts, there would be a concerted and violent chemical reaction between the lithium and the thionyl chloride.

In figure 5-16, the comparative performances of two solid cathode cells, Li-(CF)$_n$ and Li-MnO$_2$ of 2/3 A-size, are shown. The data are for room temperature performance. There is little effect on service hours at higher and lower temperatures, except below 100 ohm/cell. At the resulting higher current drains, service hours are decreased, as is average discharge voltage. Figure 5-17 shows relative voltage-time curves of 2/3 A-size Li-(CF)$_n$ and Li-MnO$_2$ cells discharged at 300 ohm and room temperature.
Figure 5-16. Li-(CF)$_n$ and Li-MnO$_2$ cell performance at 21°C (2/3 A cells)—load versus service hours.

Figure 5-17. Li-(CF)$_n$ and Li-MnO$_2$ cell performance at 300 ohm and room temperature—typical discharge curves.

5.6.7 Safety

Subsection 5.6 describes some of the safety hazards associated with lithium anode batteries. The following subsection provides controls which have been effective in prior applications.
5.6.7.1 Controls

a. Thermal controls: Cell/battery temperatures must be controlled below the manufacturer's stated upper temperature limit (e.g., 72°C for Li-BCX). Testing should be done to verify safe performance at such limits. An account must be given of both external heat sources and heat generated by the cells due to internal losses on discharge (see subsection 4.4.1). Methods of thermal control are given in subsection 4.4.3.

b. Short circuit controls: Overcurrent protection devices must be provided such as fuses or circuit breakers, regardless of whether or not the cells have self-contained fuses. Protective devices should be rated above the highest likely load current, but well below the short circuit capability of the battery as established by testing (see subsection 4.1.3).

c. Overdischarge protection: This does not apply to single-cell batteries in applications where no external series power supply can be applied to the cell. Wherever more than one cell is used in series, all cells must have one or more shunt diodes attached to them (depending on redundancy requirements) so that the diodes become conductive at the smallest possible negative voltage. Conservatively current-rated Schottky barrier rectifiers have been used on Orbiter equipment using Li-BCX batteries since they conduct at -0.25 to -0.3 V, whereas silicon diodes require -0.5 to -0.6 V for conduction. It is important to strive for the least negative value. A concern for short circuiting of the cell by shorting diodes is addressed by the typical cell self-contained fuse; or by the provisioning of fuses in the diode bypass circuit. A low voltage cutoff circuit may be used wherever analysis supported by testing demonstrates that the cutoff operates to remove the load from the battery whenever any single cell in the battery nears zero voltage. (Before it was determined that the optimum design of a lithium-sulfur dioxide cell required a balanced design, i.e., ampere-hour capacity of positive and negative electrodes being equal, reversal often resulted in venting. Besides methane and excess electrolyte, the formation of "popcorn polymer" resulted from the action of excess lithium on the acetonitrile.)

d. Charge prevention: The basic control is to avoid paralleling batteries, or strings of cells within a battery, either of which may force a charging current through a stack of cells containing a weak or dead cell (or cells). However, if parallel strings of cells must be used, each string must contain two blocking diodes. One of the failure modes of diodes is to fail short circuited. Batteries which must be paralleled with external power sources must have charge current blocking devices. The special case of cells used to back up power supplies to memory circuits (e.g., complementary metal oxide silicon (CMOS), random access memories (RAM) and timers) follows in subsection 5.6.7.2.

e. Do not solder leads directly to a lithium cell, as damage to the separator can result. If the cell does not have tabs, use a spot welder to attach leads.

f. The use of prepackaged multicell lithium batteries should be avoided. If they are used, however, it is imperative that documentation be provided which shows that the hazard controls stated above are incorporated.
5.6.7.2 Lithium Batteries in Backup Power Applications

Small lithium batteries and button cells are used as backup sources for microwatt and milliwatt circuits such as clocks, CMOS, counters, and RAM. A typical circuit is shown in figure 5-18. A high value resistor (kiloohms) may also be included at position A, and a fuse may be included at position B.

