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DESIGN, DEVELOPMENT, PERFORMANCE, AND RECONDITIONING OF Ni–Cd BATTERIES USING POLYPROPYLENE SEPARATORS

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Summary

This paper relates the experience with the 1975 Viking Mars Lander program sealed, sterilizable, eight ampere hour (A h) nickel–cadmium (Ni–Cd) batteries using nonwoven polypropylene separator material

Included in the discussion are cell and battery properties, design and development testing information (including environment testing), life test data, and shallow and deep discharge reconditioning results

Insights into such problems as separator wettability, optimizing electrolyte quantity, and plate carbonate reduction are provided. Thermal considerations are discussed, including the special requirement for withstanding sterilization temperatures of up to 275 °F (135 °C) for 40 h Other environmental design and test requirements, including the mission requirements and constraints are included.

The cell characteristics are identified, and the approach to cell matching and selection are explained. Life data based on actual mission experience identifies performance, degradation and the results of first, a series of shallow discharge reconditioning cycles, and later an intensive program of deep discharge reconditioning

A brief discussion of the power system and the software modeling of the batteries, as well as modeling of the power system, provide the background for some of the discussions

Introduction

Secondary Ni–Cd batteries have long been the mainstay of Earth-orbiting and planetary spacecraft orbiting missions. Typically, the cell separator material used was nylon and was expected and was found to last three to five and more years in the intended applications.

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Environmental requirements included temperature cycling, sinusoidal vibration, random vibration, acoustic shock, and pyrotechnic shock for survival of launch environments For space environment survivability, thermal–vacuum testing was required. Charge/discharge cycling was used for cell matching and selection and certification of design life Except for minimal variations in the above test requirements, based on peculiarities of different launch vehicles or anticipated spacecraft or satellite environments, no severe requirements or constraints were imposed on the design or material selection for the cells or batteries until the introduction of the Viking Mars Lander program

In addition to the customary launch, orbiting, and life design requirements, a planetary quarantine (PQ) constraint restricting introduction of Earth-originating biota to the Martian surface environment imposed a high temperature sterilization requirement on the design of the cells as well as on the entire spacecraft Material selection for such things as cell separators became a concern Traditional nylon separators would not satisfactorily survive the sterilization temperature cycling, so other materials had to be considered.

Polypropylene was investigated and was ultimately selected as the separator and the design was begun

Requirements

The mission design required batteries that would survive not only the environments described in Table 1, but also an eleven month Earth–Mars cruise mission, a Mars orbit duration (approximately one month) for Lander

TABLE 1

Electrical and environmental requirements for flight cells and batteries

Test requirements	Cell tests	Battery tests	Test
Seal leakage	X	X	He gas detection ($< 1 \times 10^{-8}$ std cm^3/s)
Electrical characteristics	X	X	Voltage/time at different rates
Cycle life	X		10 000 LEO* cycles (0 - 40 °C) of flight-type cells
Sterilization	X	X	111 °C for 54 h 123 °C for 40 h
Landing shock		X	30 g peak, 1/2 sine pulse 22 ms duration
Random vibration		X	10 g rms, 5 min/axis
Sinusoidal vibration		X	1 016 cm double amplitude 7.5 g, 19 - 250 Hz, back at two octaves/min

*LEO low earth orbit

site selection, a descent to the Martian surface (approximately 4 - 6 h) resulting in up to 75 percent depth of discharge (DOD), and a 90-day landed mission

The mission objectives were many, but primarily were concerned with the determination of the existence of life, past or present, characterization of the Martian atmosphere, and surface composition in the Martian environment (approximately 0.38 of Earth's gravity) The landed mission would require many cycles of 20 - 40% DOD which would result in elevated battery operating temperatures.

Power system

Figure 1 is a block diagram of the Viking Lander power system [1]. During the cruise mission, the Viking Orbiter supplied unregulated solar panel power to the Bioshield Power Assembly (BPA), which conditioned the raw power and provided equipment and battery charging power at a charge rate of *C*/15 or *C*/40. During the landed mission two series-connected 35 W radioisotope thermoelectric generators (RTG) supplied the equipment and the battery recharging energy. Redundant shunt regulators dissipated the excess RTG power when not required for equipment loads or battery charging. Batteries were sequentially charged one hour out of every four at a charge

