

CHAPTER 4

CHEMICAL STORAGE AND GENERATION SYSTEMS

1. Introduction

Spacecraft power can be viewed as the ultimate requirement of portable or remote energy storage devices. Energy storage must be accommodated in the spacecraft power system to provide power for the various mission requirements. The mission requirements determine the various types and levels of energy storage. Both primary (one discharge) and secondary (rechargeable) batteries have been used in space applications. The latter is generally recharged using the photovoltaic array on the spacecraft. Fuel cells provide power for primary Shuttle operations and life support as well as power for other equipment, instruments, and spacecraft in the storage bay. Fuel cells are similar to primary cells in that the stored energy is limited to the fuel and oxidant.

The electrochemical cells in the battery are the basic source of the stored energy. The electrically, mechanically, and thermally connected cells form the battery. Each electrochemical cell is a self-contained device that releases stored chemical energy as electrical energy on demand from an electrical load. When the load is connected across its terminals, one electrode in the cell will spontaneously release electrons while the other spontaneously and simultaneously accepts them. The circuit is closed within the cell by the flow between both electrodes of charged species (ions) in the electrolyte. The number and capacity of the connected cells in the battery determine the energy and power capability.

In a primary cell the reactions are irreversible and therefore the chemical energy can be converted to electrical energy only once. In a rechargeable cell the reactions are reversible, and thus, by reversing the flow of electrons (e.g., from a solar array during the sunlight period), the reactions are reversed, restoring the potential energy difference of the electrodes as chemical energy. The ability to reverse the discharge-charge process thousands of times is a function of the cell chemistry.

The fuel cell system (often referred to simply as the 'fuel cell') has been used for manned missions and is the primary power source for the Shuttle. The fuel cell system includes a number of fuel cells electrically assembled like the cells in a battery to form the fuel cell stack. The remainder of the system includes the external fuel and oxidant tanks, water collection apparatus, and the associated electrical, valving, and plumbing hardware.

The difference between the individual battery cell and the individual fuel cell is that in the former the chemical energy is stored and converted to electrical energy within

each cell case. In the fuel cell, the chemical energy is stored in the form of hydrogen gas or more recently methanol (the fuel) and oxygen gas (oxidant) in tanks external to the cells. The energy output of each fuel cell is the result of hydrogen gas or methanol reacting at one electrode releasing electrons on demand from the load and the spontaneous and simultaneous reaction of oxygen gas and the electrons at the other electrode. The circuit is closed within the cell by the flow between both electrodes of charged species (ions) in the electrolyte. The product is pure water which can be used for consumption. Like the battery, the voltage of the fuel cell stack is the sum of the individual fuel cell voltages required for the spacecraft power. However, the fuel cell system energy storage capability is limited in life by the quantity of H₂ and O₂ gasses in the external storage tanks.

2. Inventions

A chronological list of the primary inventors and major events in electrochemical energy storage are given in Table 4.1.

Table 4.1 List of Electrochemical Cell Inventions

Date	Inventor	Type	Couple
1786	Galvani	Galvanic Cell	Cu/Fe
1800	Volta	Voltaic Pile	Ag/Zn
1836	Daniell	Cell in H ₂ SO ₄	Cu/Zn
1839	Grove	Fuel Cell	H ₂ /O ₂
1860	Plante	Rechargeable	PbO ₂ /Pb
1868	LeClanche	Dry Cell	Zn/MnO ₂ /C
1900	Edison	Storage Battery	Ni/Fe
1901	Jungner	Sealed battery	Ni/Cd
1945	Ruben	Mercury Cell	Zn(Hg)/MnO ₂ /C
1962	Kummer	Sodium/ Sulfur	Na/S
1961	Miracle	Lithium SO ₂	Li/SO ₂
1962	Watanabe	Li-Carbon Monofluoride	Li/(CF) _x
1965	Dunlop	Nickel-Hydrogen	Ni/H ₂
1968	Methlie	Lithium- MnO ₂	Li/MnO ₂
1973	Will	Nickel/Metal Hydride	Ni/MH
1979	Crotzer	Sodium/Nickel Chloride	Na/ZnCl ₂
1981	Goodenough	Lithium/Cobalt Oxide	Li/CoO ₂
1981	Goodenough	Lithium/Nickel Oxide	Li/NiO ₂
1981	Hunter	Lithium/Manganese Oxide	Li/MnO ₂
1983	Blomgren	Li-Thionyl Chloride	Li/SOCl ₂

3. Evolution of batteries in space

Silver-Zinc was the battery of choice in the early days of space missions. Nickel-Cadmium batteries became the major energy storage device over the next 20 years because of their long cycle life. The Nickel-Hydrogen battery started to play a role in the 1980s. Lithium-ion batteries are being baselined for JPL's planetary missions. A chronological history of first uses of batteries in space applications appears in Table 4.2.

The earliest use of a battery in an orbital spacecraft was the primary silver-zinc battery used in the Russian spacecraft, Sputnik I, launched October 4, 1956. The primary battery provided power for communication and spacecraft operations. There were no solar cells available for charging and thus when the energy was depleted, communication was terminated. The Ag-Zn primary battery exhibits reasonably high specific energy, and therefore the battery was intended to provide power to the 84 kg spacecraft for up to three weeks, although the spacecraft actually remained in orbit for three months. The second Sputnik, launched a month later, carried the dog known as Laika. It was six times larger and lasted five months. It also utilized a much larger Ag-Zn battery. In November 1961, the U.S. spacecraft, Ranger 3, containing two 14-cell, 50 Ah batteries for the main power and two 22-cell, 50 Ah batteries for the TV camera power, was placed into solar orbit and took photographs of the Moon. Mariner 2, containing one 18-cell, 40 Ah Ag-Zn battery, launched August 27, 1962, was the first successful interplanetary mission to Venus.

The first U.S. spacecraft to be launched was the Vanguard Test Vehicle 3. It utilized zinc-mercuric oxide primary batteries (in the form of 'D' sized cylindrical cells) and solar cells to provide power. Unfortunately, it failed to orbit. However, Explorer 1, the first of several Explorer spacecraft, was launched February 1, 1958. It was successful in discovering the Van Allen radiation belt. The spacecraft was a cylinder 80 inches in length and 6 inches in diameter containing 5 kg of instruments, batteries (primary mercury type), and a radio.

Explorer 6, launched in August 1959, was the first successful launch of Nickel-Cadmium (Ni-Cd) cells. In August of that year Pioneer, the first stage of the lunar probe, contained Ni-Cd and Ag-Zn cells. The first time Ni-Cd batteries were used for prime power was in February 1960. Transit 1B containing two packs of 28, 5 Ah cylindrical Ni-Cd cells produced by the Sonotone Company, Elmsford, New York, failed to launch. However, in April 1960, the weather satellite TIROS I was successfully launched. It contained three strings of 21 Ni-Cd cylindrical cells. These cylindrical F-5 cells contained glass-to-metal seals to insulate the positive terminal from the metal case. These cells were also fitted with a threaded base which was used to screw into threaded holes in the battery baseplate. The spacecraft operated in a 90 to 110 minute orbit. The spacecraft electrical loads were designed to remove only a conservative 3% of the capacity from the battery during the 30 or so minute eclipse period. The low depth-of-discharge (DOD) is a significant factor in extending life. However, it also means a

Table 4.2 Chronological List of First Use of Batteries in Space

Date (m/d/y)	Satellite	Duration	Type	Comments
10/4/56	SPUTNIK I	3 months	Ag/Zn	1W for 3 weeks
12/6/56	VANGUARD	Failed	Zn/HgO	First U.S. launch
2/1/58	EXPLORER 1	3.8 months	Zn/HgO	Van Allen Radiation Belt
8/6/59	EXPLORER 6	2 years	Cyl Ni/Cd	First earth photos
3/13/61	IMP 1	3.5 years	Ag/Cd	Non-magnetic
1/26/62	RANGER 3	Solar orbit	Ag/Zn	Moon photos
4/26/62	ARIEL I	14 years	Pris Ni/Cd	First LEO mission
8/27/62	MARINER 2	Venus probe	Ag/Zn	Venus mission
6/23/63	SYNCOM-2	Communications	Cyl Ni/Cd	First GEO
5/20/65	APOLLO CM	Short	Ag/Zn	LTD cycle life
6/23/66	NTS-2	5 years	Ni/H ₂	12 hour polar
9/23/66	USAF	Classified	Ni/H ₂	LEO
2/14/80	SOLAR MAX	8 years	Ni/Cd	Standard battery
4/4/83	STS-3	Days	Li-BCX	Astronaut use
5/19/83	INTELSAT V	14 years	Ni/H ₂	GEO
4/6/84	LDEF	6 years	LITHIUM	Exposure to space
10/18/89	GALILEO	Hours	Li-SO ₂	Jupiter probe
4/25/90	HST	In orbit	Ni/H ₂	NASA LEO
6/10/90	LEASAT	Orbiting	Super Ni/Cd	GEO
1/25/94	CLEMENTINE	5 months	SPV Ni/H ₂	Lunar mapping
1/25/94	TUBSAT-B	4 years	2 Cell CPV	Store messages
5/19/95	CENTAUR	1st mission	Li-SOCl ₂	28V, 250AH battery
5/5/96	IRIDIUM-1	Commercial	50Ah SPV	34 to date-LEO
12/4/96	Mars Lander	JPL mission	Ag/Zn	40AH rechargeable
12/4/96	Mars Rover	JPL mission	Li-SOCl ₂	3 'D' cell batteries
11/19/97	FLIGHT EXP	USAF experiment	Na/S	Wakeshield platform

much larger battery is required for the low DOD requirement. This is a high price to pay in inefficiency and cost.

In November 1964, the first prismatic Ni-Cd cells produced by Gulton Industries were flown on Explorer 23. Each cell was a box-like configuration which provided a means for producing an efficient battery design in which the cells were lined up in a close knit battery pack held together with end-plates and metallic rods. The cells also were designed with two insulated terminals such that the cells were electrically floating. General Electric (G.E.) of Gainesville, Florida, and Eagle-Picher (E-P) Company in Joplin, Missouri, succeeded in developing and flying Ni-Cds in space.

In 1966, the OAO-series of spacecraft developed by the prime contractor, Grumman Aerospace, utilized three batteries of 20 Ah prismatic Gulton cells uniquely assembled into two battery frames. Pairs of cells were interspersed between the two assemblies to minimize temperature variation. This power system utilized a V_T (temperature-compensated voltage) charge control system that applied a constant voltage to batteries during charge. The preset V_T limited the charge, resulting in a safe and reliable charge condition. This is a condition in which the batteries return to full charge but are not excessively overcharged. The selected voltage limit was based on a parallel set of temperature-compensated voltage curves (V_T curves). The V_T curve selection used to limit the charge voltage provided flexibility to account for unexpected high depths of discharge and/or imbalance between cells and/or batteries.

In the mid 1970s, NASA undertook a program to develop 'standard' flight hardware including 'standard' cells and batteries, a Modular Power System (MPS), an Attitude Control (ACS), Computer and Data Handling (C&DH), tape recorders, etc. To this end, Goddard Space Flight Center (GSFC) was responsible for developing the 'standard' Ni-Cd cell and then the 'standard' battery. Four companies were given the opportunity to develop prismatic 20 Ah 'standard' Ni-Cd cells. Cells from the four manufacturers would then be capable of being assembled into the 'standard battery' structure produced by McDonnell Douglas with the end use in the MPS. The battery was designed to meet all NASA mission and launch requirements including vibration and shock. The competing manufacturers included General Electric, Eagle-Picher, Yardney Technical Products (YTP), Pawcatuck, Connecticut, and Saft Corp., Valdosta, Georgia. Each company submitted cells for evaluation; however, only the G.E. cells were selected as 'NASA standard cells.' The cells were accompanied by a 'Manufacturing Control Document' (MCD) which was intended to provide a consistent process and reliable product. The first lot of 'standard' 20 Ah cells in 'standard' 20 AH batteries were flown successfully on the Solar Max Mission (SMM) for more than eight years. Subsequently, the technology was extended to 50 Ah cells which were used on several NASA spacecraft, e.g., Landsat, TOPEX, UARS, and GRO.

Also in the 1960s, a technology was discovered that made use of the NiOOH electrode from the Ni-Cd cell and the H₂ electrode from the fuel cell. The Individual Pressure Vessel (IPV) Ni/H₂ cell was contained in a pressure cylinder configuration due to

the buildup of hydrogen during charge; as much or greater than 400-800 psi. The replacement of the cadmium electrode with a hydrogen electrode reduced weight and increased energy, thus almost doubling the specific energy over the Ni-Cd cell. However, because of the cylindrical configuration and the wider spacing of the cells on the baseplate, the energy density (Wh/liter) of the battery was similar to that of the Ni/Cd battery. However, the Ni-H₂ system offered the capability of extended life at higher DOD. Comsat was the first to develop this battery and use it in the Intelsat spacecraft in a GEO mission. In 1983, Eagle-Picher was successful in combining two cells in the same cylinder. This Common Pressure Vessel (CPV) cell was first used in JPL's Mars Global Surveyor mission in 1994. The next step resulted in the development of a rechargeable Single Pressure Vessel (SPV) Ni-H₂ battery in which 22 cells were mounted in the same structure. It was used for the first time in 1994 in Clementine, a Navy satellite which circled the Moon. Ni-MH cells using chemically bonded hydrogen in the form of a hydride have been used in a few rocket experiments, but have not been used in any major flight program. However, because of the low pressure these cell cases do not require high pressure cylinders.

Lithium primary cells were used in space during the 1980s. Li-(CF)_x was one of the first used for range safety on launch vehicles. Li-BCX (Li-SOCl₂ cells with bromine chloride additive), produced by Wilson Greatbatch Limited, Clarence, NY, was selected by NASA/Johnson Space Center for use in astronaut equipment, specifically the helmet lights and TV camera. Later, Li-SO₂ batteries from Alliant TechSystems were selected for the probe on the Galileo mission to Pluto that required nine years of storage before use. Seven kWh Li-SOCl₂ (250 Ah, 28 V, batteries were developed by Saft and Yardney for the Air Force Centaur launch vehicles to replace the Ag-Zn batteries in order to extend operating time in placing payloads in orbit. Smaller 'D' size cells based on this technology were used by JPL in the Mars Rover in 1997.

In the 1980s, JPL initiated development of a rechargeable Lithium cell in an in-house program. The Lithium-Titanium Disulfide (Li-TiS₂) used pure lithium as the anode. The specific energy achieved 100 Wh/kg or 2 times the NiH₂ or Ni-MH system and was cycled more than 1000 times at 50% DOD. However, the use of the metallic lithium foil concerned the users. In the follow-on lithium-ion cell development effort in the 1990s, coke or graphite replaced the Lithium anode foil and several cathode materials, e.g., cobalt, nickel or manganese oxides, replaced the undesirable titanium disulfide. There was no lithium metal in the cell. This new system made use of the difference in concentration of Li ion between anode and cathode. The potential of each cell is 4.0 volts and the specific energy greater than 125 Wh/kG. This new technology is being considered for a number of NASA and AF programs. A diagram of the Ni-Cd, Ni-H₂, and Li-Ion batteries stages is shown in Figure 4.1.

	1958-69	1970-79	1980-89	1990-97
NI-CD	'59 EXPLORER-6 (CYLINDRICAL) '62 ARIEL-1 LEO (PRISMATIC) '63 SYNCOM2 GEO		'80 SOLAR MAX NASA 20 AH STD '82 LANDSAT -D STD 50 Ah	'90 LEASAT GEO SUPER NI-CD
NI-H₂		'77 NTS-2 & AF FIRST IPV USE	INTELSAT 5 IPV GEO	'90 HUBBLE IPV '94 CLEMENTINE SPV '94 TUBSAT CPV
LITHIUM			'83 STS- LI-BCX '89 GALILEO Li-SO ₂	'95 CENTAUR '96 PATHFINDER

Figure 4.1 Major Steps in the Development of Ni-Cd, Ni-H₂ and Li-Ion Batteries

4. Fundamentals of electrochemistry

Electrochemistry, for the most part, is based on thermodynamics. As given in Eq. (4.1), electrical work (W) equals the quantity of electricity (Q) multiplied by the electric potential or electromotive force (E).

$$W = Q \times E = I \times t \times E \quad (4.1)$$

In the operation of an electrochemical cell, Q is equal to the current (I) integrated over time (t). This value of $I \times t$ is generally defined as the product of ampere-seconds (coulombs) or ampere-hours. It is related to n, the number of moles of electrons produced by one mole of reactant, E, the electrochemical potential, and F, the Faraday constant (units of ampere-seconds or coulombs):

$$W = n F E \quad (4.2)$$

If the components are at unit activity, then $E = E^\circ$, where E° is the Standard Electrochemical Potential, and furthermore if the cell operates reversibly, then $w = w_{max}$. Because electrical work is non PV work (useful work), $w_{elec,max} = -\Delta G$ (Gibbs Free Energy). Thus, Eq. (4.2) becomes:

$$\Delta G^\circ = -n F \Delta E^\circ \quad (4.3)$$

4.1 Standard electrode potential and free energy

E° is the standard electrochemical reaction at unit activity and standard temperature and pressure conditions (25°C and 1 atm) given in Table 4.3. Thus, ΔG° , a thermodynamic property, can be determined from the difference (ΔE°) between half-cell reactions. By the adopted conventions, if ΔG° is a negative value the reaction is spontaneous and exothermic (heat released). If ΔG° is positive, the reaction will be non-spontaneous and endothermic (heat required). Standard half-cell (single electrode) electrode potentials are generally shown as reduction reactions, i.e., reactions use electrons to produce a product having a lower valence state. Reactions written in the reverse will have reverse polarity. A spontaneous reaction will occur within a cell when the reaction is written in such a way that the ΔE° is positive. To obtain a positive ΔE° , the reactions have to be

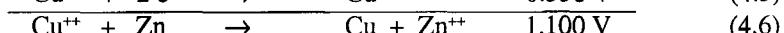
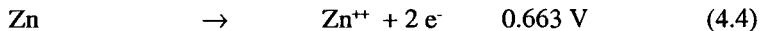
Table 4.3 Representative Standard Electrode Potentials
(In Acid Solutions)

Element	Oxidized Form		Reduced Form	Reduction Potential E° (V)
Potassium	$K^+ + e^-$	=	K	- 2.925
Calcium	$Ca^{2+} + 2e^-$	=	Ca	- 2.86
Sodium	$Na^+ + e^-$	=	Na	- 2.614
Magnesium	$Mg^{2+} + 2e^-$	=	Mg	- 2.36
Aluminum	$Al^{3+} + 3e^-$	=	Al	- 1.66
Manganese	$Mn^{2+} + 2e^-$	=	Mn	- 1.18
Zinc	$Zn^{2+} + 2e^-$	=	Zn	- 0.663
Iron	$Fe^{2+} + 2e^-$	=	Fe	- 0.440
Cadmium	$Cd^{2+} + 2e^-$	=	Cd	- 0.040
Cobalt	$Co^{2+} + 2e^-$	=	Co	- 0.266
Nickel	$Ni^{2+} + 2e^-$	=	Ni	- 0.250
Lead	$Pb^{2+} + 2e^-$	=	Pb	- 0.126
Hydrogen	$2H^+ + 2e^-$	=	H ₂	0.000
Copper	$Cu^{2+} + 2e^-$	=	Cu	+ 0.336
Iodine	$I_2 + 2e^-$	=	2I ⁻	+ 0.536
Silver	$Ag^{2+} e^-$	=	Ag	+ 0.699
Mercury	$Hg^{2+} + 2e^-$	=	Hg	+ 0.854
Oxygen	$O_2 + 4H^+ + 4e^-$	=	2H ₂ O	+ 1.229
Chlorine	$Cl_2 + 2e^-$	=	2Cl ⁻	+ 1.356
Gold	$Au^{+} + e^-$	=	Au	+ 1.68
Fluorine	$F_2 + 2e^-$	=	2F ⁻	+ 2.86

(In Basic Solutions)

Hydrogen	$2H_2O + 2e^-$	=	$H_2 + 2OH^-$	- 0.828
β NiOOH	$\beta NiOOH + H_2O + e^-$	=	$Ni(OH)_2 + OH^-$	+ 0.490
Oxygen	$O_2 + 2H_2O + e^-$	=	$4OH^-$	+ 0.401
Silver	$Ag_2O + H_2O + 2e^-$	=	$2Ag + 2OH^-$	+ 0.345
Cadmium	$Cd(OH)_2 + 2e^-$	=	$Cd + 2OH^-$	- 0.809
Zinc	$ZnO_2^{2-} + H_2O + 2e^-$	=	$Zn + 4OH^-$	- 1.216

written in such a manner that the sum is positive. This requires that reactions be written such that the electrons used are the same number as that released. As an example, using Table 4.3, the following oxidation and reduction reactions can be arranged to show a positive E° .



