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The NASA Aerospace Battery Safety Handbook

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ABSTRACT

This handbook has been written for the purpose of acquainting those involved with batteries with the information necessary for the safe handling, storage and disposal of these energy storage devices. Included in the document is a discussion of the cell and battery design considerations and the role of the components within a cell. The cell and battery hazards are related to user- and/or manufacturer-induced causes. The JSC Payload Safety Guidelines for battery use in Shuttle applications are also provided.

The electrochemical systems are divided into zinc anode and lithium anode primaries, secondary cells, and fuel cells. Each system is briefly described, typical applications are given, advantages and disadvantages are tabulated, and most importantly, safety hazards associated with its use are given.

GLOSSARY

ABBREVIATIONS AND ACRONYMS

ARC	Ames Research Center
BL	butyrolactone
CF	carbon polymonofluoride
DME	1,2 dimethoxythane
DMI	dimethylisoxazole
DMSI	dimethylsulfite
DOD	depth of discharge
DOT	Department of Transportation
ELT	electronic locating transmitter
EPA	Environmental Protection Agency
EVA	extravehicular activity
GEO	geosynchronous orbit
GAS	getaway special
GSFC	Goddard Space Flight Center
HR	high rate
IATA	International Air Transport Association
ICAO	International Civil Aviation Organization
JPL	Jet Propulsion Laboratory
JSC	Johnson Space Center
KSC	Kennedy Space Center
LaRC	Langley Research Center
LDEF	Long Duration Exposure Facility
LeRC	Lewis Research Center
LEO	low earth orbit
LR	low rate

MF	methylformate
MMU	Manned Maneuvering Unit
MSFC	Marshall Space Flight Center
NASA	National Aeronautics and Space Administration
NEG	negative
NIOSH	National Institute for Occupational Safety and Health
PC	propylene carbonate
POS	positive
SLA	sealed lead acid
SMM	Solar Max Mission
THF	tetrahydrofuran
Wh/kg	mass energy density
Wh/L	volume energy density

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SECTION 1

SCOPE

This document includes discussion of numerous electrochemical energy storage systems, their composition, chemical reactions, advantages and disadvantages and, primarily, their safety considerations. The cell and battery electrochemistries have been divided into zinc anode primary, lithium soluble cathode primary, lithium solid cathode primary, and secondary cells including lithium anode and regenerative level cells. The information is intended to provide a user or novice in cell/battery technology with a general knowledge of the concerns and problems inherent in the use of each cell/battery type.

Included also are the payload safety guidelines for use of batteries on the Shuttle, safety design philosophy, electrochemical cell examples, and design considerations. The user- and manufacturer-induced safety problems and a checklist of potentially unsafe conditions are also provided.

SECTION 2

INTRODUCTION

In addition to the background and objective, this section gives the Shuttle Safety Guidelines as required by JSC. The remainder of the publication addresses the types of electrochemical systems and the associated safety issues.

2.1 BACKGROUND

There have been many requirements for spacecraft batteries which have demanded a variety of different characteristics. The differences in requirements include power, energy, safety, cost, operational life (both calendar life and cycle life), shelf life, and efficiency. The result has been that many different generic types of batteries, both primary and secondary, are in use. The cells and batteries described herein differ widely in their operational and safety aspects. It is the intent of this handbook to acquaint the user with potential hazards of cells and batteries and recommended ways of handling them. In general, electrochemical cells are safe when operated in the manner for which they were designed. The major causes of safety problems are related to misuse, mishandling, or poor design. This publication is intended to serve as a guide to the proper handling of spacecraft batteries.

2.2 OBJECTIVE

This handbook is written for technicians, engineers, and scientists who handle or use batteries. Batteries and the cells of which they are comprised provide a means of storing electrical energy in a chemical form. These electrochemical devices are capable of releasing energy, both electrical and/or chemical, in a manner that can result in hazards to nearby personnel and equipment. Therefore, it is essential that the user identify which electrochemical power sources are being used and understand the hazards involved with their operation, handling, and disposal.

In order to facilitate use of this handbook, it is organized into primary cells (zinc anode type and lithium anode type); secondary cells (nickel hydroxide, silver oxide, lead acid, lithium, and sodium-sulfur types); and fuel cells.

2.3 PAYLOAD SAFETY GUIDELINES FOR BATTERIES (JSC)

Sections 2.3.1 to 2.3.4 appear as paragraph 3.4.1.2 in the Johnson Space Center (JSC) Document, "Space Transportation System Payload Safety Guidelines Handbook" (JSC 11123), change 1, September 1978. It describes the guidelines and requirements that must be followed prior to consideration for acceptance of any battery aboard the Shuttle. The Power Generation Branch of the Propulsion and Power Division at JSC has the review responsibility and makes the appropriate recommendations to the Shuttle Payload Safety Panel for their approval. The Introduction and Definition portions of JSC 11123 are taken directly from the document and appear in the Appendix.

2.3.1 Battery Types

The broad spectrum of power and energy storage requirements for payload power provisioning requires the use of many types of batteries. Listed below are primary and secondary types which have potential payload application:

Primary batteries

- Zinc-manganese dioxide-Leclanche ($Zn-MnO_2$)
- Zinc-manganese dioxide alkaline ($Zn-MnO_2$)
- Zinc-mercuric oxide ($Zn-HgO$)
- Zinc-oxygen ($Zn-O_2$)
- Zinc-silver oxide (silver-zinc) ($Zn-Ag_2O$)
- Lithium-organic
- Lithium-inorganic

Secondary batteries

- Nickel-cadmium ($NiOOH-Cd$)
- Nickel-hydrogen ($NiOOH-H_2$)
- Nickel-zinc ($Ni-Zn$)
- Silver-cadmium ($AgO-Cd$)
- Silver-zinc ($AgO-Zn$)
- Silver-hydrogen ($AgO-H_2$)
- Lead-acid (lead-lead dioxide) ($Pb-PbO_2$)

The above listing covers the range of available technology from commercial off-the-shelf cells/batteries to spaceflight hardware types to advanced development types. Most of these will require various degrees of design modification to make them acceptable for payload applications from both a performance and a safety viewpoint. Proper consideration must be given to required battery enclosures, seals, vents, type and amount of electrolyte, type and amount of gas generated on stand and during operation, operating temperature capability, pressure environment, and many other factors involved in a battery selection activity. Careful consideration should be given to the applicable Department of Transportation shipping requirements. Note that there is an exemption for lithium batteries from regulations for the transportation of hazardous materials, DOT-E-7052 (4th revision), contained in Code of Federal Regulations, Title 49, parts 100-199.

2.3.2 Primary Hazards

Regardless of the type of battery selected, the primary hazards are the buildup of flammable, corrosive, or toxic gases and reaction products and the expulsion of electrolyte, which also may be corrosive and/or toxic. These hazards are in the form of (1) hydrogen and oxygen generated by nickel-cadmium, silver-zinc, lead-acid, and other types of batteries; (2) harmful reaction products from organic and inorganic electrolyte systems of the lithium batteries; and (3) electrolytes which are both caustic (potassium hydroxide) and acidic (sulfuric acid and reaction products of sulfur dioxide).

2.3.3 Battery Safety Design Philosophy

The battery design philosophy relative to safety should consider the capability of the design to survive a single failure mode of the battery without creating any of the payload hazards defined in paragraph 2.3.4 of this publication. Primarily, these hazards include contamination, corrosion, explosion, fire, injury, and illness. They require consideration for all mission phases and ground operations with associated ground crew operations. Listed below are the major failure modes, any one or combination of which could possibly cause venting of toxic, corrosive, and/or flammable materials with associated fire or explosion.

(1) Overtemperature (from battery self-heat or environmental heat).

(2) Short circuit (external or internal to the battery).

(3) Reverse current (inadvertent charging).

(4) Cell reversal (overdischarge).

(5) Cell/battery leakage (gases and/or electrolyte).

(6) Cell grounds (moisture, potting outgassing, electrolyte leakage).

(7) Cell internal shorts (foreign material, separator degradation).

(8) Overpressure.

These potential failure modes require special attention during the selection and design of the battery. Again, the design approach should preclude any of the above occurrences. If a failure does occur, however, the design should preclude, if possible, resultant venting, fire, or explosion. If venting cannot be prevented in the event of a major failure, it is the responsibility of the payload developer to demonstrate that venting will occur in a manner that is not hazardous to the Orbiter.

2.3.4 Safety Guidelines

The following safety guidelines are provided for consideration in the design and selection of cells and batteries. They are grouped according to preventive design functions relative to the major failure modes and their possible effects already discussed. Since a wide range of battery types is discussed, all guidelines will not apply to all batteries. The guidelines given below are not considered to cover every conceivable contingency requiring special attention to design safety features. Hence, the NASA safety review of any specific design may disclose features requiring correction or features considered deficient for the particular battery in its proposed use.

2.3.4.1 Battery/Cell Structural Design And Pressure Vessel Considerations.

(1) Cell types that may generate excessive gas during open circuit stand and operation should have positive pressure relief capability for each cell and for the battery case.

(2) The design of batteries and cells should take into account their inherent function as pressure vessels, and should include analysis/tests to determine structural capability. Both mechanical pressure from swelling of cell elements and gaseous pressure should be considered in these analyses/tests. Special precautions should be observed in designing these vessels because of their function as energy storage containers in a harsh chemical and physical environment. Annealing of molded plastic cases, for example, may be required for stress relief.

(3) Structural design margins should involve proper consideration of ground and flight mechanical environments (shock, vibration, and acceleration).

(4) A fracture mechanics analysis should be performed to ensure, as a minimum, the compatibility of the case with the electrolyte (and other materials in contact with the case such as potting material, etc.), particularly where pressure/ mechanical forces may occur.

(5) Basically, pressure buildup should not present a hazard.

2.3.4.2 Electrolyte Containment in the Battery/Cells.

(1) Electrolyte quantity should be optimized to the minimum amount required to meet capacity requirements.

(2) Cell cases should be designed to avoid electrolyte access to vent mechanisms to help prevent electrolyte ejection.

(3) Battery cases with pressure relief plugs should incorporate provisions (i.e., porous plugs, standpipes, baffles, etc.) to help prevent ejection of accumulated electrolyte.

(4) Battery and cell cases for vented cell systems should be designed to contain all the electrolyte during overpressure conditions such as those caused by overload or internal shorts.

(5) Use hermetically sealed cells wherever the application permits.

2.3.4.3 Design Protection From Vented Electrolyte or Other Vent Products.

(1) As a first approach, battery cases should be designed to contain vented electrolyte or vent products from all but the

most catastrophic events. If necessary to vent, the battery case vents should be located so as to preclude damage to adjacent equipment or injury to operating personnel.

(2) A battery case constructed of metal should be internally coated to make it resistant to electrolyte attack and electrically nonconductive. Since vent plugs are normally metallic, they should be electrically isolated from the case by use of an insulating insert.

(3) All internal battery electrical connectors, components, and wiring should be encapsulated (e.g., conformally coated, etc.) for protection against electrolyte or moisture. This coating, however, must not interfere with a required venting or rupture function of the component.

(4) The resulting vent products from various postulated failure modes should be identified for evaluation of the potential safety hazard.

2.3.4.4 Gas-Handling Design Considerations.

(1) Free volume within battery cases should be decreased to a minimum to reduce the accumulation of gas.

(2) Exposed circuitry, such as relay contacts, should not be used inside the battery case nor adjacent to a battery vent. Such components often cause sparking and arcing and can ignite flammable mixtures of gases emitted by certain batteries.

(3) Consider the inclusion of an explosion and detonation overpressure suppression material (highly porous, fully reticulated foam) or an explosive energy absorptive material in the headspace of a battery.

2.3.4.5 Electrical Design Considerations.

(1) Paralleled batteries or strings of cells should be isolated from each other by series diodes, particularly for primary battery systems.

(2) Whenever applicable, individual cells should incorporate shunt bypass diodes as protection against possible cell reversal.

(3) Whenever practical, batteries should be fused to protect against extreme overloads. This might be accomplished with an automatically resettable thermal switch or circuit breaker to preclude losing the battery for the entire mission in the event of a one-time momentary short.

(4) Battery thermal design should be capable of withstanding the maximum continuous load without causing cell venting or rupture.

(5) Thermally actuated electrical switches should be incorporated to prevent electrically induced thermal overloads.

(6) An explosion prevention demonstration should be conducted to ensure the functionality of the internal (electrochemical design) or external (bypass electronics) means for preventing excessive pressure buildup or rupture.

2.3.4.6 Ground and Flight Operational Considerations.

(1) Batteries should not be connected with a load applied since sparking and arcing could result.

(2) Battery cases should be marked to indicate the type and quantity of electrolyte they contain. Markings should refer to the appropriate activation and safety procedures.

(3) Battery connections to equipment should not be of dissimilar metals since corrosion between mating surfaces would result.

(4) Batteries should be physically designed to preclude polarity reversal when connecting terminals are installed. Decals or markings should clearly indicate positive (POS) and negative (NEG) terminals when lug and bolted terminal connections are used. Decals or markings should state the order (POS or NEG first) of mating and demating of battery terminals to the vehicle terminals. Such instructions reduce the possibility of inadvertent grounding of the battery by installation tools, or other means.

(5) Battery temperature limits for safe operation and storage should be indicated on the battery case.

(6) The programmed use of a battery should provide for a sufficient capacity margin to preclude end-of-capacity cell problems.

(7) Suitable operating and handling procedures should be provided for the use and disposal of expended batteries.

(8) For each pressurized volume contained in a battery, a pressure leak check capability should be provided.

(9) All tools used for battery activation, installation, removal, handling, and similar operations should be made of, or coated or wrapped with, an insulating or dielectric material to prevent inadvertent shorting of battery, cells, or vehicle buses.

SECTION 3

CELL DESIGN

A discussion of the electrochemical principles governing energy storage and the internal and external cell construction considerations is given in this section.

3.1 ELECTROCHEMICAL CELL PRINCIPLES

The electrochemical cell is a device for storing electrical energy in a chemical form. The cell consists of two dissimilar electrodes (anode and cathode) and electrolyte to allow conduction of the charged species from one electrode to the other inside the cell. When the external circuit is closed either directly (short) or through a load, there is an instantaneous current flow. The basis for this can be described in a stepwise manner. Starting with the ANODE, usually a metal, e.g., zinc or lithium, a reaction occurs that produces positively charged species in the electrolyte (m^+). Electrons are simultaneously released from that electrode to the terminal. The electrons then flow through the load to the CATHODE where they are used in the cathodic electrochemical reaction to produce species of an opposing charge, thus closing the circuit.

The anode reaction is called an oxidation reaction and is the negative terminal. The cathode reaction is the reduction reaction and is the positive terminal. Each cell contains a separator which is used to maintain physical separation of the electrodes and in some cells to immobilize the electrolyte. In other cells the electrodes are completely covered with electrolyte and the separator serves to physically separate the plates. When the electrodes are flooded with electrolyte, the cell is considered a "FLOODED" cell. In the cells in which the electrolyte is immobilized (as in a sponge) in the separator and plates, the quantity of electrolyte is limited to allow gas (oxygen) recombination in the cell. This cell is referred to as a "semi-dry," "semi-wet," or "STARVED" cell.

Because of thermodynamics, one electrode is always a preferred anode when compared to another electrode and vice versa. This difference in ability to produce or accept electrons is given the term potential difference or VOLTAGE. The quantity of "ACTIVE MATERIAL" (the parts of the electrode that are not structural) in the anode and cathode determine the amount of electrical energy stored (ampere hours) in the cell. If the anode material runs out of chemicals to produce electrons at the same time the cathode material is used up in accepting electrons, the cell is considered a "BALANCED" design. If one or the other runs out first it is either ANODE-LIMITED or CATHODE-LIMITED.

A PRIMARY battery is not designed or intended to be recharged, regardless of the possibility that limited capability for recharging, using special care and controls, may exist. A SECONDARY, or rechargeable, battery is one that is specifically designed to permit recharging, regardless of the number of charge/discharge cycles actually obtainable.

A power supply or alternate source of energy is used to supply the electrons back into the electrode serving as the negative terminal while extracting electrons from the positive terminals. The current flow is opposite to electron flow.

The potential difference (voltage) between the two electrodes during discharge (while the cell is providing energy to the load) is usually positive when connecting the positive lead of the voltmeter to the cathode (+) and negative lead to the anode (-). When one or the other electrode runs out of active material, new reactions can occur, most often by electrolysis of the electrolyte. This change in reactions and products alters the potential differences occurring between anode and cathode and results in a negative potential (voltmeter leads unchanged). This is termed "CELL REVERSAL" which can lead to undesirable, usually gaseous products which can result in a cell hazard. For this reason, the discharge must be terminated before the cell reaches complete discharge.

A similar event occurs when a cell is charging and all of the active material is in its fully charged state. If electrons continue to be forced into the cathode and withdrawn from the anode, new reactions will occur; this increases the potential (difference) and causes new and sometimes undesirable reactions to take place. Thus a "CHARGE CONTROL" network is necessary to fully charge the battery but limit the overcharge which is provided to account for electrochemical inefficiencies.

3.2 CELL CONFIGURATIONS

Electrochemical cells are available in a variety of configurations which include button, cylindrical construction (bobbin* and cylindrical spiral wound**), and prismatic. The type of configuration determines to some extent the cell capability and the application. Both primary and secondary batteries have been manufactured in all four configurations. For example, the lead acid cell appears as a "D" size cylindrical spiral wound cell and a large prismatic cell (as in the automobile). The primary lithium-thionyl chloride (Li-$SOCl_2$) cell has been produced in the button, bobbin, spiral, and prismatic configurations.

3.3 CELL DESIGN CONSIDERATIONS

The cell mechanical design considerations comprise several factors including the seal, tabs, electrode/separator pack assembly, case, and pressure relief vent.

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*Bobbin construction is the type in which one electrode is in the center in the form of a post and the other electrode is the outer cylinder.

**Spiral wound is the type in which both anode and cathode, mechanically separated by a separator, are rolled into a cylinder and inserted in a cell.

3.3.1 Seal

The seal utilized in hermetically sealed aerospace applications is a glass/metal or ceramic/metal seal. However, the seal design is a separate consideration for each type of cell. In the zinc anode primary cells, the ability to provide a hydrogen escape while at the same time avoiding electrolyte leakage (especially in the case of alkaline electrolytes) is a difficult task. Among the other considerations for a seal are:

(1) Stability.

(2) Method of installation/assembly.

(3) Placement.

(4) Terminal size.

(5) Thermal expansion.

(6) Compatibility with the other components.

(7) Welding of tab to terminal.

3.3.2 Tabs

The tabs provide access to the plates containing the active material. Their conductivity and placement in the cell are factors in the mechanical configuration. Among the tab criteria of interest are:

(1) The number of tabs per electrode.

(2) Placement.

(3) Welding to terminal.

(4) Welding to plate.

(5) Strength.

(6) Stress relief.

(7) Electrical and thermal conductivity.

(8) Compatibility with other cell components.

(9) Load requirements (amount of current).

3.3.3 Electrode Pack

The pack assembly comprising the electrodes and separator involves the following considerations:

(1) Extent of overlap of electrodes.

(2) Possible shorting through the separator.

(3) Possible shorting of electrode edges.

(4) Uniformity of compaction and interelectrode spacing throughout pack.

(5) Pack thickness.