![Figure 5-18. Typical lithium cell backup circuit.](image)

A safety problem can exist in these various circuits if the blocking diode fails by short circuiting, and resistor A and fuse B have inadequate ratings to prevent significant charging currents from flowing into the lithium battery from the parallel power supply. Tests have shown that such charging currents can cause certain types of lithium cells to explode violently. Not all of the wide variety of lithium-based cells have been tested, and only limited quantities of any particular type have been tested. Hence, for equipment to be flown in manned space vehicles, certain circuit modifications have been necessary to ensure safe operation. These modifications are in lieu of lengthy, expensive testing to determine the hazardous nature of any and all types of lithium cells.

In order to assess the safety of a particular battery circuit, without extensive tests of the many batteries necessary to disclose a low rate of failure, the following data are necessary:

a. The current which the cell will pass in the charging direction when the lowest and highest power supply voltages to reach the cell are applied. This would be the low and high ends of the power supply output voltage tolerance, minus any impedances between the power supply and the cell (diode assumed shorted).
The charge currents should be determined using samples of five or more cells from each of two or more manufacturing lots in order to evaluate variability.

b. Nominal current supplied to the load by the cell at its operating voltage with the power supply off.

c. Minimum voltage to operate load.

With these data, a decision can be made concerning the addition of a fuse at position B on figure 5-18. Any fuse has a blow-time which is virtually instantaneous at some value of current larger than its rating. For example, Littlefuse picofuses blow within 5 sec of applying a current equal to 200 percent of the fuse rating. Thus, a picofuse rating should be determined that is equal to half, or less, of the cell charging current determined previously. If this rating exceeds the nominal load current supplied by the battery, it is a satisfactory fuse to insert at position B in the battery circuit of figure 5-18, and the battery will be considered safe even if the diode fails short. However, when the fuse blows, there is no longer a backup power source available.

If the fuse rating determined in the method previously mentioned is less than the nominal load current supplied by the battery, such a fuse clearly cannot be used. In such a case, series redundant diodes must be used. Two series diodes are required for fail-safe (FS) operation; three series diodes are required for FS/FS operation. The additional diode (or diodes) will reduce the voltage available from the battery circuit. Hence, it is necessary to evaluate the resulting voltage available versus the minimum voltage required to operate the load. If insufficient voltage is available, it will be necessary to add a cell in series with the existing cell. This, in turn, introduces the possibility of overdischarge of one of the series cells, which has been shown to result in violent venting of some types of lithium cells. Therefore, the use of more than one cell in series will result in a further requirement to install an appropriately rated, protective shunt diode on each cell. One diode per cell is sufficient for FS operation; two diodes per cell are necessary for FS/FS operation. These arrangements are shown in figure 5-19.

![Figure 5-19. Typical lithium cell backup circuit with hazard controls.](image-url)
The use of a current-limiting resistor at position A of figure 5-18 in lieu of shunt diodes where more than one cell is used, or in lieu of a fuse at position B where a fuse can be used, requires a determination of the minimum value of cell charging current below which no hazard can occur due to charging. Such a determination requires lengthy testing of a large number of sample cells if a low failure rate exists. Therefore, the use of a limiting resistor is not recommended unless such data are available. Underwriters Laboratory (UL) data can be used to meet this requirement if the cell in question has undergone the UL testing. The amount of possible charging current must still be determined, either by test or analysis, in order to use the UL data, however. Also, a means must be provided to check out the redundant diodes to verify continuing redundancy.

To summarize, the following hazard controls are necessary. They are shown in order of simplicity and assume avoidance of lengthy battery tests:

a. A blocking diode in the battery circuit is mandatory.

b. A current limiting resistor may be used if data exists to support its use.

c. A fuse rated as determined previously must be added if the relationship between fuse rating and load current permits it.

d. If a fuse cannot be used due to incorrect relationship between the fuse rating and the load current, series redundant diodes must be used.

e. If the use of series redundant diodes requires compensation of voltage drop by an additional cell (or cells), shunt diodes must be used on the cells.

From all of the foregoing information, it should be clear that it would be simpler to use less energetic types of cells requiring fewer or no hazard controls in this application. Button cells or small cylindrical cells are available (made with silver-zinc, zinc-manganese alkaline, zinc-air, or even zinc-mercuric oxide couples) that can provide the required service, usually in nearly the same volume.