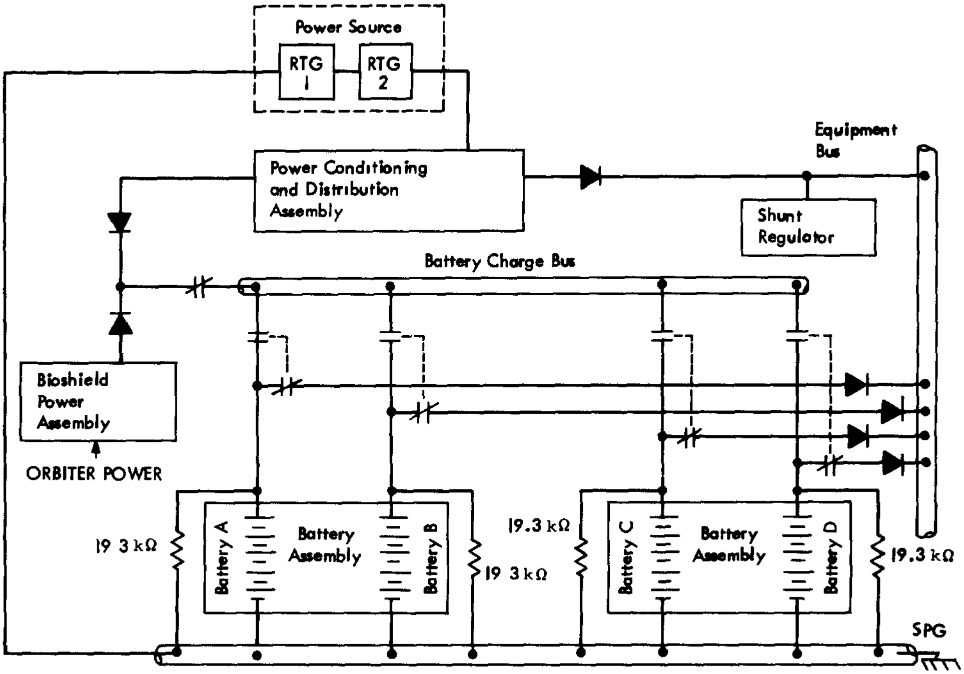

Fig 1 Viking Lander Power System block diagram [1]

rate of $C/15$ - $C/8$. Power conditioning and distribution to the subsystems was provided through the power control and distribution assembly (PCDA) electronics

The PCDA contains redundant converter/chargers, one being maintained in a standby mode, which provide regulation of the low voltage RTG output and draw constant power from the RTGs The redundant battery chargers are a constant voltage design set at 34 8 V (d.c).

The charge control logic in the PCDA senses charge bus voltage and battery temperature, and controls the charge enable and discharge enable relays to prevent damage to the batteries and to optimize the utilization of power. The PCDA uses redundant charge control circuits to prevent a single failure from causing a loss of charge control capabilities

Each charge control circuit has four temperature sensing channels, one for each battery. As a battery is connected to the charge bus, the appropriate temperature sensing channel is activated.

Batteries

The energy storage system of each Lander consisted of two assemblies containing two 24-cell, series-wired, 8 ampere hour (A h) nickel–cadmium (Ni–Cd) cells. Each battery weighed 23 kg (50.5 lb). Operational requirements for the Mars mission dictated that the batteries be heat sterilized at 112 °C (233 °F) for 54 h For this reason a non-woven polypropylene separator system was selected. The charge control used a voltage/temperature compensated system. During all ground testing of the batteries, individual cell monitoring and control were performed During the mission, only battery temperature and voltage were available Table 2 lists the battery characteristics [2]

TABLE 2

Battery characteristics [2]

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2 - 24 cell, 8 A h batteries/assembly
2 battery assemblies/spacecraft
Battery weight 50 5 lb (22.9 kg)
Heat sterilization 54 h at 233 °F (112 °C)
Charge conditions
  Voltage/temperature control
  $C/15$ — In cruise from Orbiter
  $C/160$ — Trickle
  $C/8$ — Typical landed operation
Monitoring
  Temperature — flight
  Battery voltage — flight
  Cell voltage — ground only

Selection of four, 8 A h batteries (A, B, C, and D) was based on an initially predicted maximum depth of discharge (DOD) of 75% during the descent of the Lander to the surface.