3.3.4 Vent

Pressure relief/release in some cells is necessary to avoid a high internal pressure (venting) situation. Although less important in primary zinc anode, lithium-solid cathode, and lithium-solid electrolyte cell types, it can have application in lithium-soluble cathode, rechargeable silver zinc, and lead acid cells/batteries. The considerations for a pressure relief vent include:

(1) Pressure setting.

(2) Reproducibility.

(3) Type; i.e., vent plug, diaphragm, scored case.

(4) Placement.

(5) Method of installation.

3.4 BATTERIES

A battery consists of one or more cells in series or parallel in order to provide the required voltage and capacity (ampere hours). In a series string, cells are connected so that the positive terminal of one cell is attached to the negative terminal of the other. The battery voltage is the sum of the cell voltages and the battery capacity is the same as the cell capacity. A parallel arrangement occurs when the positive terminal of one cell or series string of cells is connected to the positive terminal of a second or third cell or series of cells. The negative terminal of the last cell in each series string is connected to the negative terminal of the other strings. In this case the voltage of the battery is the same as the voltage of each cell or string of cells with which it is in parallel. However, in the parallel case, the capacity of the parallel cells or strings is additive. The larger the number of cells, the greater is the energy available for use and the greater is the concern for safety.

Batteries are available in many sizes and shapes for a wide range of applications. If not available, an assembly can be designed to meet the volume, mass, structure, and shape requirements.

3.5 CELL/BATTERY SELECTION

Several factors need to be considered in selecting a cell or battery for a specific application. The list includes, but is not limited to the items in Table I.

Table I. Selection Factors

- Mass
- Volume
- Cost
- Rechargeability
- Availability
- Maintenance
- Temperature
- Rate
- Capacity
- Safety
- Duty cycle
- Physical design
- Mass energy density (Wh/kg)
- Volume energy density (Wh/L)
- Efficiency
- Reliability
- Voltage regulation
- Environmental

These are given in random order because each user places the priorities on the factors that are most important to him/her. The ideal battery is one that is low cost, operates over a wide temperature range, can provide unlimited energy and power levels, has unlimited shelf life, and is safe. Unfortunately, the more energetic the system, the greater the hazards, and usually the greater the cost.

The user will survey the candidate cell/battery electrochemical systems and consider a series of trade-offs. Among the specific questions that must be answered are:

(1) What is the total energy (watt hours) required?

(2) What is the voltage requirement of the load?

(3) What is the power profile?

(4) What current will be required by the load continuously and under pulsed load?

(5) What are the mass, volume, and physical limitations?

(6) What temperature range is expected?

(7) What is the shelf life requirement?

(8) Is recharging necessary and available, and if so, what is the current available?

(9) Is replacement possible?

(10) What cost is projected?

(11) Is it to be used in manned or unmanned applications?

(12) What are the potential hazards?

(13) What are the shock and vibration requirements?

The answers to these questions will result in one or more candidate electrochemical systems capable of meeting the requirements of the application. The reader is requested to consult the list of references at the end of this handbook for a broader, more in-depth view of the selection, operation, performance and capabilities of the various electrochemical cells.

SECTION 4

CELL AND BATTERY SAFETY HAZARDS

As described in this safety handbook, there are many electrochemical cell variations. They differ in configuration, performance characteristics, and operational requirements (use), depending on the electrochemical couple and electrolyte. The various types of cells will be described later in this handbook. However, there are general safety concerns ascribed to electrochemical cells and batteries that will be covered here.

4.1 CLASSIFICATION OF HAZARDS

The cell and battery hazards of concern can be classified into four groups.

(1) Leaking of electrolyte or gas through flaws in seals, welds, or cases.

(2) Mild venting of gases and electrolyte through seals, welds, cases, or burst disc caused by buildup of internal pressure.

(3) Violent venting or rupture of the cell, sometimes with explosion and fire, caused by undesirable reactions in the cell as in a thermal runaway condition or accumulation of explosive gaseous products such as hydrogen and oxygen.

(4) Excessive heating of the cell/battery or associated equipment caused by inadvertent cell shorting.

The extent to which these hazards occur depends on the type of system and the extremes in operating conditions. The causes are described in the next section.

For the most part, cells and batteries are considered safe, except for design flaws that appear when they are utilized in the manner recommended by the manufacturer. Even the newer higher energy storage cells are safe if operated as prescribed. The responsibilities for the safety problems with electrochemical cells and batteries can therefore be placed in two categories: user-induced and manufacturer-induced causes.

4.2 USER-INDUCED SAFETY PROBLEMS

With regard to the user-induced causes given in Table II, the problems arise because the user does not always have the knowledge or the understanding of the selected battery limitations and hazards, especially with the large number of different types available. Also, the user is not always in control of the battery use. The battery is a portable stand-alone device and there is no guarantee that when it is placed in the intended equipment and/or transferred to others that all the operational limitations and safety requirements will be followed. Unfortunately, it is the ultimate user that suffers the consequences although others may be severely impacted because of inability to meet mission requirements.

Table II. User-Induced Causes of Safety Hazards

- Use in abusive environments or conditions.
- Improper handling, storage, transportation, or disposal.
- Extended use beyond the cell/battery capability.
- Improper design of battery-operated equipment.

One solution to the user-induced causes for battery safety hazards is to educate all involved with designing, handling, purchasing, application, and use of batteries and their associated equipment. The batteries and associated equipment should be qualified at higher levels than the maximum expected performance requirements in order to evaluate the equipment under extended use. In addition, safety abuse tests are necessary to determine the equipment limitations in the event of an unusual excursion. The abuse test results are to be used as a guide in determining the safety limitation of the cells and batteries in use, not as operating limits.

4.3 MANUFACTURER-INDUCED SAFETY ISSUES

The manufacturer has the major responsibility for safety. It is the design construction techniques and quality control that determine if the product, even if used properly, will present a safety hazard. Proper manufacturing can provide confidence that the cell or battery will be safe. The manufacturer-induced causes for safety hazards are given in Table III.

Table III. Manufacturer-Induced Causes of Safety Hazards

- Cell design not safety oriented.
- Improper use of materials/equipment.
- Use of impure or unacceptable chemicals/materials/components.
- Lack of adequate quality control processes.
- Insufficient nondestructive and destructive tests.
- Inadequate configuration control documentation and management.

The manufacturer, once having tested the cell or battery under extreme conditions to prove safety, must be certain that products coming off the assembly line are the same as those tested; and further, that there is a high enough degree of consistency between samples. Quality assurance and control with adequate sampling and inspection points and qualification of assembly and operators are essential to a product which can be considered safe. Remember that the higher the energy, the greater the safety concern and therefore the greater the need for quality standards throughout the entire process, from incoming materials to final product and packaging.

4.4 UNIVERSAL CAUSES OF CELL/BATTERY HAZARDS

From paragraph 4.1 it is seen that there are certain operating conditions that affect the safety of all cells, although to different degrees: from leakage of mild salt-solutions to explosion. The general undesirable operating conditions that affect safety include:

(1) Excessive high and low temperature. (paragraph 4.4.1)

(2) Excessive high current (external short). (paragraph 4.4.2)

(3) Extended discharge/reversal. (paragraph 4.4.3)

(4) Cells of unequal capacity/voltage. (paragraph 4.4.4)

(5) Charging of primary cells. (paragraph 4.4.5)

4.4.1 Excessive High and Low Temperature

High temperature excursion or operation has several consequences. First, it can increase the gas pressure within a cell and simultaneously increase the vapor pressure of the electrolyte, thus adding to the pressure on the seals and welds. Second, it can cause an increase in solubility of active materials, thus resulting in a loss in capacity, or increase in the rate of dendritic growth which can result in an internal short. Third, it can cause undesirable reactions to occur, sometimes with the production of large quantities of heat which in turn cause additional side heat generating reactions, thus producing a thermal runaway condition. Fourth, it can cause degradation of the separator and other materials within the cell which can result in reduced performance or internal short. Without going into greater detail, the extreme temperature of flame/fire is not only detrimental but can result in violent explosions. Low temperature can also play a role in cell safety because it can cause the desired electrochemical reactions to become inefficient and instead cause generation of gaseous products (e.g., hydrogen), which can be hazardous when the gas accumulates. Extreme low temperatures can also cause structural problems in the cell and battery case containment, resulting in cell case cracks and electrolyte leakage.

4.4.2 Excessive High Current

High current on discharge can cause safety problems for three reasons. First, each cell has an internal impedance which affects conductivity from one terminal through the cell to the other terminal. The heating effect is increased by the square of the current (I^2R), thus causing the internal temperature to rise. The heat is increased further by exothermic reactions such as those on discharge, further enhancing the possibility for the extreme high temperature safety problems described above. Second, high rates of discharge (or charge for a secondary cell) can cause an increase in cell degradation or a possible reversal condition, generating undesirable gases or products. Third, for a rechargeable cell, a high rate charge can result in abnormally high operational voltages (overvoltage) resulting in undesirable side reactions such as the buildup of gases. Even more basic is that the touch temperature limit (45°C) of the cell/battery and of the equipment it supplies may be exceeded, creating a burn hazard to the user.

4.4.3 Extended Discharge/Reversal

If a cell is reversed, its performance is permanently affected. Of even more concern, undesirable reactions can occur, resulting in accumulation of products which can react, creating potentially unsafe conditions. Reversal cannot occur on a single cell under load because when it runs out of energy there is no way to continue the discharge without forcing current through with a power supply. However, if a low capacity or low voltage cell (or a failed cell) is in a series with other "good" cells, the voltage of the "good" remaining cells can force current through the discharged cell, causing it to go into reversal. The production of undesirable products has caused safety problems in the high energy lithium cells, in particular, and is a problem of significant concern.

4.4.4 Cells of Unequal Capacity/Voltage

A related concern occurs in a battery with a string of series-connected cells in parallel with another string(s). If one cell in one of the strings runs out of energy during discharge, it can cause the other good string(s) of cells to force current (charge) into the string with the bad cell in an attempt to bring the voltages to the same level. This may result in charging of the entire string with the bad cell. If this is a primary cell battery, the charging can cause undesirable product formation and a buildup of heat, which is a potential safety problem.

In parallel secondary cell batteries the loss of a cell in a string will result in greater energy storage removal from the unaffected string(s) which may have long-term performance effects but not a safety effect.* However, on charge, the current normally shared equally will be forced from the power supply or solar array primarily through the deficient battery, resulting in extreme overcharge, high temperatures, and a high potential for a hazard condition.

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*Unless the resulting higher current brings on the hazard.

4.4.5 Charging of Primary Cells

Because most of the primary cells consist of nonreversible electrochemical constituents, charging of a cell produces heat and may induce undesirable products to form. These products can be permanent, and potentially hazardous whether in the gaseous or solid/liquid phase.

4.5 POTENTIALLY HAZARDOUS CONDITIONS TO AVOID - A CHECKLIST

This checklist applies to all cells, although the extent of hazard depends on type of system and nature of hazard. Specific potential hazards are described separately for each cell type in Section 5. Lithium anode hazards and safety checklist are given in paragraph 5.2.1.7.

(1) Do not use or store in areas where there is heat or flame.
  - Cold storage is preferred.

(2) Do not place or store on metal shelf or bench.
  - Use insulated/wood tables.

(3) Do not encapsulate or pot vents of cells or batteries.
  - Allow for expansion and breathing.

(4) Do not charge primary cells.
  - They have the capability to be discharged only once.

(5) Avoid mixing cell sizes or types in a battery unless specifically required.
  - Cells must operate uniformly.

(6) Do not reverse.
  - Disconnect cells from the line when the cell is no longer working at normal operating voltage or provide battery under voltage sensor.

(7) Do not severely overcharge secondary cells.
  - The recharge (charge to discharge ratio) should be controlled and minimized when possible.

(8) Do not heat cells to rejuvenate them.
  - This is an unsafe method.

(9) Do not dispose of cells in fire.
  - Possibility of violent detonation exists.

(10) Do not allow metallic tools, wires, or loose hardware to bridge the positive and negative terminals.
  - Discharges cell and may cause venting or explosion.

(11) Handle groups of cells carefully to avoid short circuit or unexpected discharge.
  - Exercise care in handling cells where terminals can come in contact with each other.

(12) Do not store depleted or partially used cells in equipment.
- Discard or place in storage immediately after use.

(13) Assure all intercell connectors and connections are bolted, welded, crimped or soldered correctly.
- This avoids high resistance (minimizes voltage loss) and therefore large heat buildup.

SECTION 5

THE PRIMARY CELLS, THEIR CHARACTERISTICS AND POTENTIAL HAZARDS

For purposes of simplifying this discussion, the primary cell and battery types have been divided into these three categories:

(1) Zinc anode primary cells/batteries.

(2) Lithium anode-soluble cathode primary cells/batteries.

(3) Lithium anode-solid cathode primary cells/batteries.

As described earlier, primary cells can be discharged only once and then are no longer useful.

5.1 ZINC ANODE PRIMARY CELLS/BATTERIES

Many of the zinc anode cells have been and are available commercially to the consumer. They are by far the most familiar and often used in toys, flashlights, and other well-known applications. Primarily they are low in cost, used in low rate* (<C/10)** applications and are relatively safe. These include the familar zinc-manganese dioxide-Leclanche cell, the zinc-manganese dioxide-alkaline cell, and the zinc-mercuric oxide cell. Zinc-air and zinc-silver oxide cells are higher in energy density and are capable of operating at higher rates. Zinc-air cells/batteries have applications only in oxygen environments or wherever it is supplied and have been used in space in the Shuttle cabin. They are attractive because of their high volume energy density. Primary zinc-silver oxide batteries are available in low rate (button cell) designs and also have been used in space in both flooded electrolyte starved and reserve configurations. These offer the highest discharge rate capability of the zinc anode cells. See Table IV for the characteristics of this cell type. In these cell types the zinc anode is always the negative electrode relative to the opposing electrode on discharge because it is the electrode that provides the electrons to the load during discharge.

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*For purposes of this report:

	Low rate will be	< C/10
	Moderate rate	C/10-C/4
	High rate	> C/4

However, bear in mind that high rate for one type of cell, i.e., lithium anode types, may be moderate rate for another type; i.e., aqueous secondary cells.

**C/t is a term used to designate the rate (charge or discharge current) that will completely discharge a cell in t hours. C is the nominal capacity of a cell. For example, for C = 20 ampere hour cell the C/10 rate is 2 amperes.

Table IV. Zinc Anode Primary Cell Characteristics

Name	Anode	Electrolyte	Cathode	OCV (V)	(NOM) (V)	Specific Energy (Wh/kg)	Energy Density (Wh/L)	Operating Temp °C	Comments
A. Leclanche	Zn	$NH_4Cl/ZnCl_2$	MnO_2/C	1.6	(1.3)	65	100	- 5 to 45	Low cost, sloping voltage
B. Alkaline	Zn	ZnO/KOH	MnO_2/C	1.6	(1.3)	95	220	-20 to 55	Greater drain rate, sloping voltage
C. Mercury	Zn	ZnO/KOH	HgO	1.35	(1.3)	105	325	0 to 55	Level voltage
D. Zinc-air	Zn	KOH/NaOH	O_2(Air)	1.5	(1.4)	290	905	0 to 50	Highest available energy of zinc anode cells
E. Silver-zinc	Zn	KOH/NaOH	Ag_2O/AgO	1.8	(1.6)	200	515	-20 to 55	High drain rate, high cost

5.1.1 Zinc-Manganese Dioxide-Leclanche ($Zn-MnO_2$)

5.1.1.1 Description. This cell, sometimes called the zinc-carbon cell, utilizes an aqueous solution of ammonium chloride (NH_4Cl) and/or zinc chloride ($ZnCl_2$) as the electrolyte. Its reaction is given as:

$$Zn + 2MnO_2 + 2NH_4Cl \rightarrow 2\ MnOOH + Zn(NH_3)_2Cl_2 \qquad (5-1)$$

However, the reaction products differ depending on the rate of discharge and electrolyte composition. The metallic zinc amalgamated electrode forms the inner wall of the cell case. Carbon is mixed with the MnO_2 powder to form the cathode. The separator is a gelled paste or gel coated paper.

5.1.1.2 Applications. It is generally found in the cylindrical (bobbin) and wafer type constructions and therefore is of limited electrode area. Thus, it is limited to low rate (<C/100) applications. This cell has wide consumer application in toys, flashlights, radios, flashers, and instruments. One can remove 50 percent of the capacity to 1.0V at the C/50 rate and 100 percent at the C/400 rate.

5.1.1.3 Advantages and Disadvantages.

Advantages

(1) Low cell cost.

(2) Low cost per watt-hour.

(3) Large variety of shapes, sizes, battery voltages, and capacities.

(4) Wide distribution and availability.

(5) Long tradition of reliability.

Disadvantages

(1) Low energy density.

(2) Poor low-temperature service.

(3) Poor leakage resistance under abusive conditions.

(4) Low efficiency under high current drains.

(5) Limited shelf life.

(6) Voltage falls steadily with discharge.

5.1.1.4 Potential Hazards And Controls.

(1) Hydrogen gas can accumulate in a sealed battery case during discharge.
  - Allow cell to breathe so that hydrogen mixes with air.
  - Avoid areas where there are open electrical contacts, arcing, or sparking.

(2) Cells can expand due to pressure and vent.
  - Do not encapsulate cell vent or place in tight container.

(3) Cells can leak salt-solution electrolyte.
  - Grounding of cells to the metal battery case can result in a low or high rate short.

(4) See paragraph 4.5 for a checklist of hazardous conditions to avoid.

5.1.2 Zinc-Manganese Dioxide-Alkaline ($Zn-MnO_2$)

5.1.2.1 Description. This cell is similar to the Leclanche cell except that it utilizes a strong solution of potassium hydroxide (KOH) for electrolyte. Its reaction is given as:

$$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3 \qquad (5-2)$$

In this cell the zinc anode is a pressed powder amalgamated with small amounts of mercury and a binder to form a gel or pressed as a dry powder. The mercury supresses the hydrogen gassing. The cathode is similar to the Leclanche cathode mixed with acetylene black. The separator is a microporous woven or felted material. The 25 to 50 percent KOH electrolyte is immobilized in a gel.

5.1.2.2 Applications. Available in a wide variety of sizes in the consumer market, it is used for higher drain rate application than the Leclanche cell. Applications may include but are not limited to portable TV and radio cassette recorders and players. It is produced in cylindrical and button cell configurations. It has a factor of four times the rate capability of the Leclanche cell and therefore has a broader range of applications.

5.1.2.3 Advantages and Disadvantages.

Advantages

(1) Better (than Leclanche) low-temperature service.

(2) Higher efficiency under high discharge loads.

(3) Good shelf life (4-year storage - 80 percent of capacity).

(4) Wide availability.

(5) Moderate cost (higher than Leclanche).

Disadvantages

(1) Hydrogen gassing rate higher than Leclanche.

(2) Shorted cells result in high temperatures (100°C) due to high rate capability.

(3) Sloping discharge curve (better than Leclanche).

5.1.2.4 Potential Hazards and Controls.

(1) Hydrogen gas can accumulate during discharge to a greater extent than Leclanche.
- Allow cell to breathe so that the H_2 gas mixes with air.
- Avoid areas where open contacts exist.

(2) Expansion of cells due to pressure buildup possible.
- Do not encapsulate.
- Leave room for can expansion.

(3) Leakage of electrolyte.
- Strong alkali is more corrosive and harmful than the salt-solution of Leclanche cell.
- Can burn the skin or corrode nearby equipment or personnel.