The reaction is balanced and both electrons released in the Zn oxidation reaction (4.4) are used in the Cu reduction reaction (4.5). The +1.100 V for ΔE° of the net reaction (4.6) will result in a negative ΔG and therefore the reaction as shown is spontaneous to the right. This is also expected in practice wherein copper will plate out in the presence of an active metal such as zinc (provided the electrolyte contains Cu^{++} ions). ΔG° can be calculated for this reaction as follows:

$$\Delta G^\circ = -n F \Delta E^\circ \quad (4.7)$$

using 23.06 kcalories/volt for the Faraday constant,

$$\Delta G^\circ = 50.73 \text{ Kcal} \quad (4.8)$$

4.2 The Nernst equation

The Nernst Equation for a half cell reaction is given in Eq. (4.9). The terms a_{products} and $a_{\text{reactants}}$ refer to the activity of the constituents. The approximation shown in Eq. (4.10) can also be used for the oxidation/reduction reactions for a full cell. It takes into account the variation from standard conditions due to temperature and concentration of reactants and products shown as moles per liter.

$$E = E^\circ - RT/nF \ln a_{\text{products}} / a_{\text{reactants}} \quad (4.9)$$

or

$$\Delta E = \Delta E^\circ - 0.059 \log [\text{products}] / [\text{reactants}] \quad (4.10)$$

where ΔE is the calculated voltage, ΔE° is the reversible equilibrium voltage (difference in half cell reactions) for the net reaction, R is the gas constant (1.986 Cal/deg C/mole), T is the absolute temperature ($25^\circ\text{C} = 298 \text{ K}$), n is the number of electrons per mole, and F is the Faraday constant (23,06 Cals/Volt).

$$\frac{RT}{nF} \ln \left(\frac{\text{Zn}^{++}}{\text{Cu}^{++}} \right) = 0.59 \log \left(\frac{\text{Zn}^{++}}{\text{Cu}^{++}} \right) \quad \text{at } 25^\circ\text{C}, n=1 \quad (4.11a)$$

In the above example of the Cu and Zn reactions:

$$\Delta E = 1.100 - 0.059 \log [Zn^{++}] / [Cu^{++}] \quad (4.11b)$$

Representative values for theoretical voltages, specific energy, and energy density are shown in Table 4.4, along with the two types of fuel cells for comparison.

4.3 Capacity and the Faraday relationship

The capacity available from stored active materials is usually expressed in coulombs (ampere seconds) or ampere hours (Ah). It is based on the Faraday expression which relates the number of coulombs (96,494) required to plate 1 gram equivalent (112.41g) of silver (Ag) from a solution at unit activity and concentration of silver ion (Ag^+) according to Eq. (4.12).



Cell and battery capacity is generally described in terms of ampere hours. The Faraday constant is 26.8 Ah per equivalent. For reactions where more than one electron is involved, the atomic or molecular weight is divided by the number of electrons to determine the equivalent weight. In the example of the copper reaction, Eq. (4.5), the reaction requires two electrons to plate 63.5 g of copper. The atomic weight of copper is 63.5. Therefore, 26.8 Ah would result in 31.8 grams of plated copper.

5. Cell and battery mechanical design

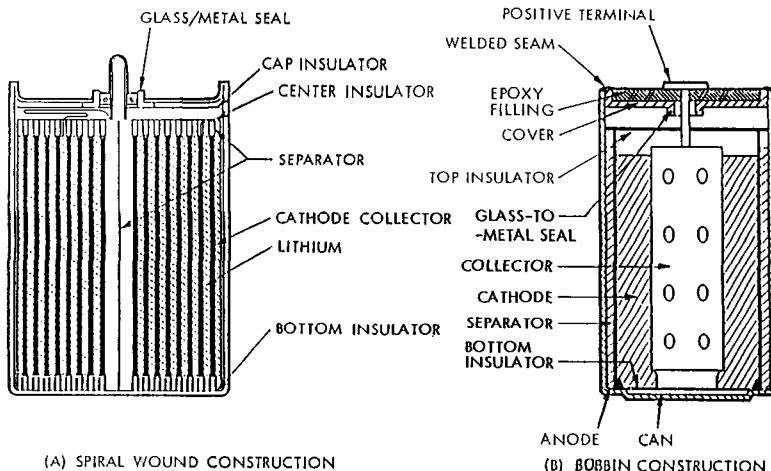
The discussion below provides the basis for understanding cell and battery design concepts.

5.1 Cell design

An electrochemical cell consists of two electrodes (anode and cathode), electrolyte, separator, insulator, insulated seal(s), terminals, and case. The anode and cathode electrodes, each comprised of one or more plates, contain active material of opposing potential energy and polarities. Plates of different polarities are alternated and separated from each other with a separator which provides electrical insulation and in some cases serves as a container for the electrolyte. Each plate contains electrochemically producing ac-

Table 4.4 Theoretical Voltage and Capacity of Major Battery Systems (from Linden, 1984)

Battery	Reaction Mechanism	V	Theoretical Capacity g/Ah	Ab/kg	Wh/kg
PRIMARY CELLS					
LeClanche	$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$	1.6	4.46	224	358
Alkaline MnO ₂	$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$	1.5	4.46	224	336
Mercury	$Zn + HgO \rightarrow ZnO + Hg^-$	1.34	5.26	190	254
Silver Oxide	$Zn + Ag_2O + H_2O \rightarrow Zn(OH)_2 + 2Ag$	1.6	5.55	180	288
Zinc/Air	$Zn + 2O_2 \rightarrow ZnO$	1.65	1.55	658	1320
Lithium/Sulfur Dioxide	$2Li + 2SO_2 \rightarrow Li_2S_2O_4$	3.1	2.64	369	1175
Lithium/Thionyl Chloride	$4Li + 2SOCl_2 \rightarrow SO_2 + 4LiCl + S$	3.6	2.48	403	1471
Li/Manganese Dioxide	$Li + Mn^{4+}O_2 \rightarrow Mn^{4+}O_2(Li^+)$	3.5	3.50	286	1001
SECONDARY CELLS					
Lead-Acid	$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$	2.1	8.32	120	252
Nickel/Cadmium	$Cd + 2NiOOH + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$	1.35	5.52	181	244
Silver/Zinc	$Zn + AgO + H_2O \rightarrow Zn(OH)_2 + Ag$	1.85	3.53	283	523
Nickel/Hydrogen	$H_2 + 2NiOOH \rightarrow 2Ni(OH)_2$	1.5	3.46	289	433
Nickel/Metal Hydride	$MH + NiOOH \rightarrow M + Ni(OH)_2$	1.35	6.50	206	278
Silver/Cadmium	$Cd + AgO + H_2O \rightarrow Cd(OH)_2 + Ag$	1.4	4.41	226	318
Li / Cobalt Oxide	$LiC_6 + CoO_2 \rightarrow 6C + LiCoO_2$	4.00	6.08	164	656
Li / Nickel Oxide	$LiC_6 + NiO_2 \rightarrow 6C + LiNiO_2$	3.90	6.08	164	640
Li/Manganese Oxide	$LiC_6 + MnO_2 \rightarrow 6C + LiMnO_2$	4.50	9.18	109	491
Sodium/Sulfur	$2Na + 3S \rightarrow Na_2S_3$	2.10	2.65	377	792
Sodium/Nickel Chloride	$2Na + NiCl_2 \rightarrow 2NaCl + Ni$	2.58	3.28	305	787
FUEL CELLS					
H ₂ /O ₂	$H_2 + O_2 \rightarrow H_2O$	1.23	0.336	2965	3662
MeOH/ O ₂	$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$	1.21	0.199	5025	6080



LITHIUM PRIMARY CYLINDRICAL CELL CONFIGURATIONS

Figure 4.2 Diagrams of Cylindrical Cell Construction

tive material in contact with a current collector from which the electrons either enter or exit from the cell. A porous conductive substrate is used in some cases to house the active material. Cylindrical cells are either spirally wound to provide higher rate capability or of bobbin construction which utilizes a center anode or cathode with the alternate electrode surrounding the center rod. A diagram of the two types of cylindrical cells is given in Figure 4.2.

A cell pack consists of the electrodes and separator in close contact to minimize ohmic losses. Exiting from the plates is an electrically conducting metallic tab for making electrical contact to the terminal inside the cell. The tabs of the same polarity are connected together directly or via a busbar and can easily be welded to their designated terminal within the cell during the cell assembly process. An example of a Ni-Cd cell pack is shown in Figure 4.3.

The non-woven nylon or polypropylene separator, which is chemically inactive in the cell environment, is used to maintain separation of plates thus avoiding shorting. It also has the function of providing a path for ions in the electrolyte to diffuse between plates and thus maintain optimum conductivity. In the case of a 'starved' (semi-dry) cell design wherein the electrolyte volume is limited in the cell, the separator can also serve as a sponge to maintain contact between the plates. The separator material must be chemically and thermally stable as well as have a minimal effect on the resistance to flow of ions within the cell.

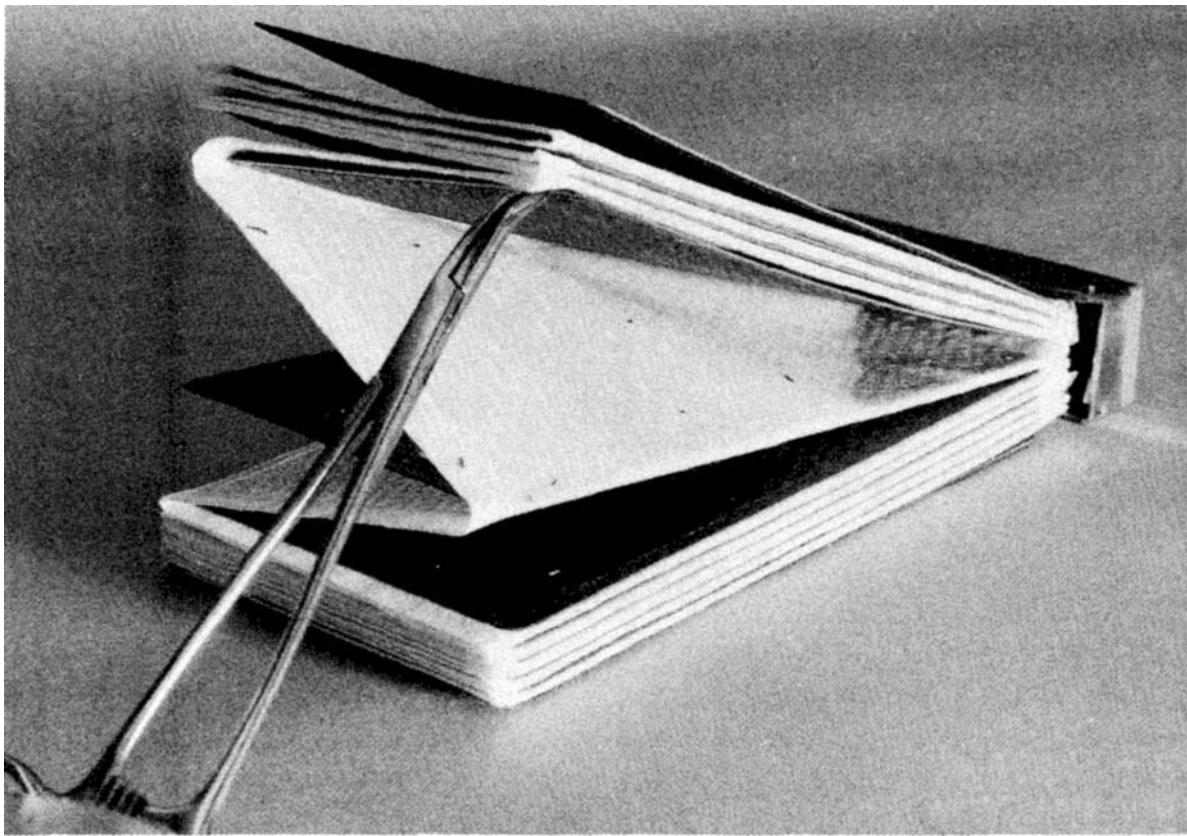


Figure 4.3 Prismatic Cell Constituents

The cell pack is inserted into a polymeric or metallic type case. Hermetically sealed cells desired for space applications use low carbon 304 stainless steel for the case and cover and a polymeric liner is used to insulate the pack from the case. The terminals designated positive and negative, depending on the polarity of the electrodes, exit through the cover where metal seals are in place to prevent leakage of the electrolyte or reaction products. Such a leakage would lead to a failure of the cell.

The cover also contains a fill tube for electrolyte addition that can be welded or sealed. Prismatic cells require compression on their flat surfaces to maintain inter-electrode spacing within the cell and thus avoid expansion of the case due to internal pressure. Cylindrical cells usually provide a structure that can withstand internal pressure. In this case, the cell pack is wrapped taut around a mandrel before insertion into the cylindrical case. The case provides the strength to maintain interelectrode spacing.

Activation of the cell is accomplished by addition of the electrolyte, an ionically conducting solution that provides the ion movement between plates. The electrolyte provides the means for completion of the electrochemical oxidation/reduction reactions and thus completes the electrochemical circuit. The electrolyte consists of ionic species (salt, acid, or alkali) specific to the electrochemical nature of the electrodes dissolved in a solvent. The combination must provide maximum conductivity and be chemically, electrochemically, and thermally stable. The solvent can be aqueous, inorganic or organic, and liquid or solid. In some cases, specifically in the lithium primary cells, the solvent also serves as the cathode active material, referred to as 'catholyte,' and is consumed during the discharge.

5.2 *Battery design*

A battery consists of a number of cells electrically connected in a series or parallel arrangement, a housing and baseplate, connectors, and sensors. The battery structure contains the intercell wiring, thermal fins, voltage and temperature sensors, and connectors for power, signals from the sensors, and voltage monitoring. Although surprising to some, the battery is only a structure that contains the electrochemical cells in the desired voltage arrangement and does not store energy in and of itself.

The prime requirement for a battery is to be capable of providing the required power and energy at the desired voltage and over the required period of time. Among the overriding requirements are those of minimum size, volume, and cost to meet spacecraft requirements. *Caution:* On occasion the spacecraft designers will dictate the allowed volume, mass, and cost prematurely and without due consideration for the real long-term energy storage capability and the usual growth of the power budget.

From a configuration standpoint, for space use a battery must be mechanically configured to withstand a wide range of shock and vibration, be capable of dissipating heat and maintaining a uniform temperature between cells and across the battery, utilize wire

size and intercell connectors to minimize voltage drop, be equipped with sensors to provide the power system with the data with which to make decisions, and include connectors to interface power, sensing, and controls to the spacecraft.

The size of a battery will depend on the voltage and capacity required. These in turn determine the number and size of cells. The design of a battery can be initiated after selecting (described later) the cell capacity and configuration (prismatic, cylindrical) required to meet mass, volume, voltage life, and energy storage requirements with adequate margin. It is essential that the cells in a battery and between batteries in parallel be of the same type and capacity to avoid discontinuous performance leading to early battery failure. In addition, it is most important that the cells be from the same manufacturing lot so as to assure consistent performance across and between batteries and to assure mission reliability.

The battery base-plate size will be determined by the cell configuration and space-craft requirements. Prismatic cells offer the best packaging factor because the cells can be placed in a close-packed arrangement. Thermal dissipation and control occur through the wide flat face of the cell through thermal fins between the cells to the baseplate. Endplates on both ends of the cell stack maintain compression on the cells and connection to the baseplate. The battery-to-cell weight ratio for a prismatic cell battery can be expected to be as low as one to 1.15. However, for a cylindrical cell battery the ratio is more like one to 1.5. Although each cylindrical cell is structurally sound, mounting the cells into a battery configuration onto a baseplate leads to inefficient packaging. The cylinders also have to be arranged so that adequate heat is removed through the baseplate which adds to the inefficiency and complexity of heat removal.

6. Performance metrics

Considerations for the selection of a cell and battery to meet mission goals depend on performance characteristics and other practical and safety factors. These are listed in Table 4.5. The electrical parameters used to characterize battery performance are described below.

Table 4.5 Battery Selection Factors

Mass	Voltage	Capacity	Specific Energy
Volume	Rate Capability	Cycle Life	Energy Density
Design	Maintenance	Availability	Depth of Discharge
Cost	Efficiency	Environmental	Temperature Range
Safety	Storage	Voltage Profile	Voltage as f(Temp)

6.1 Voltage

The number and type of cells in a series or parallel arrangement determine the battery voltage. Therefore the discussion that follows relates to cell voltage. The voltage of a cell depends on the potential energy difference of the active materials stored in the anode and cathode as described above.

Open circuit

The open circuit voltage of a cell is the voltage measured without a current drain. It is near the equilibrium voltage of the anode and cathode reactions in contact with the electrolyte. However, even at open circuit, the voltage of a cell will depend to a small extent on the relative quantities of charged and discharged active materials in those electrodes. For a fresh or fully charged cell at open circuit, the potential energy difference between both electrodes is at its highest, and this results in a high open circuit voltage. The nearer to the end of discharge, the closer the potential energy of the electrode active materials and therefore the lower the equilibrium open circuit voltage. The measured equilibrium voltage is also dependent on temperature. The Nernst Equations (4.9, 4.10) describe the effect of temperature on voltage.

Voltage during discharge and charge

Cell voltage during discharge and charge is affected by several factors. Once discharge or charge is initiated, voltage moves from the open circuit value. During discharge, cell voltage will fall continuously toward zero volts where there is little potential energy difference between the electrodes. During charge, electrons are being forced into the cell to return the active materials in the anode and cathode to the state of highest potential energy difference. Therefore, the cell voltage will increase above its equilibrium voltage. If the charging continues without a charge control mechanism, additional reactions can occur within the cell which result in undesirable products that can exceed the safe operating conditions.

The term ‘polarization’ is used to describe the voltage deviation from equilibrium caused by current flowing through the cell and its constituents. The voltage offset is due to electrical, ionic, and/or kinetic ‘impedance’ within the cell or its chemical reactions. The three types of polarization experienced in electrochemical reactions are: ohmic (η_{IR}), activation (η_{Act}), and concentration (η_{Conc}) polarization. All three are also influenced by temperature, the higher the temperature the less the effect of the polarization and the less the offset from equilibrium voltage. Figure 4.4 describes how the three factors affect polarization.

The voltage change introduced by ohmic polarization (η_{IR}) is caused by current flowing through the inert parts of the cell from one terminal to the other. This change occurs the instant the current is drawn or applied and is sometimes used to measure the resistance of a cell by subjecting it to a current pulse ($\Delta E / \Delta I = R$). The η_{IR} remains relatively constant during charge and discharge.

Activation polarization (η_{Act}) is a kinetic phenomenon that is related to the charge transfer step of the electrochemical reaction. In viewing this phenomenon on an oscilloscope, a curve similar to the capacitor discharge curve is seen. This mimics the ca-

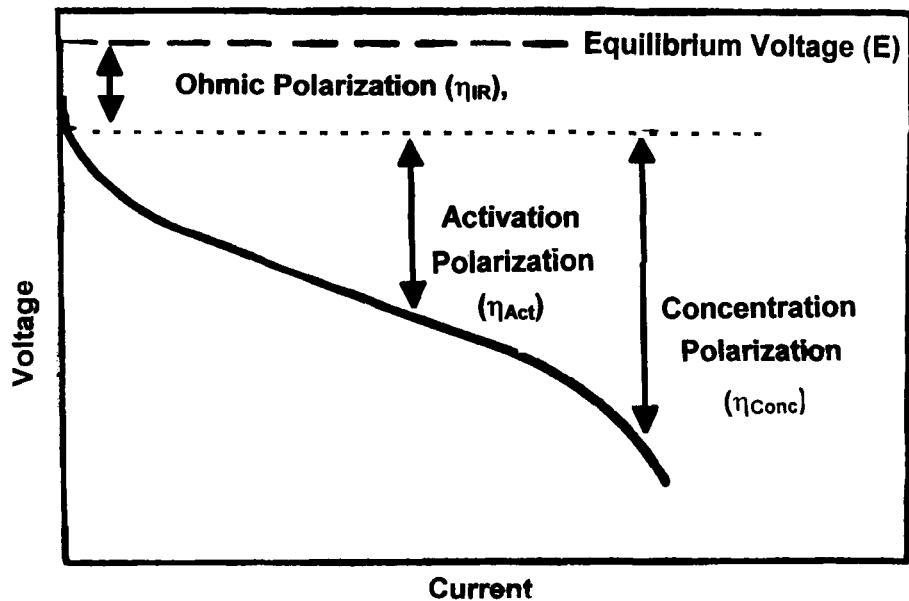


Figure 4.4 The Types of Polarization

pacitor action in that the ions and electrons are aligned at the electrode surface and undergo conversion to the desired products at the active electrode site.

Concentration polarization (η_{Conc}) refers to the effect on conductivity of the ionic species in the electrolyte and active material. It is most predominant at low concentrations and at the end of discharge where the quantities of the charged active materials are low. At higher concentrations the electrolyte tends to be more conductive than at lower

concentrations. Also, aqueous electrolytes tend to be more conductive than organic or other inorganic electrolytes. The higher the concentration the less the affect on voltage. As the active material in either electrode is depleted, the voltage during discharge will fall slowly until one of the active ingredients has been exhausted. At that time the voltage will fall precipitously toward zero volts.

The greater the capacity removed during discharge, the greater the effect of the polarization factors. Because there is less active material to convert, the electrolyte may become depleted, and/or some active materials may become passive, thus increasing the resistance to current flow. This is another way of bringing up the subject of depth of discharge. The greater the quantity of total cell capacity removed on a percentage basis (DOD), the closer to the depletion of active material, the lower the cell voltage, and the closer to cell failure. The reverse is true during charge.

6.2 Capacity and energy

The capacity refers to the number of hours the required load current can be sustained during the discharge (for cells and batteries the units are ampere hours). It is derived from the Faraday relationship. (See Section 4.3 for a description of the basis for capacity determination.) Except for laboratory testing, rarely is the current constant during a mission. With equipment and heaters turning on and off and pulsing from the controls, the battery cells have to be capable of providing a wide range of current within the time or orbit requirement.

Electrical engineers can view the battery capability to store and deliver energy as related to a capacitor. Capacitors store energy like a battery; however, the energy is released in fractions of a second. The energy storage materials are on the surface of the electrode and are controlled by the dielectric within the case. They are rated in terms of microfarads and exhibit characteristics relative to known discharge/time relationships. On the other hand, the comparable metric for energy storage is on the order of Farads. It equates to the quantity of stored energy in a cell or battery released over a time period of minutes to hours. As long as there are chemically active stored materials within both electrodes, the cell voltage will be maintained and the battery will release or store energy over a period of time depending on rate.