The batteries were launched in a discharged state, each with a 19.3 kΩ resistor connected across its terminals for telemetry monitoring purposes An additional purpose of this operational mode was elimination of the memory effect and reduction of capacity degradation. Early in the cruise Earth–Mars mission one battery was maintained in a partially charged state to enable power transfer from orbiter to Lander in the event of orbiter battery charger failure

Cell

The cell characteristics are listed in Table 3 [3]

The use of polypropylene separator material, the incorporation of a heat treatment to improve separator wettability, the performance of final electrolyte quantity adjustment after heat treatment, and the plate carbonate reduction process were the significant differences between these cells and standard cells using nylon separators

An end-of-mission capacity of 8 A h dictated a design of 9.5 A h beginning-of-life. The cell is identified as an 8 A h (nameplate capacity) cell

TABLE 3

Cell characteristics [3]

Cell capacity	8 A h (rated)
Cell weight	273 g — Lot average
Cell size	7 589 cm × 2 27 cm × 8 651 cm (including terminals)
Case material	304L stainless steel
Case wall thickness	0 48 ± 0 05 mm
Insulated terminals	Positive and negative
Terminal type	Nickel post with ceramic insulator GE — all nickel braze
Auxiliary electrode	None
Separator material	Pellon FT2140 nonwoven polypropylene
Separator thickness	0 216 mm
Plate pack wrap	Pellon FT2140 nonwoven polypropylene
Case liner	0 127 mm solid polypropylene sheet
Electrolyte	KOH + H_2O
Electrolyte concentration	34% KOH
Electrolyte quantity	21 5 - 23 5 cm^3
Plate substrate	0 191 mm perforated steel sheet
Sinter porosity	80% nominal
Number of plates	Pos 11 Neg 12
Plate size	7 0 ± 0 03 × 4 9 ± 0 03 cm
Plate thickness	Pos 0 066 - 0 071 cm Neg 0 078 - 0 081 cm

The cell plates were given a (General Electric Company proprietary) carbonate reduction process These cells exhibited a lower end-of-charge voltage (10 - 15 mV) and a reduced voltage spread, and delivered 0 5 A h more than previously accepted cells.

The quantity of electrolyte used in each cell ranged from 21 5 to 23 5 cm^3 and was closely controlled to prevent premature cell dryout due to inadequate electrolyte or to prevent an inadequate oxygen recombination rate due to excessive electrolyte

The quantity of potassium carbonate allowed in the electrolyte before filling is limited to two grams per liter Due to the introduction of a heat treatment process during the final manufacturing tests to improve separator wettability, a change was made to the procedure to add electrolyte to the initial quantity supplied This was accomplished during a 48 h $C/10$ overcharge test Sufficient electrolyte was added to achieve a nominal pressure of 20 psig (1 406 kgf/cm^2). The process, performed during fabrication, permitted an increase in the electrolyte quantity from 1 5 to 2 cm^3 over the quantity supplied in non-heat-treated cells, while still avoiding the excessive pressure during overcharge.

A method of sterilizing the cells, which introduced little or no degradation in cell performance, was developed. Prior to sterilization the cells were discharged at a $C/2$ rate to 1.0 V followed by application of a 1 Ω load to each cell for 24 h. During exposure to heat the cells were maintained in an open-circuit condition. Cells sterilized in any other condition suffered extensive capacity loss and, in some cases, physical damage.

Long-duration trickle-charging effects at a $C/160$ rate to maintain state-of-charge (SOC) during portions of the 11 month cruise mission were evaluated. It was determined that the batteries would still deliver nameplate capacity, but there was a significant degradation in cell voltage during the first discharge after removal of the trickle charge. This degradation can be removed after several cycles of charge/discharge.

Because of the requirement to function in numerous modes of operation including open-circuit charged stand, open-circuit discharged stand, trickle charging, and cycling to 75 and then 50% DOD, and combining these requirements with the use of polypropylene separator material having a low wettability characteristic and the high temperature sterilization requirement, cells were matched to within ±1% of the average cell capacity This would minimize the potential effects of cell capacity dispersion which would result in cell reversal or complete cell discharge.

Cells were not matched from cell acceptance data supplied from the manufacturer It was determined during development testing that after 60 - 70 charge/discharge cycles the rate of change of cell characteristics and capacities decreases significantly.

Based on these data, 64 cycles were selected for the cell matching program. Constant current charging was used to a timed cutoff for charge phases using $C/15$, $C/10$, and $C/7.5$ rates. A standard $C/2$ discharge to a 1.0 V cutoff was selected for all discharges for uniformity. The test sequences subjected the cells to both overcharging and deep discharging to induce a significant amount of stress and degradation under temperature control

Previous tests had indicated that cells in an inactive state for long periods of time tend to operate at higher voltages than normal during the first charge Using a low charge rate for the first charge prevents the development of the high voltages

Cell matching was based, in order, on W h capacity, A h capacity, and cell voltage at the end of charge and during discharge. Actual cell selection consisted of the selected 24 cells from the W h capacity list with a minimum spread in W h capacity.