(4) See paragraph 4.5 for a checklist of hazardous conditions to avoid.

5.1.3 Zinc-Mercuric Oxide (Zn-HgO)

5.1.3.1 Description. This cell utilizes either 30 to 45 percent potassium hydroxide (KOH) or sodium hydroxide (NaOH) saturated with zinc oxide (zincate) as the electrolyte. The reaction is given as:

$$Zn + HgO \rightarrow ZnO + Hg \tag{5-3}$$

The cell is available in different forms that determine the structure of the zinc electrode; e.g., corrugated strips or pressed powder amalgamated with Hg. The cathode consists of mercuric oxide mixed with graphite. Layers of cellulose are used for the separator. The zinc-mercuric oxide cell is manufactured in three basic structures: a) wound anode, b) flat pressed powdered electrode and c) cylindrical pressed powder type.

5.1.3.2 Applications. The zinc-mercuric oxide cell is available in a button cell or cylindrical cell configuration. Because of a higher volume-energy density than the previous two systems, it has application where rate is low and volume is minimized. This includes pacemakers, hearing aids, detectors, and sensors.

5.1.3.3 Advantages and Disadvantages.

Advantages

(1) Higher volume-energy density.

(2) Long shelf life.

(3) Flat discharge curve over a wide range of current drains.

(4) High resistance to impact, acceleration, and vibration.

Disadvantages

(1) Relatively higher cost.

(2) Disposal problems because of Hg produced on discharge.

(3) Electrolyte creep may result in leaks.

5.1.3.4 Potential Hazards and Controls.

(1) Tendency for hydrogen, caused by zinc oxidation, to accumulate during discharge.
- Do not place cell in sealed area or encapsulate it. Allow cell to breathe so that H_2 can mix with air.

(2) The presence of Hg is of concern because of its toxic nature, particularly in the vapor phase.
- Extra care must be taken to avoid cell damage during handling, shipment, and storage to prevent Hg exiting from the cell. Short circuit or any excess heating of the cell can result in Hg vapor.
- Do not solder leads directly to the cell terminals unless proper precautions are taken and the manufacturer has approved the procedure.

(3) Opening and/or disposal of the cell must be performed under controlled conditions.
- If open, place entire contents under water in a polyethylene or polypropylene container.
- Spent zinc-mercuric oxide cells can be disposed of by insulating and disposing in trash.
- Do not dispose of cells in a fire.

(4) Electrolyte (strong alkali) leak from cell shall be neutralized.
- If it comes into contact with skin or metallic parts, it can be neutralized with a saturated solution of boric acid. If solution is unavailable, rinse in large quantities of water.

(5) See paragraph 4.5 for a checklist of hazardous conditions to avoid.

5.1.4 Zinc-Air (Zinc-Oxygen) ($Zn-O_2$)

5.1.4.1 Description. This cell also utilizes a potassium hydroxide (alkaline) electrolyte and an amalgamated zinc powder sometimes with a gelling agent as the anode. The cathode referred to as an air cathode remains intact (does not undergo reaction) throughout the discharge reaction. Oxygen from the air enters the cell through openings in the case, flows through diffusion and hydrophobic membranes and is reduced at the carbon or sintered nickel structure impregnated with a catalyst, sometimes platinum. The reaction is given simply as:

$$Zn + 1/2\ O_2 \rightarrow ZnO \qquad (5\text{-}4)$$

5.1.4.2 Applications. Large zinc-air batteries with the appearance of an automobile battery having sheet zinc anodes (low rate) have been used for railroad signal switching, telecommunication, and beacons. Recently, they have been utilized by NASA in the Shuttle cabin, in a button cell configuration. The small cells have been used in portable communications gear and hearing aids.

5.1.4.3 Advantages and Disadvantages.

Advantages

(1) High volume-energy density.

(2) Flat discharge voltage at low rates.

Disadvantages

(1) Capacity highly dependent on load.

(2) Cell drying out due to accessibility to air.

(3) Anode area limits power output.

(4) Dependent on environmental conditions.

(5) Pulse capability limited.

5.1.4.4 Potential Hazards and Controls.

(1) Strong alkali in electrolyte may leak (primary hazard).
  - Use saturated solution of boric acid or dilute vinegar (acetic acid) to neutralize.

(2) Hydrogen evolution can occur because of the electrochemical reduction of zinc.
  - Because the cells and batteries are "pressure relieved," they are usually designed such that the accumulation of hydrogen is minimized in the cell and battery case.

(3) See paragraph 4.5 for a checklist of hazardous conditions to avoid.

5.1.5 Zinc-Silver Oxide (Silver-Zinc) ($Zn-Ag_2O$)

5.1.5.1 Description. This cell utilizes a porous electro-formed amalgamated zinc electrode, and a porous silver oxide electrode and a 35 to 45 percent solution of KOH. To prevent silver migration in the cell, the separator system is constructed of multiple layers of cellophane and nylon fabric. Sometimes radiation-grafted polyethylene is used to extend wet life. The cell reaction is given as:

$$Zn + Ag_2O \rightarrow 2Ag + ZnO \tag{5-5}$$

5.1.5.2 Applications. Because of its high energy density it has found wide use in electronic equipment, hearing aids, watches, calculators, and other instruments requiring extended life. In space it has been used to power the tools used to repair the Solar Max Mission (SMM) spacecraft and to power the Manned Maneuvering Unit (MMU) required to propel the astronaut during extravehicular activity (EVA). Most of the primary batteries on Apollo and Skylab were zinc-silver oxide. A cell/battery can be recharged a limited number of times to allow checking of performance or associated equipment. It is available in button, prismatic, and reserve configurations.

5.1.5.3 Advantages and Disadvantages.

Advantages

(1) High energy density.

(2) Good voltage regulation - flat discharge voltage.

(3) Comparatively good low-temperature operations.

(4) Good shock and vibration resistance.

(5) On a limited basis, can be charged and discharged to determine capacity.

Disadvantages

(1) Relatively high cost.

(2) Active cell shelf life limited to 1 year or as little as 30 days (except for reserve types).

5.1.5.4 Potential Hazards and Controls.

(1) Strong alkali may leak through pressure relief valve.
  - Use saturated boric acid solution to neutralize effects of alkali on skin and metals.

(2) Hydrogen can accumulate on open circuit stand and especially at low voltages (<0.3V).
  - Silver has a low hydrogen overvoltage; thus when the silver electrode potential falls there is a greater tendency for hydrogen to be evolved. Do not allow discharge below 1.0V.
  - On the prismatic cells there is a pressure relief valve to allow gas escape.
  - Assure adequate ventilation for pressure-relieved hydrogen.

(3) Zinc dendrites can form (on charge).
  - Even with the multiple layers of separator it is possible for zinc to work its way through during charging and create an internal short.
  - Internal shorts can produce heat which increases pressure within the cell. (Most shorts are high impedance and thus current is limited to low levels.)

(4) See paragraph 4.5 for a checklist of hazardous conditions to avoid.

5.2 LITHIUM ANODE PRIMARY CELLS/BATTERIES

Various cells with lithium anodes and non-aqueous electrolytes are rapidly gaining importance for consumer and space related applications. The reason is that they offer the highest specific energies (Wh/kg), highest volume energy densities (Wh/L), and longest storage life of any electrochemical cell thus far developed. Like the zinc anode cells described in paragraph 5.1, most of the lithium anode cell technologies to date are for primary cell applications.

The main reason for the continued growth in interest in lithium cell technology over the past several years is large energy storage capability and lengthy shelf life of lithium itself. Ironically, the same reasons are also the cause of the safety hazards associated with this technology. The basis for lithium's energy storage capabilities are the magnitude of its oxidation potential (3.01V) compared to other metals such as zinc (0.76V), and its large capacity per unit weight (3.86 ampere hours/gram) again compared with zinc (0.82 ampere hours/gram). Together they provide the largest watt hour/gram material known. The basis of the lengthy storage life is the protective film formed on the lithium surface when it is in a suitable non-aqueous media. The film protects it against corrosion and loss of energy experienced in all aqueous electrochemical systems.

The inherently large energy storage capability is quite desirable when the total electrochemical cell system is under control and used in applications and within limits for which it was intended. However, if subjected to abnormal operation or conditions, the large quantity of energy can be released quickly, sometimes with violence, resulting in venting and or explosion on rare occasions. For this reason, the soluble cathode lithium anode cell should only be used in applications where the zinc anode cell will not meet performance requirements. In the three groups of cells described below, those designed for the highest discharge rates (soluble cathode type) are the most susceptible. The safety issue is of considerable concern. A vast amount of testing, including abuse testing, has been conducted. The results and complications specific to lithium anode cells are included in the discussion of hazards (paragraph 5.2.1.7).

The lithium cell groups are divided into three categories:

(1) Soluble cathode cells.

(2) Solid cathode cells.

(3) Solid electrolyte cells.

The soluble cathode types include lithium-sulfur dioxide ($Li-SO_2$), lithium-thionyl chloride ($Li-SOCl_2$), and lithium-sulfuryl chloride ($Li-SO_2Cl_2$). The lithium-thionyl/chloride (bromine chloride) (Li-BCX) cell utilized in Shuttle applications is the lithium-thionyl chloride type with a bromine chloride additive which influences its characteristics. The basis of the soluble cathode technology is that the cathode material is used up during the discharge reaction. These cells have the capability of being discharged at rates as high as C/10 and higher. The majority of safety issues are related to this group of lithium anode cells.

There are numerous solid cathode cells ranging in voltage from 1.5V to 3.3V. These are gradually replacing the zinc anode cells because of the higher energy storage capability. They utilize a cathode material that remains in the solid condition during operation and are used in applications where rate requirements are low (<C/100).

The lithium-iodine cell is one of the few solid electrolyte cells in production. It has the lowest rate capability of the lithium systems and is quite safe, except at temperatures above 186°C (lithium melting point), where it can explode.

Because lithium is an active metal, it reacts with moisture. Therefore, the assembly of the lithium cells must be accomplished under moisture-free, dry room conditions to optimize performance and safety. Thus, the quality control of materials and processes is critical to success.

Finally, as in the zinc anode cell designation, the lithium anode is the negative electrode relative to the opposing electrode because it provides the electrons to the load during discharge. The three types of lithium electrochemical cells are described below.

Table V. Lithium Soluble Cathode Cell Characteristics*

Name	Anode	Electrolyte	Cathode	OCV (V)	(NOM) (V)	Specific Energy (Wh/kg)	Energy Density (Wh/L)	Operating Temp °C	Comments
Li-SO_2	Li	CH_3Cn/LiBr	SO_2/C	3.0	(2.9)	280	440	-55 to 70	Most advanced of soluble cathode type
Li-$SOCl_2$	Li	$SOCl_2$/$LiAlCl_4$	$SOCl_2$/C	3.6	(3.5)	600	900	-40 to 70	Highest energy density
Li-BCX	Li	$SOCl_2$/$LiAlCl_4$/BrCl	$SOCl_2$/C	3.9	(3.5)	430	960	-40 to 70	BrCl reported to prevent formation of S
Li-SO_2Cl_2	Li	SO_2Cl_2/$AlCl_4$	SO_2Cl_2/C	3.9	(3.5)	500	1000	-40 to 70	In early stages of production

*Cylindrical spiral wound (jellyroll) construction.

5.2.1 Lithium Anode-Soluble Cathode Cells/Batteries

The four electrochemical cell types comprising this group are lithium-sulfur dioxide (Li-SO_2), lithium-thionyl chloride (Li-$SOCl_2$), lithium-thionyl/chloride (bromine chloride) (Li-BCX) (Li-$SOCl_2$ with halogen additive), and lithium-sulfuryl chloride (Li-SO_2Cl_2). They are similar in that they comprise cathode active materials that are used up during the discharge process, sometimes forming reactive discharge products. They are capable of rates up to C/10 (and higher) because the active materials are in direct contact with the carbon current collector. The carbon electrode is porous and serves as the storage site container for some of the discharge products. In addition to the improved energy and storage performance capability, they have a characteristic which must be considered in their use: voltage delay. This is the delay, after the load is switched on, of the cell/battery voltage reaching its normal operating voltage after the initial power surge. This drop in voltage depends on the cell's previous storage temperature, time, discharge rate, and temperature of the application. A number of corrective actions have been taken to avoid this problem, including pulsing the battery before intended use and, more recently, the inclusion of additives of various types to the cell components. See Table V for the pertinent characteristics of each of the four cells discussed below.

5.2.1.1 Lithium-Sulfur Dioxide (Li-SO_2). This cell, available in a spiral-wound construction, utilizes a polypropylene separator between layers of lithium foil and porous carbon structures of roughly equivalent size. The carbon cathode is prepared to size by pressing or rolling a mixture of carbon and Teflon (as a binder) over a nickel screen with a lubricant (isopropyl alcohol). The result is an 80 percent porous structure that provides the necessary surface area for the discharge reaction to occur and volume for discharge products to deposit. The discharge product is lithium dithionite. The net reaction is given as:

$$2Li + 2SO_2 \rightarrow Li_2S_2O_4 \qquad (5\text{-}6)$$

The electrolyte consists of a solvent, acetonitrite (CH_3CN), to store the SO_2, and a salt (LiBr) to enhance the conductivity. The internal pressure of the cell at the start is in the range of 3 to 4 atmospheres (3-4 x 10^{-5} pascals). A glass to metal seal is used for hermetic sealing, and a pressure vent is used to release the pressure when it reaches a preset level of 27 to 30 atmospheres (at temperatures of 93 to 107°C).

5.2.1.2 Lithium-Thionyl Chloride (Li-$SOCl_2$). The lithium-thionyl chloride cell is composed of a lithium foil anode and a cathode current collector of carbon-Teflon composition as described for the lithium-sulfur dioxide cell. The liquid $SOCl_2$ serves as the cathode active material (catholyte) and as the solvent in which 1.5 mol $LiAlCl_4$ is dissolved to form the electrolyte. The separator is a nonwoven glass held together with an inert binder. The reaction is given as:

$$4Li + 2SOCl_2 \rightarrow 4LiCl + S + SO_2 \qquad (5\text{-}7)$$

The LiCl discharge product deposits in the pores of the cathode. It eventually clogs enough pores to render the cathode inactive (passivated) and thus causes the cell to fail. (For further discussion see design considerations for the influence of this factor on safety, paragraph 5.2.1.8.) The SO_2 is evolved as a gas and reaches a pressure of 1 atmosphere at the end of discharge at 20°C. Because the solvent is consumed during discharge, an adequate volume of electrolyte is required when the cell is manufactured to assure that the $SOCl_2$ will not run out before discharge is completed. These cells have been produced in button cell (very low rate applications), bobbin cylindrical cell construction to replace the alkaline cell applications (moderate rate), spiral wound cylindrical cells for higher rate applications, reserve types (high rate) where the acidic electrolyte increases the discharge rate capability, and in prismatic types to the 10,000 ampere hour size.

5.2.1.3 Lithium-Thionyl/Chloride (Bromine Chloride) (Li-BCX). This cell is produced almost exactly like the lithium-thionyl chloride cell except for the addition of BrCl. The BrCl additive is said to scavenge the free sulfur (S) formed during the early stages of discharge, thus minimizing potential hazardous reactions.

5.2.1.4 Lithium-Sulfuryl Chloride (Li-SO_2Cl_2). This electrochemical system (in its development stage) is similar to the soluble cathode cells described above. However, the cathode of the lithium-sulfuryl chloride cell evidently is not optimized for this system. From early indications it offers a higher rate capability than the lithium-thionyl chloride cells but presently exhibits a higher loss in capacity on stand. Its reaction is given as:

$$2Li + SO_2Cl_2 \rightarrow 2LiCl + SO_2 \qquad (5-8)$$

As in the case with lithium-thionyl chloride cells, the SO_2 is gaseous and the clogging of the carbon by LiCl can limit the discharge.

5.2.1.5 Applications. The lithium soluble cathode cell group offers the user a power source that can be used in applications with a specific energy and energy density 8 times greater than the present Leclanche cells over a wide range of temperatures, and in addition offers a long shelf life. Cells of bobbin construction, which are considered low rate because of their limited electrode surface, are in production and have been made available to the public. However, few of the high rate (spiral wound, large surface area) cells have been made available to the consumer bcause of the safety issues. However, the lithium-sulfur dioxide cell was approved by the FAA for use in electronic locating transmitters (ELT) for private noncommercial aircraft, and the lithium-thionyl chloride cells are used in oilwell logging tools. Almost all other applications are military.

The size and configuration of a cell determines its application. Lithium-thionyl chloride cells in flat disc (button) cells containing multiple plates have been used by the military in multicell batteries for several portable applications. The cylindrical lithium-sulfur dioxide (spiral-wound) cells and lithium-thionyl chloride (spiral and bobbin) cells have been used in a wide variety of military applications. The lithium-sulfur dioxide cell has better low-temperature rate capability than the lithium-thionyl chloride cell, which has higher energy density (Wh/kg) and is capable of operating at higher temperatures. The spiral type is used in radios, transceivers in sonobuoys, and a wide range of portable power equipment. The lithium-thionyl chloride bobbin type (low rate) has been used for small instruments and computer memory applications. The reserve lithium-thionyl chloride cell offers an extremely high current within seconds of activation and is being considered for monitors and missile activation. The very large prismatic (10,000 ampere hour) size has been used as a standby power source in missile silos. There is also the flat disc cell which is available in 50 to 2000 ampere hour sizes. To date, soluble cathode cells that have been approved for NASA use in the Shuttle include the lithium-thionyl/chloride (bromine chloride) cell used on the astronaut's helmet to power the TV camera and the EVA lights, lithium-sulfur dioxide cells for the Galileo Probe and Long Duration Exposure Facility (LDEF), and a few low rate AA, 1/2 MA and C bobbin construction types in various applications. The safety of these spiral-wound "D" cells is assured by the use of a diode across each cell, a fuse in each cell, under-voltage battery cutout for the TV camera battery and thermostatic switches, and adequate heat sinking.

5.2.1.6 Advantages and Disadvantages.

Advantages

(1) High energy storage capability including specific energy, energy density, and operating voltage.

(2) Lengthy storage life.

(3) High rate capability for lithium cells.

(4) Good low-temperature performance of lithium-sulfur dioxide.

(5) Relatively flat discharge voltage.

Disadvantages

(1) Inherently higher hazard potential.

(2) Safety precautions necessary.

(3) Internal cell pressure increases rapidly as temperature increases (especially lithium-sulfur dioxide).

(4) Reversal and charging can result in venting or explosion.

(5) Catholyte and electrolyte are toxic if cell is opened.

(6) Disposal, handling, and transportation procedures must meet safety requirements of Department of Transportation (DOT) and Environmental Protection Agency (EPA) and must be carefully scrutinized.

(7) Voltage delay possible depending on temperature and time of storage and rate and temperature of application.

5.2.1.7 Potential Hazards and Safety Issues (see paragraph 4.5 for a checklist of general potential hazards). The subject of safety immediately comes to mind when the use of a lithium cell is contemplated. What is it about these cells whose energy and performance is well beyond that of the present aqueous electrochemical systems? The conclusion is obvious: lithium is one of the most electrochemically energetic of the elements. In addition, the non-aqueous constituents used in the cell and the lithium are toxic and produce complex products whose reactivity, composition, and role in the cells is not well-understood.

It is known that lithium cells are not as tolerant as aqueous cells to design flaws and abuse. The hazards associated with these cells were identified earlier in this manual as user-induced and manufacturer-induced causes (paragraphs 4.2 and 4.3). Assuming a cell has been designed properly and has been manufactured under the quality control required to meet the specified applications, the safe use of the cell/battery is of primary concern.