A list of the theoretical capacities and specific energy of electrochemical cells used in space was given in Table 4.4. The theoretical specific energy (Wh/kg) is determined by the product of the voltage and the value for Ah/kg. The practical values for these is shown in Table 4.6.

The list includes a number of primary cells that have been used in Shuttle instruments and astronaut equipment. The secondary cells include types that have either been used for space or have been evaluated for use in space. The Lead-Acid characteristics are listed for comparison. In addition, the capacity numbers are provided in the Table.

The use of H₂ or methanol offers a ten-fold increase of energy over that of primary and rechargeable batteries.

Capacity is affected by temperature, discharge rate, charge rate, and charge control methodology. It is also dependent on the relative quantities of active material in the two electrodes. The electrode with the limiting capacity is the one that determines which electrode will have its active material depleted first.

Energy is simply the integral of the voltage and current over time. In general, an estimate of the energy of a battery can be made by taking the product of the average voltage, average current, and time.

6.3 Specific energy and energy density

Important metrics to the spacecraft engineers are specific energy (SE), a function of the total energy of a battery or cell per unit weight, and the energy density (ED), the total energy of a battery or cell per unit of volume. These parameters enables the engineer to

Table 4.6 State of Art Operational Characteristics of Major Cell Types

Battery System	Anode	Cathode	Cell Voltage (V)	Nominal Specific Energy (Wh/kg)	Energy Density (Wh/l)
<u>PRIMARY CELLS</u>					
LeClanche	Zn	MnO ₂	1.5	85	165
Alkaline-MnO ₂	Zn	MnO ₂	1.5	125	330
Mercury	Zn	HgO	1.3	100	460
Silver Oxide	Zn	Ag ₂ O	1.6	120	500
Zinc/Air	Zn	O ₂ (air)	1.5	340	1050
Li/SO ₂	Li	SO ₂	3.0	260	415
Li/SOCl ₂	Li	SOCl ₂	3.6	320	600
Li/MnO ₂	Li	MnO ₂	3.0	230	550
Li(CF) _n	Li	(CF) _n	3.0	220	410
<u>SECONDARY (RECHARGEABLE) CELLS</u>					
Lead-acid	Pb	PbO ₂	2.0	35	60
Nickel-Cadmium	Cd	NiO ₂	1.2	35	80
Nickel-Metal hydride (MH)		NiO ₂	1.2	50	65
Nickel-hydrogen	H ₂	NiO ₂	1.2	55	60
Silver-Zinc	Zn	AgO	1.5	90	180
Silver-cadmium	Cd	AgO	1.1	55	100
Zinc-Air	Zn	O ₂ (air)	1.5	150	160
Lithium-Ion	C	LiCoO ₂	4.0	90	125
Lithium-Organic	Li	Mn ₂ O ₄	3.0	120	230
Lithium-Polymer	Li	V ₆ O ₁₃	3.0	200	150
Sodium-Sulfur	Na	S	2.0	160	110
Zebra	Na	NiCl ₂	2.3	120	110

make an estimate of what can be expected of a particular battery chemistry. Generally, primary batteries are higher in both parameters than rechargeable. For example, a Lithium-Thionyl Chloride primary cell has a theoretical specific energy of 1471 Wh/kg compared with 656 Wh/kg for Lithium-Cobalt Oxide. The actual specific energy and energy density can be expected to be 20-30% of the theoretical value. Lithium-Thionyl Chloride has demonstrated capability for 300-600 Wh/kg (depending on rate) while the Lithium - Cobalt Oxide cell has demonstrated 100-120 Wh/kg.

The theoretical values in Table 4.4 are based on the active materials only, and therefore do not include the electrolyte, terminals and mechanical hardware. Specific energy and energy density can be determined by multiplying the capacity per unit weight or volume by the voltage. Considering that cells comprise a case, electrode structures with current collectors, busbars, and other components, these values are not actually achievable. A rule-of-thumb for a well-developed electrochemical cell is 25% of the theoretical energy. Practical operating voltages and demonstrated values of specific energy and energy density are given in Table 4.6.

6.4 Life and performance limitations

The metric that best describes the life of a cell or battery in an aerospace application is the cycle or point in time when the energy storage requirement of the spacecraft can no longer be met. That implies that the voltage and current (power) during discharge will be depleted and unable to meet planned spacecraft operations.

The process for avoiding this condition or assuring that the mission can be met is to incorporate enough margin to the selection of the cell capacity and voltage so that the expected cell degradation will be offset by excess capacity and voltage. Selection of a larger capacity cell and battery impacts efficiency of mass and volume. An optimum in balance between the efficiency and life requirements needs to be considered when making a selection for a mission. This implies that for a GEO mission, where only 100 cycles per year are required, the battery DOD can be high (as much as 75%). For a LEO mission requiring 5000 cycles per year, the DOD usually is below 30%. Figure 4.7 provides a generalized relationship between cycle life and DOD.

The factors that play an important role in cell life are rate, temperature, depth of discharge, charge control, and voltage limits.

Effect of rate

Rate plays an important role on capacity and battery life because it influences the conversion of products to reactants and vice versa (for rechargeable cells). The effect of

cell charge and discharge rate on life is related not only to the current flowing through the cell but more specifically to the current density (mA/cm^2) at the surface of the plates.

Some electrochemical cell types, particularly primary cells, generally operate at low current densities ($<1 \text{ mA/cm}^2$). Rechargeable Ni-Cd and Ni-H₂ cells operate reversibly and relatively efficiently at 10 mA/cm^2 . At high rates, some of the active material in either or both electrodes may not be accessible because of plate construction or polarization losses which prevent the desired reaction from taking place. The result is that some of the material is disconnected from the active material and becomes 'inactive'. Under this condition the cell will appear to have an unusually low voltage and will exhaust one of the electrodes sooner resulting in cell failure. Thus, the general trend is that higher rate results in lower capacity as shown in Figure 4.5. However, most electrochemical cells are relatively forgiving when operated within the rates for which they were designed.

The higher the discharge rate, the greater the voltage drop due to ohmic losses that exist in the cell and electrical circuitry including wire and internal and external cell connections. During charge, the measured battery voltage is higher at higher rates. With regard to 'state-of-charge' as the cell or battery is depleted, the voltage on discharge will steadily drop (less in cells with a flat discharge voltage). However, there will be a sharp drop in voltage when the capacity is close to depletion (approaching 'failure') indicating the potential differences are approaching equality (0.0 volts). If the load on the battery continues, the battery voltage will drop below the bus voltage resulting in a significant spacecraft problem.

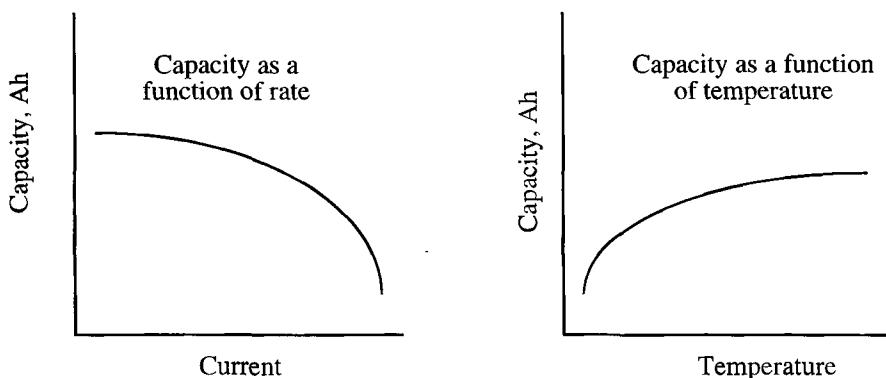


Figure 4.5 General Trends for the Effect of Rate and Temperature on Capacity

Low rate generally results in high capacity. However, at very low rate, products may be formed which are not reversible. In the case of rechargeable cells the long term effect of operating at low rate can result in shorter operating life.

Effect of temperature

Temperature plays a role similar to rate. The two are actually related in that high rate tends to result not only in higher IR polarization but I^2R heating as well. Increased heating can reduce activation polarization losses because it improves the kinetics and reduces concentration polarization losses by enhancing the conduction of the ions. The result is a lowering of the cell voltage charge (i.e., closer to the equilibrium voltage). However, excessive heating can also result in permanent loss of reactants or products and in fact can lead to a condition in a rechargeable cell known as 'thermal runaway'.

Thermal runaway can occur if the V_T charging method (see Section 6.5) is used. The charge voltage limits are set by the V_T curves, shown above, which are in the power system. Heating results in a lower cell voltage which will result in higher current from the solar array to raise the battery voltage to the preset V_T charge voltage. This results in more heat which lowers the battery voltage even further, causing the power system to impose higher current to reach the voltage set point, and so on. This produces 'thermal runaway' which most often results in venting, at times with violence. This can also happen if one cell in a battery experiences a short. Unless this is recognized and the V_T level is lowered, the power system will continue to view the full battery as a 28 V. system and overcharging of the remaining cells will occur.

The effect of temperature on a Ni-Cd cell is given in Figure 4.6. Note that lower temperature ($0\text{--}5^\circ\text{C}$) extends Ni-Cd life significantly. Low temperatures generally result in increased polarization resulting in lowering of reaction rate and ion flow within the electrolyte; therefore, at temperatures below ambient, the voltage of a battery will be lower on discharge. On charge, because the current (electron flow) is reversed, it takes a higher voltage to return the same current to the cell or battery.

Depth of discharge

The depth of discharge is the percent or fraction of the cell or battery capacity removed during a discharge. Primary cells are usually discharged completely; thus, this parameter is used for rechargeable cells. It is well known that there is a strong relationship between DOD and life. The greater the depth of discharge on a regular basis, the sooner the cell will fail to deliver the required voltage for the time period required. The relationship can be described as asymptotic. An example of this is the ability of a Ni-Cd cell to undergo 40,000 cycles at 13% DOD in the Solar Max Spacecraft that orbited the earth

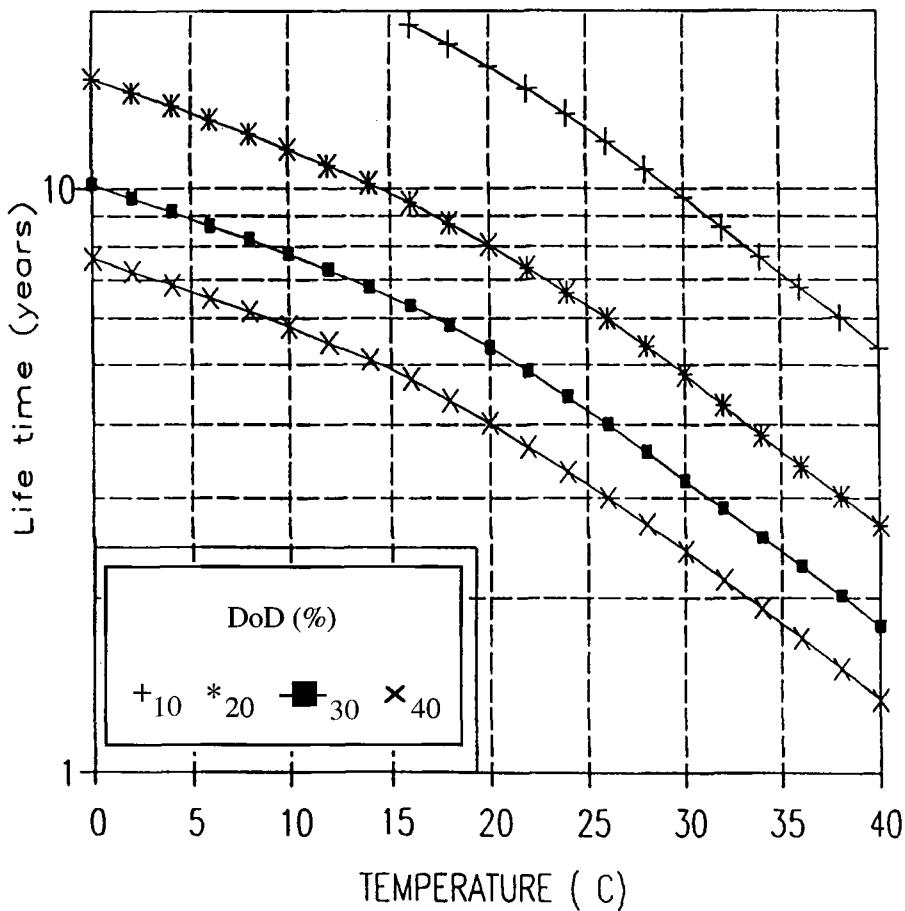


Figure 4.6 Effect of Temperature on Cycle Life

for eight years and 1000 cycles at 50% DOD. It should be recognized that some batteries have a stronger relationship than others. This metric also depends on cell construction, e.g., thickness and number of plates and quantity of active material which affects the current density. An accepted relationship between depth of discharge and cycle life is shown for a Ni-Cd Cell in Figure 4.7.

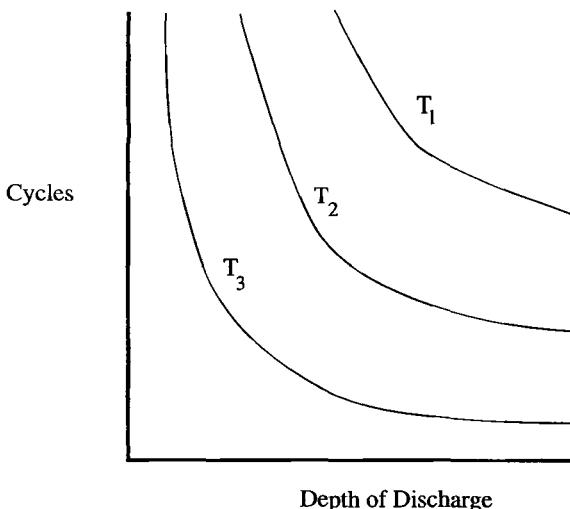


Figure 4.7 Generalized Relationship Between Depth of Discharge and Cycle Life

6.5 Charge control

To recharge a cell is to return the active materials to the condition of highest potential energy difference between anode and cathode. This requires forcing electrons from the solar array, or other source of electrons, into the battery. The voltage of the solar array and the voltage at the input of the battery has to be large enough to overcome polarization, however, not so large that the input voltage forces unwanted reactions to take place. From this it is easily seen that charge control methodology is an essential contributor to the battery life.

A number of methods have been used for charge control. All types make use of a voltage limit to avoid undesirable reactions that can be caused by excessive voltage. To a great extent the mission orbital schedule determines the size of the battery, and the size of the solar array determines the rate of charge of the battery. In a LEO orbit, the energy removed during the 35 minutes of eclipse has to be replaced within the 65 minutes in sunlight without exceeding the safe voltage limit. Charge control is a major consideration for this orbit that occurs 5000 times per earth year. In the GEO orbit, the spacecraft is in the Sun for three full months; then the batteries provide energy in increasing amounts each Earth day to a maximum of 45 minutes, then in decreasing amounts until the spacecraft returns to full Sun. This occurs twice each Earth year resulting in only 100 charge/discharge cycles per year.

Methods used for charge control include constant current, maximum current to a temperature compensated voltage limit followed by current taper (V_T control), and mul-

tiple step charge. The former has been used in GEO orbits because the sun time is in excess of 23 hours during each shadow period. During the sun period trickle charge current is used to offset the self-discharge experienced. This also minimizes the chance for excessive voltage.

The V_T method is used most often for Ni-Cd and other types of battery charging using the maximum solar array power. A large fraction of the solar array power is used for the loads. The remainder is used to charge the battery. When the battery voltage reaches a preset level determined by laboratory tests, the voltage is held constant to minimize the overcharge. Any of several voltage levels can be selected for operation depending on the condition of the batteries and the spacecraft operational conditions. Also, they can be used for operation when unusual battery characteristics are present, i.e., high or low DOD or a cell short condition. The V_T levels used in the Modular Power Subsystem (MPS) flown in TOPEX, Landsat, UARS, Solar Max, and other space conditions are shown in Figure 4.8.

During the constant voltage period, the current is allowed to taper to a low value depending on the ability for the battery to accept current at that voltage. This provides a means of reducing the current when the cell reaches the fully charged condition where the inefficiency results in gassing, heating, and/or undesirable reactions. The V_T level is selected so as to minimize or eliminate overcharge. For a Ni-Cd battery the recommended charge to discharge ratio as a function of temperature is shown in Figure 4.9. The ratios take into consideration the charging inefficiency due to the O_2 competing reaction that occurs when charging at temperatures above $0^\circ C$.

Figure 4.10 shows the use of a V_T operation of a Ni-Cd battery at Level 5 and $10^\circ C$. This was the selected condition for operating a healthy Ni-Cd battery in space for 25% DOD. If the voltage is set too high, the maximum current available from the solar array would continuously charge the battery until the higher voltage level was reached.

As described above, if the voltage is too high and the current is high, heating occurs and thermal runaway results. The multi-step method provides a mechanism for reducing the current in steps as the charge voltage reaches preset limits. It takes the place of an automated V_T operation except that the current is decreased in a stepwise manner when preset voltage limits are reached.

6.6 Efficiency and thermal properties

Coulombic (Electrochemical) and energy efficiencies are the key factors in determining cell and battery performance. The former is used to describe the reversibility of the electrochemical reactions as a function of temperature, the effect of competing reactions, and the effect of self-discharge factor. Primary cells contain reactants that are mostly irreversible. Rechargeable cells are by their very nature highly reversible. How-

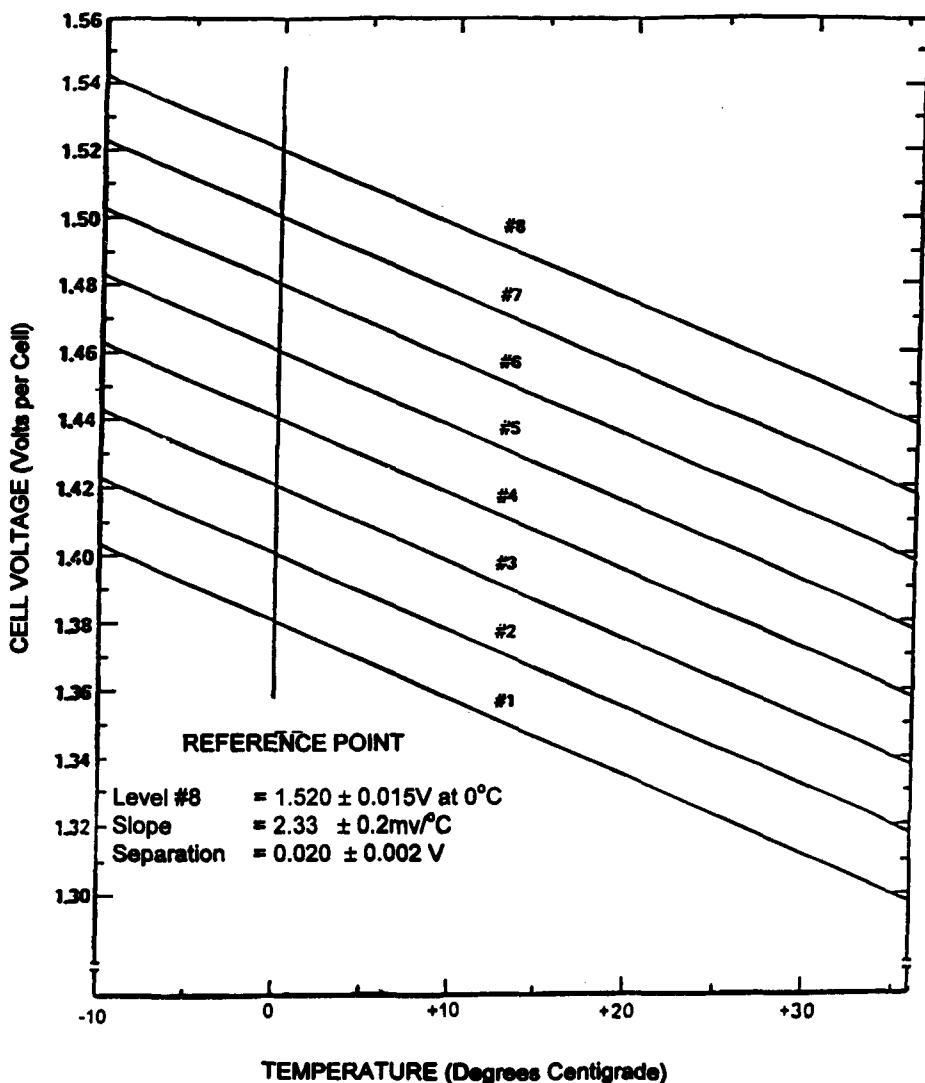


Figure 4.8 Temperature-Compensated Voltage Curves Used for V_T Charging

ever, increases or decreases in temperature can change the reversibility and result in competing reactions.