5.6.7.3 Qualification and Acceptance Testing of Lithium Batteries

a. Given that one of the functions of qualification tests is to verify the effectiveness of hazard controls (see subsection 6.1), qualification tests as detailed in section 6 should be performed on all lithium batteries and cells intended for space applications. In many instances, except for hazard controls, qualification can be facilitated by the use of analysis and other valid test data.

b. Acceptance testing should also be required for lithium anode flight batteries as described in section 7, with emphasis placed on the specific provisions for lithium batteries detailed in subsection 7.2.1d.
5.6.7.4 Personnel Certification

Personnel who are required to handle lithium batteries or cells must know the safety hazards associated with lithium batteries and must be trained in appropriate controls against such hazards before they may routinely handle lithium batteries.

5.6.8 Shipping, Handling, and Disposal of Lithium Batteries

5.6.8.1 Shipping

Transportation of both new and used lithium batteries is governed by the federal regulations relating to the shipment of hazardous materials. The regulations are published in paragraphs 172.101, 173.206(e)(1), and 175.3 of Title 49, Code of Federal Regulations. The research and special program administration of the U.S. Department of Transportation (DOT), Washington, DC 20590, has issued exemptions to allow for the shipment of lithium cells and batteries if detailed requirements regarding cell size, test results, and packaging are met. Fresh batteries, alone or in equipment, may be shipped by motor vehicle, rail freight, cargo vessel, and cargo-only aircraft under exemption DOT-E-7052. Any company or group shipping under this exemption must be explicitly registered with the DOT as a party to this exemption prior to shipping batteries by any mode. Exemption DOT-E 8441 permits the shipments of waste lithium batteries to a disposal site only by a motor vehicle. (See also subsection 5.6.8.4)

Exemption 7052 requires the proper shipping name, "Batteries Containing Lithium Metal," to be on each shipping container. It prohibits the shipping of cells containing more than 0.5 g of lithium each by passenger aircraft. Each cell and battery must be equipped with an effective means of preventing external short circuits and must incorporate a safety venting device or be designed in a manner that precludes a violent rupture.

For cells or batteries made from cells containing less than 0.5 g of lithium, paragraph 173.206F of Title 49, Code of Federal Regulations is applicable. Such cells are unregulated and may be transported by passenger carrying aircraft.

5.6.8.2 Packaging

Some of the important guidelines for packaging cells and batteries are as follows:

a. Cells and batteries must be packed in strong inner fiberboard (corrugated) containers limited to a maximum of 500 g of lithium in one inner container. No cell containing more than 12 g of lithium may be shipped under exemption 7052.

b. When drums are used, the inner containers must be separated from each other and from all inner surfaces of the drum by at least a 1-in. thickness of vermiculite or other equivalent noncombustible cushioning materials.

c. For shipment by cargo-only aircraft, the outside container must be a DOT specification 17H or 17C series removable-head drum and be equipped with a gaslight gasket.
d. For shipment by water, motor vehicle, or rail freight, the outside container must be a strong wooden box.

The information given regarding packaging and transporting lithium cells and batteries is for general information only. Any shipper of lithium cells and/or batteries should purchase and maintain updated regulation guides from DOT, the International Air Transport Association (IATA), and the International Civil Aviation Organization (ICAO) in order to have a thorough and current understanding of proper shipping methods.

5.6.8.3 Storage

Special care is needed for storage of lithium cells and batteries. It is desirable for storage facilities and fire fighting provisions to be reviewed and approved prior to storage of lithium cells in any area. Once the storage area is established, the quantity of cells and batteries added or removed from storage must be monitored. Partially discharged, fully discharged, or reversed cells and batteries (e.g., lithium-sulfur dioxide and lithium-thionyl chloride) have been reported to be more hazardous than fresh ones. Hence, fresh and used cells and batteries should be stored separately. The following precautions are recommended for storing new and used cells and batteries.

Store new lithium batteries as follows:

a. Lithium batteries shall be stored in their original shipping containers in a cool ventilated shelter.

b. The storage area shall be isolated from other hazardous and combustible material and used only for the storage of unused lithium batteries.

c. Lith-Ex fire extinguishment material should be on hand in case of fire. In addition to a dry chemical fire extinguisher, the Lith-Ex may be stored in a pail together with a small shovel for smothering burning lithium.

d. Sustained storage above 25°C should be avoided, as should any excursions above 54.5°C. The optimum storage temperature is -10°C to 0°C.

e. Special care shall be exercised in handling and moving containers to prevent crushing or puncturing them.