5.2.1.7.1 The Causes. In evaluating the causes for lithium cell safety problems, it can be concluded that during discharge, temperature, whether internally or externally imposed, is responsible for the unsafe behavior of lithium cells, some types to a greater extent than others. Increases in temperature can:

(1) Increase internal gas pressure; i.e., $p = f(T)$.

(2) Increase vapor pressure of solvent or other volatile constituents, thus further increasing internal pressure.

(3) Increase the rate of reactions, resulting in additional heat and pressure.

(4) Cause lithium to melt and react with other constituents and/or products, producing highly exothermic reactions and causing extremely rapid temperature and pressure increases.

(5) Result in thermal runaway leading to venting of gases (methane from lithium-sulfur dioxide cells) and explosion.

NOTE

The construction of the cell and battery determines the heat dissipation rate, and thus the rate at which the cell temperature increases.

Other kinds of operation or abuse that would cause the above chain of events to occur include:

(1) High rate discharge or external short, producing heat generation from the exothermic discharge reactions and from the

I^2R cell heating losses as current flows from one terminal through the cell to the other terminal.

(2) Operation in a high-temperature environment which increases the internal cell temperature.

(3) Potting or thermally insulating a cell in such a manner that even at low rates and reasonable temperatures, heat cannot be adequately dissipated.

(4) Internal low-resistance shorts of the type initiated by puncturing, crushing, bridging of terminals or parts within the cell, or other physical/mechanical abuse in which the rapid I^2R heating raises the cell temperature.

(5) Charging a cell, thus producing gases and other products while generating heat or causing unexpected reactions to occur which in themselves are heat-initiated.

(6) Continuing the discharge beyond the point at which the cell's useful capacity is depleted (reversal or overdischarge) so that abnormal exothermic gas-producing and other reactions take place, thus increasing the temperature or causing other reactions to occur.

(7) Depleting the soluble cathode (SO_2, $SOCl_2$, SO_2Cl_2) at the end of discharge so that dry conditions are created, resulting in increased impedance and localized dry spots leading to dangerous localized intense heating.

NOTE

The merits of an anode-limited vs cathode-limited design are still being debated.

For the most part the discussion above is directed at the soluble cathode cells designed for high rate capability. Caution with the low-rate cells is also advised; however, due to the limited reaction rate capability, these cells would be dangerous only if exposed to an environment where the temperature exceeds the melting point of lithium (186°C); e.g., fire or if the cell is punctured or crushed violently.

Numerous abuse tests have been performed including exposure to flame, impact, penetration, and rapid high temperature heating, to name a few. It is the consensus that cell venting is not objectionable as long as it does not occur in areas where personnel are affected, such as the Shuttle cabin. However, explosion or detonation is totally unacceptable and all effort must be made to insure against this event. For example, the lithium-thionyl/chloride (bromine chloride) cell appears to offer a measure of added safety and performance over the lithium-thionyl chloride cell. However, heat-tape tests performed recently on these cells in which the temperature was increased at a high rate (10°C/sec), resulted in total detonation of the lithium-thionyl/ chloride (bromine chloride) cell whereas the lithium-thionyl chloride cell was found to vent its products, otherwise remaining intact.

Controversy remains over the subject of whether a cell that vents is safer than one without a vent. The latter cells can release internal products only by violation of the cell case usually designed for up to 1000 psi. The selection of a cell type depends on the application and related environmental considerations.

5.2.1.7.2 The Safety Precautions - A Checklist (see paragraph 4.5 for a checklist of general potential hazards).

Cells, Non-Operational

(1) The cell/battery must be designed to meet the application requirements for rate, temperature, and environment.

(2) All personnel involved, from the designer and engineer to those using, transporting, storing, disposing, operating, and working in the vicinity of use, shall be instructed on the precautions and actions to take in an emergency.

(3) An approved safety plan defining the conditions for storage, handling, use, and disposal, shall be in effect and followed.

(4) Each cell shall be hermetically sealed for space use with 100 percent verification. Use of other types of seals shall be evaluated for the application.

(5) The cells shall never be placed on a metal table, bench, or cabinet in which bridging of cell terminals is possible.

(6) Extended storage and temperatures greater than 60°C (45°C for lithium-sulfur dioxide is undesirable because of seal corrosion/ bridging and capacity loss.

(7) The pressure relief vent shall never be potted or otherwise sealed to avoid extreme pressure buildup in the cell.

(8) Partially discharged cells, or cells with open circuit voltage less than specified, shall be removed from equipment or shelf and properly disposed of.

(9) Requirements for handling and disposal must be understood by all who come in contact with the cells/batteries.

(10) Cells should never be punctured, crushed, mutilated, impacted, or disposed of by incineration unless performed by approved methods and personnel.

(11) Leaking cells shall be handled by trained personnel with adequate protection of hands and face.

(12) The cases of all cells must be electrically isolated from one another.

(13) Acceptable quality control methods including screening, selection, first piece buyoff (such as the JSC certification of lithium-thionyl/chloride (bromine chloride) cells) must be in effect to assure quality of product before lot acceptance is made.

(14) The manufacturer shall have a process that is well-documented, including configuration control steps. Verification (through the use of travelers, inspection reports, etc.) must be in effect to assure the product meets the intended application.

Cells, Operational

(1) The recommended operating temperature shall be maintained within the -20°C to 40°C range (or within the manufacturer specification) whenever possible, unless adequate precautions are taken for the higher temperatures.
- Limit current drain with suitable electronics.
- Use a thermal fuse to terminate operation when temperature limits are exceeded.
- Use solid cathode or solid electrolyte cells which are self-rate limiting.

(2) To terminate discharge, select an appropriate voltage which occurs prior to reaching the knee of the voltage/time curve to avoid reversal.
- Limit the rate of discharge by electrical fuse or thermal fuse to avoid premature cell failure.
- Use of bypass diodes or individual cell voltage cutouts is required for series-connected cells.

NOTE

A bypass diode or diodes in parallel with the cell provides a means for current to bypass the cell when the cell voltage falls below a predetermined level signifying a discharged cell. Precaution must be exercised in selecting the diode(s) because it can drain current from the cell, thereby discharging the very cell it is intended to protect. Also there has been concern about uniformity of bypass diodes, requiring suitable selection tests to be performed.

(3) Minimize the rate of discharge specifically <C/10 (unless designed for higher rates) to minimize heat generation.
- Use of self-rate limiting solid cathode or solid electrolyte cells will reduce the hazard.
- Use of individual cell fuses will offset the effect on external short or high rate excursion. An electronic or thermal fuse built into a cell is suggested. Opening of internal tabs by melting is not sufficient.

(4) Prevent charging a cell, thus eliminating gas generating and other reactions.
    - Use of diodes in series will protect the cell (see Batteries below).

Batteries

(1) For high-rate applications, a fuse shall be incorporated in both legs. As a minimum, one shall be incorporated, preferably in the ground leg. For multivoltage battery designs, each tap shall be fused in addition to the ground leg fuse.

(2) In a battery where parallel strings are used, each string shall contain a diode to avoid a string of good cells charging another string with one bad cell.

(3) Use of a thermal fuse or thermostat in a series cell string is advisable in cases where environmental temperatures may exceed safe operating limits. However, caution must be used in its selection and a decision must be made as to whether a resettable or non-resettable switch is desired for the application.

(4) Monitoring of each cell's voltage to insure cells are not reversed is desirable but not practical. A battery discharge low voltage cutout shall be selected so that impending failure of one cell will terminate the discharge.

NOTE

The alternative method to increase sensitivity to a failing cell in a series string is to utilize a preselected value of the Δ 1/2 battery voltage (the voltage of one-half the cells in the battery minus the other half) to terminate the discharge.

(5) Battery packaging shall be such as to maximize the thermal dissipation and yet assure there is proper electrical isolation of the cells. The latter criterion supersedes the former.

(6) A decision must be made as to whether the battery case can prevent the products from venting its cells or whether it too must have a pressure relief vent.

(7) Backfilling of battery cases shall be accomplished with dry N_2 gas, vacuum, or dry air to avoid corrosion.

5.2.1.8 Design Considerations. The cell/battery design quality depends on the electrochemical design as well as the mechanical design. These are discussed below.

5.2.1.8.1 Electrochemical. The electrochemical design involves the role, quantities and reactivity of active materials and electrolyte in the cells. The capacity and safety of a cell (and its performance characteristics to some extent) depend on which of the components (anode, cathode, or electrolyte) will be limiting on discharge. In theory, depletion of anode and cathode simultaneously is desired, with enough electrolyte remaining to maintain adequate conductivity.

In practice, the anode and cathode respond to rate and temperature differently. Although there are numerous types, sizes, shapes, and designs of cells and batteries, there is no universal type that can be expected to perform exactly as intended for all cell applications and conditions.

There are safety-related considerations that can be given to a cell design in order to optimize safety and performance. For the lithium soluble cathode cells, these issues are of primary concern because of the reactions that can take place on reversal of anode-limited, cathode-limited, or carbon-limited cells. The anode-limited cell refers to the situation where the lithium is depleted before the catholyte, leaving only a screen current-collector used in its support. The cathode-limited cell refers to the case where catholyte is depleted and lithium is left at the anode. The carbon-limited design implies that, although there is adequate catholyte and lithium, the carbon current collector wherein the cathode reaction takes place has lost its activity (passivated) due to pore clogging. At low rates, similar to those seen in the solid cathode or solid electrolyte cells, there is a possibility of achieving a balanced cell design; i.e., one in which anode and cathode materials are depleted simultaneously when the cell comprises stoichiometrically equal quantities of cathode and anode active materials. At moderate to high rates, one can expect that even though the cell is of a balanced cell design, the cell will become carbon-limited, leaving excess lithium and catholyte present.

In the early days of the lithium-sulfur dioxide cell development, a large excess of lithium (1.8 times SO_2) was added to the cell to optimize its output characteristics. When the cell became fully discharged, the SO_2 was depleted, leaving a large excess of lithium when the cell went into reversal.

During discharge and reversal, products were formed which on continued reversal became, under various conditions and especially at higher temperatures, highly reactive with lithium, resulting in venting or even explosion with methane formation (one of the discharge products). Today, ampere hour capacity of positive and negative electrodes in lithium-sulfur dioxide cells is balanced within a ratio of 1 $\pm$0.1.

The design of greatest concern in the lithium-thionyl chloride cell is the cathode- or $SOCl_2$-limited case. Because the $SOCl_2$ serves as the solvent as well as the catholyte, its depletion can result in a dry cell whose conductivity is adversely affected and whose soluble salts and products are no longer in solution. The local hot spots, increased impedance, and continued reversal can lead to energetic reactions involving chemical reaction of the lithium and the remaining observed species. Lithium dendrite formation is possible once the voltage drops below 0.1 volts and current continues to flow. This can result in an internal short, either intermittant or direct, resulting in a hazardous condition.

In summary, reversal conditions must be avoided. However, in remote or unattended applications there is the possibility that one cell in a series string will be forced into reversal through the load by the remaining cells. The type of cell and electrochemical design (balanced, anode, cathode or carbon-limited) can affect the ultimate safety of the associated equipment and adjacent areas.

There is still a concern for lithium dendrite shorts reported by several researchers and for the shock or impact characteristics of lithium-thionyl chloride cells having undergone reversal. Reports of detonations indicate a serious cause for concern regarding these cells. Warming lithium-sulfur dioxide cells that were reversed when cold has also resulted in explosions.

5.2.1.8.2 Mechanical. Refer to paragraph 3.3 for mechanical design considerations of importance not only for the safety of lithium soluble cathode primary cells but for other electrochemical systems as well.

5.2.2 Lithium Anode-Solid Cathode Primary Cell/Batteries

Several electrochemical systems are contained in this group of cells. As indicated, the cells utilize a lithium anode in combination with an electrochemically reducible material, in some cases mixed with carbon to enhance conductivity. They are available in flat disc (button) cells, cylindrical cells, and as flat prismatic types in prismatic batteries. They have low to moderate rate capability which is self-limiting by the surface area of the electrodes available for reaction. Thus, except for highly unusual conditions, they are considered safe and with acceptable safety screening tests for verification. The characteristics of the various types are given in Table VI and are discussed individually below.

5.2.2.1 Lithium-Manganese Dioxide (Li-MnO_2). This cell utilizes an electrolyte composed of propylene carbonate (PC) and 1,2 dimethoxyethane (DME) with lithium perchlorate ($LiClO_4$) salt which enhances the conductivity. The reaction is given as:

$$Li + Mn^{4+}O_2 \rightarrow Mn^{3+}O_2(Li^+) \qquad (5\text{-}9)$$

where the lithium ion (Li^+) enters the MnO_2 lattice.

The cathode is either pressed powder or a thin pasted electrode on a conductive support.

5.2.2.2 Lithium-Carbon Monofluoride (Li-$(CF)_x$). The active components are a lithium anode and solid carbon polymonofluoride (CF) formed by reaction of carbon monoxide with fluorine gas. Several electrolytes have been used, including lithium hexafluorarsenate ($LiAsF_6$) in dimethyl sulfide (DMSI). Other

Table VI. Lithium Solid Cathode Cell Characteristics*

Name	Anode	Electrolyte	Cathode	OCV (V)	(NOM) (V)	Specific Energy (Wh/kg)	Energy Density (Wh/L)	Operating Temp °C	Comments
Li-$\mathrm{Mn0_2}$	Li	$\mathrm{PC/DMI/LiAlCl_4}$	$\mathrm{Mn0_2/C}$	3.0	(2.8)	200	400	-20 to 55	Earliest use, can store at elevated temp
Li-$\mathrm{(CF)_x}$	Li	$\mathrm{DMS1/LiAsF_4}$ $\mathrm{BL/DME/THF/LIBF_7}$	$\mathrm{(CF)_x/C}$	3.1	(2.5)	250	600	-20 to 60	First used commercially, highest reservation specific energy
Li-CuS	Li	$\mathrm{DME/1,3D/LiCl0_4}$ $\mathrm{THF/DME/LiCl0_4}$	CuS	2.1/1.7	(1.8)	135	335	-10 to 70	2X capacity of Zn-$\mathrm{Mn0_2}$
Li-Cu0	Li	$\mathrm{PC/THF/LiCl0_4}$	Cu0/C	2.2	(1.5)	300	600	-10 to 70	High volumetric energy density
Li-$\mathrm{FeS_x}$	Li	$\mathrm{PC/DME/LiCl0_4}$	$\mathrm{FeS,FeS_2/C}$	1.7	(1.5)	125	370	-10 to 45	Replacement for Zn-$\mathrm{Ag_20}$ temperature dependance
Li-$\mathrm{Bi_2Pb_20_5}$	Li	$\mathrm{1.3D/LiCl0_4}$	$\mathrm{Bi_2Pb_20_5/Pb}$	2.3	(1.5)	150	400	-10 to 45	Replacement for Zn-$\mathrm{Ag_20}$
Li-$\mathrm{Ag_2Cr0_4}$	Li	$\mathrm{PC/LiCl0_4}$	$\mathrm{Ag_2Cr0_4/C}$	3.3/2.5	(1.5)	275	750	-10 to 55	Very low (~10y) discharge rate
Li-$\mathrm{V_20_5}$	Li	$\mathrm{MF/LiA_sF_6}$ $\mathrm{MF/LiBF_4}$	$\mathrm{V_20_5/C}$	3.4	(2.8)	200	600	-40 to 60	Very long storage life (~10y)
Li-$\mathrm{I_2}$	Li	LiI	$\mathrm{I_2/P2PV}$	2.8	(2.7)	120	600	0 to 150	Low drain rate

*			
PC	Propylene Carbonate	1,3 D	Dioxolane
DME	1,2 Dimethoxyethane	THF	Tetrahydrofuran
DMSI	Dimethylsulfite	MF	Methylformate
		BL	Butyrolactone

electrolytes have included lithium tetrafluoroborate ($LiBF_4$) salt in butyrolactone (BL), tetrahydrofuran (THF) or propylene carbonate (PC) and dimethoxyethane (DME). The simplified reaction is given as:

$$Li + (CF)_x \rightarrow x\ LiF + xC \qquad (5\text{-}10)$$

where the CF acts as an intercalation compound.

5.2.2.3 Lithium-Copper Sulfide (Li-CuS). This cell consists of a lithium anode and copper sulfide cathode in an electrolyte of $LiClO_4$ in 1,2 dimethoxyethane (DME) and 1,3 Dioxalane (1,3,D) and 2.5 dimethylisoxazole (DMI). The reaction is given in two steps with the final step:

$$4Li + 2Li_xCuS \rightarrow 4Li^+ + 2Li_xCu + 2S^{2-} \qquad (5\text{-}11)$$

5.2.2.4 Lithium-Copper Oxide (Li-CuO). The lithium sheet on a nickel grid (anode) and pressed copper oxide pellet, mixed with acetylene black and a Teflon binder (cathode) are in an electrolyte consisting of $LiClO_4$ in propylene carbonate (PC) and tetrahydrofuran (THF). The cell reaction is given as:

$$2Li + CuO \rightarrow Li_2O + Cu \qquad (5\text{-}12)$$

5.2.2.5 Lithium-Iron Sulfide (Li-FeS or Li-FeS_2). The construction is similar to zinc-silver oxide cells with the lithium anode and a FeS or FeS_2 cathode mixed with graphite and a PTFE (Teflon-based) binder. The electrolyte consists of a solvent of propylene carbonate (PC) and 1,2 dimethoxyethane (DME) and lithium perchlorate ($LiClO_4$) salt. The separator is polypropylene.

The reactions are given as:

$$FeS_2 + 4Li \rightarrow Fe + 2Li_2S \qquad (5\text{-}13a)$$

$$FeS + 2Li \rightarrow Fe + Li_2S \qquad (5\text{-}13b)$$

5.2.2.6 Lithium-Lead Bismuthate (Li-$Bi_2Pb_2O_5$). This system uses a lithium anode and a cathode consisting of $Bi_2Pb_2O_5$ mixed with lead powder and Teflon binder. The electrolyte is $LiClO_4$ in 1.3 Dioxolane (1,3D). The reaction is given as:

$$10\ Li + Bi_2Pb_2O_5 \rightarrow 5Li_2O + 2Bi + 2Pb \qquad (5\text{-}14)$$

5.2.2.7 Lithium-Silver Chromate (Li-Ag_2CrO_4). The lithium film anode is opposed by a cathode of silver chromate and graphite. The electrolyte is $LiClO_4$ in propylene carbonate (PC). The discharge reaction is given as:

$$2Li + Ag_2CrO_4 \rightarrow Li_2CrO_4 + 2Ag \qquad (5\text{-}15)$$

5.2.2.8 Lithium-Vanadium Pentoxide ($Li-V_2O_5$). This cell is sometimes used as a reserve cell because the electrolyte will degrade the cell. However, it consists of a lithium anode and a V_2O_5 cathode mixed with carbon and Teflon. The electrolyte consists of a mixture of lithium hexafluoroarsenate ($LiAsF_6$) or lithium tetrafluoroborate ($LiBF_4$) salts in methylformate (MF). The electrolyte is sealed in an ampule within the cell which is easily shattered without affecting the cell. The separator is polypropylene and the reaction is given as:

$$4Li + V_2O_5 \rightarrow 2Li_2O + V_2O_3 \quad (5\text{-}16)$$

5.2.2.9 Applications. These solid cathode cells are generally used in low to moderate drain applications in small flat (button) or cylindrical configurations. Such applications include watches, calculators, computer memory, clocks, telemetry, and tape recorders. They range in voltages of 1.5-1.6V per cell for lithium-copper oxide; 2.8V for lithium-iron sulfide, lithium-manganese dioxide, and lithium-vanadium pentoxide, and 3.0V for lithium-silver chromate. A list of the individual cell configurations and applications is given in Table VII.