For example, the reactions of the electrodes in the Ni-Cd cell are quite reversible. However, near the end of the charge, the oxidation of Ni(OH)_2 to NiOOH competes with the oxidation of OH^- to O_2 . The competition results in the inefficient use of elec-

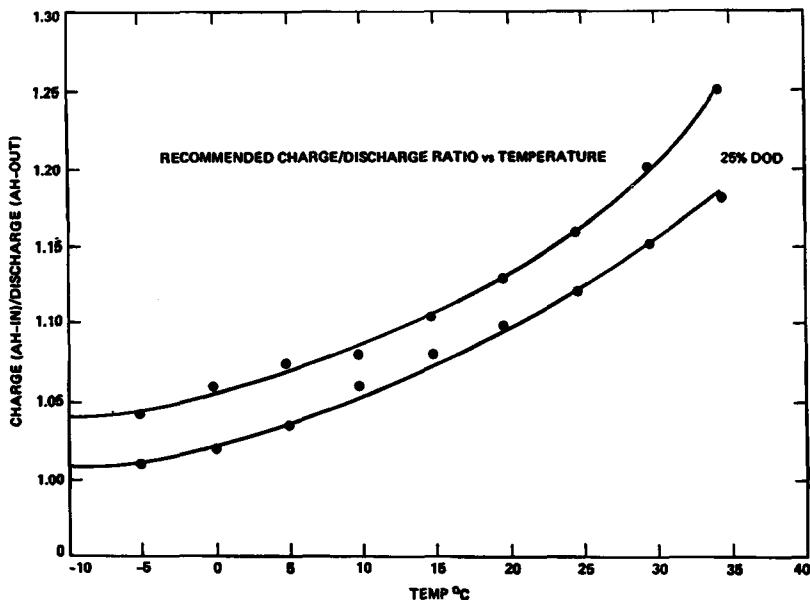


Figure 4.9 Recommended Charge to Discharge Ratio for a Ni-Cd Cell

trons for the $\text{Ni}(\text{OH})_2$ reaction. To account for this, the charge process is therefore continued beyond that of 100% reversibility. The extent of overcharge is strongly affected by temperature. As the temperature rises, the overpotential of the OH^- reaction increases faster than the $\text{Ni}(\text{OH})_2$ reaction resulting in larger quantities of O_2 production. Thus, the higher the temperature the greater is the electrochemical inefficiency. For this system the coulombic efficiency decreases from 0.98 at 5°C to 0.85 at 20°C. The Li-Ion cell is practically free of competing reactions to the point at which the cell is fully charged over the same temperature range. Thus, its coulombic efficiency is relatively constant at 0.98.

Energy efficiency depends on the same coulombic factor and the voltage of the cell. Cell voltage, affected by polarization, increases during charge and decreases during discharge. The ratio of the integral of the voltage and current during discharge to that on charge provides the energy efficiency. For the Ni-Cd cell, the energy efficiency at 5°C is 0.84, while that of the Li-Ion cell is 0.95. The result of inefficiency is heat generation that is taken into consideration in the power system thermal design.

7. Electrochemical cell types

Except for a limited number of cases, primary cells can only be discharged once. These include the lithium primary battery systems. However, Ag-Zn cells on the Shuttle backpack can be recharged a few times. This helps to provide the engineers with the information that the batteries can meet the capacity requirements and are acceptable for flight. However, most primary systems do not have this capability. They are considered a primary cell because the reactions during discharge cannot be reversed.

7.1 Primary cells

Initially, the short demonstration missions used primary cells for prime power to minimize cost and complexity. Several space applications still require the use of primary

Table 4.7 Primary Cells Used in Shuttle Missions

Zinc Anode Primary Cells/ Batteries

- Zinc - Manganese Dioxide-LeClanche (Zn - MnO₂)
- Zinc - Manganese Dioxide Alkaline (Zn - MnO₂)
- Zinc - Mercuric Oxide (Zn - HgO)
- Zinc - Oxygen (Zn - O₂)
- Zinc - Silver Oxide ('Silver-Zinc') (Zn - Ag₂O)

Lithium Anode-Soluble Cathode Primary Cells/ Batteries

- Lithium - Sulfur Dioxide (Li - SO₂)
- Lithium - Thionyl Chloride (Li - SOCl₂)

Lithium Anode-Solid Cathode Primary Cells/ Batteries

- Lithium - Carbon Monofluoride (Li - (CF)_x)
 - Lithium - Manganese Dioxide (Li- MnO₂)
-

batteries. Some of these are used in Shuttle applications to support astronaut equipment, for instrument power, and for experimental packages such as the Get-Away Special (GAS). Small-size rechargeable batteries have also been used for Shuttle applications in OEM and instrument power. In addition, they have been used in landers, penetrators, and probes in planetary missions. A list of the primary cells used in Shuttle missions is given in Table 4.7.

The broad spectrum of power and energy storage requirements for payload power provisioning requires the use of many types of batteries. All batteries require approval by the Johnson Space Center Safety Office before use. Many will require various degrees of design modification and safety tests to make them acceptable for aerospace

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. Listed below are primary types that have been used in payload applications:

A comparison of specific energy of primary batteries used in space is shown in Table 4.4 for theoretical energy and in Table 4.6 for actual use. From the initial use of these cells, new technologies have resulted in an increase in voltage and energy capability. Specific characteristics of the zinc anode cells are shown in Table 4.8.

Zinc anode primary cells/batteries

Many of the zinc anode cells have been and are available to the consumer for use in toys, flashlights, and other well-known applications. Generally, they are low in cost, used in low rate (<C/100) applications, and are relatively safe. These include the familiar Zn-MnO₂-LeClanche cell, the Zn-MnO₂-alkaline cell, and the Zn-HgO oxide cell. All the zinc anode cells, except the LeClanche, type use alkaline electrolyte (aqueous potassium hydroxide) which enhances the conductivity and improves rate capability and voltage during discharge.

Zn-O₂ (air) and Zn-Ag₂O cells are higher in energy density, and the Zn-Ag₂O is capable of operating at higher rates than typical primary cells. Zn-O₂ batteries have been used in space in the Shuttle cabin. The zinc cells are attractive because of their high volume energy density. Primary Zn-Ag₂O 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. In zinc anode cells, the zinc anode is always the negative electrode because it provides the electrons to the load during discharge. A more detailed description of each of the types follows.

Zinc-Manganese Dioxide-LeClanche (Zn-MnO₂)

This cell, sometimes called the zinc-carbon cell, utilizes an aqueous solution of ammonium chloride (NH₄Cl) and/or zinc chloride (ZnCl₂) as the electrolyte. Its reaction is given as:



Table 4.8 Zinc Anode Primary Cell Characteristics

Name	Cell Designation	Nom. Volt. (V)	OCV (V)	Energy Density (Wh/kg)	Temp. °C	Comments	
LeClanche	Zn // NH ₄ Cl / ZnCl ₂ // MnO ₂ / C	1.6	(1.3)	65	100	-5 to 45	Low cost, sloping voltage
Alkaline	Zn // ZnO / KOH // MnO ₂ / C	1.6	(1.3)	95	220	-20 to 55	Greater drain rate, sloping voltage
Mercury	Zn // ZnO / KOH // HgO	1.35	(1.3)	105	325	0 to 55	Level voltage
Zinc-Air	Zn // KOH/NaOH // O ₂ (Air)	1.5	(1.4)	290	905	0 to 50	Highest available energy of Zn anode cells
Silver-Zinc	Zn // KOH / NaOH // Ag ₂ O/AgO	1.8	(1.6)	200	515	-20 to 55	High drain rate, high cost

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.

It is generally found in the cylindrical (bobbin) and wafer type constructions and therefore is of limited electrode area, restricting it to low rate ($<\text{C}/100$) applications. This cell has wide consumer applications in toys, flashlights, radios, flashers, and instruments. One can remove 50 percent of the capacity at the $\text{C}/50$ rate and 100 percent at the $\text{C}/400$ rate. This type of cell has been used in some Shuttle applications for instruments, flashlights, and radios.

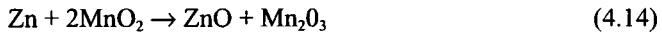
The advantages include: 1) low cell cost, 2) low cost per watt-hour, 3) large variety of shapes, sizes, battery voltages, and capacities, 4) wide distribution and availability, and 5) reliability.

The disadvantages include: 1) low energy density, 2) poor low-temperature service, 3) leakage under abusive conditions, 4) low efficiency under high current drains, 5) limited shelf life, and 6) sloping voltage.

The potential hazards include: 1) H_2 gas accumulation during discharge needs relief (do not encapsulate), and 2) cells can leak salt-solution electrolyte (avoid contact to metal).

Zinc-Manganese Dioxide-Alkaline ($\text{Zn}-\text{MnO}_2$)

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:



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 suppresses 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.

Available in a wide variety of sizes in the consumer market, it is used for higher drain rate application than the LeClanche cell. Applications in space are primarily for OEM equipment including radios and recorders. 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.

The advantages include: 1) improvement of low-temperature service over LeClanche, 2) higher efficiency under high discharge loads, 3) good shelf life (4-year storage with

80 percent of capacity), 4) wide availability, 5) moderate cost (higher than LeClanche), and 6) sloping discharge curve (better than LeClanche).

The disadvantages include: 1) hydrogen gassing rate higher than LeClanche, and 2) shorted cells (high rate) can produce high temperatures (100°C).

The potential hazards include: 1) H₂ gas accumulation during discharge needs relief (do not encapsulate), and 2) leakage of corrosive alkaline electrolyte.

Zinc-Mercuric Oxide (Zn-HgO)

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:



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.

The 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 applications where rate is low and volume is minimized. It also exhibits a level voltage during discharge which makes it ideal for a memory storage or time standard. It is also used in pacemakers, hearing aids, detectors, and sensors.

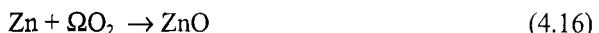
The advantages include: 1) higher volume-energy density, 2) long shelf life, 3) flat discharge curve over a wide range of current drains, and 4) high resistance to impact, acceleration, and vibration.

The disadvantages include: 1) somewhat higher cost than Zn-MnO₂, 2) disposal of Hg produced on discharge, and 3) electrolyte creep may result in leaks.

Potential hazards include: 1) because of zinc oxidation, a tendency for H₂ to accumulate during discharge (do not encapsulate), 2) the toxic nature of Hg vapor (avoid cell damage during handling, shipment, and storage to prevent Hg loss), 3) short circuit or any excess heating of the cell can result in Hg vapor release (do not solder leads directly to the cell terminals without proper precautions), 4) the need to open and/or dispose of the cell under controlled conditions to prevent the escape of Hg vapor (if there is a need to open, one should place the entire contents under water in a polyethylene or polypropylene container), and 5) possible electrolyte (strong alkali) leak from cell (neutralize with a saturated solution of boric acid or large quantities of water).

Zinc-Oxygen (Zn-O₂ or Zn-Air)

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 wintered nickel structure impregnated with a catalyst, sometimes platinum. The reaction is given simply as:



Large zinc-air batteries with the appearance of an automobile battery having sheet zinc anodes (low rate) have been used for railroad signal switching, telecommunications, 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.

The advantages include: 1) high volume-energy density, and 2) flat discharge voltage at low rates, while the disadvantages include: 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, and 5) pulse capability limited.

There are two potential hazards: 1) electrolyte leakage (use saturated solution of boric acid or dilute vinegar to neutralize), and 2) H₂ evolution can occur because of the electrochemical reduction of zinc (do not hermetically seal).

Zinc-Silver Oxide (Silver-Zinc) (Zn-Ag₂O)

This cell utilizes a porous electro-formed amalgamated zinc electrode, 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:



Because of its high energy density it is widely used in electronic equipment, hearing aids, watches, calculators, and other instruments requiring extended life. In space, it has been used in several important applications: as a primary battery for launch vehicle controls and communications, to power the tools to repair the Solar Max Mission (SMM) spacecraft, and for the Manned Maneuvering Unit (MMU) required to propel the astronaut during extravehicular activity (EVA). This battery, if assembled with adequate

separator and design, is considered a limited use rechargeable cell. A cell/battery can be recharged a limited number of times to allow checking of performance or associated equipment. As a reserve battery it has been used in some long term missions where the electrolyte is maintained in a bellows leaving the cell dry until activation. In space, most of the primary batteries on Apollo and Skylab were zinc-silver oxide, a limited cycle life rechargeable battery. A 40 Ah, 28 V. battery was recently used to provide prime power for the Mars Lander to meet a 30 day mission. It actually lasted 100 days. A photo of the battery appears in Figure 4.11. The Zn-Ag₂O system is available in button, prismatic, and reserve configurations.

The advantages: 1) high energy density, 2) good low-temperature operation, 3) good shock and vibration resistance, and 4) can be charged and discharged to determine capacity. The disadvantages: 1) relatively high cost, 2) active cell shelf life limited to 1 year or as little as 30 days (except for reserve types), and 3) two voltage plateaus associated with Ag₂O and AgO discharge product.

The potential hazards include: 1) strong alkali may leak through pressure relief valve (use boric acid solution to neutralize), 2) need to vent H₂ accumulated on open circuit stand and at low voltages (< 0.3V, Ag has low H₂ overvoltage), and 3) zinc dendrites can form (on charge) creating internal short (internal shorts can produce heat which increases pressure within the cell).

Lithium anode primary cells/batteries

Various cells with lithium anodes and non-aqueous electrolytes have gained 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 above, most of the lithium anode cell technologies in use today are for primary cell applications. Rechargeable lithium cells are presently being developed for space and commercial use.

The main reasons 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 bases for lithium's energy storage capabilities are the magnitude of its oxidation potential (3.01V) compared to other metals such as zinc (0.66V) 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.

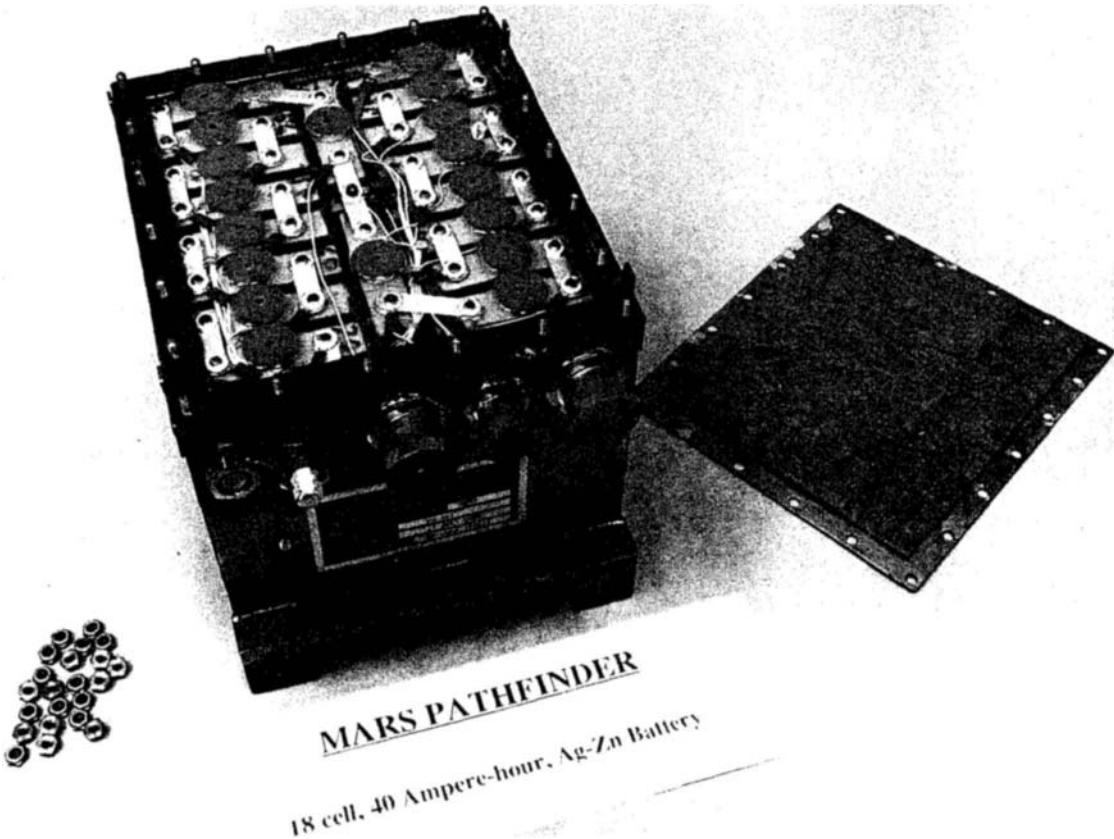


Figure 4.11 The 40Ah, 28V Ag-Zn Battery Used in the Mars Pathfinder Lander

The lithium cell groups can be divided into three categories:

- (1) Soluble cathode cells.
- (2) Solid cathode cells.
- (3) Solid electrolyte cells.

Lithium cells use either solutions of organic or inorganic electrolyte. In the soluble cathode type, the solvent containing a conductive salt, 'catholyte', also serves as the active energy producing material for the cathode reaction. A porous inert carbon electrode provides the reaction site and stores the product deposit. Lithium metal foil is the source of the anode reaction. Compatible salts are dissolved in the solvent to enhance conductivity. 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. In these cells the active material of the cathode is also in contact with the anode, thus providing capability for relatively high discharge rate for primary cells but also concern for safety. These cells are used by the DOD and NASA but are not available for commercial use.

The soluble cathode types used in space applications include lithium-sulfur dioxide (Li-SO_2) and lithium-thionyl chloride (Li-SOCl_2). Lithium-sulfuryl chloride ($\text{Li-SO}_2\text{Cl}_2$) has been considered, but presently the Li-SO_2 and Li-SOCl_2 have been used for various applications. A variation of the Li-SOCl_2 cell (Li-BCX) containing bromine chloride has been utilized in astronaut Shuttle applications.

The inherently large energy storage capability is quite desirable when the electrochemical cell system is properly designed for the application and used within the limits for which it was intended. However, if subjected to abnormal operations or conditions, the large quantity of energy can be released quickly, sometimes with violence, resulting in venting or, on rare occasions, explosion. For this reason, the soluble cathode lithium anode cell should be used only in applications where the zinc anode cell does not meet performance requirements.

Solid cathode cells ranging in voltage from 1.5 V to 3.3 V have been developed over the years. Although a number of types have been identified, only a few have become common. 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 they are used in applications where rate requirements are low (<C/100).

One of the few solid electrolyte cells in use is the lithium-iodine cell. It has the lowest rate capability of the lithium systems because of the conductive path through solid electrolyte. Thus, it is the safest of lithium cells, except at temperatures above 186°C (lithium melting point) where it, like the other lithium cells, can be hazardous.

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 in Table 4.9.

Lithium Anode Soluble Cathode Cells/Batteries

The electrochemical cell types comprising this group are lithium-sulfur dioxide (Li-SO_2), lithium-thionyl chloride (Li-SOCl_2), and lithium-thionyl chloride with bromine chloride (Li-BCX). 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 for short periods 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, these cells have a characteristic which must be considered in their use: voltage delay. The delay is due to the lithium film formed on the lithium metal surface which provides a protective layer. When a load is switched on, the cell responds as if it contained a high resistance between electrodes. Thus, after the initial power surge, the cell or battery voltage drops well below the operating voltage for a short period, seconds to minutes depending on operating conditions, before the cell or battery reaches its normal operating voltage. This drop in voltage depends on the cells 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.

Reversal of these cells, as with most electrochemical cells, produces undesirable reactions which not only result in loss of cell use but may result in a hazard condition. Diodes are used in parallel strings to avoid one of the strings forcing current through the other string resulting in a reversal. Diodes are also occasionally used across cell terminals to bypass the current when its voltage drops below a preset point.

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 eight 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 (center electrode with thick surrounding opposing electrode) are considered low rate because of their limited electrode surface. However, high rate (spiral wound, large surface area) cells are used by the U.S. Army

Table 4.9 Lithium Soluble Cathode Cell Characteristics*

Name	Cell	Nominal Voltage (V)	OCV (V)	Specific Energy (Wh/kg) (Wh/l)	Operating Temperature (°C)	Comments
Li-SO ₂	Li // CH ₃ CN / LiBr // SO ₂ /C	3.0	(2.9)	280	440	-55 to 60 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 60 Highest energy density
Li-BCX	Li // SOCl ₂ / LiAlCl ₄ // BrCl // SOCl ₂ /C	3.9	(3.5)	430	960	-40 to 60 BrCl reported to prevent formation of S
Li-SO ₂ Cl ₂	Li // SO ₂ Cl ₂ // AlCl ₄ // SO ₂ Cl ₂ /C	3.9	(3.5)	500	1000	-40 to 60 In early stages of production

*Cylindrical spiral wound (jellyroll) construction.

for a number of field applications. Also, the lithium-sulfur dioxide cell was approved by the U.S. Federal Aviation Administration for use in electronic-locating transmitters (ELT) for private noncommercial aircraft, and the lithium-thionyl chloride cells are used in oil well 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-type (button) cells containing multiple plates have been used by the military in multi-cell batteries for several portable applications. These cells have been used in the Mars Rover and are planned for the DS-2 probe into the surface of Mars. They were also developed using flat plate electrodes into 250 Ah 28 V batteries for the Centaur launch vehicle. Their designs include 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.

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, as well as in the Galileo and Cassini probes. 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 in the astronaut helmets 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 M, 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.

Lithium-Sulfur dioxide (Li-SO₂)

This cell is available in spiral wound construction. It 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

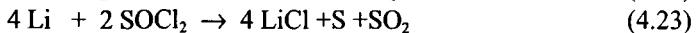
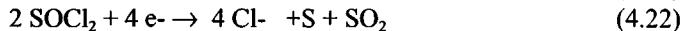
is an 80% porous structure that provides the necessary surface area for the discharge reaction to occur and volume for the discharge product (lithium dithionite) to deposit. The reactions are :



The electrolyte consists of a solvent acetonitrile (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 3-4 atmospheres ($3-4 \times 10^5$ 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 26-30 atmospheres (at temperatures of 93-106°C). Cells of this type developed by Alliant Techsystems have been used in the Galileo probe to Jupiter. A photo of one of the three probe batteries is shown in Figure 4.12. A similar design was launched in 1997 on the Huygens probe on the Cassini spacecraft to Saturn.