Store used lithium batteries in the following manner:

a. Used lithium batteries shall be packaged in accordance with subsection 5.6.8.2.

b. A remote collection point and storage area, separate from other combustible material, shall be established for batteries awaiting disposal.

c. Used lithium batteries are not to be commingled with normally generated refuse.

d. Used lithium batteries shall not be burned, dropped, dismantled, modified, or otherwise carelessly handled, short-circuited, charged, or reused.
Storage space shall be properly ventilated. When a storage space is entered in which lithium batteries may have vented gas, air respirators or self-contained breathing apparatus approved by the National Institute for Occupational Safety and Health (NIOSH) shall be worn.

5.6.8.4 Disposal

Used (and new) lithium batteries are considered hazardous materials by the Environmental Protection Agency (EPA). Additionally, improper disposal of lithium batteries can be very dangerous. The various safety problems in the disposal of lithium batteries include venting of toxic gases and liquids, violent explosions, and fire. These hazards are basically due to the extreme reactivity and the toxic nature of cell components and discharge products. A rough estimate of the explosive hazard of one D cell (approximately 0.1 lb. of lithium and catholyte) is assumed to be equivalent to 0.1 lb of trinitrotoluene (TNT). Some partially or fully discharged cells are reported to be more hazardous than new cells. Hence, it is necessary to take great care in the disposal of these cells and batteries. It is advisable to seek the assistance of concerned authorities (i.e., the EPA of the state concerned) before disposing of the cells. They must be disposed of per the established and recommended procedures. The transport of hazardous waste is regulated by 40 CFR Part 263, which provides for the proper identification of the transporter and manifesting of the waste. The various methods attempted so far for the disposal of the cells fall into one of the following categories:

a. Controlled rupture and incineration with adequate scrubbers by EPA-approved disposal companies (preferable mode)

b. Disposal in landfills after discharging them and packing in vermiculite filled drums (do not dispose of cells with normally generated refuse.)

c. Keeping the cells in disposal ponds or lagoons
Section 6
Qualification Testing

6.1 Requirement

Qualification testing of primary batteries for use in critical applications should be performed, even though the selected battery may be commonly available to the general public through ordinary commercial outlets. This is to ensure adequate performance capabilities in the specific ground and space environments of the intended application. It is also to ensure that the batteries have effective hazard controls designed into and onto them for all hazards associated with the particular battery type and that these controls work in the expected environments.

6.2 Test Configuration

An essential aspect of space battery qualification testing is that tests must be performed with the batteries installed in the equipment in which they are to be used or in an accurate physical and thermal simulation thereof. This is necessary to ensure that adverse interactions between the batteries and the equipment are discovered and accommodated. This requirement becomes especially important with regard to the thermal environment and performance of the batteries.

6.3 Test Objectives

Qualification testing must verify the following capabilities and conditions.

a. The ability to provide the required energy (watt-hours) at the required power levels (watts) must be verified under the environmental extremes of the intended application.

b. The ability to remain within the required voltage regulation during power drain transients, within the sensing capability of voltage sensitive equipment, must be verified. That is, severe undervoltage lasting 0.1 sec is of no consequence to a device which cannot respond to an undervoltage in less than 0.2 sec.

c. The ability to deliver the required energy after subjection to all reasonably projectable periods and conditions of storage prior to being placed on load must be verified. This includes both prelaunch and postlaunch storage.

d. Qualification test documentation must demonstrate that the batteries subjected to qualification testing are physically, electrochemically, and electrically the same as batteries which will be flown. It must also demonstrate that the qualification test articles are manufactured by the same manufacturer using the same methods, procedures, processes, and manufacturing equipment that will be used on flight batteries, to the extent such verification is possible. This may be difficult or impossible to verify in the case of some commercially available cells for which the flight batteries are a small fraction of the vendor's business or the vendor uses proprietary processes and materials he is unwilling to disclose. In such cases, qualification and engineering test data must be obtained to develop requirements for acceptance tests to be performed by either the vendor or the buyer on battery
purchases intended for flight. These acceptance tests shall essentially be incremental qualification tests and shall emphasize the tests which verify continued resistance to known hazards. See section 7 for further information on these requirements.