Table VII. Cell Configurations

D,C	$Li-MnO_2$	Camera flash, toys, watches, cameras, small motors
D,C	$Li-(CF)_x$	Watches, calculators, solid rocket booster
*	Li-CuS	Medical applications
C	Li-CuO	Clocks, telemetry, high temperature application
B	$Li-FeS_x$	Watches, cameras, calculators
B	$Li-Bi_2Pb_2O_5$	Electronics, watches
B,C,P	$Li-Ag_2CrO_4$	Medical implantables, computer memory
*	$Li-V_2O_5$	Medical, military
*	$Li-I_2$	Medical, implantable

Key: B = Button, D = Disc, C = Cylindrical, P = Prismatic, * = Special

5.2.2.10 Advantages and Disadvantages. The major advantage of these cells is the high specific energy and volume energy density, long storage life and operation capability over a wide range of temperatures. Even with a lithium anode, they are considered safe after proper safety verification tests, except when exposed to fire. The major advantages of each system are given below:

Lithium-Manganese Dioxide (Li-MnO_2)

Advantages

(1) Good performance at moderate to low discharge rates over wide range of temperature.

(2) 3V cell.

(3) Cost-competitive with conventional batteries.

(4) Capable of elevated temperature storage.

Disadvantage

(1) Low rate.

Lithium-Carbon Monofluoride (Li-$(CF)_x$)

Advantages

(1) Theoretically highest specific energy.

(2) Low internal impedance.

(3) High pulse capability.

Disadvantage

(1) Exhibits voltage delay.

Lithium-Copper Sulfide (Li-CuS)

Advantages

(1) Good low-temperature performance.

(2) Favors intermittent discharge.

(3) Good capacity retention.

Disadvantages

(1) Limited availability.

(2) Two-plateau voltage curve.

Lithium-Copper Oxide (Li-CuO)

Advantages

(1) Highest volumetric energy density.

(2) No voltage delay.

(3) 10-year storage life at 20°C.

(4) High-temperature storage capability.

(5) Good charge retention of partially discharged cells.

Lithium-Iron Sulfide (Li-FeS)

Advantages

(1) Good low-temperature storage.

(2) Relatively low cost.

Disadvantage

(1) Lower power capability than silver-zinc cells.

Lithium-Lead Bismuthate (Li-$Bi_2Pb_2O_5$)

Advantages

(1) Improved shelf life over conventional cells.

(2) Lighter weight and lower cost.

(3) Pulse load capability.

Lithium-Silver Chromate (Li-Ag_2CrO_4)

Advantages

(1) High volume energy density.

(2) Lengthy storage life (~10 years).

(3) Low rate capability.

Disadvantage

(1) Higher cost.

Lithium-Vanadium Pentoxide (Li-V_2O_5)

Advantages

(1) High volume energy density.

(2) Lengthy storage life (~10 years).

Disadvantage

(1) Two-step discharge due to two reduction voltages.

5.2.2.11 Potential Hazards and Safety Issues (see paragraph 4.5 for a checklist of general potential hazards). These cells contain lithium and care must be exercised in their handling, storage, use, transportation, and disposal. There are two major safety issues: high-temperature explosions and leakage of electrolytes, catholytes, or products.

They are self-limiting in their discharge rate capability and therefore cannot generate their own internal temperatures. However, subjecting the cells to high temperatures; i.e., > 186°C, the melting point of lithium, can result in a venting or explosion.

The second safety issue involves the leakage of the various electrolytes, some of which are toxic and others that can burn or cause personal harm. Caution must be exercised in the use of these cells in applications where the electrolyte can set off side reactions.

5.2.3 Lithium Solid Electrolyte Cells.

There is only one electrochemical cell of this type available today: the solid-state lithium-iodine cell.

5.2.3.1 Lithium-Iodine (Li-I_2). The lithium-iodine cell uses a solid lithium anode and an iodine charge transfer complex as the cathode. The cathode consists of a mixture of the iodine and poly-2-vinylpyridine. The electrolyte is solid lithium iodide. The reaction is given as:

$$2Li + I_2 \rightarrow 2LiI \qquad (5\text{-}17)$$

See Table VI for its characteristics.

5.2.3.2 Applications. Because of its very low discharge rate capability, the primary use of this cell is in pacemakers. However, these cells have application in comparative circuits or computer memory retention, watches, and calculators, and have been used in several such applications in the Shuttle Orbiter.

5.2.3.3 Advantages and Disadvantages.

Advantages

(1) Excellent storage capability (~10 years).

(2) Sealed - no leakage.

(3) Wide operating temperatures.

Disadvantages

(1) Low current drain only.

(2) Low power capability.

5.2.3.4 Potential Hazards. This system is even less hazardous than the solid cathode cells because electrolyte leakage is not a concern. Placing the cell in a flame could result in a venting or deformation.

5.2.4 Handling of Lithium Cells (see paragraph 5.2.1.7.2)

5.2.4.1 Shipping. Transportation of both new and used batteries is governed by the federal regulations relating to the shipment of hazardous materials. The regulations are published in 49CFR 172.101, 173.206 (e) (1) and 175.3. Research and special program administration of the U.S. Department of Transportation, Washington, D.C. 20590, has issued exemptions to allow for the shipment of lithium cells and batteries if detailed requirements regarding cell size and 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, Appendix A. Any company or group shipping under this exemption must be explicitly registered with the Department of Transportation 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.

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 gram of lithium) by passenger aircraft. Each cell and battery must be equipped with effective means of preventing external short circuits and must incorporate a safety venting device or be designed in such manner that will preclude a violent rupture.

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

5.2.4.2 Packaging. Some of the important guidelines for packaging of cells and batteries are given below.

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

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

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

(4) For shipment by water, motor vehicle, or rail freight, the outside container must be a strong wooden box.

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

5.2.4.3 Storage. Special care is needed for the storage of lithium cells/batteries. It is desirable that the storage facilities and firefighting provisions be reviewed and approved prior to storage of lithium cells in any area. Once the storage area is approved and established, the quantity of cells and batteries that is added or removed from storage must be monitored. Partially, fully discharged, or reversed cells/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/batteries should be stored separately. The following precautions are recommended for the storage of new and used cells/batteries.

New lithium batteries shall be stored as follows:

(1) Lithium batteries shall be stored in their original shipping containers in a cool, sprinkler protected, ventilated shelter.

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

(3) Since the effect of mass storage on the degree of hazard is not known, the quantity stored in any area shall be kept to a reasonable minimum.

(4) Lith-EX fire material should be on hand in case of fire.

(5) Batteries in storage shall be retained in unit packages, preferably shipping containers, to prevent heat transfer between batteries.

(6) Storage temperature above 54.5°C shall be avoided (to optimize performance, 27°C).

(7) Special care shall be exercised in handling and moving containers to prevent crushing or puncturing.

Used lithium batteries shall be stored in the following manner:

(1) Used lithium batteries shall be packaged in accordance with paragraph 5.2.4.2 above.

(2) A remote collection point and storage area, sprinkler protected (if feasible), and separate from other combustible material shall be established for batteries awaiting disposal.

(3) Used lithium batteries shall not be allowed to accumulate and disposal shall be effected promptly (no more than 30 lbs. or 30 days).

(4) Lithium batteries are not to be disposed of or transported with normally generated refuse.

(5) Used lithium batteries shall not be burned, dropped, cannibalized, dismantled, modified, or otherwise carelessly handled, short-circuited, charged, or reused.

Storage spaces shall be properly ventilated. When entering a storage space 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.

5.2.4.4 Disposal. Improper disposal of lithium batteries can be very hazardous. The various safety problems one may come across in the disposal of lithium batteries are venting of toxic gases and liquids, violent explosions, and, sometimes, fire. These hazards are basically due to extreme reactivity and the toxic nature of cell components and discharge products. A rough estimate of the explosive hazard of 10 to 15 "D" size cells (200 ampere hours) is assumed to be equivalent to 0.25 lb. of TNT. Partially/fully discharged cells are reported to be more hazardous than new cells. Hence, great care is needed in the disposal of these cells/batteries. They cannot be discarded like alkaline zinc-manganese dioxide cells. It is advisable to seek the assistance of concerned authorities (Environmental Protection Agency of the state concerned) before disposing of the cells. They must be disposed of per the established and recommended procedures. The various methods attempted so far for the disposal of the cells fall into one of the following groups.

(1) Disposal in land fills.

(2) Keeping the cells in disposal ponds or lagoons.

(3) Disposal into municipal sewage after deactivation and neutralization.

(4) Controlled incineration with adequate scrubbers by approved disposal companies.

Detailed discussion of these methods is beyond the scope of this publication.

SECTION 6

THE SECONDARY CELLS, THEIR CHARACTERISTICS AND POTENTIAL HAZARDS

Secondary cells and batteries differ from the primary cells and batteries in that the chemically stored energy used up during the discharge can be returned by recharge. Secondary cells/batteries require additional circuitry to provide the means for recharging. Depending on type of electrochemical cell application and temperature, cells can be cycled (charged/discharged) hundreds of times to tens of thousands of times.

The most often used secondary system for space applications is the nickel-cadmium (NiOOH-Cd) type. Because of its reversibility and long life it has been used in the majority of low Earth orbiting (LEO) and geosynchronous orbiting (GEO) spacecraft. During eclipse it provides power to the spacecraft, the instruments, and electronics. During Sun periods the solar array provides spacecraft energy requirements and also recharges the battery. An alternative nickel electrode electrochemical system is the nickel-hydrogen ($NiOOH-H_2$) battery which has received much attention in recent years. The other rechargeable systems used in space are based on the silver oxide electrode. These include the silver-cadmium (AgO-Cd), silver-zinc (AgO-Zn) and silver-hydrogen ($AgO-H_2$) types. The five types are similar in that they use a strongly alkaline electrolyte. The lead acid secondary cell/battery uses strong acid (sulfuric) as the electrolyte. The lead acid battery, the most commonly known because of its consumer applications, is one of the few electrochemical systems using an acid electrolyte. It has been utilized as a sealed cylindrical cell in getaway special (GAS) applications. There are also two lithium systems now in the developmental stage: lithium-titanium disulfide ($Li-TiS_2$) and lithium-molybdenum trisulfide ($Li-MOS_3$). Only the lithium-titanium disulfide system is discussed here.

Because these cells are commonly designated as nickel- and silver- and in order to be consistent with the designation of the primary cell on discharge, the nickel hydroxide, silver oxide, and lead dioxide electrodes are the cathodes on discharge and are positive in voltage with respect to the opposing electrodes. On charge the role of anode/cathode is reversed with the opposing electrode. However, they maintain the same polarity as that during discharge.

The batteries constituting the secondary group are divided as follows:

Nickel hydroxide cells/batteries
Silver oxide cells/batteries
Lead acid cells/batteries
Lithium cells/batteries
Sodium-sulfur cells/batteries

Refer to Table VIII for their characteristics.

Table VIII. Secondary Cell Characteristics

Name	Anode*	Electrolyte	Cathode*	OCV (V)	(NOM) (V)	Specific Energy (Wh/kg)	Energy Density (Wh/L)	Operating Temp °C	Cycle Life** @ 80 percent DOD
NiOOH-Cd	Cd	KOH	NiOOH	1.29	1.25	30	80	-10 to 35	-2000
$\mathrm{NiOOH-H_2}$	H_2	KOH	NiOOH	1.32	1.25	55	60	-10 to 35	-2000
NiOOH-Zn	Zn	KOH	NiOOH	1.73	1.69	60	120	-20 to 60	200-300
AgO-Cd	Cd	KOH	$\mathrm{Ag_2O/AgO}$	1.41	1.3/1.1	55	110	-25 to 70	400
AgO-Zn	Zn	KOH	$\mathrm{Ag_2O/AgO}$	1.86	1.7/1.5	90	180	-20 to 60	100
$\mathrm{AgO-H_2}$	H_2	KOH	$\mathrm{Ag_2O/AgO}$	1.39	1.2	80	90	0 to 50	400
$\mathrm{PbO_2-Pb}$	Pb	$\mathrm{H_2SO_4}$	$\mathrm{PbO_2}$	2.1	2.0	30	70	-40 to 60	300-500
$\mathrm{Li-TiS_2}$	Li	organics	$\mathrm{TiS_2}$	2.4	2.0	125**	150**	-20 to 55	New couple
Na-S	Na	alumina	S	2.1	1.75	187**	304**	350	New couple

* On discharge

** Projected

Note: The values for Specific Energy, Energy Density and Cycle Life refer to the same battery in each case. Different trade-offs can be made between energy and life with the result that these values can vary over a wide range in most cases.

6.1 NICKEL HYDROXIDE CELLS/BATTERIES

The nickel hydroxide cells include nickel-cadmium and also the nickel-hydrogen, nickel-zinc, and nickel-iron types. The former two have been or are in space use. The latter two have been used, or considered for use, in electric vehicles, load leveling, and photovoltaic power generation systems and will not be discussed here.

6.1.1 Nickel-Cadmium (NiOOH-Cd)

6.1.1.1 Description. The nickel hydroxide electrode (+) is produced in either a sintered plate or pressed powder form for this cell. For space use and for the nickel-hydrogen cell, the sintered plate is required. An 80 percent porous nickel plaque or a nickel screen or perforated sheet serves as the current collector. The active material (nickel hydroxide) deposited into the pores by a series of steps fills approximately 40 percent of the remaining space in the plaque. The cadmium hydroxide electrode (-) is produced in the same manner. A 31 percent aqueous solution of potassium hydroxide is used as the electrolyte and the separator is a nonwoven nylon or polypropylene material. The cell is hermetically sealed with two ceramic/metal terminal seals. The cell reaction is given as:

$$2NiOOH + Cd + 2H_2O \underset{\text{chg}}{\overset{\text{disch}}{\rightleftarrows}} 2Ni(OH)_2 + Cd(OH)_2 \qquad (6\text{-}1)$$

6.1.1.2 Operation. In order to replace the energy removed from the cell on discharge the cell must be recharged to the full state of charge and then must receive an overcharge which offsets the charge inefficiency. The inefficiency is a function of rate and temperature and is a result of the production of oxygen gas during the charge process, primarily near the end. The gas evolution occurs at the nickel hydroxide electrode. In the flooded/vented cells, the gas produced by the electrolysis of the aqueous alkaline solution is allowed to escape. The water/electrolyte must be replaced periodically as in the nonsealed automobile lead acid batteries.

In the hermetically sealed (semi-dry or starved) type, the electrolyte is immobilized in the separator and plates, allowing the gas to distribute itself around and within the cell pack. The evolution of the oxygen gas is offset by its recombination at the cadmium hydroxide electrode, which contains cadmium metal (Cd) because it is being charged. The oxygen recombines according to the following reaction:

$$O_2 + 2Cd + 2\,H_2O \rightarrow 2Cd(OH)_2 \qquad (6\text{-}2)$$

Thus when the charging process has converted most of the active materials to NiOOH and Cd as given in (6-1) and oxygen evolution occurs, the oxygen reacts with the charged Cd via (6-2) to discharge the cadmium electrode by the same amount.

The aerospace cell is referred to as positive-limited on charge (and discharge). If it were to be negative-limited on charge, the negative electrode would evolve hydrogen gas which is not recombined in this cell. A high internal pressure and therefore potential safety problem would result. The discharge is positive-limited because of more rapid degradation of the negative electrode. There is always excess negative capacity and therefore the cell capacity is limited by the positive electrode.

The most efficient charge scheme is to use a high current (>C/4) at the start of charge and convert to constant voltage (current taper) at a prescribed voltage limit until the current drops to a C/15 rate. The cells can generally be charged at the C/10 rate constantly without producing excessive pressure. However, this charge rate results in a temperature increase based on I^2R heating. The discharge process results in a thermal inefficiency of 16 to 18 percent which must be provided for in a system design.

6.1.1.3 Applications.

Nickel-cadmium cells are available in a number of shapes and sizes for consumer and space applications. The sealed button and cylindrical cells have found their way into many portable power devices (radios, telecommunication, lighting, switching, hearing aids, pacemakers, calculators, tooth brushes, instrument tools, etc.). The cells/batteries used for space applications are the hermetically sealed prismatic type. Cells/batteries are also available in a vented, flooded type which offers an improved power capability. These have been used in aircraft turbine engine and diesel engine starting as well as other mobile military equipment.

Because there is a rapid decrease of cell cycle life with high depths of discharge (DOD)*, operation has been limited in aerospace applications to 25 percent DOD for LEO applications and 65 percent for GEO applications.

6.1.1.4 Advantages and Disadvantages.

Advantages

(1) Maintenance-free sealed cells.

(2) Long cycle life.

(3) Rugged/sealed.

(4) High rate/power capability.

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*Depth of discharge is the percent of nominal (rated) capacity removed from the cell during a discharge.

(5) Flat discharge.

(6) Long storage - discharged/shorted.

(7) Large data base.

Disadvantages

(1) Relatively high cost.

(2) Memory effect/double plateau - may need reconditioning.

(3) Charge control methods necessary.

(4) Poor charge acceptance at high temperature or low charge rate.

(5) Poor capacity retention on storage, charged.

(6) Prismatic sealed cells require end-plates to prevent expansion due to internal pressure.

6.1.1.5 Potential Hazards.

(1) Pressure buildup in sealed case on charge.
- Use adequate temperature, rate, and charge controls.
- Ratio, balance and stability of active materials must be considered in design.

(2) Leakage of alkaline electrolyte.
- Prevent by performing seal and cell testing.
- White encrustation on seal or case is an indication of leak.
- Inspection and welder certification, qualification, and calibration is necessary.
- Use nylon/cotton gloves in handling electrolyte.

(3) Leakage of oxygen can cause imbalance problems resulting in dangerous H_2 buildup.
- Use reliable ceramic/metal seals.
- Perform helium leak test on each cell.

(4) Internal shorting can result in hot spots, arcs, etc. leading to potential explosion.
- X-ray cell.
- Use "clean" methods in cell assembly.
- Inspect plates for sharp edges, burns, etc.

(5) Cell reversal can result in H_2 and/or O_2 evolution which cannot be recombined as in the charge condition.
- Monitor each cell during operation (not practical).
- Undervoltage cutout can be utilized.
- Use a Δ 1/2 battery voltage to monitor changes in individual cell characteristics (voltage of 1/2 battery subtracted from other half).

(6) External shorts can cause very high-rate, high-temperature excursions which can lead to a violent venting.
  - Use tools and equipment that are insulated to prevent bridging.
  - Coat cell terminals to prevent inadvertent metal contact.
  - Use fuses and other protective circuitry.

(7) See paragraph 4.5 for a checklist of potential hazards.