All flight batteries were delivered with capacities exceeding 10 A h at the beginning of life Battery capacity exceeded cell capacity because of several reconditioning cycles applied to the cells before assembly into a battery and as a prerequisite to sterilization

Battery behaviour and conditioning after launch

During the cruise portion of the mission, each battery was conditioned by charging it once at *C*/15 until the voltage/temperature compensated charge control logic detected full charge and terminated the charge. The battery was then discharged through a 19.3 Ω resistance to 27.3 V, at which time the discharge sensors terminated the discharge. The 27.3 V minimum was a conservative minimum value that would reasonably ensure that no cell would be reversed The battery was then allowed to cool for a period of time before being recharged

Battery C was considered to be in the best condition and would provide one extreme with respect to degradation. It was the first to be discharged.

The discharge/recharge cycle was performed 227 SOLs after landing and indicated that 7% degradation had occurred since the cruise conditioning performed one year earlier A SOL is a Mars solar day and is equivalent to 24.67 Earth hours.

Until approximately 1400 SOLs after landing, battery degradation was insignificant and less than expected Load sharing was within 0 1 A with any combination of three batteries on the equipment bus. At that time, batteries C and D developed depressed voltages and began exhibiting higher operating temperatures. They supplied less of the equipment bus demand load

Figures 2 and 3 display the energy storage decay since the cruise conditioning. Batteries A and B degraded in capacity at a very slow rate at first, with C and D degrading very rapidly. The batteries appeared to respond to shallow discharge (to >1.0 V per cell), but that was short lived.

Deep discharge reconditioning was then attempted with apparent great gains in energy storage capacity, but the gains were of short duration Within four to five months up to 50% of the gains were again lost. Tables 4 through 7 provide a tabular summary of the results of all reconditioning cycles since