e. It must be verified that all hazard controls are working. This includes abuse testing which provides conditions requiring hazard controls to function and/or actuate while under extremes of environment, energy delivery, and/or fault conditions.

f. Sufficient test articles for extended life storage tests must be provided to perform shelf-life tests which yield capacity retention data over several time increments from the date of manufacture (e.g., 6 months, 12 months, and 18 months). These tests do not require pass/fail criteria or completion prior to certification of the battery for flight, as long as fresh batteries are used for flight. The data obtained shall be used to establish allowable storage times prior to use.

g. In complying with the conditions and capabilities mentioned above, some qualification requirements may be met by producing analyses supported by related test data, if technically justifiable. The exception to this shall be any requirement consisting of, or relatable to, safety requirements and hazard controls.
Section 7
Acceptance Testing

7.1 Purchasing

Arranging and enforcing the acceptance testing discussed in this section is easily accomplished in the case of special battery designs, which are developed and qualified under contract with a battery manufacturer and purchased in flight quantities from that manufacturer. In the case of common commercial cell and/or battery types available to the general public, procurement should be made directly from a manufacturer, in lieu of a jobber or distributor. Two benefits accrue from such a practice: fresh batteries with known manufacturing dates can be required, simplifying control of shelf life, and the possibility is increased of obtaining an agreement with the manufacturer that defective material found in acceptance testing (by the seller or the buyer) will be replaced by the manufacturer.

7.2 Types of Acceptance Tests at Delivery

Formal acceptance testing should be performed by the seller or buyer as a condition of acceptance at the time batteries are offered for delivery or on receipt of shipment, depending on the contractual agreement reached with the seller.

Since primary batteries are single-discharge (one-shot) devices, destructive tests or tests which expend a significant part (or all) of a battery's capacity must be performed on a sampling basis. Nondestructive acceptance testing can be completed on 100 percent of batteries to be delivered. Recommended tests of both types are given in the following subsections. Use of any particular test will depend on the type of battery purchased.

7.2.1 Tests Performed on all Batteries Submitted for Acceptance

a. Each cell or battery must be examined for cleanliness, evidence of leakage or damage, and variance from design configuration. Flaws of a purely cosmetic nature may be permitted at the buyer's discretion. Each cell shall be labeled with the manufacturer's name and the cell model number. If not on the label, the voltage, capacity, and type chemistry should be noted on the accompanying paperwork.

b. All dimensions (length, width, height, and diameter) and weights must be verified as correct, depending on the buyer's requirement for such information.

c. It must be verified that the cell open circuit voltage is at an acceptable level. This test and the loaded voltmeter test (discussed in the next paragraph) obviously cannot be performed on cells which are purchased dry and to which the electrolyte will be added later by the buyer (e.g., manually or automatically activated silver oxide-zinc primary cells and batteries). In the latter case, continuity checks should be made between the terminals of each cell to verify that no internal short exists. The continuity test can be performed with an ohmmeter or a dielectric tester at the discretion of the buyer. Checking the open circuit voltage only reveals that the cell is at the proper state of charge and is not internally short-circuited. No information is obtained on the amount of energy available, except on a gross estimate basis.

7-1
d. A loaded voltmeter test must be applied to show that the load voltage is at or above a minimum acceptable level, based on prior test data. This test is conducted by applying a known resistive load for a fixed time and reading the voltage at the end of that time. The fixed time should be brief (30 to 90 sec) so that the capacity expended on the test is negligible relative to the expected full capacity. The resistive load should be at or near the load of the intended application. Again, the loaded voltmeter test reveals nothing about energy delivery to be expected. It shows whether or not the tested cell has any supranominal internal impedance and whether or not it should be expected to deliver the load at an acceptable voltage level.

e. For batteries enclosed in metal cases, dielectric checks must be performed between each of the main battery terminals and the case (but not between the battery terminals themselves). This is to ensure the lack of grounds between cells and case, and is not feasible unless the cells contain their electrolyte.

f. Dry charged multicell batteries (usually silver-zinc type) should be checked to ensure there are no loose intercell connections, and at the connector, pin by pin to ensure the proper wiring sequence.

g. Potting should be examined to ensure that vents are not blocked.

h. Dry charged batteries should be received with premeasured filler kits of electrolyte.

i. In some instances, individual cell X-rays are required. Applicable circumstances are