6.1.2 Nickel-Hydrogen ($NiOOH-H_2$)

6.1.2.1 Description. This cell, like the nickel-cadmium cell, is quite reversible. It utilizes a nickel hydroxide electrode produced by electrochemical deposition of nickel hydroxide into the pores of a sintered nickel plaque with screen support. The hydrogen electrode comprises a Teflon bonded platinum black on a nickel mesh screen to allow the reduction and oxidation of hydrogen. A gas diffusion screen is used to facilitate hydrogen diffusion. The electrolyte is 30 to 35 percent aqueous potassium hydroxide by weight. An asbestos fuel cell bidirectional separator is used. The cell configuration is such as to contain 800 to 1000 psi of hydrogen on full charge. The reaction is given as:

$$2NiOOH + H_2 \underset{chg}{\overset{disch}{\rightleftarrows}} 2Ni(OH)_2 \tag{6-3}$$

A plasma sprayed zirconia oxide is sometimes used to coat the inside of the cylindrical pressure vessel to enhance electrolyte distribution. It has the potential for greater depth of discharge and higher rate capability than the nickel-cadmium.

6.1.2.2 Operation. The cell can be charged at a relatively high rate constant current (~ C/2) similar to the nickel-cadmium cell. During charge, hydrogen is evolved at a rate consistent with the charge rate. Pressure builds up to 800 to 1000 psi. During overcharge the O_2 generated in place of the $Ni(OH)_2$ oxidation reaction reacts with the hydrogen generated according to the reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{6-4}$$

thus maintaining the high pressure at a constant value. The cells are in a cylindrical pressure vessel container that can withstand up to 2400 psi. On discharge, the hydrogen recombines in the cell according to (6-3). If discharged to 100 percent DOD, the cell pressure returns to its original value.

The nickel-hydrogen is reported to be an improvement over the nickel-cadmium because the cadmium electrode, which degrades with life and depth of discharge, is replaced by the H_2 electrode. However, this has not yet been proven.

6.1.2.3 Applications. This type of cell has had one major application, that of replacing the nickel-cadmium in GEO spacecraft. The enhanced specific energy (Wh/kg) over nickel-cadmium cells offers a greater opportunity for increasing the spacecraft capability of reducing total mass. GEO orbit (22,000 miles above the earth) is one in which there are only two eclipse periods per year, thus requiring ~100 cycles/year. The nickel-cadmiums are operated to 65 to 75 percent DOD. The nickel-hydrogen cells are projected to reach 85 percent DOD. Small nickel-hydrogen cells have been designed for a number of other specialized applications. However, the nickel-hydrogen offers an improvement in cell sizes greater than 50 ampere hours while the nickel-cadmium is more efficiently used below this value. There is also interest in their use in LEO where their capability for greater DOD would provide a distinct advantage. While the specific energy of nickel-hydrogen cells is greater than nickel-cadmiums, the volume energy density is less.

6.1.2.4 Advantages and Disadvantages.

Advantages

(1) State of charge directly related to pressure.

(2) Specific energy/power greater than nickel-cadmium.

(3) Higher depth of discharge than nickel-cadmium projected (not yet proven).

(4) Can tolerate overcharge and reversal at controlled rates.

Disadvantages

(1) High cost.

(2) Self-discharge proportional to decrease H_2 pressure.

(3) Volume energy density and power << nickel-cadmium.

6.1.2.5 Potential Hazards.

(1) High rate charging and heat buildup.
  - Use charge control and thermostatic devices.

(2) High pressure buildup.
  - Use strain gage to monitor pressure.

(3) Leakage of strong alkaline electrolyte.
  - Prevent by performing seal and cell testing.
  - White encrustation on seal or case acid is an indicator of a leak.
  - Inspection and welder qualification and calibration necessary.
  - Use rubber gloves in handling electrolyte.

(4) Gas (H_2 or O_2) leakage creates cell imbalance - potential of exceeding pressure limit.
- Perform helium leak testing on each cell.
- Use high reliability well tested seals.

(5) External shorting can result in very high-rate, high-temperature excursion leading to a violent venting.
- Use fuse and other protective circuitry.

(6) See paragraph 4.2 for a checklist of potential hazards.

6.2 SILVER OXIDE CELLS/BATTERIES

There are three types that comprise this group: silver-cadmium, silver-zinc, and silver-hydrogen. The first two have found application in space for limited mission life. The silver-cadmium cell is nonmagnetic and is used in applications where magnetometers are among the spacecraft instruments. Silver-zinc (also known as silver-oxide zinc and zinc-silver oxide) cells have been used in mid-altitude with relatively short-life spacecraft where the high specific energy plays a part in helping to reduce spacecraft weight. The cell is similar to that described in paragraph 5.1.5 on zinc anode cells except that it is rechargeable. The silver-hydrogen cell is similar to the nickel-hydrogen type described in paragraph 6.1.2, with silver replacing the nickel.

As described earlier, the silver oxide electrode is the cathode on discharge and anode on charge (polarity + on both charge and discharge). The zinc, cadmium, and hydrogen are the anodes on discharge and cathode on charge (polarity - on both charge and discharge). See Table VIII for the cell characteristics.

6.2.1 Silver-Cadmium (AgO-Cd)

6.2.1.1 Description. The silver electrode is prepared by sintering silver powder on a silver grid after molding or continuous rolling. Pasted or pressed plates have also been used. The cadmium electrodes are produced by the same processes using cadmium oxide or hydroxide on a silver or nickel grid. The electrolyte is 40 percent KOH. The plates are wrapped with multiple layers of separators to prevent silver migration, which is one of the life-limiting processes. The reaction is given as:

$$AgO + Cd + H_2O \underset{\text{chg}}{\overset{\text{disch}}{\rightleftarrows}} Cd(OH)_2 + Ag \qquad (6\text{-}5)$$

A second discharge plateau noted in silver cells is due to the discharge of Ag_2O according to:

$$Ag_2O + H_2O + Cd \underset{\text{chg}}{\overset{\text{disch}}{\rightleftarrows}} Cd(OH)_2 + 2Ag \qquad (6\text{-}6)$$

6.2.1.2 Operation. The charging of silver-cadmium cells occurs at two voltage levels. Conversion of Ag to Ag_2O and AgO charge is best performed at constant current at the C/20 - C/10 rate to 1.6V/cell. Thereafter, O_2 is generated at the silver electrode (anode on charge) as with the nickel hydroxide electrode (anode on charge) of a nickel-cadmium cell. Hydrogen is also generated on the cadmium electrode via electrolysis of water during the overcharge, if not prevented by cutoff voltage. There is little or no gas recombination so that the overcharge capability of the silver-cadmium is not possible. Hydrogen evolution appears to be less of a problem with the silver-cadmium cells than the silver-zinc secondary cells.

6.2.1.3 Applications. The cells are usually available in polymeric cases in the prismatic configuration and their use has been primarily on magnetic spacecraft and in military applications.

6.2.1.4 Advantages and Disadvantages.

Advantages

(1) Higher specific energy than nickel-cadmium.

(2) Higher volume energy density than nickel-cadmium and nickel-hydrogen.

(3) Nonmagnetic.

(4) Less sensitive to overcharge than silver-zinc.

Disadvantages

(1) Relatively high cost.

(2) Short cycle life (better than silver-zinc).

(3) Operation strongly dependent on temperature.

(4) Lower voltage than silver-zinc.

6.2.1.5 Potential Hazards.

(1) High rate charging and heat buildup.
- Use charge control and thermostat devices.

(2) High-pressure buildup - some cell pressure relieved.
- Use strain gage to monitor pressure.

(3) Leakage of strong alkaline electrolyte.
- Prevent by performing seal and cell testing.
- White encrustation on seal or case is an indicator of a leak.

- Inspection and welder qualification and calibration are necessary.
- Use rubber gloves in handling electrolyte.

(4) Gas (H_2 or O_2) leakage creates cell imbalance - potential to exceed pressure limit.
- Perform helium leak testing on each cell.
- Use high-reliability, well-tested seals.

(5) External shorting can result in very high-rate, high-temperature excursion leading to a violent venting.
- Use fuse and other protective circuitry.

(6) See paragraph 4.2 for a checklist of potential hazards.

6.2.2 Silver-Zinc (AgO-Zn)

6.2.2.1 Description. The cell is a modified version of the primary silver oxide-zinc cell. The silver electrode is the same type described in paragraph 6.2.1.1 on silver-cadmium cells. The zinc electrode is prepared by pressing a paste or slurry of zinc oxide binder, or by electrodeposition in plating tanks onto metallic grids. As in the silver-cadmium cell, the plates are also wrapped with layers of separator to prevent silver migration and zinc dendrite formation. The inner separator serves as an electrolyte reservoir and barrier to minimize AgO oxidation of the separator. The outer separator stabilizes the zinc electrode and retards zinc penetration. The outer separator is cellophane but is being replaced by radiation-grafted polyethylene in some applications. The electrolyte is 40 percent KOH. The two-step reaction is given by:

$$AgO + Zn + H_2O \underset{\text{chg}}{\overset{\text{disch}}{\rightleftarrows}} Zn(OH)_2 + Ag \qquad (6\text{-}7a)$$

$$Ag_2O + Zn + H_2O \underset{\text{chg}}{\overset{\text{disch}}{\rightleftarrows}} Zn(OH)_2 + 2Ag \qquad (6\text{-}7b)$$

6.2.2.2 Operation. The charge and discharge are similar to that of the silver-cadmium cell. In this case charge is terminated at 2.0V to avoid the generation of gas which cannot be recombined and zinc dendrites. The high rate capability is due to the electrical conductivity of the silver grid and the conductivity of the positive electrode.

6.2.2.3 Applications. These cells are available in button cell, cylindrical cell, and prismatic cell configurations. The capacities available are very low up to thousands of ampere hours as in military equipment. High rate (HR) and low rate (LR) versions exist. These cells are usually specially ordered to meet the requirements. HR cells were used in the tools and MMU on the SMM repair mission in April 1984. The silver-zinc battery is also available in reserve configuration for very long storage periods prior to use. Cells with active electrolyte will lose capacity. Several planetary missions have used these cells to meet long term inactive cruise requirements.

6.2.2.4 Advantages and Disadvantages.

Advantages

(1) Highest specific energy and power of presently available secondary batteries.

(2) Highest volumetric energy and power of presently available secondary batteries.

(3) Very low self-discharge.

Disadvantages

(1) High cost.

(2) Limited cycle life.

(3) Poor low-temperature performance.

(4) Two-step voltage plateau.

6.2.2.5 Potential Hazards.

(1) High rate charging and heat buildup.
- Use charge control and thermostat devices.

(2) High pressure buildup possible.
- Cells may be pressure relieved.
- Use strain gage to monitor pressure.

(3) Leakage of strong alkaline electrolyte.
- Prevent by performing seal and cell testing.
- In vented designs, absorb electrolyte before it escapes from the battery.
- White encrustation on seal or case is an indicator of a leak.
- Inspection and cell assembler qualification and calibration are necessary.
- Use rubber gloves in handling electrolyte.

(4) External shorting can result in very high-rate, high-temperature excursion leading to a violent venting.
- Use fuse or other protective circuitry.

(5) See paragraph 4.5 for a checklist of potential hazards.

6.2.3 Silver-Hydrogen ($AgO-H_2$)

6.2.3.1 Description. This cell utilizes the silver electrode of the type used in the silver-zinc cell, paragraph 6.2.2, and an electrocatalytic gas electrode similar to that used in the nickel-hydrogen cell (see paragraph 6.1.2.1). The silver oxide electrode, which has higher energy per unit weight than the nickel-hydrogen electrode, offers a higher energy density than the nickel-hydrogen type. The reaction is given as:

$$AgO + H_2 \underset{\text{chg}}{\overset{\text{disch}}{\rightleftarrows}} Ag + H_2O \tag{6-8}$$

The electrolyte is a 25 to 30 percent aqueous KOH solution. The cell case is cylindrical construction and uses polymeric "Ziegler" seals for each of the electrodes. One 50 ampere hours type was developed for NASA in the late 1970's.

6.2.3.2 Operation. The charge and discharge operation is analogous to the nickel-hydrogen cell operation (see paragraph 6.1.2.2).

6.2.3.3 Applications. This electrochemical system has yet to be used in aerospace or other applications for several reasons: cost, energy density less than silver-zinc, and concern because the silver migration limits cycle life. However, the silver electrode performs well in applications where the low rate charge is maintained for lengthy periods.

6.2.3.4 Advantages and Disadvantages.

Advantages

(1) Highest energy density aqueous system except for silver-zinc.

(2) Moderate power capability.

(3) Good low-temperature performance.

Disadvantages

(1) Silver electrode limits cycle life.

(2) Limited data base.

(3) High cost.

(4) Longer charge times relative to nickel-cadmium or nickel-hydrogen.

6.2.3.5 Potential Hazards.

These are the same as those given for the nickel-hydrogen cell (paragraph 6.1.2.5).

6.3 LEAD ACID CELLS/BATTERIES

Lead acid is the most familiar of all of the electrochemical cell types because of its consumer use. Where the cell/battery is charged, the positive plate consists of lead dioxide (PbO_2) and metallic lead is the major constituent of the negative electrode. The grid is constructed of either pure lead, lead alloyed with antimony, or lead with calcium. Tin and arsenic and other metals are also used to enhance the grid. The separator is a phenolic/cellulosic material, PVC, or nonwoven polypropylene. Sulfuric acid is the electrolyte. The reaction is given as:

$$Pb + PbO_2 + 2H_2SO_4 \underset{\text{chg}}{\overset{\text{disch}}{\rightleftarrows}} 2PbSO_4 + 2H_2O \qquad (6\text{-}9)$$

It is obvious that the concentration of the acid electrolyte varies with the state of charge of the cell or battery. The cell type of most interest for space is the sealed cell, which is discussed below.

6.3.1 The Sealed Lead Acid (SLA) Battery

Lead acid cells that are considered for space include the SLA cell and gel cell.

6.3.1.1 Description. The lead acid battery has recently been made available in a sealed (not hermetically sealed) design version. It operates via the same reaction. However, unlike the nickel-cadmium cell, it is pressure-relieved. The lead-calcium alloy improves the structural strength of the PbO_2 electrode in the presence of antimony. During overcharge, the O_2 evolved is recombined at the negative (Pb) electrode. In order to do this the cell must be in the "starved" condition, i.e., all of the electrolyte is immobilized in the felted glass separator and plates. However, unlike the nickel-cadmium, small amounts of hydrogen gas are evolved from the negative electrode which must find its way through the seals at very low rates to avoid pressure buildup and yet avoid cell dryout. The electrodes are spirally wound.

6.3.1.2 Applications. The SLA cells are manufactured in "D" and other cylindrical and prismatic shapes. They can be used for toys, portable tools, appliances, lighting, and alarm systems. The larger cells use tubular plates. SLA cells were used in several GAS Shuttle experiments; J, D, and X sizes have also been used.

6.3.1.3 Advantages and Disadvantages

Advantages

(1) Maintenance-free.

(2) Low heat generation on discharge.

(3) Voltage is a function of state of charge.

(4) Low self-discharge rates.

(5) Long float-life capability.

(6) Low cost.

Disadvantages

(1) Cannot be stored discharged.

(2) Capacity influenced by discharge rate.

(3) Energy density comparable to nickel-cadmium.

(4) Subject to freezing at low states of charge.

6.3.1.4 Potential Hazards.

(1) O_2, H_2, or CO_2 pressure accumulation in the cell.
- Use recommended charge current only.
- Operate at prescribed temperature.
- Do not reverse cells.
- Do not place near open switch or equipment where a spark is accessible.
- Do not seal cell(s) in gastight containers.
- Allow adequate thermal dissipation.

6.3.1.5 Handling. The same general considerations apply as were discussed in section 5.2.1.7.2. In addition, special care should be taken not to subject these cells to subfreezing temperatures while they are in a low state-of-charge.

6.3.1.6 Shipping. An important difference exists between sealed lead acid cells and sealed nickel-cadmium cells during shipping and storage. Whereas nickel-cadmium cells are best shipped and stored in a completely discharged state in order to avoid the hazards of accidental shorting, lead-acid cells, after activation with electrolyte, must be kept charged. Sealed cells are never sold in a dry charged state.

Care should also be exercised while shipping cells and batteries when the terminals are not covered. The cells should be packed tightly, preferably with separations between each cell, so that they cannot fall over and short out against each other. These batteries are extremely heavy and require substantial packaging materials in order to keep the package intact during shipment. If there is any doubt as to the safety of the product during shipment, the open tabs should be covered with an insulating material.

6.3.1.7 Storage. Storage shall be in a cool, dry environment. A means must be provided for maintaining a float charge in order to prevent damage caused by long storage in a discharged or partially discharged condition. Either constant potential (preferred) or constant current may be maintained on the cells. At 25°C, a constant potential of 2.18 to 2.20 V/cell is recommended. This corresponds to 0.0006C to 0.001C overcharge. As the storage temperature is decreased, the potential must be increased by 0.10V for each 25°C temperature decrease.

6.4 THE SECONDARY LITHIUM CELL, ITS CHARACTERISTICS AND POTENTIAL HAZARDS

Recent advances in electronic devices and continuing increase in power requirements of space missions have necessitated the development of high energy density rechargeable batteries. Among various electrochemical systems, batteries utilizing lithium have received widespread attention because of the high electropositive nature of lithium and its low equivalent weight. A number of soluble and insoluble materials have been examined as candidate cathode materials. Even though soluble cathode materials offer a number of advantages (such as rate capability, low sensitivity to overcharge, etc.), these cells exhibit high rates of self-discharge. SO_2 is an example of this type of cathode material, and is currently being investigated. One of the insoluble cathode materials being investigated is TiS_2.

The electrode reaction of these materials involves an intercalation process; i.e., introduction of a guest species into a host lattice without structural modification of the host. Among the various insoluble cathode materials, TiS_2 has been investigated very extensively because of its physical and chemical properties that ideally satisfy the various criteria required of a cathode material. Secondary lithium cells are in the stage of development and are therefore not as readily available as the other electrochemical cells.

6.4.1 Lithium-Titanium Disulfide (Li-TiS_2)

6.4.1.1 Description. In this electrochemical system, lithium is the negative electrode (anode) action material and TiS_2 the positive electrode (cathode) action material. Lithium electrodes are fabricated by pressing two pieces of lithium foil (10 to 20 mil) against each side of a nickel screen. TiS_2 electrodes are currently made by pressing or coating techniques. TiS_2 is initially mixed with a suitable binder material (5 to 10 percent) such as Teflon or rubber based polymers, and the resultant mass is pressed/coated onto a nickel screen.

A solution of 1-2M $LiAsF_6$ in two methyltetrahydrofuran (2 Me-THF) is currently being used as the electrolyte for this system. Investigation of many new electrolytes is in progress. During discharge lithium intercalates into TiS_2 and deintercalation of lithium takes place during discharge. The overall cell recharge is:

$$Li + TiS_2 \overset{\text{disch}}{\underset{\text{chg}}{\rightleftarrows}} LiTiS_2 \qquad (6\text{-}10)$$

6.4.1.2 Operation.

Lithium-titanium disulfide cells are not yet commercially available. However, there is the potential for future use because of their higher energy density. Cells are presently being made only at the laboratory level for development purposes. The operating voltage of this system is between 1.7 - 2.5V. The cell cannot tolerate overcharge or overdischarge. Even though experimental cells built at JPL have achieved 700 cycles, cell capacity has been found to decrease upon cycling. Both Li and TiS_2 electrodes and the electrolyte have been undergoing physical and chemical changes and these changes are assumed to be responsible for capacity degradation with cycling. Work is in progress at JPL and other labs to alleviate this problem.