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 similar to the Li-SO_2 cell. The liquid SOCl_2 serves the dual role as the cathode active material (catholyte) and the solvent. The conductivity is provided by the 0.5 m LiAlCl_4 dissolved in the electrolyte. Occasionally other salts or higher concentrations are added to enhance the performance. The separator is a nonwoven glass held together with an inert binder. The reactions are given as:



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. 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. 250 Ah Li-SOCl_2 cells and batteries have been used recently in space for launch vehicle power on the Centaur launch vehicle to double the mission capability over the Ag-Zn batteries. Two types of cells and batteries were developed for this purpose. The flat pancake design of Saft (France) as seen in Figure

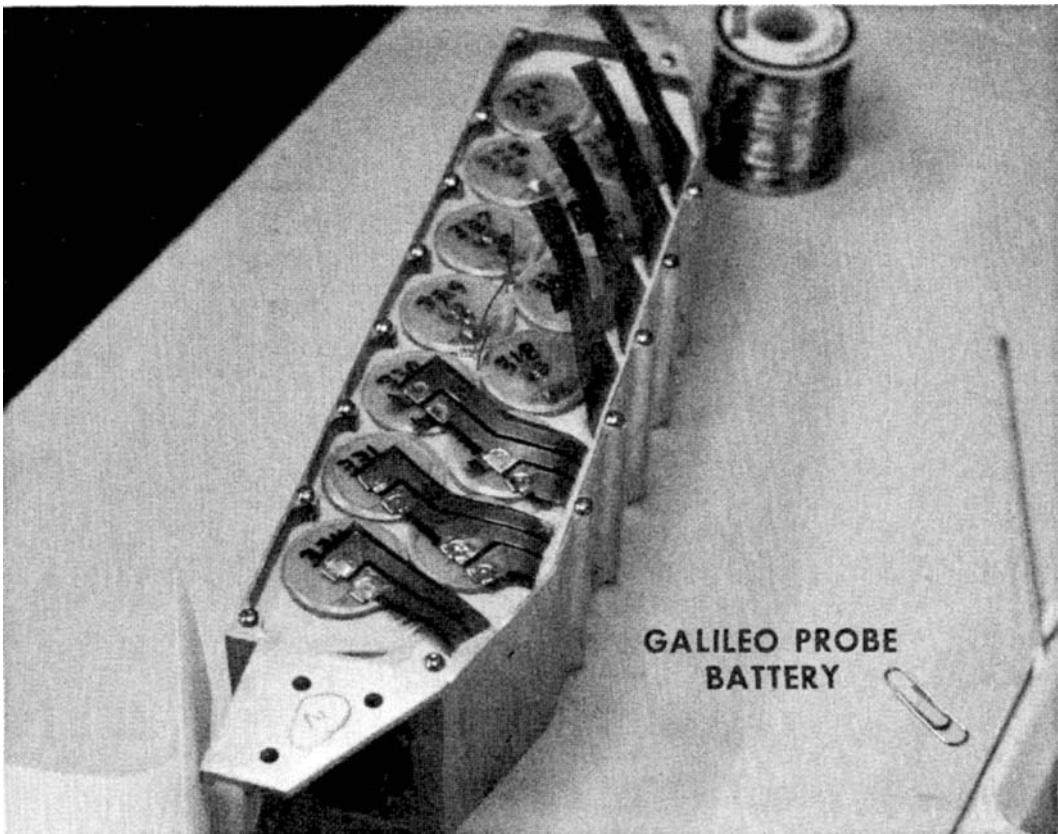


Figure 4.12 Galileo Probe Li-SO₂ Battery

4.13, was selected for the first Centaur mission. Both designs passed a myriad of strenuous hot and cold temperature tests and several vibration and shock levels associated with a launch vehicle.

A more recent application is the Li-SOCl₂ Mars Pathfinder Rover battery, Figure 4.14, which used a 'D' cell design. It served as the power source for experiments on the Rover that could not be handled by the solar array on the top of the Rover.

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. As is the case with lithium-thionyl chloride cells, the SO₂ is gaseous and the clogging of the carbon by LiCl can limit the discharge. These cells have been successfully used in a number of astronaut applications in 'C', 'D', and 'DD' configurations.

The advantages include: 1) high 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, and 5) relatively flat discharge voltage. The disadvantages include: 1) inherently higher hazard potential, 2) safety precautions necessary, 3) internal cell pressure increases rapidly as temperature increases (especially Li-SO₂), 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 U.S. Department of Transportation (DOT) and the U.S. Environmental Protection Agency (EPA), and (7) voltage delay is possible depending on temperature and time of storage and rate and temperature of application.

The potential hazards are based on the concern for the reactivity of lithium. 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 Chapter as user induced and manufacturer-induced. 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.

The hazards include excessive temperature during storage and operation which can:
1) increase internal gas pressure, i.e., $p = f(T)$, 2) increase vapor pressure of solvent or

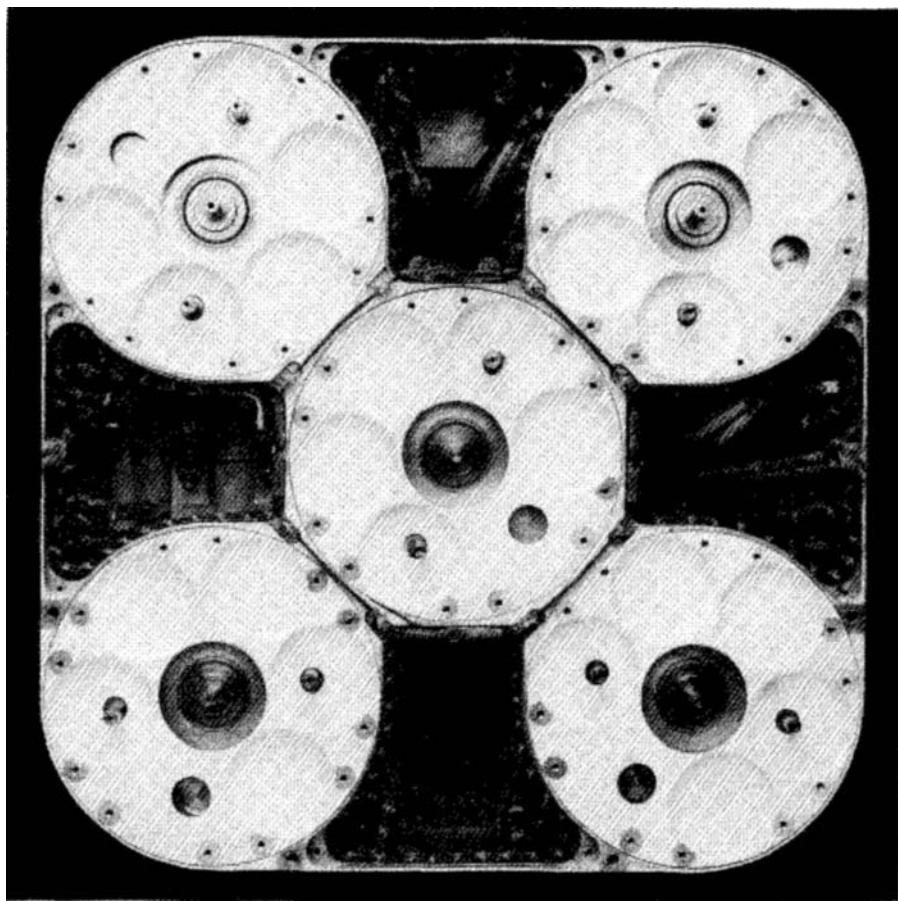


Figure 4.13 Top View of Saft 250 Ah, 28V Centaur Battery

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, 6) charge a cell, thus producing gases and other products while generating heat or causing unexpected reactions to occur which in themselves are heat initiated, 7) continue the



Figure 4.14 The Mars Pathfinder Rover Battery with Li-SOCl₂ Cells

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, and 8) deplete 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 that the construction of the cell and battery determines the heat dissipation rate, and thus the rate at which the cell temperature increases; the merits of an anode-limited vs cathode-limited design are still being debated.

Numerous abuse tests have been performed, including exposure to flame, impact, penetration, and rapid high temperature heating. 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. 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. 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 ultimately depends on the application and related environmental considerations.

Lithium Anode Soluble Cathode Cells/Batteries

Lithium-Manganese Dioxide (Li-MnO₂)

This cell utilizes an electrolyte composed of propylene carbonate (PC) and 1,2 dimethoxyethane (DME) with lithium perchlorate (LiClO₄) salt which enhances the conductivity. The reaction is given as:



where the lithium ion (Li⁺) enters the MnO₂ lattice. The cathode is either pressed powder or a thin pasted electrode on a conductive support. It has been used for memory backup and small light loads.

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

The active components are a lithium anode and solid carbon polynonofluoride (CF) formed by reaction of carbon monoxide with fluorine gas. Several electrolytes have been used, including lithium hexafluorarsenate (LiAsF₆) in dimethylsulfide (DMSI). Other electrolytes have included lithium tetrafluoroborate (LiBF₄) salt in butyrlactone (BL) tetrahydrofuran (THF) or propylene carbonate (PC) and dimethoxyethane (DME). The simplified reaction is given as:



where (CF_x) acts as an intercalation compound. Li- (CF_x) cells were initially used in a launch vehicle safety application. However, since the Shuttle accident, use has been discontinued.

Lithium Solid Electrolyte Cells

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

Lithium-Iodine (Li-I₂)

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:



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

The advantages include: 1) excellent storage capability (~10 years), 2) sealed (no leakage), 3) wide operating temperatures, and 4) safety. The disadvantages include: 1) low current drain only, and 2) low power capability. The potential hazards include placing the cell in a flame could result in a venting or deformation.

7.2 Rechargeable cells and batteries

Rechargeable or secondary cells and batteries differ from the primary cells and batteries in that the chemically stored energy used during the discharge can be returned to the chemical form by recharge. This is accomplished by causing a source of electrons from the solar array or power supply to flow in the reverse direction from that of the discharge direction. When this occurs the reactions are reversed and therefore the electrode that served as the anode on discharge becomes the cathode on charge. The cathode where reduction took place during discharge becomes the anode where oxidation occurs. Similarly the anode becomes the cathode. Even though the reactants and products are changing, the polarity remains the same as that during discharge because the quantities of active materials are primarily in the charged state. A diagram of charge and discharge configurations is shown in Figure 4.15 for the Ni-Cd cell.

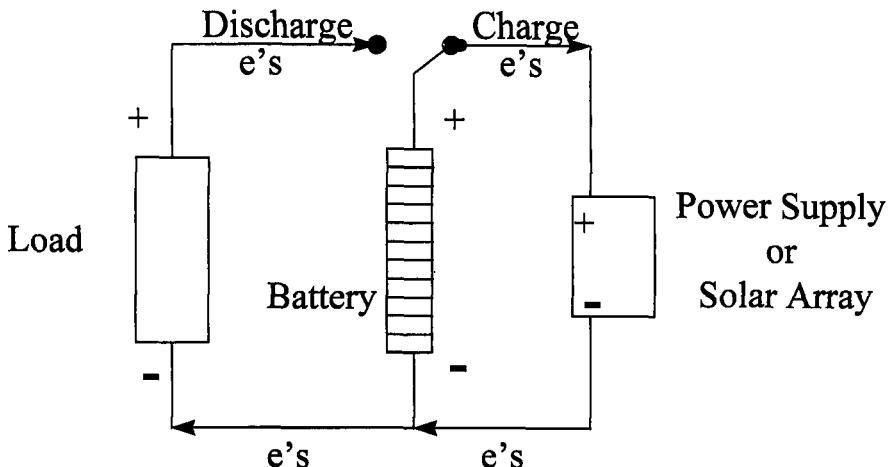


Figure 4.15 Charge and Discharge Configurations For Rechargeable Cells

Secondary cells/batteries require additional circuitry to provide the means for charging. Depending on type of electrochemical cell application and temperature, cells can be cycled (charged/discharged) hundreds of times to tens of thousands of times. Because of its reversibility and long life this battery type has been used in the majority of low Earth orbiting (LEO) and geosynchronous orbiting (GEO) spacecraft.

It is essential for long life missions that the cells in the battery be hermetically sealed to maintain their chemical and electrochemical balance. The rechargeable batteries that have seen the most use in space are those that consist of nickel hydroxide as the discharged active material. These are the 'nickel-cadmium (Ni-Cd)' and 'nickel - hydrogen (Ni-H₂)' types. They have demonstrated long cycle life in LEO and GEO mission applications. During eclipse, they provide power to the spacecraft, the instruments, and electronics. During Sun periods, the solar array is adequate enough to provide spacecraft energy requirements and recharge the battery.

A second type is based on the silver oxide electrode. These batteries have been used in more limited applications because of their limited cycle life. Specifically, these include silver-cadmium (AgO-Cd) and silver-zinc (AgO-Zn) batteries. The silver-hydrogen (AgO-H₂) battery has received some attention because of its higher specific energy but has not been used in space. The nickel and silver oxide based cells are similar in that they use a strongly-alkaline electrolyte.

Although the most well known rechargeable battery is the lead acid system, it is not truly a sealed system and therefore use in space is not practical for long term missions; its use in space has been limited to short term shuttle applications in a cylindrical configuration.

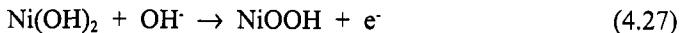
Recent developments have resulted in cells based on lithium, with the initial designs using lithium foil. However, their use is a safety concern. Even though the primary cells use lithium foil, the replating of the lithium during charge was determined to be unsafe. A lithium-based cell that provides an adequate level of safety is the lithium-ion cell, in which lithium metal is absent.

Sodium-Sulfur (Na-S) cells operate at temperatures of 350°C where the constituents are in the molten condition. The electrodes are separated by a beta alumina separator which allows sodium ions to flow between electrodes. Although they have demonstrated long cycle life in ground tests, concern for the reliability of the high temperature system has limited its use to a single flight experiment. Sodium-Nickel Chloride (Na-NiCl₂) cells which operate at 250°C have also shown long life in commercial ground tests and are being considered for electric vehicle applications but have not had any space use.

A comparison of the characteristics of rechargeable cells is shown in Table 4.10. A comparison of the characteristics based on 28 V space batteries, given in Table 4.11, reflects the improvement in specific energy and energy density. The other factors that need to be considered in selecting a battery for a mission, such as cycle life and LEO or GEO, are also given.

Nickel hydroxide cells/batteries

There are three types of nickel hydroxide cells/batteries. These are identified as the cells containing Ni(OH)₂ as the discharged active material and NiOOH as the oxidized active material in the charged state. The Ni(OH)₂ exhibits a positive polarity in this type of cell. The reaction is:



The types of nickel hydroxide cells include Ni-Cd and Ni-H₂ and have been used extensively in space. Nickel-Metal Hydride (Ni-MH), a version of the Ni-H₂ type in which the hydrogen is bonded chemically as a hydride as compared to pressurized H₂, has until now received little attention as a space battery. Nickel-zinc (Ni-Zn) and nickel-iron (Ni-Fe) types are also in the nickel hydroxide family but with higher specific energies than Ni-Cd and Ni-H₂. However, they are not sealable. 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.

Table 4.10 Secondary Cell Characteristics

Name	Design	Anode*	OCV (V)	Nominal Voltage (V)	Specific Energy (Wh/kg) (Wh/l)	Operating Temp. C	Cycle Life 80% DOD
NiOOH-Cd		Cd // KOH // NiOOH	1.29	1.25	30 80	-10 to 35	-2000
NiOOH-H ₂	(IPV)	H ₂ // KOH // NiOOH	1.32	1.25	55 60	-10 to 35	-2000
NiOOH-H ₂	(CPV)	H ₂ // KOH // NiOOH	1.32	1.25	55 60	-10 to 35	-2000
NiOOH-H ₂	(SPV)	H ₂ // KOH // NiOOH	1.32	1.25	55 60	-10 to 35	-2000
AgO-Cd		Cd // KOH // Ag ₂ O / AgO	1.41	1.3/1.1	55 110	-25 to 60	400
AgO-Zn		Zn // KOH // Ag ₂ O/AgO	1.86	1.6/1.5	90 180	-20 to 60	100
PbO ₂ -Pb		Pb // H ₂ SO ₄ // PbO ₂	2.1	2.0	30 60	-40 to 60	100
Na-S		Na // b" alumina // S	2.1	1.65	186** 304**	350	1000
Na-NiCl ₂		Na // b" alumina // NiCl ₂	2.4	2.3	120 110	275	1000
Li-CoO ₂		Li // EC / DMC / CoO ₂	4.00	3.64	120 125	-20 to 50	1000

* 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, in most cases, these values can vary over a wide range.

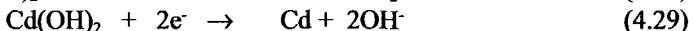
Table 4.11 A Comparison of 28V Battery Characteristics

CHEMISTRY	Ni-Cd	SUPER Ni-Cd	IPV Ni-H ₂	2 CELL CPV Ni-H ₂ (3.5")	22 CELL SPV	Li-ION	Ag-Zn
NUMBER OF CELLS	18	18	18	18	22	8	18
NOMINAL VOLTAGE	21.6	21.6	22.5	22.5	27.5	28.8	27
CAPACITY (Ah)	18	20	20	20	15	5	40
SPECIFIC ENERGY (Wh/Kg)	25	25	29	31	44	90	72
ENERGY DENSITY (Wh/L)	35	31	16	18	38	140	86
CYCLE LIFE	30000 LEO	30000	> 30000	~ 10000	N/A	~ 1000 (> 80% DOD)	< 100 (> 80% DOD)
WEIGHT (Kg)	16	17.9	13.8	13.1	9.6	1.6	15
VOLUME (L)	11.4	14.4	13.6	11.4	8.6	1.0	12.6
BATTERY DIMENSIONS (in)	12.3 x 7.3 x 7.7	13.5 x 8.1 x 8.4	25.0 x 17.6 x 3.5	18.0 x 14.5 x 4.5	21.0 x 5.0 dia.	N/A	12.0 x 8.0 x 8.0
HERITAGE	LEO / GEO	LEO / GEO	LEO / GEO	MARS GLOBAL SURVEYOR	MARS '98	NEW MILLENIUM	MARS PATHFINDER

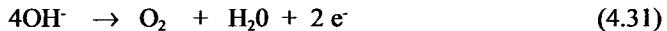
Nickel-Cadmium (Ni-Cd)

In the Ni-Cd cell, cadmium hydroxide, $\text{Cd}(\text{OH})_2$, is the active material of the negative electrode. The $\text{Cd}(\text{OH})_2$ negative electrode active material like the $\text{Ni}(\text{OH})_2$ material is contained within an 80 percent porous nickel plaque containing a perforated sheet or nickel screen which serves as the current collector. The active material is deposited into the pores by a series of steps filling approximately 40 percent of the remaining space in the plaque. 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 electrode and net cell reaction shown as a charge reaction is:

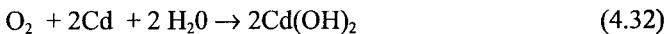
Charge



In order to replace the energy removed from the cell during 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 at the nickel hydroxide electrode produced primarily near the end of the discharge. The reaction resulting in the inefficiency at the positive electrode is:



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 negative electrode which contains a significant quantity of cadmium metal (Cd) because it is being charged. The oxygen recombines chemically according to the following reaction:



Thus, when the charging process has converted most of the active materials to NiOOH and Cd as given in Eqs. (4.28-4.30) and oxygen evolution occurs, the oxygen reacts with the charged Cd via Eq. (4.32) to discharge the cadmium electrode by the same amount resulting in no net change of reactants and products thus preserving the electrode balance.

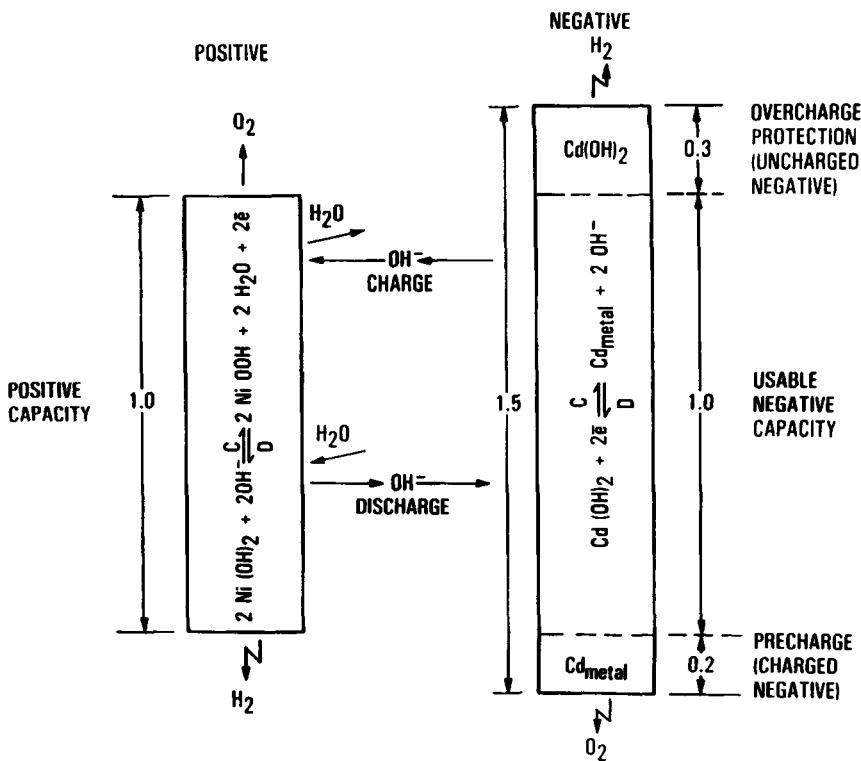


Figure 4.16 Active Material Balance in a Ni-Cd Cell

The aerospace cell is referred to as positive-limited on charge (and discharge). If it were to be negative-limited on charge, as in electrolysis, the negative electrode would evolve hydrogen gas which is not recombined in this cell. A high internal pressure and 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 balance between the active materials in the Ni-Cd cell is given in Figure 4.16.