1. High reliability and/or safety are critical.

2. Presence and configuration of critical cell components are discernible on X-ray pictures.

3. Adequate standard X-ray pictures of good and bad cells are available to assist in discerning anomalous internal configurations.

j. High temperature dimensional and electrical stability of cells must be verified. For example, Li-BCX cells bought by JSC are each soaked at 72°C for 2 hours as a condition of acceptance. This is the manufacturer's upper limit of use. No leakage or dimensional changes are permitted, and cells must meet open circuit and load voltage test criteria after cooling to room temperature.

k. An example of testing for leakage on a 100 percent basis is given by the normal test performed for commercial alkaline cells for Shuttle flights; namely, subjecting all incoming cells to a pressure (vacuum) of <0.1 psia for 6 hours, then performing a visual inspection for leakage.
7.2.2 Tests Performed on Samples

a. Sample sizes should be based on a known sampling system such as MIL-STD-105 or some other system endorsed by the buyer's quality assurance organization.

b. Capacity (electrical life) tests should be performed at the discharge rate (or rates) used in the intended application.

c. If batteries are to be exposed directly to a vacuum, the capacity test samples should be tested under vacuum conditions, including the time of storage on orbit prior to use. Any high temperature expected in use should also be applied.

d. For lithium batteries, tests should be performed to verify continued resistance to abuse and continued efficacy of hazard controls (observe safety precautions during tests); for example:

1. Resistance to short circuits must be verified with or without thermal shunts, depending on the manner in which qualification testing was performed. The short circuit load should be $\leq 50$ m$\Omega$, unless prior testing has shown that higher resistances provide worse cases of abuse.

2. It must be verified that integral fuses, if used in the battery design, function according to design intent. In lieu of this test, the manufacturer's acceptance data performed at the component level when he received the fuses into his stock may be used if he has maintained fuse lot traceability from acceptance test to installation.

3. Overdischarge tests must be performed which verify continued efficacy of shunt diodes in preventing hazards due to overdischarge. Stress should be applied during such a test through exposure to high or low temperature extremes, depending on findings of prior testing.

4. Cells must be exposed to a high temperature just below the temperature which resulted in failure during prior testing. (Failure can include dimensional distortion, leakage, venting, or explosion, depending on criteria defined by the buyer.) The purpose is to confirm that failures do not occur at the acceptance test temperature: for example, 72°C for Li-BCX cells. LiBCX cells must also withstand 149°C for 15 minutes without failing except for bulging at the bottom. No leaking, venting, nor rupture is allowed.

5. Random vibration tests must be performed on each lot.

7.3 Preflight Acceptance

a. At the latest possible time prior to installing batteries in their launch position, a final check of acceptability must be performed. This check should include the open circuit voltage, loaded voltmeter test, and dielectric tests of 7.2.1.c, d, and e and the visual examination of 7.2.1.a.
b. If the battery is to power critical equipment or a critical system, telemetry should be provided from the time it is installed in its launch position until launch (as a minimum). Postlaunch telemetry may also be required. Telemetry should typically include battery voltage, current, and temperature. Where possible, telemetry should also provide monitoring of individual cell voltages. Prelaunch limits (redlines) for each telemetry channel should be established, by which continued acceptability of the battery can be judged. Critical, in the sense of this paragraph, means that loss of the battery could result in loss of primary mission goals, loss of the flight vehicle, or harm to ground crews or flight crews.
Section 8
References


* NHB 8060.1C may be obtained by NASA employees through field installation Directives Officers; others may submit requests to the NASA Headquarters Information Center, Code JOB-24, National Aeronautics and Space Administration, Washington, D.C. 20546-0001.

** NSTS 1700.7B may be obtained by JSC employees from JSC Distribution/PS34, by NASA-affiliated requesters and payload customers through the Payload and Crew Equipment Branch, Code NS2 at Johnson Space Center, Houston, Texas 77058. Other interested parties may contact the authors of this document at the numbers listed in the preface.
Appendix A

First Aid for Exposure to Electrolytes
First Aid for Exposure to Electrolytes

Reference should be made to the appropriate Material Safety Data Sheet (MSDS) provided by suppliers for detailed information.

1. Potassium Hydroxide (KOH)

   **Eye exposure:** Immediately irrigate the exposed eyes with copious amounts of water for at least 30 minutes, holding the lids apart to get complete washing. Follow this with treatment by an ophthalmologist.