6.4.1.3 Applications.

These cells will reportedly find application as energy storage devices in future GEO and LEO spacecraft. These cells are also being considered as sources of electrical power/storage energy devices for various defense applications. If they can be produced economically, they may replace nickel-cadmium cells in consumer applications. These are only projected or anticipated applications and they are possible only after improving the cell performance.

6.4.1.4 Advantages and Disadvantages.

Advantages

(1) High energy density.

(2) Higher cell voltage.

(3) Low self-discharge.

(4) Projected low cost.

Disadvantages

(1) Poor performance at high discharge rates.

(2) Poor cycle life performance.

(3) Sensitivity to overcharge and overdischarge.

(4) Disposal problems.

6.4.1.5 Safety. Little is known about the safety of rechargeable lithium cells in general, and lithium-titanium disulfide cells in particular. However, they are reported to be inherently safer than lithium primary cells such as lithium-sulfur dioxide and lithium-thionyl chloride. No hazards are reported when the cells are short-circuited or driven into reversal. However, there are some reports of venting, can bulging, etc., upon continuous charging at high rates. One area for modest concern involves disposal after use, which needs detailed investigation.

6.5 SODIUM-SULFUR CELLS/BATTERIES

This is a high-temperature (350°C) technology that has generated significant interest over the past several years since its announcement by Ford Motor Company. Significant resources have been allocated for this work for both electric vehicles and load leveling. Two technologies are being evaluated as candidates for space use: the Ford beta alumina and the Dow hollow fiber system. The discussion in this section is based on projected characteristics and plans.

6.5.1 Sodium Sulfur (Na-S)

6.5.1.1 Description. The system requires a high temperature (350°C) to maintain its anodic material, sodium, and cathodic material, sulfur, in the molten state. Solid beta alumina or glass acts as both the separator and the electrolyte, in which the sodium ions produced on discharge diffuse through the ion selective material to produce the product sodium sulfide according to:

$$2Na + xS \underset{chg}{\overset{disch}{\rightleftarrows}} Na_2Sx \qquad (6\text{-}11)$$

The depth of discharge and operation determines the value of x which ranges from 5 to 2.

6.5.1.2 Operation. The projected operation appears to be rather straightforward. The cell is designed to operate at 90 percent energy efficiency. However, the impedance and therefore open circuit voltage varies with state of charge/discharge. Charging is terminated once the cell resistance equals twice the discharge endpoint resistance.

6.5.1.3 Applications. Interest in this projected high specific energy system makes it a candidate for several applications, including electric vehicles and space. The major difficulty is the weight penalty that is associated with the thermal management of the system at 350°C and as such it is geared for large systems. The materials problems associated with this temperature have not been solved and the impact on safety also represents an unresolved issue.

6.5.1.4 Advantages and Disadvantages.

Advantages

(1) Adapted to large energy systems.

(2) High peak power.

(3) Support for development is relatively high.

(4) Large specific energy and energy density for a secondary system.

Disadvantages

(1) Operation at 350°C.

(2) Materials and safety problems associated with high temperatures.

(3) Beta alumina technology needs refinement.

(4) Heat management required.

(5) Cost will be high.

(6) Weight penalty for thermal management.

6.5.1.5 Potential Hazards. The hazards of this system have been assessed; however, with experience the problems associated with the molten technology will become more evident.

SECTION 7

PRIMARY AND REGENERATIVE FUEL CELLS, THEIR CHARACTERISTICS AND POTENTIAL HAZARDS

7.1 ALKALINE AND ACID FUEL CELLS

Fuel cells may be classified along with batteries as electrochemical energy storage devices. The major difference between the two is in the type of active materials (those materials that participate in the electrochemical reaction) as well as the products of reaction of these materials, their location, and transport. In the case of batteries these materials are generally solids or liquids (such as NiOOH, Cd, AgO, Zn, $SOCl_2$, and Li) that are located and remain within the power-producing cell or battery. The products of the battery reactions are also solids and liquids (such as $Ni(OH)_2$, $Cd(OH)_2$, Ag, $Zn(OH)_2$, SO_2, S, and LiCl) that also remain within the power-producing cell after use. In the case of fuel cells, the reactants are gases (H_2 and O_2) that are stored within separate containers and transferred to the power-producing fuel cell stack where they undergo electrochemical reaction as in a battery. The producer of the fuel cell reaction, liquid H_2O, is removed from the fuel cell stack and stored in another container.

Two major categories of fuel cells consist of primary and secondary or regenerative types. The primary type operates only in the power-producing or discharge mode and consumes the reactants in the process. The regenerative type operates in both the power-producing or discharge mode as well as the secondary or recharge mode. In the former discharge mode this type consumes reactants as a primary fuel cell. In the recharge mode the regenerative type employs an electrolyzer to decompose the product water back into reactants H_2 and O_2. Power for this process is supplied by a photovoltaic or other source. As such, the regenerative fuel cell operates in essentially the same manner as a secondary battery.

Fuel cells may be further broken down into two categories consisting of the acid and alkaline versions. The major difference between these is the type of electrolyte employed within the cells. This may be either acid or alkaline. Other differences between these are the materials of construction, which are selected on the basis of tolerance to either the acid or alkaline environment.

7.1.1 Description

The primary fuel cell power plant is comprised of several elements consisting of the fuel cell stack, H_2 and O_2 storage tanks, condenser, gas flow control system, power conversion equipment, and thermal control equipment. The most important element of this complete system is the fuel cell stack in which the power-producing electrochemical reactions take place. The stack is comprised of a group of thin bipolar plates with electrodes on either side and a layer of electrolyte between each. The plates are machined with holes on their outer edges along with grooves on their surfaces so as to form a manifold and gas distribution system when assembled into the stack. Hydrogen is fed to one side and oxygen to the other side of each plate through this manifold system. Upon entering their respective compartments, the gases come in contact with the catalyzed electrode/electrolyte interfaces where the electrochemical reactions take place.

In both the acid and alkaline types the catalyst employed within both anodes and cathodes is a finely divided form of platinum black. Different amounts are incorporated within each electrode of each type. Other materials of construction for the acid type consist of carbon black and Teflon for the electrodes and a solid polymeric electrolyte (an acid type ion exchange membrane material). Other materials of construction for the alkaline type consist of carbon and nickel for the electrodes and a porous asbestos layer containing aqueous KOH solution as the electrolyte. Operating temperatures of both types of fuel cells are near 100°C.

Regenerative fuel cells are comprised of the primary fuel cell power plant in conjunction with a water electrolysis unit. These two elements are integrated into a complete rechargeable type system. The fuel cell portions of these are essentially the same as described above. The only major difference is that the gases are stored under pressure in steel containers. The electrolyzers are in both cases very similar in configuration to the fuel cells. These are comprised of bipolar stacks of cells with gas manifolds. Product water from the fuel cells (collected in a reservoir tank) is fed to the electrolyzer where it is decomposed into H_2 and O_2 gases which, in turn, are stored in the high-pressure tanks.

7.1.2 Operation

In the primary fuel cells, the H_2 and O_2 gases from the storage reservoirs are fed via manifolds to the anodes and cathodes of the cell stacks. Here the gases react electrochemically to produce electrical energy. The specific electrochemical reactions that take place within the cells depend on whether they are of the acid or alkaline type. For the acid type the reactions are as follows:

$$\begin{array}{ll}
\text{Anode:} & 2H_2 \rightarrow 4H^+ + 4e^- \\
\text{Cathode:} & O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \\
\hline
\text{Overall:} & 2H_2 + O_2 \xrightarrow[\text{disch}]{} 2H_2O
\end{array}$$

For the alkaline type the reactions are as follows:

$$\begin{array}{ll}
\text{Anode:} & 2H_2 + 4(OH)^- \rightarrow 4H_2O + 4e^- \\
\text{Cathode:} & O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^- \\
\hline
\text{Overall:} & 2H_2 + O_2 \xrightarrow[\text{disch}]{} 2H_2O
\end{array}$$

The product water formed within the cells is removed by a gas recirculation scheme wherein water vapor is transferred to the hydrogen stream and then removed externally in a condenser. Thermal management is provided by circulating a coolant around the cell stack to absorb heat and then removing the heat in a radiator. Small heaters are incorporated to provide for heating the stack up to operating temperature during startup. Fans and pumps are used to circulate the gases and coolants. Hydrogen and oxygen are stored as cryogenic liquids in metal storage tanks (titanium, Inconel, or aluminum).

In the regenerative fuel cells, the product water from the fuel cell stack is fed to an electrolysis unit where it undergoes electrochemical decomposition into H_2 and O_2 gases. The specific reactions that take place within the electrolyzer again depend upon whether it is of the acid or alkaline type.

In the acid electrolyzer:

$$\begin{array}{lccc}
\text{Anode:} & 2H_2O & \rightarrow & O_2 + 4H^+ + 4e^- \\
\text{Cathode:} & 4H^+ + 4e^- & \rightarrow & 2H_2 \\
\hline
\text{Overall:} & 2H_2O & \underset{\text{charge}}{\leftarrow} & 2H_2 + O_2
\end{array}$$

In the alkaline electrolyzer:

$$\begin{array}{lccc}
\text{Anode:} & 4(OH)^- & \rightarrow & O_2 + 24_2O + 4e^- \\
\text{Cathode:} & 4H_2O + 4e^- & \rightarrow & 4(OH)^- + 2H_2 \\
\hline
\text{Overall:} & 2H_2O & \underset{\text{charge}}{\leftarrow} & 2H_2 + O_2
\end{array}$$

The gases from the electrolyzers are first passed through a condenser to remove water and then transferred to their respective storage tanks. The water is transferred to the water reservoir tank. Both the fuel cell and electrolyzer portions generate heat during operation and must be cooled. This cooling is provided by circulating a coolant through the outer shells of each to a heat exchanger and then to a radiator. During some conditions it is necessary to supply heat to one or the other units to maintain operating temperature. This is provided by circulating the hot coolant from one to the other via the heat exchanger.

7.1.3 Applications

Primary fuel cells have been used as the primary power source for all manned spacecraft since the 1960's. They have provided all the power required for life support, housekeeping, propulsion and control, instruments, experiments, etc.

The first units were of the acid type and were employed on the Gemini spacecraft. Three of these 30-kg units aboard the Gemini produced 1 kW during the missions, which lasted up to 14 days.

Subsequent units were of the alkaline type used on the Apollo missions in the late 1960's and early 1970's. These employed three fuel cell assemblies, each weighing 110 kg and capable of delivering up to 1.4 kW. They were designed to operate for periods approaching 3 weeks. The power plant on Apollo logged 440 hours, including some time on the surface of the Moon.

Most recently, advanced alkaline fuel cells have been used for power on the Shuttle Orbiter. These are somewhat lighter and have more power than the earlier alkaline versions. Three such power plants are located aboard the Orbiter. These are designed to provide nominal power output of 2 to 12 kW (average 7 kW) and can produce peak power up to 21 kW. The units are designed to operate for approximately the same length of time (~ 2+ weeks) as the earlier versions. In addition, the units are intended for refurbishment and have been reused on subsequent Shuttle flights.

The regenerative fuel cells are intended for use on long-term orbital missions requiring very high power levels up to 500 kW. These missions include a wide range from low Earth orbit to geosynchronous orbits. In these applications the cells serve the same function as rechargeable batteries; i.e., to provide power during eclipse periods to all spacecraft loads. The cells are recharged during the light period.

7.1.4 Advantages and Disadvantages.

Primary Fuel Cells

Advantages

(1) Very high energy density.

(2) Few moving parts.

(3) Moderate operating temperature.

(4) Oxygen can be used for life support.

(5) High thermal efficiency.

Disadvantages

(1) High cost.

(2) Complex assembly - numerous interconnecting parts.

(3) Complex operation - many controls required.

Regenerative Fuel Cells

Advantages

(1) High energy density (mass).

(2) Projected high cycle life.

(3) Built-in state of charge indicator.

Disadvantages

(1) Low volumetric energy density.

(2) High cost.

(3) Relatively low energy efficiency.

(4) Complex assembly - numerous interconnecting parts.

(5) Complex operation - many controls required.

7.1.5 Potential Hazards

Potential Hazards of Primary Fuel Cells

(1) External H_2 leaks can produce explosive conditions.

(2) Internal H_2 and O_2 leaks can cause local hot spots and also explosive conditions.

(3) External O_2 leaks can cause fires.

(4) Shunt currents can cause internal generation and mixing of gases with resultant heating.

(5) Blockage of manifolds can cause cell reversal and subsequent generation and mixing of gases with resultant heating.

(6) Inadequate cooling can cause thermal runaway.

(7) Thin bipolar cell stacks can be readily shorted without proper insulation and handling.

(8) Alkaline electrolyte is corrosive and toxic.

Potential Hazards of Regenerative Fuel Cells

(1) All of the same hazards of primary fuel cells above.

(2) External leakage problems are enhanced by high pressure storage and numerous gas plumbing connections.

SECTION 8

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SECTION 9

DEFINITIONS

Ampere hours	The number of amperes times the number of hours provided during the discharge or charge process.
Anode	An electrode at which an oxidation reaction (loss of electrons) occurs. In primary cells, the negative electrode of the cell. In secondary cells, either electrode may become cathode or anode, depending upon the direction of current flow (charge or discharge).
Battery	Two or more cells connected in series, parallel, or a combination of both, or a single cell used as a single-cell battery.
Binder	A material, usually organic, used to promote adhesion between the particles of a powder.
Capacity:	The number of ampere hours of stored energy in a single cell.
Rated Capacity	The nominal or nameplate capacity (manufacturer specified) as stated for specific conditions of temperature, current and end voltage.
Standard Capacity	The capacity as measured under a standardized charge-discharge cycle.
Theoretical Capacity	The number of ampere hour equivalents of stored chemical mass.
Measured Capacity	The capacity as measured under other than standard conditions.
Cathode	An electrode at which a reduction reaction (gain of electrons) occurs. In primary cells, the positive electrode of the cell. In secondary cells, either electrode may become cathode or anode, depending upon the direction of current flow.
Catholyte	In batteries having separate electrolyte solutions surrounding the anode and cathode, the electrolyte solution surrounding the cathode or electrolyte containing cathodic active material in solution (as in lithium-thionyl chloride).
Cation	A positively charged ion.
Cell	An electrochemical device consisting of an anode and a cathode in a common electrolyte solution, or in separate electrolyte solutions connected by an ionic bridge. Each anode or cathode may consist of one or more parallel-connected electrodes.
Cell Reversal	A forced reversing of the polarity of the terminals of a cell due to overdischarge.

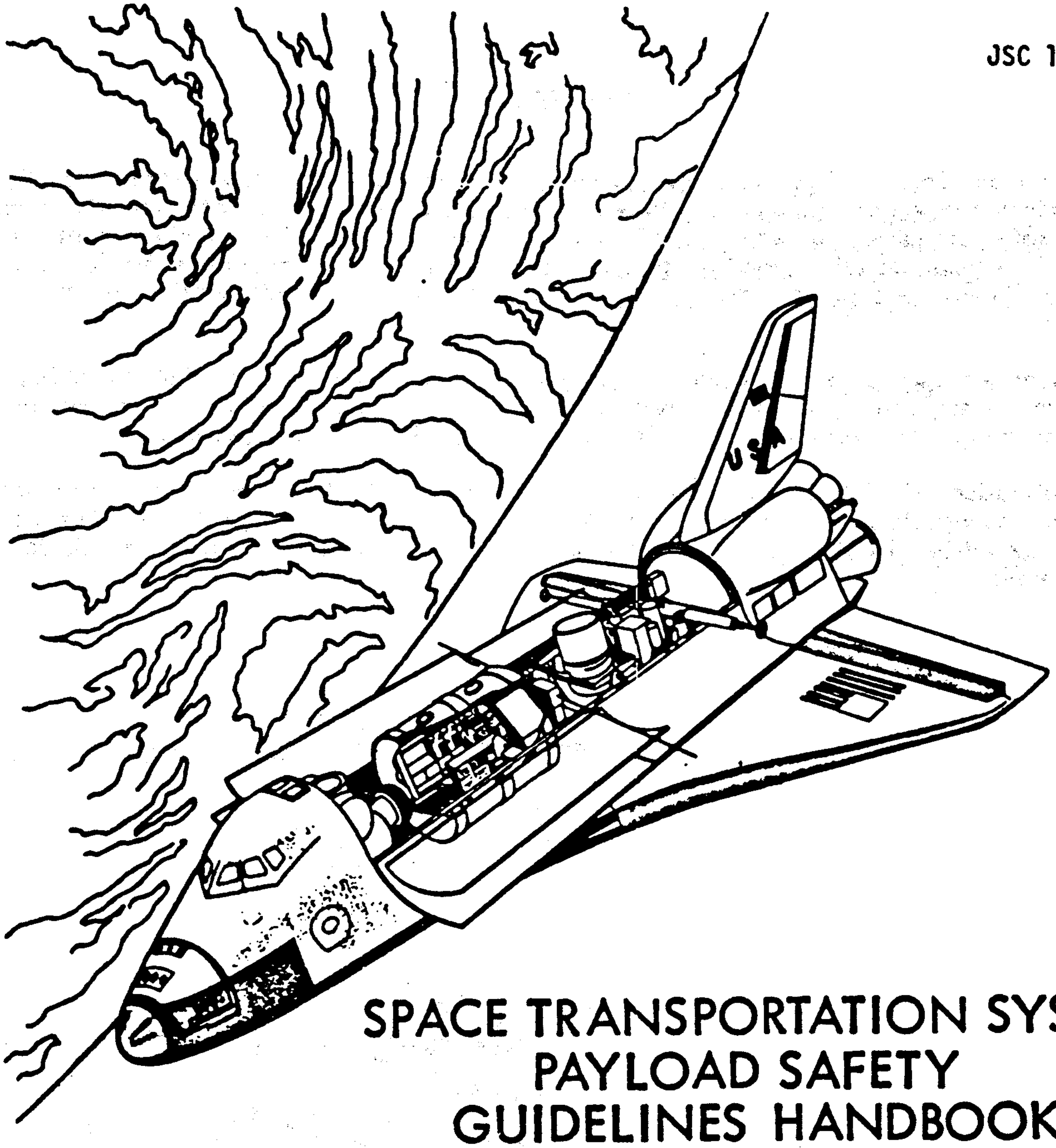
Charge	The process of storing electrical energy in a secondary (rechargeable) battery by forcing current to flow through the battery in the charge direction, which restores discharged material to its charged state.
Current Density	Current per unit electrode area (amperes/centimeter squared).
Cycle Life	The number of cyclic operations (charge-discharge) which a cell or battery will tolerate prior to failure.
Cycling	Repetitive charge-discharge operation of a battery.
Dendrite	A needlelike or treelike branched crystalline growth.
Discharge	The process of obtaining electric power from a battery by connecting a load across the battery terminals, allowing the voltage of the battery to force current through the load.
Discharge Plateau	The relatively flat portion of a discharge curve occurring at the middle of the discharge period.
Efficiency	Ratio of output energy to input energy.
Thermodynamic Efficiency	Ratio of electrical work output to total heat content change.
Electrical Work Efficiency	Ratio of electrical work output to total free energy change.
Watt-Hour Efficiency	In secondary batteries, the ratio of electrical work output (on discharge) to electrical work input (on charge); i.e., watt-hour out/watt-hour in.
Ampere-Hour Efficiency	In secondary batteries, the ratio of measured charge output (on discharge) to total charge input (on charge); ampere-hour out/ampere-hour in.
Utilization Efficiency	That fraction of the mass of electrode active materials that is electrochemically available for discharge at useful voltages.
Electrode	A metallic or nonmetallic conducting body through which the current enters or leaves an electrochemical cell.
Electrolyte	1. An ionic salt dissolved in a solvent to form an ionically conductive solution. 2. The ionically conductive solution itself.