The most efficient charge scheme is to use a high current ($>\text{C}/4$) at the start of charge and convert to constant voltage (current taper) at a prescribed voltage limit until the current drops to a $\text{C}/15$ rate. The cells can generally be constantly charged at the $\text{C}/10$ rate 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. Because there is a rapid decrease of cell cycle life with high depth of discharge (DOD), operation has been limited in aerospace applications to 25 percent DOD for LEO applications and

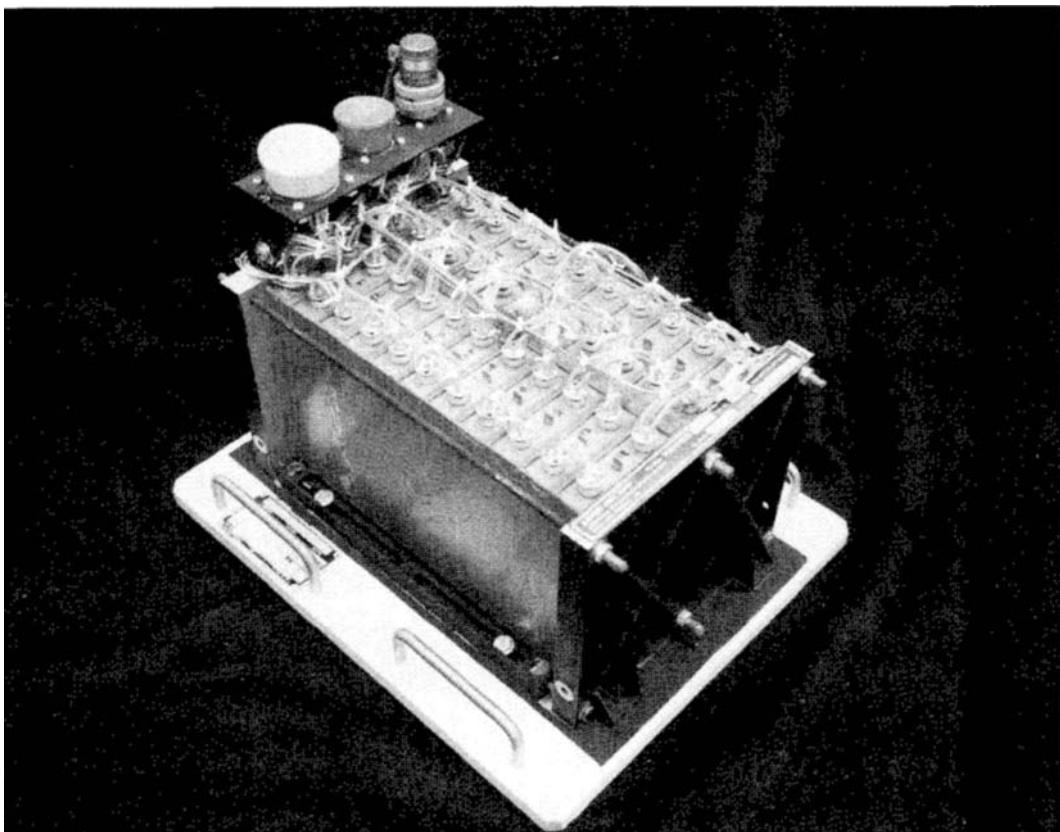


Figure 4.17 The NASA Standard 20 Ah Battery used on the Solar Max Spacecraft

65 percent for GEO applications. The NASA Standard 28 V battery, developed by McDonnell-Douglas and containing the NASA Standard 25 Ah G.E. prismatic hermetically sealed cells, was used on the Solar Max Mission. That mission lasted more than 8 years in LEO orbit (See Figure 4.17).

The advantages of this design are: 1) maintenance-free sealed cells, 2) long cycle life, 3) rugged/sealed, 4) high rate/power capability, 5) flat discharge, 6) long storage life and 7) a large operational data base. The disadvantages include: 1) a relatively high cost, 2) a memory effect/double plateau (may need reconditioning), 3) the need for charge control methods, 4) poor charge acceptance at high temperature or low charge rate, 5) poor capacity retention on storage, and 6) prismatic sealed cells require end-plates to prevent expansion due to internal pressure.

There are several potential hazards: 1) pressure buildup in sealed case on charge (adequate temperature, rate, and charge controls required because of an undesirable ratio, balance, and stability of active materials), 2) leakage of alkaline (white encrustation on seal or case is an indication of leak (inspection and welder certification, qualification, and calibration is necessary as is the use of nylon/cotton gloves in handling electrolyte), 3) leakage of oxygen can cause imbalance problems resulting in dangerous H 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 results in gas evolution and irreversible electrode imbalance, making it necessary to monitor each cell during operation (either the undervoltage cutout can be utilized, or one can use a 1/2 battery voltage to monitor changes in individual cell, and 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 protective circuitry). Please note that although the potential hazards are concerns to be considered, the Ni-Cd cell and battery has been the battery most often used in space from the 1960s to 1990s.

Nickel-Hydrogen (Ni-H₂)

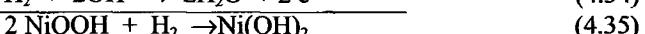
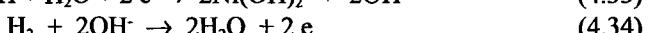
The Ni-H₂ battery has been selected for GEO and some planetary missions. The Hubble Space Telescope mission also uses these batteries. Three types of NiOOH-H₂ cells have been demonstrated for space missions. These include the Individual Pressure Vessel (IPV), the Common Pressure Vessel (CPV), and the Single Pressure Vessel (SPV). The Ni-H₂ battery has a higher specific energy, greater depth of discharge capability, and longer life than the Ni-Cd battery because the cadmium electrode, which degrades with life and depth of discharge, is replaced by the H₂ electrode. However, its energy density is generally less than the Ni-Cd battery because the Ni-H₂ cylindrical cell configuration has a significantly lower packing density.

The single IPV Ni-H₂ cell was the first configuration used in space in a GEO application. Eagle-Picher, one of the manufacturers of CPV Ni-H₂, found that they could install two cells in the same pressure cylinder thus increasing the specific energy and energy density. The SPV involved containment of all 22 cells in a single pressure cylinder thus enhancing the specific energy and energy density. Since its first use by the Naval Research Laboratory, the IPV has been used for commercial purposes as well.

This cell, like the Ni-Cd cell, is quite reversible. The positive Ni(OH)₂ plates are also similar in construction to those described above. The hydrogen electrode comprises a Teflon bonded platinum back on a nickel mesh screen to allow the reduction and oxidation of hydrogen. A gas diffusion screen is used to facilitate hydrogen diffusion. 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. The electrolyte is 30 to 35 percent aqueous potassium hydroxide by weight. An asbestos fuel cell bidirectional separator is used.

The IPV, CPV, and SPV cell configurations use a pressure cylinder to contain 600 to 1000 psi of H₂ at full charge. The cell discharge reaction at the NiOOH electrode is the same as that in the Ni-Cd cell. The H₂ recombination reaction with NiOOH at the negative during discharge is given in Eq. (4.34). The net reaction is given in Eq. (4.35). The reaction on discharge shows that the H₂ built up on charge decreases during the discharge.

Discharge



During charge, H₂ Pressure during charge builds to the design level of 600 - 800 psi. During the overcharge period O₂ is also evolved as shown in reaction at the positive Nickel electrode Eq. (4.35). The O₂ produced reacts with the water to produce OH⁻ according to Eq. (4.36) resulting in no net reaction (Hydrogen evolution reaction is suppressed) and thus the cell pressure remains constant once full charge is reached.



The two gases are combined at the fuel cell electrode at the same rate as they are being produced and thus electrode balance is maintained. The pressure remains at the maximum until the start of discharge when the O₂ reaction subsides. The H₂ then reacts until the end of discharge when pressure is at the minimum as shown in Eq. (4.34). The

cell can be charged at a relatively high rate constant current (~ C/2) similar to the Ni-Cd cell.

This type of cell has had one major application, that of replacing the Ni-Cd in GEO spacecraft. The enhanced specific energy (Wh/kg) over Ni-Cd cells offers a greater opportunity for increasing the spacecraft capability while 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 Ni-H₂ cells are projected to reach 85 percent DOD during the longest eclipse period (about 75 minutes) which occurs twice each Earth year. There is also interest in using this cell in LEO where its capability for greater DOD would provide a distinct advantage. While the specific energy of Ni-H₂ cells is greater than Ni-Cd cells, the volume energy density is less because of the cylindrical gas canister design.

Two types of Ni-H₂ cells were developed initially: the Comsat 35 Ah design (Figure 4.18) used in the U.S. Navy NTS-2 spacecraft and the U.S. Air Force 50 Ah baseline design developed by Hughes Aircraft. The second generation design combined the best of both designs. Eagle-Picher produced an 80 Ah design and Gates Energy Products 3 Ah cell used for Intelsat. Figure 4.19 is a photo of the Intelsat Ni-H₂ battery containing IPV cells produced by Ford Aerospace.

Figure 4.20 shows the concept of the two-cell common pressure vessel cell used for the Mars Global Surveyor Mission and the 22-cell single pressure cell used in the Clementine Mission. The SPV design has been used on more than 40 Iridium™ communications spacecraft developed by Motorola.

This cell offers several advantages, including: 1) state of charge directly related to pressure, 2) longer cycle life at higher DOD than Ni-Cd, 3) specific energy/specific power greater than Ni-Cd, 4) higher depth of discharge capability than Ni-Cd, and 5) the ability to tolerate overcharge and reversal at controlled rates.

The disadvantages include: 1) high cost, 2) self-discharge proportional to decrease H₂ pressure, 3) higher cost than Ni-Cd, and 4) volume energy density and power density less than Ni-Cd. The potential hazards are: 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, 4) gas (H₂ or O₂) leakage creates cell imbalance leading to excessive pressure (perform helium leak testing on each cell and use high reliability well tested seals), and 5) external shorting can result in very high-rate, high temperature excursion leading to a violent venting (use fuse and other protective circuitry).

Silver oxide cells/batteries

Three types comprise this group: silver-cadmium (Ag-Cd), silver-zinc (Ag-Zn), and silver-hydrogen (Ag-H₂). The first two have found applications in space for limited

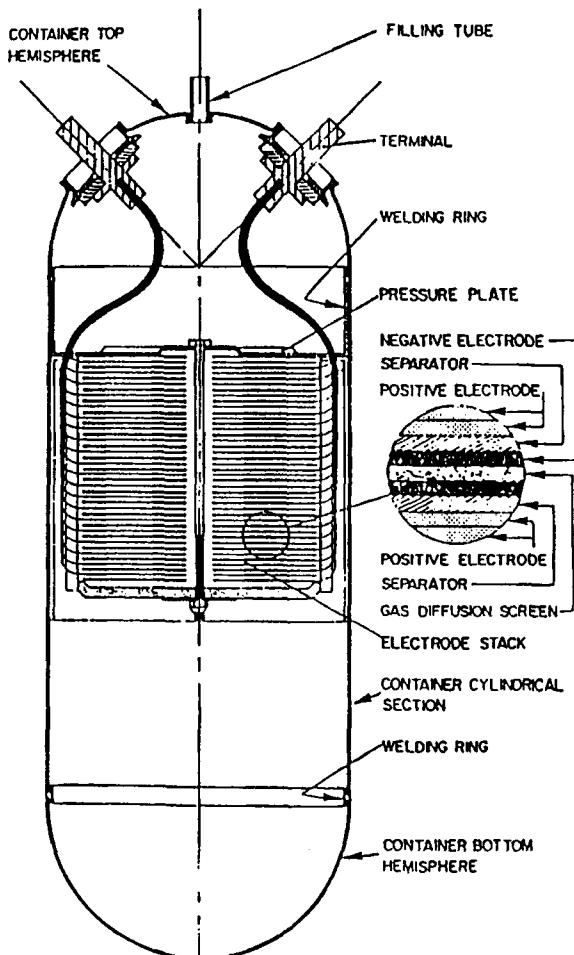


Figure 4.18 Comsat IPV Ni-H₂ Cell Design

mission life. The latter has not been developed for space. The Ag-Cd cell is nonmagnetic and, although not extensively used, was favored in applications in which magnetometers are among the spacecraft instruments. Ag-Zn (also known as silver oxide-zinc and zinc-silver oxide) cells have been used in mid-altitude orbits with relatively short-life spacecraft where the high specific energy plays a part in helping to reduce spacecraft weight. Ag-Zn batteries have been used in launch vehicles for communication and control until the spacecraft is placed in orbit (i.e., during the insertion phase). The cell is similar to that described above under zinc anode primary cells except that it can be



Figure 4.19 Intelsat-V Battery with 30 Ah IPV Cells

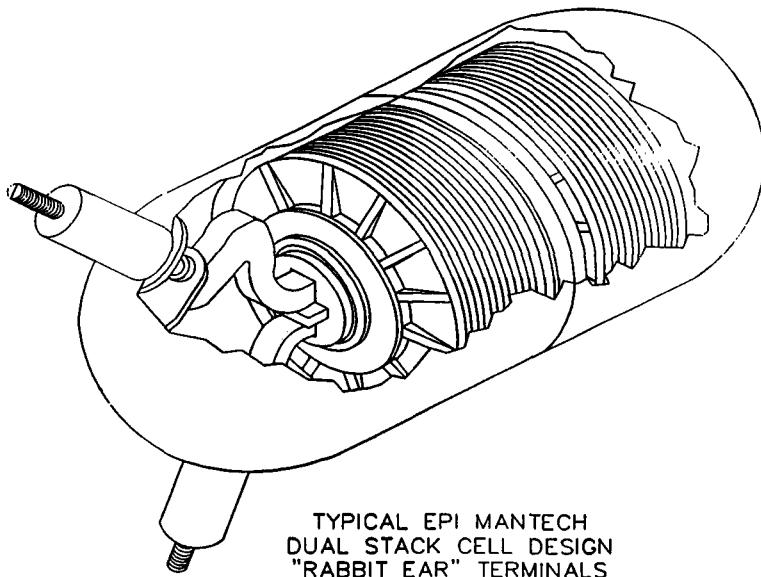


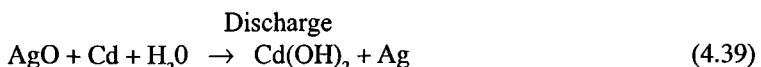
Figure 4.20 CPV Design Concept

recharged. However, because of the inefficiencies caused by gaseous reactions at the electrodes pressure relief vents are used in these cells.

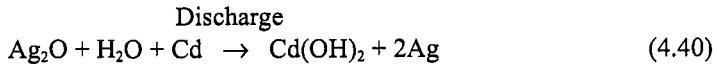
As described earlier, the silver oxide electrode is the cathode on discharge and anode on charge (polarity + on both charge and discharge). The zinc, cadmium, and hydrogen are the anodes on discharge and cathode on charge (polarity - on both charge and discharge). See Table 4.10 for the cell characteristics.

Silver-Cadmium (AgO-Cd)

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 process 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 a life-limiting process. The discharge reaction is given as:



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



The charging of AgO-Cd 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). H_2 is also generated on the Cd 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. H_2 evolution appears to be less of a problem with these cells than the Ag-Zn cells. 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.

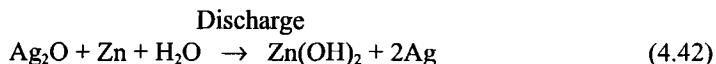
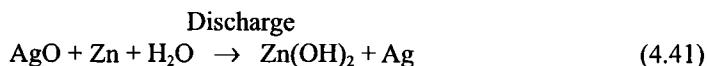
The advantages of this cell are: 1) higher specific energy than Ni-Cd , 2) higher volume energy density than Ni-Cd and Ni-H_2 , 3) nonmagnetic, and 4) less sensitive to overcharge than silver-zinc, while the disadvantages include: 1) short cycle life (better than Ag-Zn), 2) operation strongly dependent on temperature, and 3) lower voltage than Ag-Zn .

The potential hazards and suggested cautions are: 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 (prevented by performing seal and cell testing; white encrustation on seal or case is an indicator of a leak), 4) inspection and welder qualification and calibration are necessary (use rubber gloves in handling electrolyte), and 5) gas (H_2 or O_2) leakage creates cell imbalance leading to excessive pressure (perform helium leak testing on each cell; use high reliability, well-tested seals; external shorting can result in very high-rate, high temperature excursion, leading to a violent venting; use fuse and other protective circuitry).

Silver-Zinc (Ag-Zn)

The cell is a modified version of the primary Ag-Zn cell. The silver electrode is the same type as previously described. 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 Ag-Cd cell, the plates are also wrapped with layers of separator to prevent silver migration. Zinc dendrite formation is the major cause of life limitation. 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 discharge reaction is given by:



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

These cells are generally prismatic in configurations. The capacities available range from very low 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 Ag-Zn battery is also available in reserve configuration for very long storage periods prior to use. Cells with active electrolyte will lose capacity and therefore storing the electrolyte outside the cell will prevent the high self-discharge rate. Several planetary missions have used batteries of this type to meet long term inactive cruise requirements. Figure 4.11 is a photo of the Mars Pathfinder Lander Ag-Zn battery that landed on Mars, July 4, 1997.

Again, the advantages are: 1) highest specific energy and power of presently available secondary batteries, and 2) highest energy density and power of presently available secondary batteries. The disadvantages: 1) high cost, 2) limited cycle life, 3) poor low-temperature performance, and 4) a two-step voltage plateau. The potential hazards and mitigating actions are: 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 gauge 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; search for white encrustation leak, which requires inspection and cell assembler qualification and calibration; use rubber gloves in handling electrolyte), and 4) external shorting can result in very high rate, high temperature excursion leading to a violent venting (use fuse or other protective circuitry).

Lithium ion cells/batteries

Initially, rechargeable lithium cells were comprised of lithium foil as the anode material. A number of cathode materials were also investigated. Limited cycle life cells were demonstrated with Li-TiS₂ and Li-V₆O₁₃, however, concern for the safety of the lithium foil as a rechargeable electrode led to the conclusion that further development for space was not advisable.

An increase in power requirements for space missions has necessitated the development of high energy density rechargeable batteries. Among the 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 candidates for 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.

The development of a lithium ion cell, absent of lithium metal, offers an opportunity to significantly increase the specific energy and energy density, thus reducing battery mass and volume. The three types presently under development are the Lithium-Cobalt Oxide (Li-CoO₂), Lithium-Manganese Oxide (Li-Mn₂O₄), and Lithium-Nickel Oxide (Li-NiO₂). Of the three, only the first has demonstrated the potential for cycle life required for space. A major advantage of this system is the cell voltage of near 4 V per cell, a specific energy of 100 Wh/kg, and energy density in excess of 250 Wh/l.

The cell potential is based on the difference in potential between a cathode material containing lithium ion, such as Lithium Cobalt Oxide (LiCoO₂) and a carbon electrode that can intercalate lithium ion. When the lithium ions are in the carbon anode the cell is charged, and when the lithium ions return to the cathode matrix the cell is discharged. The most familiar of these is the Lithium-Cobalt Oxide (Li-CoO₂) cell. Although the lithium -ion cell has not been used in space to date, it has been added to the manifest of upcoming planetary missions, e.g., the Mars missions.

The basis for the Lithium-Ion cell concept appears in Figure 4.21. The cell is assembled with the Li⁺ intercalated in the cathode material, e.g., LiCoO₂, and a layered carbon or graphite anode. The cell is activated by charging, i.e., forcing the Li⁺ to flow into the anode structure. When the charging step is completed the potential difference is approximately 4.0 V. During discharge the Li⁺ flows back into the cathode during which time the cell voltage decreases. During the initial charge process there is some loss of the Li⁺ in the structure of the anode.

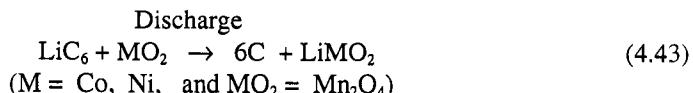




Figure 4.21 Examples of Li-Ion Cells

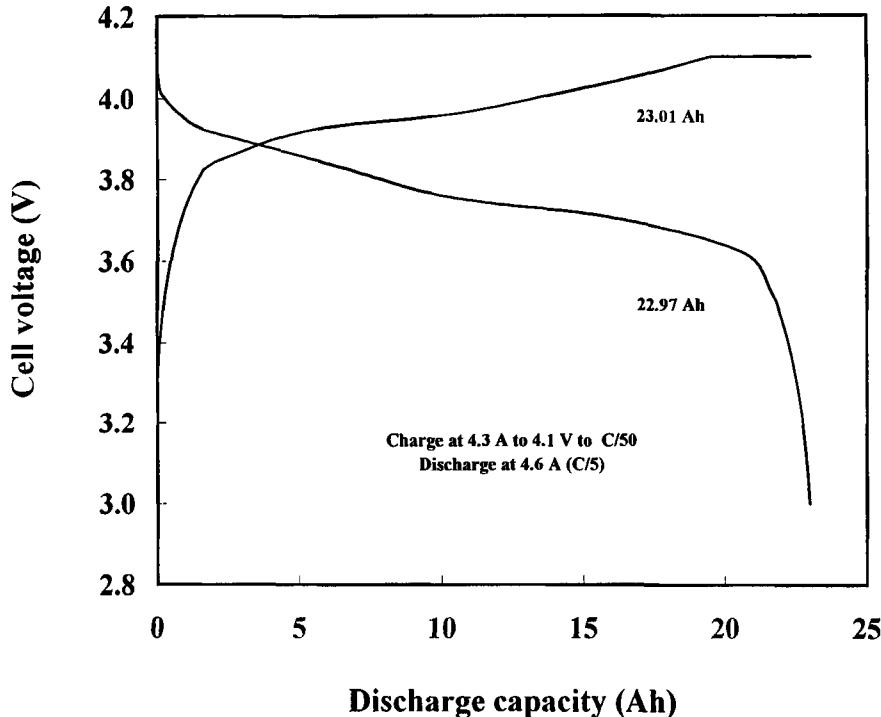


Figure 4.22 Charge and Discharge Curves of the Blue Star Li-CoO₂ Cell at the C/5 Rate

The electrolyte is generally a solvent mixture of Ethylene Carbonate (EC), Diethyl Carbonate (DE), and Dimethyl Carbonate (DMC), with a salt such as LiPF₆ or LiBF₄. Examples of flat plate, cylindrical, and prismatic design Li-Ion cells appear in Figure 4.21. The prismatic cells are from Yardney Technical Products and the cylindrical cell from Blue Star Batteries. The charge and discharge curves for the Blue Star LiCoO₂ battery at a C/5 rate are shown in Figure 4.22.