   **Inhalation exposure:** Move patient to fresh air. Check patient for respiratory distress; emergency airway support and 100 percent humidified supplemental oxygen with assisted ventilation may be needed. Get medical attention at once.

   **Skin contact:** For minor exposure (for example, the pads of the fingers), neutralize the caustic by rinsing the fingers with a saturated solution of boric acid (do not use acetic acid), followed by thorough washing. If exposure is more extensive, remove contaminated clothing and irrigate the exposed skin with copious amounts of water for at least 15 minutes. Get medical attention if irritation or pain persists after washing.

2. Electrolyte from certain lithium batteries (thionyl chloride, BCX, sulfur dioxide)

   These materials if spilled will be present as both liquid and gas. Move the patient to fresh air. If the patient is not breathing, give artificial respiration. If breathing is difficult, give oxygen. Remove contaminated clothing and shoes. Flush eyes and skin with running water at least 15 minutes. If splash is directly to the eyes, flush eyes for at least 15 minutes with lids held open. Keep patient quiet and maintain normal body temperature. Get prompt medical attention. If exposure is by inhalation, respiratory distress may not appear for 24 hours.
Appendix B

Air-Permeable Electrolyte Repellent Fabric for Lining Zinc-Air Battery Cases
Appendix B

Air-Permeable Electrolyte Repellent Fabric for Lining Zinc-Air Battery Cases

A material which has been found satisfactory for lining the inside of zinc-air battery cases is GORE-TEX® fabric, manufactured by W. L. Gore and Associates, Inc., Membrane Products Division (part number L11517). This material has been used to make lightweight, waterproof tents, and windbreakers that "breathe." The material has three layers of material bonded together. The two outer layers are woven nylon and the inner layer is a thin sheet of microporous polytetrafluoroethylene (PTFE). The material has been purchased and installed according to the specifications and sketches shown on JSC Drawing SED33103430. Although the manufacturer has supplanted this material with a polyester-PTFE laminate, a limited supply of the original sheet is available in JSC bonded stores.
Appendix C

Standard for Restrictions on Mercury Use
STATEMENT OF STANDARD

The use of equipment containing mercury in liquid or vapor form (such as manometers, lights, thermometers, etc.) shall be avoided where the mercury could come in contact with the spacecraft or spaceflight equipment at any time during manufacturing, assembly, testing, checkout, or flight. Where the use of equipment containing mercury cannot be avoided, the following information shall be documented in a waiver for approval by the Program Manager:

1. A list of equipment containing mercury to be used during manufacturing, assembly, testing, and checkout, along with justification for each use
2. The amount of mercury contained in the equipment
3. The protection provided to prevent the release of mercury
4. A plan for decontamination in the event the mercury is released. The plan must note the following:
   a. An environment containing mercury vapor in concentration of 0.005 mg/m³ (or greater) is not acceptable for continuous occupancy. Equipment used to detect mercury in the crew compartment must be able to measure concentrations below this level.
   b. Mercury must not be removed from metal surfaces with any abrasive cleaning method. The removal of oxide films on the metal will cause immediate mercury penetration.

REMARKS

Mercury is a particularly hazardous liquid because of its toxicity and tendency to penetrate joints and amalgamate structure materials. Corona discharge can occur at low potentials in the presence of mercury vapor.

Metal contaminated while under high stress will receive greater penetration of mercury and degradation of ability to withstand stress than will metals under relatively low stress.

This standard supersedes JSCM 8080 standard 116 and incorporates SSP 30213 no. M/P-15.
Primary Battery Design and Safety Guidelines Handbook

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This handbook provides engineers and safety personnel with guidelines for the safe design or selection and use of primary batteries in spaceflight programs. Types of primary batteries described are silver oxide zinc alkaline, carbon-zinc, zinc-air alkaline, manganese dioxide-zinc alkaline, mercuric oxide-zinc alkaline, and lithium anode cells. Along with typical applications, the discussions of the individual battery types include electrochemistry, construction, capacities and configurations, and appropriate safety measures. A chapter on general battery safety covers hazard sources and controls applicable to all battery types. Guidelines are given for qualification and acceptance testing that should precede space applications. Permissible failure levels for NASA applications are discussed.