Energy Density	A figure of merit in common use with batteries, expressing the stored energy as a function of volume (watt-hours per cubic centimeter or watt-hours per cubic inch).
Float	The process of maintaining full charge using low-charge current to offset self-discharge.
Flooding	Filling of a cell containing porous electrodes with electrolyte solution, thereby preventing access of gases to the electrode surface.
Formation Cycle	A series of charge and/or discharge operations performed on a newly manufactured cell electrode to condition it for service.
Fuel Cell	An electrochemical energy-producing device employing inert electrodes to which are fed liquid or gaseous reactants, and from which the reaction products are continuously removed.
Intercalation	The process of insertion of species into the layers of the host compound such as Li into TiS_2.
Ion	A charged radical, atom, or molecule. Positive ions are formed by the loss of electrons. Negative ions are formed by addition of electrons.
Overcharge	Continued charge of the cell after it has been fully charged.
Overdischarge	Forcing current through the cell in the discharge direction after all of the active materials have been exhausted. This results in cell reversal.
Oxidation	The process of loss of electrons; one-half of a redox reaction.
Plaque	A porous body of sintered metal used as a current collector and holder of electrode active materials.
Reduction	The process of gaining electrons in a chemical reaction; one-half of a redox reaction.
Reserve Battery	A battery having very short wet-stand time but storable in the dry state. The battery is activated by addition of electrolyte and used immediately.
Self-discharge	The spontaneous discharge of a battery while standing on open circuit (without load).

Separator	A porous or microporous, single- or multiple-layered electronically nonconductive material used between cell electrodes to prevent their touching one another. It may also have other functions, such as electrolyte absorption and control of deterioration processes in the cell.
Sintered Plate Electrode	An electrode formed by sintering metallic powders to form a porous structure which contains the electrode material and current collector.
Specific Energy	The energy to mass ratio (Wh/kg) of a cell or battery.
Starved Cell	A cell containing little or no free electrolyte which enables gases to reach the electrode surfaces readily, and permits relatively high rates of gas recombination.
State of Charge	That percentage of the total available active materials of the cell that is in the charged state. (If the cell is unbalanced, this refers to the active materials of the limiting electrode.)
Substrate	A base material upon which a coating or layer is placed.
Taper Charge	A charging method which starts with a high charging current, which is reduced as the battery approaches the fully charged state. Usually similar or identical to modified constant potential charging.
Thermal Runaway	In batteries, the process by which a cell or battery will undergo a progressive and/or uncontrolled temperature increase which results in abbreviated or unexpected reaction.
Trickle Charge	A low-level constant charging current used to maintain the battery at the fully charged level (countering the self-discharge) with a minimum of damage due to overcharging.
Voltage Limit	During charge, the limit above which the battery potential is not permitted to rise during or after the charging process.

APPENDIX

JSC 11123



SPACE TRANSPORTATION SYSTEM PAYLOAD SAFETY GUIDELINES HANDBOOK

National Aeronautics and Space Administration
LYNDON B. JOHNSON SPACE CENTER
Houston, Texas
JULY 1976

PREFACE

The "Payload Safety Guidelines Handbook" has been prepared to assist STS (Space Transportation System) payload developers in achieving compliance with the documented payload safety requirements of the NASA Office of Spaceflight. The guidelines contained in this handbook apply to all payloads to be carried by the STS. They are not to be construed as requirements but are suggested design or operational options for the elimination and/or control of hazards.

The guidelines incorporate system safety experience accumulated by NASA, DOD, and aerospace industry sources on manned and unmanned spacecraft and aircraft. Of necessity, the guidelines are generic because they are intended to be applicable to any payload.

This publication will be reviewed and revised as appropriate to reflect new experience or changing emphasis to ensure continuing viability. Any questions or requests for additions and changes should be directed to Mr. J. B. Hammack, Chief, Safety Division, code NS, Johnson Space Center.

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1.0 INTRODUCTION.- The STS (space transportation system) will be used to carry into space many different types of payloads. The developers of these payloads will have varied experience and familiarity with both systems safety and manned spaceflight. The payload safety guidelines handbook has been developed at the request of the OSF/Director, Reliability, Quality and Safety and the NASA Office of Planning and Program Integration to provide the payload community with a centralized source of accumulated experience achieved in past Government and industry aerospace programs. The guidelines handbook imposes no requirements on the payload community but suggests options for the elimination and/or control of hazards.

The goal of this handbook is to promote payload safety while permitting the maximum flexibility in the control of hazards. Two key elements involved in achieving this goal are (1) effective communications between NASA and the payload community and (2) utilization of the knowledge and experience from previous programs. The payloads safety guidelines handbook is intended to provide these elements to the payload community.

This handbook provides the payload developer with a uniform description and interpretation of the potential hazards which may be caused by or associated with a payload element, operation, or interface with other payloads or with the STS. It also includes guidelines describing design or operational safety measures which suggest means of alleviating a particular hazard or group of hazards, thereby improving payload safety.

1.1 PURPOSE.- The purpose of this handbook is to assist the payload developer in achieving compliance with the documented payload safety requirements of NASA OSF. The handbook accomplishes this intent by:

a. Identifying the basic hazards involved with payloads intended for the STS.

b. Providing design and operations safety guidelines which eliminate or minimize potential hazards and thereby improve payload safety.

c. Providing the safety guidelines in a subsystem format for easy access and use.

1.2 SCOPE.- The guidelines contained in this document apply to all payloads intended to be carried by the STS. They are suggested design or operational means of avoiding hazards which if not corrected could adversely affect the safety of the STS. The STS consists of the space shuttle, spacelab, upper stages and ground sites needed to support these elements.

1.3 ORGANIZATION.- This handbook is organized into three sections: Introduction, STS Payload Hazards Definition, and Payload Safety Guidelines. Section 2.0, STS Payload Hazards Definition, defines the top level hazards affecting payloads. It also covers the various causes, failure modes, and potential effects of these hazards.

Section 3.0 of the handbook contains the safety guidelines which have been prepared to assist the payload developer in improving the design and operational safety of his particular payload. The guidelines cover STS payloads located in the orbiter payload bay, inside the crew cabin, in the spacelab, or external to the orbiter.

The guidelines are not designed for specific payloads but contain generic data which will assist individual payload designers and developers. This approach is necessary because of the wide variety, complexity, and early stage of development of the majority of payloads proposed for the STS.

The guidelines address payload design, operations during flight, and operations during ground activities including transportation, test and checkout, installation, and refurbishment. For the convenience of the developer, the guidelines are grouped by commonly understood subsystem designators such as electrical, pyrotechnics, etc., and by subject titles such as materials, human factors, and radiation.

Each subsystem guideline section is preceded by an index for that subsystem. The index identifies the main elements comprising that subsystem. The top level hazards associated with each of these main elements are identified in the index and comprise a summary of those hazards applicable to that particular subsystem element. This cross index will aid the handbook user in determining which guideline satisfies his particular application.

1.4 DATA SOURCES.- The identified hazards and the safety guidelines were developed from a data base consisting of manned and unmanned spacecraft and aircraft experience from NASA, DOD, and industrial sources. Data obtained from these sources included existing safety studies and safety standards, related payload studies, and payload description documents. The documents from which these data were obtained are listed in the bibliography section for background information, since pertinent data has been incorporated into the body of this handbook. The listing of a document in the bibliography section is not to be construed as the imposition of the document as a requirement.

2.0 STS PAYLOAD HAZARDS DEFINITION.

2.1 PAYLOAD HAZARDS.- A hazard is the presence of any potential risk situation caused by an unsafe act or condition. There are numerous potential risk situations associated with the STS payloads which directly or indirectly affect the safety of STS flight or ground personnel. One of the purposes of this handbook is to assist the payload developer in recognizing the hazards associated with STS payloads. The identification of such hazards is the necessary starting point for the development of safety guidelines which may be used to eliminate or control the hazards.

Although there may be many secondary or contributory hazards, 10 basic hazard groups were identified as the primary concerns applicable to STS payloads. These hazards have safety implications during all mission phases on ground and flight crews, the STS vehicle, or other payloads.

The hazard groups were derived from a variety of sources such as: (a) a general knowledge of STS payload energy sources which are primary sources of hazards, (b) utilization of experience gained from previous manned space programs as to hazards encountered or prevented, and (c) other representative sources of hazard grouping or categorizations. The list of hazard groups used in this handbook is in general agreement with all such sources. A difficulty common to all lists, including this one, is that there is considerable overlap between hazard groups, and the assignment of any secondary hazard to a particular group can often be arbitrary. The manner in which hazards are grouped or subdivided is therefore not particularly significant. What is important is that the payload developer be aware of all the basic hazards associated with his payload.

2.1.1 Hazard Description.- The basic hazard groups, including representative examples of their causes and effects, are discussed briefly in the following paragraphs. The groups are numbered consecutively from 1 to 10 to agree with the hazard references in each subsystem guidelines index.

1. COLLISION.- This group involves those hazards which occur when payloads or payload elements are allowed to break loose and impact STS structure, other payloads, or flight and ground personnel. These hazards are caused by structural failure, procedural error or inadequate ground handling equipment. Failure of payload attach points can create equipment projectiles that can penetrate manned compartments and injure the crew. Penetration of the cabin may result in loss of cabin pressure and crew asphyxiation. Inadequate or incorrect procedures during payload deployment, retrieval, or during EVA (extravehicular activity) can lead to collision of the payload with the orbiter or other STS elements. Damage to critical orbiter control surfaces or primary structure is possible and could prevent a successful return to Earth. Ground handling equipment such as slings, cradles, holddown arms, etc., can fail and injure personnel during ground operations.

2. CONTAMINATION.- This group of hazards is associated with the release of toxic, flammable, corrosive, condensible, or particulate matter. Contamination is caused by leakage, spillage, outgassing, loose objects, abrasion, and from the growth of fungus or release of volatile condensible materials. Leakage of hazardous fluids or gases can be initiated from cracked or worn seals, gaskets, valve seats, flanges and joints. Spillage of liquids from containers, tanks or valves can directly, or indirectly by vaporization, degrade the atmosphere or equipment operation. Many materials outgas toxic products, irritants, or foul odors which can damage the senses, and the respiratory system of crewmen. Loose objects, dirt, and abrasive action within payload components can provide a source of particles that float in the zerogravity environment of habitable areas and can enter into the eyes, ears, noses, or mouths of personnel and into sensitive equipment. Fungi growing from materials providing nutrients in moist, warm environments are bacterial infection sources and contaminants in operating equipment.

3. CORROSION.- This group involves those hazards resulting from the structural degradation of metallic and nonmetallic equipment. Material corrosion can be caused by a variety of means. leakage of corrosive or reactive material onto metallic or nonmetallic equipment can quickly degrade its usefulness. Material incompatibility or the joining of certain dissimilar metals can lead to corrosion. Environmental extremes of temperature and humidity are sources of deterioration of metals containing carbon or for most organic materials. Examples of the types of corrosive processes which can degrade metal and nonmetal equipment include stress corrosion, electrolytic corrosion, and polymerization. Causative agents will include acids, salts, solvents, halogens, etc. The effect of corrosion on equipment can lead to mechanical failures, premature wear, seizure, and short circuits. The loss of a critical function due to corrosion could lead to any of the 10 basic hazard groups identified herein, and the loss of crew, vehicle, or mission is possible.

4. ELECTRICAL SHOCK.- This group includes those hazards responsible for personnel injury or fatality because of electrical current passing through any portion of the body. Electrical shock can be caused by contact with a "live" circuit because of human error in performing an operation, a procedural error, or an equipment failure such as an insulation breakdown in exposed wiring. Other causes may be static electricity discharge, lightning strikes, or short circuits caused by moisture, bent connector pins, or wires, etc. Static electricity or lightning could be hazardous without adequate grounding or shielding protection. The effect of electrical shock can vary from a mild burn to loss of consciousness and electrocution. Cuts and bruises are possible from the involuntary reaction to the shock.

Other electrical system hazards affect the performance and operation of equipment and thereby affect the crew indirectly. Almost all payload subsystems are either electrically controlled or contain electrical components which can malfunction and cause almost any conceivable hazardous situation depending on the time and location of occurrence. For example, electrical arcing could result in fire or a faulty electrical circuit relay could cause premature activation of a pyrotechnic device. Electrical equipment malfunctions should therefore be considered as contributing factors for each of the 10 basic hazard groups.

5. EXPLOSION.- These hazards result from the the violent release of energy as a result of payload element overpressurization, fire, chemical reaction, excessive temperature, malfunctioning equipment or structural failure causing the release and collision of equipment with other structures or equipment. The overpressurization of pressure vessels, accumulators, batteries, etc., can result in explosion. Excessive temperature from a fire or a failed cooling system can result in explosion of cryogenic tanks, gas generators, pyrotechnic charges, squibs, etc. Equipment which can disintegrate explosively include pumps, motors, blowers, rocket motors, generators, lasers, etc. The effects of these explosive hazards on the crew could range from fragmentation injuries to eye or respiratory system irritation, burns, and asphyxiation. These effects would be the result of shrapnel or toxic/corrosive fluids or gases being released from the exploding component.

6. FIRE.- This group deals with the rapid oxidation of payload element combustibles. Fire can occur when a fuel and an oxidizer are exposed to an ignition source. It can also occur when hypergolics are inadvertently mixed. Fuels or combustibles consist generally of organic material, chemicals, and certain metals. Examples of these materials include rubber, wood, clothing, paint, plastics, solvents, and magnesium. Any high temperature device or source of electrical arcing or sparking can provide the ignition source for fire. Examples of these devices are bearings, motors, generators, heaters, lasers and faulty electrical wiring. The effects of fire can be catastrophic in the closed environment of a space vehicle. Death by asphyxiation, smoke inhalation, or burns are directly attributable to fire. The destruction of critical controls of life support equipment by fire can indirectly cause the loss of crewmen or the vehicle.

7. INJURY AND ILLNESS.- This group includes those hazards capable of inflicting physical injuries or illness of any sort on the flight or ground crews during all mission phases. Physical injuries may be caused by impact or collision with stationary objects having sharp edges or protruding parts or with shrapnel or projectiles from exploded tanks or accelerated loose objects. Physical injuries may also be caused by ingesting particulate matter, touching hot or cold surfaces, and by the loss of breathable atmosphere. Crew illness could result from exposure to pathogenic bacteria, toxic materials, or to excessive radiation levels.

8. LOSS OF ORBITER ENTRY CAPABILITY.- This group involves those hazards which could degrade the structural, aerodynamic, and thermodynamic integrity of the orbiter and could prevent its safe return from orbit. Such orbiter functional degradation can be caused by payload elements which cannot be retracted within the orbiter mold line or which prevent the closure of the payload bay doors. It can also be caused by payload element contact or collision with orbiter structural members, control surfaces, or primary insulation areas during payload deploy/retrieval activities. The payload elements preventing payload bay door closure include booms, antennas, solar panels, and other hinged or extendable/retractable components. Failure of such equipment may be caused by loss of electrical or hydraulic power, structural fracture, and jammed or malfunctioning retract mechanisms. Pressure vessel rupture, inadvertent firing of pyrotechnics or activation of propulsion systems could result in collision with sensitive areas of the orbiter. The eventual consequence of these hazards could be abandonment of the orbiter in space or possible loss of the crew and vehicle during an attempted entry.

9. RADIATION.- This group involves those hazards associated with the exposure of the human body and sensitive control equipment to ionizing radiation, ultraviolet or infrared light, lasers, and electromagnetic or RF (radio frequency) generating equipment. Ionizing radiation hazards may be caused by leaking or inadequately shielded radioactive equipment such as RTG's (radioisotope thermoelectric generators), particle accelerators, vidicons, liquid metal heat exchangers, etc. Overexposure of personnel to such radiation could result in tissue damage, permanent injury, or death. The crew could experience painful burns and eye damage from overexposure to ultraviolet or infrared light sources or to concentrated laser light beams. RF and electromagnetic radiation sources such as radar equipment and antennas can trigger ordnance devices or interfere with operation of critical communication equipment.

10. TEMPERATURE EXTREMES.- This group includes those hazards associated with the departure of temperature from normal. It also includes extreme heat or cold such as that generated by fire, cryogenics, and the environment of space. These hazards may be caused by insulation breakdown, short circuits, seal leaks, plumbing failures, and procedural and human error in handling or operating hot and cold generating equipment. Examples of equipment affected by temperature extremes include bearings, motors, electrical components, heaters, batteries, tanks, and lines. In addition to fire, these hazards can lead to structural degradation and mechanical equipment seizure. The ground and flight crews could suffer skin burns or frostbite as a direct result of contacting hot or cold materials. They could also be exposed to contamination hazards if overexpansion or retraction of payload components leads to the release of toxic matter.

3.0 PAYLOAD SAFETY GUIDELINES.- The payload safety guidelines in this section were prepared to assist payload developers in achieving compliance with documented safety requirements for payloads using the space transportation system. For easy access by payload developers, the guidelines are grouped into 15 generic subsystems. They provide the means for payload developers to recognize hazards and also serve as development and design aids in meeting payload safety requirements. The guidelines are a source of experience retention data for safe design and operations with a baseline of accumulated experience in manned and unmanned spaceflight as well as military and commercial operations.

Since payloads will be designed to incorporate operational safety features, most of the guidelines are design oriented. The number of generic operational guidelines included in the handbook is minimal because operations planning requires specific equipment configuration and definite mission objectives. Only the most general type of operational guidelines could be prepared and included at this early stage of payload definition. As payload equipment configuration and mission objectives are established, specific operational safety guidelines can be developed by the responsible NASA Center or by the payload developer to complement those included in the handbook.

The preparation of the payload safety guidelines consisted of four steps. (1) A data search was performed by visiting the participating NASA Centers, DOD, and the aerospace industry. (The reference sources are tabulated in the reference section of this document.) (2) The data were reviewed, and applicable safety concerns and equipment hazards were collected and categorized under the appropriate subsystems. Data were also categorized under the 10 hazards discussed in paragraph 2.1. (3) A preliminary hazard analysis was performed for each subsystem to assure that the necessary guidelines were developed for payloads. (4) The guidelines were revised for payload applicability and developer understanding .

Each of the 15 subsystem guideline subsections contains an index, a subsystem description, and the guidelines. The subsystem description contains a description of the hardware elements and their interfaces with a brief discussion of the associated hazards. The guidelines contain three main headings: design, flight operations, and ground operations. Under these three headings will be found subheadings of equipment elements. Included with the subheadings are the hazards (as defined in paragraph 2.1) which are to be controlled by the guidelines.

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16. Abstract

This handbook has been written for the purpose of acquainting those involved with batteries with the information necessary for the safe handling, storage, and disposal of these energy storage devices. Included in the document is a discussion of the cell and battery design considerations and the role of the components within a cell. The cell and battery hazards are related to user- and/or manufacturer-induced causes. The Johnson Space Center (JSC) Payload Safety Guidelines for battery use in Shuttle applications are also provided.

The electrochemical systems are divided into zinc anode and lithium anode primaries, secondary cells, and fuel cells. Each system is briefly described, typical applications are given, advantages and disadvantages are tabulated, and most importantly, safety hazards associated with its use are given.

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