The advantages include: 1) cell voltage of 4.0 V, 2) high specific energy and energy density (4 x Ni-Cd and 2 x Ni-H₂), 3) 99% charge efficiency, 4) available for commercial products, 5) operation demonstrated at -20°C, and 6) no lithium metal in the cell. The disadvantages include: 1) relatively short cycle life (compared to Ni-Cd), 2) only small size cells available for commercial products, and 3) individual cell control to maintain cell balance.

There are two noteworthy potential hazards: 1) excessive overcharge and overdischarge can result in undesirable products, and 2) cell balance must be maintained to avoid cell imbalance, resulting in undesirable reactions.

Sodium cells and batteries

The sodium cell is a high-temperature technology that has generated significant interest in recent years. The Sodium-Sulfur (Na-S) system (350°C) continues to be tested by the U.S. Air Force for a potential space application. Lengthy cycle life has been demonstrated. However, the closest to space use is in an Air Force flight experiment launched in November 1996. Significant resources were allocated for this work for both electric vehicles and load leveling, and thus transfer of the technology for flight use appeared worthwhile for large spacecraft. However, the effect on materials of the high temperature, together with the change in NASA direction to 'smaller, better, cheaper' spacecraft, resulted in reduced interest in this technology. The Sodium-Nickel Chloride (Na-NiCl₂) system with lower operating temperature (250°C) and absent of molten sulfur appeared to be worthwhile. However, with the advent of the new NASA approach, this too was dropped from consideration for space use. The Na-S system is discussed below in view of the continued, albeit low, interest.

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:



The depth of discharge and operation determines the value of x which ranges from five to two.

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. 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.

The advantages of sodium cells include: 1) adaptability to large energy systems, 2) high peak power, 3) high level of support for development is available, and 4) large specific energy and energy density ideal for a secondary system. There are several disadvantages: 1) operation at 350°C, 2) materials and safety problems associated with high temperatures, 3) beta alumina technology refinement, 4) heat management, 5) high cost, and 6) the weight penalty for thermal management.

The potential hazard includes operation at a high temperature where molten sulfur and sodium are present separated only by a ceramic separator.

8. Fuel cell systems

A fuel cell system consists of a group of cells connected in series (fuel cell stack), the fuel and oxidant stored external to the stack, and ancillaries including pumps, plumbing, sensors, and controls to process the products and reactant product. The fuel cell system differs from a battery in that the reactants are stored outside the cell in cylinders. This arrangement infers that the more fuel and oxidant available the larger the energy storage capacity and the longer the fuel cell system will operate. Battery storage capacity, however, is limited by the quantity of active material contained within the case. Fuel cell stack power is the sum of the voltages of each cell times the current. The fuel cell system uses some of the stack power for operation of the ancillaries and thus will be less than the stack power. The capacity of a fuel cell system is determined by the quantity of fuel and oxidant stored. This is a convenient system for manned flight because the fuel cell system can be supplied with enough fuel and oxidant to meet the relatively short mission length and provide water and heat for life support. For longer missions, such as LEO and GEO, rechargeable batteries are used.

The applicability of a fuel cell power plant for space use has, besides the attractive features of being a pollution-free power source based on direct conversion with immovable parts, the primary advantage of its ability to be incorporated into the ecological cycle of the space crew. Further, liquid oxygen and hydrogen are also available for propulsion on board space vehicles because of their high specific impulse. These characteristics have extended the utility of fuel cell power sources for space use in the Gemini, Apollo, Shuttle, and Spacelab programs. The H₂-O₂ alkaline fuel cell has emerged as the most attractive candidate for space use.

While making a choice among suitable alternatives to meet the requirements of a spacecraft, the factors to be considered are: 1) reliability, 2) efficiency, 3) life, 4) environmental compatibility, 5) endurance to environmental conditions in space (zero gravity, vibration, shock, acceleration, acoustic noise, etc.), 6) energy densities, 7) storage, 8) heritage, and 9) cost. The reliability of the hardware, once a choice is made, will have to consider proper choice of materials, chemicals, and components of space grade and incorporate a detailed and stringent qualification test plan.

Fuel cells have been known from the time of Grove in 1839. Since then several types of fuel cells have been developed for various stationary, vehicular, and other applications. The types of fuel cells that have been or are being considered for space use include:

Alkaline Electrolyte H₂-O₂ fuel cells (AFC) which operate at 40 - 60°C, Proton Exchange Membrane Electrolyte H₂-O₂ Fuel Cells (PEMFC) which operate at 60-80°C,

The potential hazard includes operation at a high temperature where molten sulfur and sodium are present separated only by a ceramic separator.

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and Direct Methanol/O₂, Liquid-Feed Proton Exchange Membrane Fuel Cells (DMLFFC/PEM) operating between 20°C and 90°C.

Regenerative fuel cells using the PAFC, AFC, or PEMFC, together with an electrolyzer, are being considered for applications where charge and discharge operations are required. The electrolyzer, powered by solar cells, produces the fuel and oxidant to the fuel cell when solar energy is not available. This system has yet to prove feasible for space applications.

The most common fuel cell system used in terrestrial applications is the Phosphoric Acid fuel cell (PAFC) that operates at 250°C. Higher temperature fuel cells include the Molten Carbonate Fuel Cells (MCFC) which operate at 650°C, and Solid Oxide fuel cells (SOFC) which operate near 1000°C. These have not been used in a space application.

Molecular oxygen is the oxidant in these six types of systems, and molecular hydrogen is the fuel used in the AFC and PEMFC designs. In the latest innovation, DMLFFC/PEM, aqueous methanol in the form of a liquid is the fuel. The higher temperatures of the MCFC and SOFC allow a greater variety of fuels including hydrocarbons and diesel fuel. Except for the Biosatellite missions, only the alkaline and PEMFC have been used in space, specifically for manned space applications, i.e., Gemini, Apollo, and Shuttle spacecraft.

8.1 History

The first use of a fuel cell system in space was in the Gemini program, August 21, 1962. This was the first of the seven Gemini Earth-oriented manned missions from 1962-1965. A Proton Exchange Membrane Electrolyte Fuel Cell (PEMFC), known at that time as the Solid Polymer Electrolyte Ion Exchange Membrane Fuel Cell, was used. The solid ion exchange membrane (sulfonated polystyrene resin) served as an alternative to the aqueous liquid electrolyte providing a path for the H⁺ to move from anode to cathode. Providing a mechanism for the H₂ and O₂ required the use of a platinum catalyst.

The system produced by General Electric provided 350 W for each fuel cell module. Three stacks of 32 cells were used in parallel to provide a total 1 kW for the spacecraft fuel cell system. Cryogenic H₂ and O₂ were used. The Platinum (Pt) catalyst loading was 28 mg/cm². The H₂ supply pressure was 1.6 psi above water pressure and O₂ was 0.5 psi above H₂. The efficiency was reported as 50-60%. Although the mass of the system was lower than the others, limitations of this fuel cell technology were the voltage losses due to ohmic drops in the solid electrolyte and sensitivity to water content.

The Biosatellite 2 launched September 7, 1967, utilized a similar PEMFC system, with an important change. The PEM was Nafion (perfluorosulfonic acid), a registered

trademark of the Dupont Company. Since then, Nafion has been the membrane of choice for all PEM fuel cells, including the DMLFFC/PEM.

To overcome the limitations of the Gemini PEMFC, Apollo manned flights (1968 - 72) utilized the alkaline electrolyte fuel cell (AFC). The electrolyte was potassium hydroxide (KOH) . The fuel and oxidant were H₂ and O₂. These fuel cells used an asbestos separator. The reactions for the alkaline fuel cell system are addressed in Section 8.3.

The Apollo fuel cell plant developed air and particulate contamination problems. These were trapped in the coolant system and resulted in pump cavitation. This was solved by improving servicing procedures. Another problem observed onboard was temperature oscillations due to low gravity and flow instability under certain operating conditions. This was solved by valve schedule changes. Problems in two-phase fluid handling (caused by the microgravity environment) were avoided by the use of a supercritical stage. Problems faced with insulation, heaters, pressure vessels, fans etc., were all solved by improved system design, quality control, and manufacturing/ maintenance procedures, although these failures were observed in Apollo 13.

The 1.5 kW, 26 V power plant was developed by Pratt and Whitney, a Division of United Aircraft Technologies. The total fuel cell utilized three fuel cell modules connected in parallel. The fuel cell operated at 260°C increased from the original temperature of 205°C to improve performance. A platinum catalyst was not needed. The pressure of the fuel and reactant were 60 psia. The system operated at 150 mA/cm² and the voltage was 0.72 V/cell. The peak power was 2.3 kW at 20.5 V, and the fuel cell weighed 100 kg. It operated for 690 hours without failure.

The Shuttle orbiter, developed by United Technologies Corporation and in use today, contains three H₂-O₂ alkaline fuel cell power plants supplying 12 kW at peak and 6 W average power in performance. Asbestos is also used as the separator. The operating temperature is 83-105°C. The current density is 66 - 450 mA/cm². The system is capable of 2000 hours of operation. The Shuttle orbiter fuel cell power plant was 23 kg lighter and delivered eight times the power of the Apollo fuel cell system. For additional details see Table 4.12.

In the Shuttle fuel cell plant there was a H₂ pump seizure problem which was solved by appropriate design changes followed by a 2000 hour qualification test. The magnesium separator plates in contact with water corroded, and this was solved by plating them with nickel. Cell-to-cell voltage variations resulted in a significant drop in the total voltage. These were solved by coating the electrode surfaces with special materials and leaching the asbestos matrix to remove cadmium impurities. In STS-2, water contamination resulted in non-nominal operation of the H₂ pump. By incorporating suitable filters and making changes in the recirculatory system, the problems were solved.

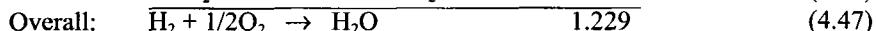
NASA is considering upgrades in the fuel cell system. Among these is the use of the Proton Exchange Membrane technology. Significant improvements have been made since their use in the Gemini mission. The PEMFC and the DMLFFC/PEM are also

being considered for use in lunar, Mars colony, and Rover applications. Another development under consideration is a rechargeable fuel cell system known as a Regenerative Fuel Cell System. It combines an electrolyzer that can produce the H₂ and O₂ during the sunlight portion of a mission using solar cells and a fuel cell stack that can provide the energy during the eclipse period. To date, the system has not met the performance requirements required for a mission.

8.2 Fuel cell system basics

In the common acid electrolyte fuel cell, fuel (H₂) reacts electrochemically at a catalyzed anode electrode/electrolyte surface to produce protons (H⁺) and electrons which flow through the load to the cathode. The protons diffuse through the electrolyte and react with O₂ to produce water at the negatively charged cathode electrode/electrolyte interface. The fuel cell useful in space applications can generally be described as consisting of two electrodes separated by and in direct contact with an electrolyte. The electrolyte can be acidic, either liquid (phosphoric acid) or solid (Nafion), or alkaline. Conductive biplates are in contact with the anode of one cell and the cathode of the adjacent cell. Thus, they separate the cells and conduct the electrons through the stack resulting in a positive terminal at one end of the stack and a negative terminal at the other end. On both sides of the biplate are flowfields that allow the fuel and oxidant to come in contact with the anode on one side and cathode on the other maximizing the contact area. The fuel and oxidant flow to the cells is provided by an internal or external manifold so that they flow into the flowfield of all cells at the same time. The fuel cell concept is given in Figure 4.23.

The reactions for the PAFC are:



The electrochemistry fundamentals and thermodynamics of this system are the same as those discussed in Section 4.4. However, there are important differences between the fuel cell parameters and those of a battery. While capacity is the parameter that best characterizes the battery cell capability, power best describes the fuel cell capability. The capacity is increased or decreased by the volume of stored fuel and oxidant. The fuel cell polarization curve is given in Figure 4.24.

Table 4.12 Comparison of Gemini, Apollo, Shuttle Fuel Cell Characteristics

	Gemini	Apollo	Shuttle
No. Flights	7 (#5-12)	All	All
Manufacturer	General Electric	P & W	United Tech. United Aircraft
Type PEMFC	AFC	AFC	
Power Module	500-620 W s	1.5 kW	14 kW
continuous	3 -350 W modules	3 modules	3 modules
1 kW Peak	Peak 2.3 kW at 20.5 V	36 kW peak	
Cell temperature	40 to 60°C	200-250°C	83 - 105°C
Voltage	23.3 - 26.5V	26 - 31 V	26.5 -32.5V
No. of sections per s/c	2	3	3
No. stacks/section	3	2	
No. cells/stack	32	31	32
Stack Size, cm	66 x 33 diam	110 x 56 diam	35 (h)x 30(w)x 01cm(l)
Battery weight, Kg	31	110	91
H ₂ / O ₂ Oper Pressure	22 /23 psia	60 / 60 psia	60 /60 psia
H ₂ Storage pressure:	210 to 250 psi	245 psi	290-290 psi
O ₂ Storage pressure	800-psi	900 psi	850-950 psi
Current density	15 (mA/cm ²)	92	67 - 450
Electrolyte	Sulfonated polystyrene	85% KOH	30 - 40 % KOH
Efficiency	50 - 60%	60%	61.8% @6 kW
Service life	400 - 800 Hrs @ .5kW	400 - 1500 Hrs @ 1kW	2000 Hrs @ 4.5 kW
Reactant used	0.41 kg/kWh	0.36 kg / kWh	450 kg / 600 L
/ 3 day Mission	Composition Rate	0.55 kg / Hr	
Time in Space	840 Hrs	1995 Hrs	Serviced 2000Hrs

Power

Power, the product of current and voltage, describes the capability of the fuel cell to convert the fuel and oxidant into the product water. The larger the electrode surface and the more active the surface, the greater is the current capability. In addition, the voltage is affected by ohmic, activation, and concentration polarization, as well as temperature. Therefore, power as a function of temperature and rate is used to describe the capability of a fuel cell or fuel cell stack.

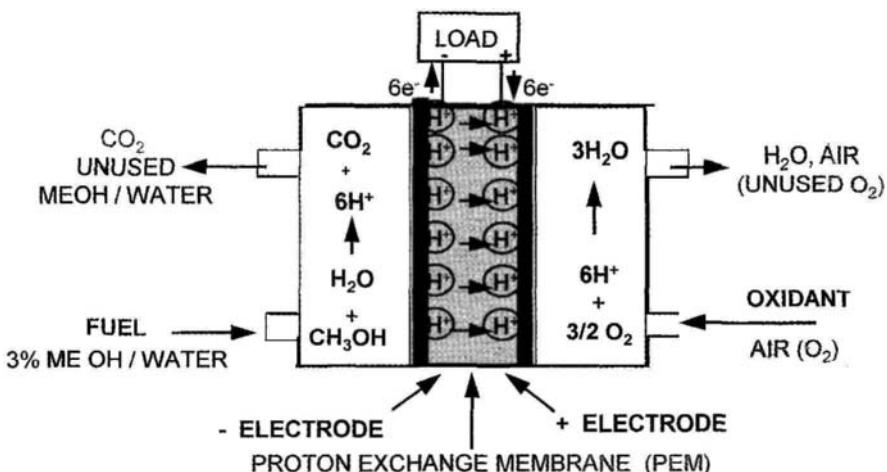


Figure 4.23 Fuel Cell Concept

Efficiency

The theoretical thermal efficiency, ϵ° at 25°C is 0.95 as determined by:

$$\epsilon_{th}^\circ = \Delta G_{298} / \Delta H_{298} \quad (4.48)$$

where ΔG_{298} , the change in free energy, is -54.63 and ΔH_{298} , the change in enthalpy, is -57.80. This equation can also be shown to be:

$$\epsilon_{th}^\circ = nFE^\circ / \Delta H_{298} \quad (4.49)$$

and thus, the actual thermal efficiency of a fuel cell can be calculated from:

$$\epsilon_{th} = nFE / \Delta H_{298} \quad (4.50)$$

where n is the number of electrons, F is the Faraday constant, E is defined as kinetic losses minus resistive losses, and ΔH_{298} is the change in enthalpy at 25°C.

The voltage efficiency can be shown as:

$$\epsilon_v = E_{meas} / E^\circ \quad (4.51)$$

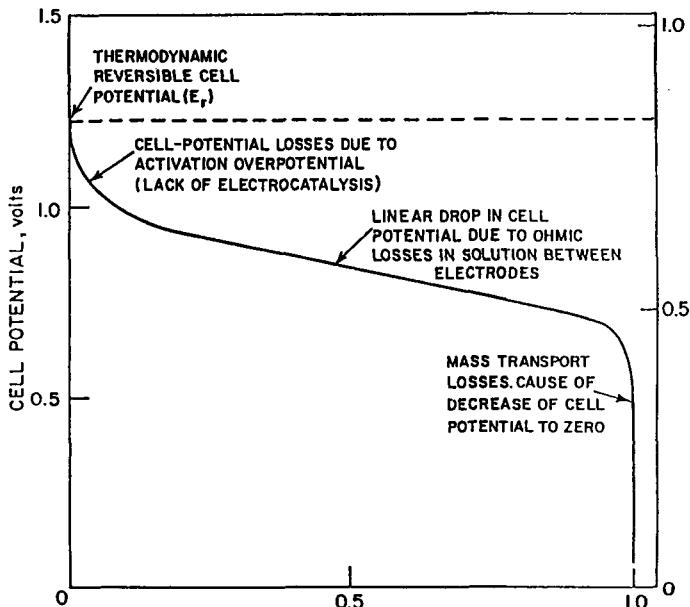


Figure 4.24 Fuel Cell Polarization Curve

The electrochemical efficiency, ϵ_{ee} , can be shown to be the product of the thermal, voltage, and current efficiencies.

8.3 Alkaline fuel cells

The reactions of the alkaline fuel cells are somewhat different from that of the acid fuel cells because of the pH. However, the E° is the same for both. The reactions are:



The fuel cell system (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 electrochemi-

cal 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.

The advantages include: 1) very high energy density, 2) few moving parts, 3) moderate operating temperature, 4) dual use for oxygen (can be used for life support), and 5) high thermal efficiency. The disadvantages include: 1) high cost, 2) complex assembly (numerous interconnecting parts), and 3) complex operation (many controls are required).

There are a number of potential hazards accompanying the use of fuel cells: 1) external H₂ leaks can produce explosive conditions, 2) internal H₂ and O₂ leaks cause local hot spots and also explosive conditions, 3) external O₂ leaks can cause fires, 4) shunt currents can cause internal generation and mixing of gases with resultant heating, 5) age of manifolds can cause cell reversal and subsequent generation and mixing of gases with resultant heating, 6) inadequate cooling can cause thermal runaway (thin bipolar cell stacks can be readily shorted without proper insulation and handling), and 7) the alkaline electrolyte is corrosive and toxic.

8.4 Proton exchange membrane fuel cells

The simplest of the fuel cell systems is the proton exchange membrane type. The electrolyte is a polymer film, Nafion (perfluorosulfonic acid), and thus the complexity of requirement for a liquid electrolyte is eliminated. The reactions are the same as in the phosphoric acid fuel cell system as is the theoretical E° for the reaction.

This system operates at a temperature to 80°C, a significantly lower temperature than the alkaline system. It was first used in the Gemini and Biosatellite spacecraft. However, it lacked the power of the higher temperature alkaline system. The operating temperature of the PEMFC is limited because of the 120°C melting point of the polymer membrane. In addition, the fuel and oxidant had to be humidified before entering the

fuel cell stack to avoid dryout and degradation of the Nafion membrane. The Gemini system also had a water control problem. For these reasons, the alkaline system was selected for the Apollo and Shuttle orbiter applications.

Because of the advantage of system simplicity, due to the solid electrolyte, this system is receiving attention as an upgrade to the orbiter and additional NASA applications.

The Gemini fuel cell stack assembly consisted of the ion exchange membrane and platinum catalyst. Each side of the membrane was covered by a titanium screen which was coated with platinum. One side of the membrane was bonded at its edges to a titanium sheet to form the cavity for the hydrogen gas. Hydrogen was introduced into the cavity through a tube connected to the edge seal. Two loops of coolant tubing were placed against the other face of the titanium sheet and wicks were placed between each pass of the tubing to remove the water produced at the cathode. These were necessary to prevent accumulation of water at undesirable places in a zero gravity environment. A total of 32 such assemblies were bolted together between end plates to form the stack assembly. Each stack contained its own hydrogen and coolant manifolding and water-oxygen separator. These stacks were installed in a cylindrical container to form the fuel cell section. Two such sections were used onboard each Gemini spacecraft.

8.5 Regenerative fuel cells

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 completely 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.

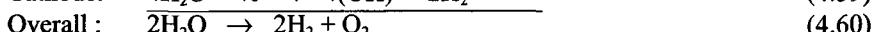
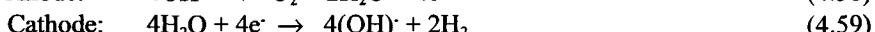
In the primary fuel cells, the H_2 and O_2 gases from the storage reservoirs are fed via manifolds to the anodes and cathodes of the cell stacks. Here the gases react electrochemically to produce electrical energy. The specific electrochemical reactions that take place within the cells depend on whether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

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 heat 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 H₂ and O₂ 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:



In the alkaline electrolyzer:



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 unity or the other to maintain operating temperatures. This is provided by circulating the hot coolant from one to the other via the heat exchanger.

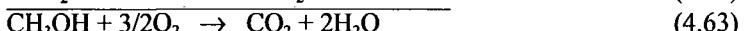
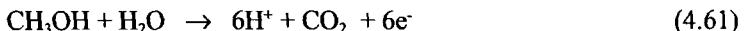
The regenerative fuel cells are intended for use on long term orbital missions requiring very high power levels up to 500 kW. These missions include a wide range, from low Earth orbit to geosynchronous orbits. In these applications, the cells serve the same function as rechargeable batteries, i.e., to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

The advantages include: 1) high energy density (mass), 2) projected high cycle life, and 3) built-in state of charge indicator. The disadvantages include: 1) low volumetric energy density, 2) high cost, 3) relatively low energy efficiency, 4) complex assembly (numerous interconnecting parts, and 5) complex operation (many controls required). The potential hazards are: 1) all of the same hazards of primary fuel cells above, and 2) external leakage problems are enhanced by high pressure storage and numerous gas plumbing connections.

8.6 Direct methanol liquid-feed fuel cell/PEM

In 1991, a breakthrough in fuel cell technology was demonstrated by the Jet Propulsion Laboratory and the University of Southern California on a U.S. DARPA-sponsored pro-

gram. This fuel cell is similar to the PEM cell described above that uses H₂ as the fuel. This technology utilizes an aqueous liquid methanol solution (presently only 3%) directly without reformer as the fuel. Methanol has a theoretical capacity of 5 kW/liter. The Direct Methanol, Liquid-Feed, Fuel Cell with Proton Exchange Membrane (DMLFFC/ PEM) uses either compressed air or oxygen as the oxidant. The only products of reaction are water and carbon dioxide. The system is being considered for use on Mars where the concentration of CO₂ is high and the product would not have an effect. The reactions of the DMLFFC/PEM are:



Laboratory versions of the fuel cell operating directly on a 3% methanol/water solution at a temperature of 90°C have delivered a continuous output of 50 A on a 4" x 6" electrode (300 mA/cm²) at 0.55 V with oxygen. The peak power of >320 mW/cm² occurs at 100 A. The size of a 5 kW stack is projected to be an 8-inch cube with a weight of less than 1 kg.

A 50 W DMLFFC/PEM full system has been demonstrated using a recently developed methanol sensor that controls the flow of methanol to the aqueous mixing tank. Two twelve-cell DMLFFC/PEM stacks (eleven cells per inch) in parallel were integrated into a complete system and continuous operation was demonstrated.

The DMLFFC/PEM concept is shown in Figure 4.25. The heart of the technology is the central section that comprises the .020-inch thick membrane electrode assembly (MEA). The MEA consists of the proton exchange membrane sealed between two carbon electrodes containing the catalyst. The 3% aqueous methanol enters the anode chamber and is converted at the electrode interface to six protons (H⁺), six electrons (e⁻), and carbon dioxide (CO₂). The protons diffuse through the membrane and react at the Cathode interface with air and the returning electrons to produce water. The theoretical energy density of methanol is five kWh/liter compared with cryogenic hydrogen of 2.7 kWh/liter. An efficiency of 34% or 1.7 kWh/liter has been achieved in a five cell stack.

The Nafion, in addition to serving as a good proton conductor, also allows methanol to diffuse from anode to cathode. The reaction at the cathode is equivalent to oxidizing methanol, with CO₂ and water as the same products as the electrochemical reaction. However, the result is a loss in efficiency of approximately 20%. A new membrane, with the same conductivity as Nafion and reduced methanol crossover to <5%, will be implemented to increase the stack efficiency from 34 to 45%.

Figure 4.26 is a closed system conceptual design. Its simplicity, compared with hydrogen or methanol-reformed systems, is due to liquid aqueous fuel circulation thus avoiding humidifiers and thermal fins (estimated at every fifth biplate) used to remove

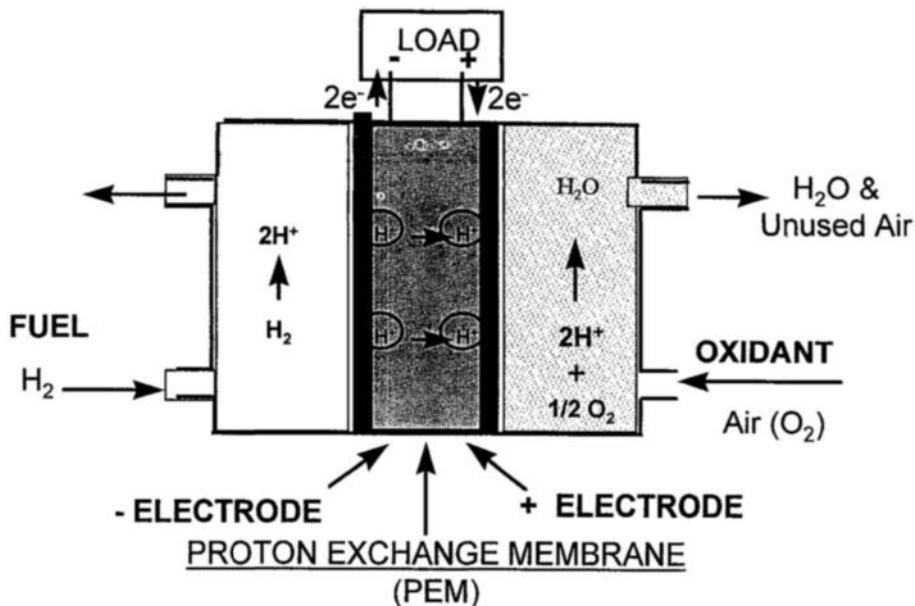


Figure 4.25 Schematic of a DMLFFC/PEM

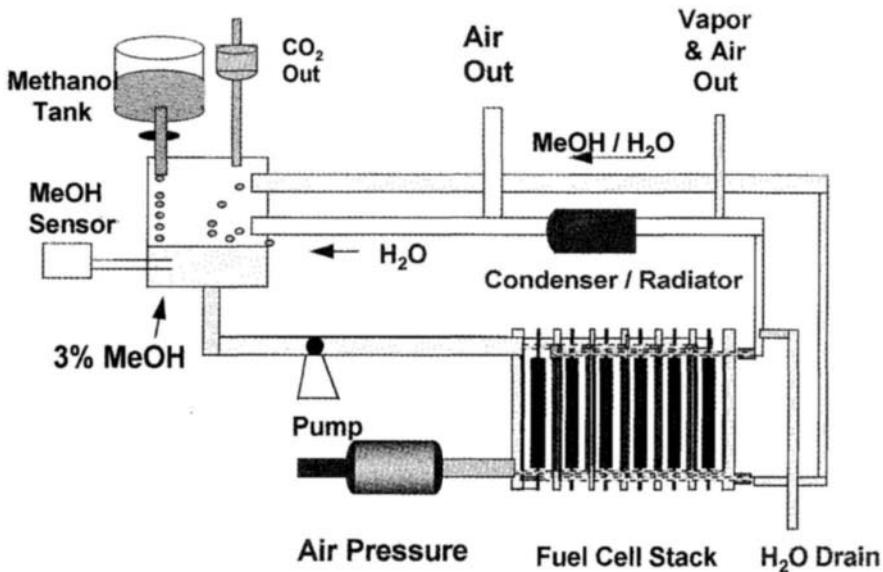


Figure 4.26 Direct Methanol, Liquid-Feed Fuel Cell Schematic

heat in the stack. Methanol from the fuel tank is mixed with recirculating water from the stack output to produce the desired concentration. The aqueous fuel is fed into a manifold that allows the fluid to flow past the anode in each cell. The aqueous fluid, less the reacted methanol, returns to the mixing tank for methanol addition. The carbon dioxide is released as a gas. Likewise, pressurized or unpressurized air flows past the cathode of each cell. The water produced is picked up in the air stream and returned to the mixing tank. Depending on temperature and application, the water can be released as a vapor or liquid. For obvious reasons, this new technology is also being considered for a number of commercial applications including electric vehicles, marine and RV use, electronic and consumer devices, and remote and emergency power.

The advantages include: 1) no harmful emissions (important for use on Mars), 2) elimination of fuel vaporizer, 3) elimination of complex and voluminous humidification systems, 4) more efficient thermal management systems, 5) significantly lower system complexity, size, and weight, and 6) a projected 45% efficiency.

There are three main disadvantages: 1) limited to use on Mars or other planetary missions, 2) lower performance compared to the AFC, and 3) the Nafion membrane allows methanol to diffuse from anode to cathode reducing efficiency

9. Definitions and terminology

Anion: A positively charged ion.

Anode: The electrode at which oxidation takes place releasing electrons to the load.

The anode can consist of many plates of the same polarity strapped together and tied to a current collector.

Battery: Two or more cells connected in series, parallel, or a combination of both, or a single cell used as a single cell battery.

C Rate: A method for describing the charge and /or discharge current relative to the cell capacity. 'C' is the manufacturer's or nominal cell capacity. Therefore, the 'C' rate is the current used to discharge a cell or battery in 1 hour, i.e., 'C'/1. To discharge the battery in 2 hours, the C/2 rate or 2 hour rate, etc. The same designation is used for charge as well.

Capacity: This is the term used to describe the electrical storage capability of an electrochemical cell or battery. It equates to the integral of the number of amperes provided by the battery over the number of hours the battery is discharged. The three terms below are used to describe capacity:

a) Theoretical Capacity (Ah_T) - The capacity of a cell as derived from the theoretical conversion of the quantity of stored electrochemical active materials to electrical energy. For example, in Eq. (4.4) above, if the mass of zinc was 65.4 g (the atomic weight), the Ah_T for the two electron reaction would be $2 \times 26.8 \text{ Ah} = 53.6 \text{ Ah}$.

b) Actual or Measured Capacity (Ah_A) - This is the capacity measured from the state of full charge until the cell or battery energy is depleted as determined by a severe voltage drop when discharging through a load similar to that for planned use.

c) Manufacturer's Rated or Nominal Capacity (Ah_R) - This is the value the manufacturer labels the cell or battery as its design capability achievable over a range of operating conditions, e.g., rate and temperature. For ambient conditions and nominal rates, the Ah_A is generally 5-20% higher than the Ah_R .

Cathode: The electrode in the cell at which reduction takes place by accepting the electrons released at the anode. The cathode can consist of many plates of the same polarity strapped together and tied to a current collector.

Catholyte: Used in cells where the electrolyte also serves as the reactant at the cathode (as in lithium-thionyl chloride cells where the solvent and the reactant at the cathode are the same - Thionyl Chloride).

Cation: A positively charged ion that reacts at the cathode.

Cell Reversal: This occurs when the polarity of the cell is reversed. The cell is driven into a negative voltage by continuing the discharge beyond the cell's useful capacity. (see *Overdischarge*).

C/D Ratio: The ratio of Ah_{in}/Ah_{out} with rechargeable cells (a way of defining inefficiency, the inverse of coulombic efficiency).

Charge Rate: This is the rate or current used during charge. It can be described in amperes or as fractions of C' rate in relation to the cell capacity, low rates are considered to be < C/50, moderate rates C/50 to C/10, and high rates > C/10. However, bear in mind that high rate for one type of cell, e.g., lithium anode types, may be a moderate rate for another type, i.e., aqueous secondary cells.

Charge Retention: The capacity remaining in a cell or battery after being on open circuit stand where it can experience self-discharge.

Charging: The process in which electrical energy removed from the battery is returned to stored chemical energy by reversing the electron flow.

Corrosion: The wasteful consumption of cell components by conversion to non active materials by the galvanic action.

Coulombic Efficiency: The ratio of the measured capacity divided by the ampere hours required to return the cell or battery to full charge (Ah_{out}/Ah_{in}). Also, known as electrochemical efficiency.

Current Collector: The low resistance metallic portion of the anode or cathode at which electrons collect and are transferred to the terminal. This is sometimes referred to as the busbar.

Current Density: Current per unit of active electrode area (Amps /cm²).

Cycle Life: The number of charge / discharge cycles the cell or battery has experienced in the regime in which it has been operated. It is occasionally reported in term of years or months.

Dendrite: The deposition of active material between anode and cathode which can serve as a means for internal discharge of a cell either temporarily or permanently.

Depth of Discharge: The 'DOD' is usually given as a percent of the total capacity removed from the cell or battery during a given cycle.

Discharge: The spontaneous removal of current from a cell or battery through a load resulting from the potential difference between electrodes.

Discharge Plateau: The relatively flat portion of a discharge curve occurring at the middle of the discharge period.

Discharge Rate: The same as charge rate except applied to discharge.

Electrochemical Efficiency: See *Coulombic Efficiency*.

Electrode: One or more electrochemically active plates in a cell containing stored chemical energy that can be converted to electrical energy and vice versa.

Electrolyte: A liquid or solid solution consisting of a solvent containing a dissolved ionic salt, thus forming an ionically conductive solution.

Energy Density: A figure of merit expressing the stored energy as a function of volume (Wh/Liter or Wh/in³).

Energy Efficiency: The ratio of output energy to input energy (Wh_{out}/ Wh_{in}).

Energy Storage: The energy storage capability of a cell or battery is given in terms of Watt hours = the integral of the voltage capacity product.

Float Charge: The process of using continuous voltage controlled low-charge current to offset self-discharge.

Flooding: Complete or almost complete filling of a cell with electrolyte to maximize the electrode/electrolyte contact. In some cell types this is detrimental because it minimizes the gas/electrode/electrolyte contact .

Formation: A series of charge and/or discharge operations performed on a newly manufactured cell or battery to condition it for service.

Grid: A metallic screen or perforated sheet that serves as a mechanical support and/or current collector within the anode or cathode structure.

Intercalation: The process in Lithium-Ion rechargeable cells wherein active species are inserted into the layers of a host compound such as Li⁺ into graphite.

Ion: A species in which there is an excess or deficiency of electrons when compared with the number of protons in the nucleus. Negative ions (Anions) are formed by an excess or addition of electrons; positive ions (Cations) have less electrons than protons.

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 wherein the reactant releases electrons that can support a reduction reaction; one-half of a redox reaction.

Plate: One of many structures containing similar anode or cathode active material. The

anode plates are strapped to a current collector to comprise the anode electrode; the same as for the cathode plates.

Packaging Factor: The ratio of battery mass or volume to mass or volume of all the cells in the battery. Prismatic cells have low packaging factors, cylindrical cells have high packaging factors.

Passivation: A process by which poorly soluble reaction products deposit on the electrode surface reducing electrode capability either by voltage or capacity loss.

Plaque: A porous body of conductive inert metal part of an electrode plate that is used as a container for active material and current collector in some cells, e.g., Ni-Cd.

Polarization: The voltage offset due to electrical, ionic, or kinetic impedance. The three types of polarization are: Resistance , Activation , and Concentration.

Reduction: The process wherein the reactant uses electrons that are released by the oxidation reaction; one-half of a redox reaction.

Reserve Battery: A dry cell or battery activated with electrolyte stored external to the cell. It is used in cases where the cell or battery exhibits a high self-discharge rate.

Sealed Cell: A cell that is sealed and isolated from the atmosphere.

Self-discharge: The spontaneous discharge of a battery while standing on open circuit (without load) due to reactions between the cell components.

Separator: An electronically insulating material which provides mechanical separation of anode and cathode plates and a path for ionic conduction. The separator can also serve as the reservoir for electrolyte in cells which contain minimum electrolyte.

Sintered Plate: An electrode formed by sintering metallic powders to form a porous structure which can contain the electrode material and current collector.

Specific Energy: The Specific Energy (SE) in Watt-hrs/kg is a parameter which describes the energy storage capability of a cell or battery in terms of terms of mass. The SE of a battery must take into account the battery mass including all electrical and mechanical parts.

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. This type of cell is sometimes referred to a 'semi-dry' or 'semi-wet' cell.

State of Charge: That percentage of the total available active material 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 conductive support used as a plate support and as a current collector. It is used as a base on which the active material is placed.

Taper Charge: A charging method wherein the charge current is reduced as the cell or 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 with a minimum of damage due to overcharging. (countering the self-discharge)

Utilization: That fraction of electrode active material mass that can be electrochemically converted from chemical to electrical energy or the reverse.

Voltage Limit: During charge, the limit above which the battery potential is not permitted to rise.

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where (CF_x) acts as an intercalation compound. Li- (CF_x) cells were initially used in a launch vehicle safety application. However, since the Shuttle accident, use has been discontinued.

Lithium Solid Electrolyte Cells

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

Lithium-Iodine (Li-I₂)

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:



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

The advantages include: 1) excellent storage capability (~10 years), 2) sealed (no leakage), 3) wide operating temperatures, and 4) safety. The disadvantages include: 1) low current drain only, and 2) low power capability. The potential hazards include placing the cell in a flame could result in a venting or deformation.

7.2 Rechargeable cells and batteries

Rechargeable or secondary cells and batteries differ from the primary cells and batteries in that the chemically stored energy used during the discharge can be returned to the chemical form by recharge. This is accomplished by causing a source of electrons from the solar array or power supply to flow in the reverse direction from that of the discharge direction. When this occurs the reactions are reversed and therefore the electrode that served as the anode on discharge becomes the cathode on charge. The cathode where reduction took place during discharge becomes the anode where oxidation occurs. Similarly the anode becomes the cathode. Even though the reactants and products are changing, the polarity remains the same as that during discharge because the quantities of active materials are primarily in the charged state. A diagram of charge and discharge configurations is shown in Figure 4.15 for the Ni-Cd cell.

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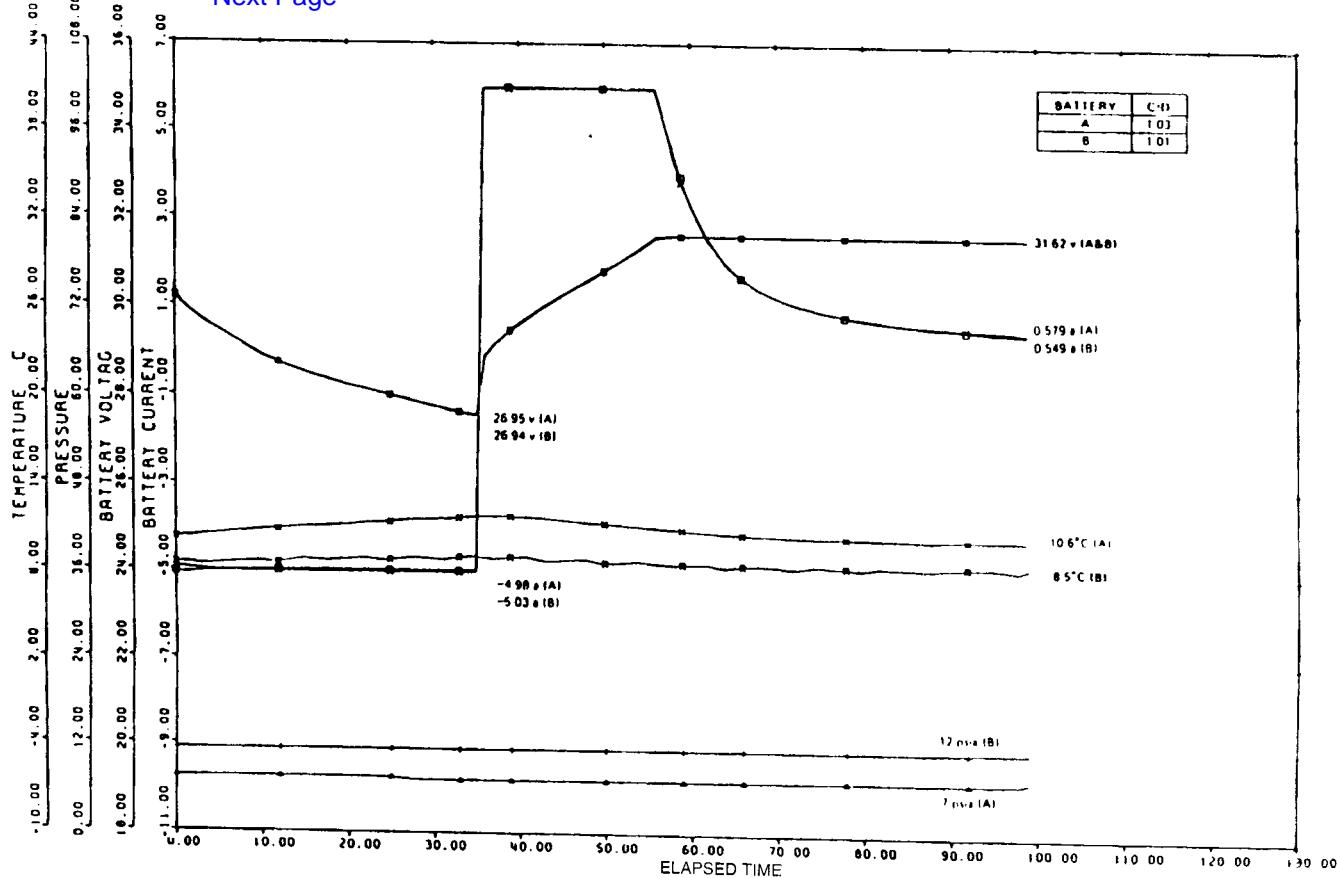


Figure 4.10 The Performance Characteristics of a Ni-Cd Battery During V_T Operation