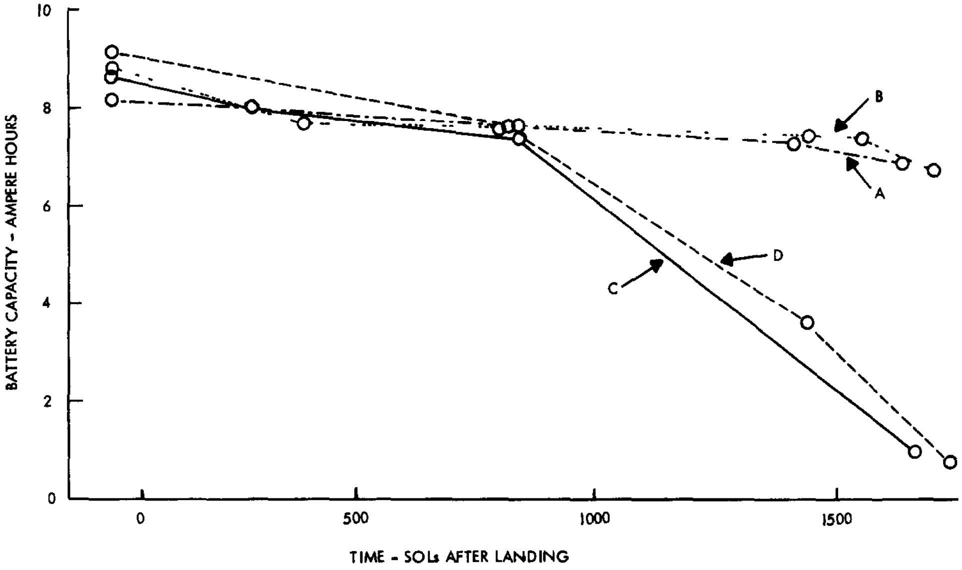

Fig 2 Viking Lander 1 battery capacity history

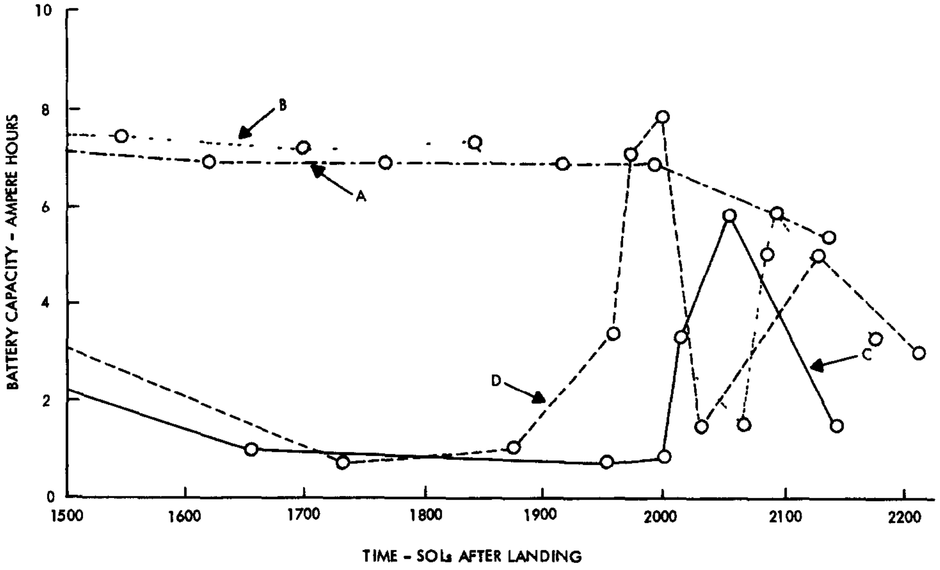

Fig 3 Viking Lander 1 battery capacity history

the cruise portion of the mission. A typical deep discharge cycle included 7 h through a 19.3 Ω resistor followed by a 21 h recharge or to voltage/temperature cutoff.

Each battery was subjected to over 500 cycles of 10 - 25% DOD and two cycles of 40 - 50% DOD early in the landed mission. In excess of 13 000 cycles of less than 10% DOD have been the battery experience to date. The

TABLE 4

VL-1 battery A degradation and reconditioning history [4]

Period	UTC date (Year/ day)	Discharge duration (h)	Average discharge voltage (V)	Discharge ampere hours (A h)	Discharge temperature °F (°C approx)	End discharge voltage (V)
CRUISE	76/128	5 6	30 2	8 10	74 9 - 83 0 (24 - 29)	27 3
SOL 802	78/295	5 1	29 4	7 64	59 2 - 60 8 (15 - 16)	27 3
SOL 1410	80/189	4 8	29 6	7 25	59 2 - 61 6 (15 - 16 5)	27 3
SOL 1618	81/037	4 6	29 6	6 93	45 2 - 48 5 (7 5 - 9)	27 3
SOL 1766	81/190	4 6	29 7	6 95	46 8 - 51 8 (8 - 11)	27 3
SOL 1914	81/342	4 5	28 5	6 79	56 7 - 64 1 (14 - 18)	27 3
SOL 1988	82/053	4 5	29 7	6 76	56 7 - 57 5 (14)	27 3
		7 0	27 5	9 87	56 7 - 59 2 (14 - 15)	24 0
SOL 2136	82/205	3 6	26 1	5 29	63 2 - 67 3 (17 5 - 19 5)	27 3
		7 0	23 6	8 97	62 4 - 67 3 (17 - 19 5)	11 0

TABLE 5

VL-1 battery B degradation and reconditioning history [4]

Period	UTC date (Year/ day)	Discharge duration (h)	Average discharge voltage (V)	Discharge ampere hours (A h)	Discharge temperature °F (°C approx)	End discharge voltage (V)
CRUISE	76/135	6 2	29 8	8 80*	73 3 - 83 0 (23 - 28 5)	27 3
SOL 382	77/228	5 4	29 4	7 80	41 1 - 47 6 (5 - 8 5)	27 3
SOL 834	78/328	5 1	29 5	7 57	47 6 - 60 8 (8 5 - 16)	27 3
SOL 1425	80/205	4 9	29 6	7 38	61 6 - 63 2 (16 5 - 17 5)	27 3
SOL 1544	80/332	4 9	29 4	7 36	57 5 - 59 2 (14 - 15)	27 3
SOL 1692	81/114	4 8	29 5	7 18	52 6 - 55 1 (11 5 - 13)	27 3
SOL 1840	81/266	4 8	29 7	7 28	59 1 - 61 6 (15 - 16 5)	27 3
SOL 2062	82/127	1 0	29 1	1 52	59 2 - 67 3 (15 - 19 5)	27 3
		7 0	17 0	6 08	59 2 - 68 1 (15 - 20)	4 2
SOL 2082	82/149	3 4	28 9	5 01	61.6 - 71.4 (16 5 - 22)	27 3
		7 0	23 8	8 04	61 6 - 76 2 (16 5 - 24 5)	12 2
SOL 2090	82/156	3 8	29 6	5 78	58.4 - 61 6 (14 5 - 16 5)	27 3
		7 0	25 4	9 05	58 4 - 67 3 (15 - 20)	13 2
SOL 2173	82/242	2 3	28 5	3 18	69.7 - 71 4 (21 - 22)	27 3
		7 0	21 7	7 62	64.9 - 71 4 (18 - 22)	7 5

*Estimated Discharge ended early by uplink command (not by PCDA logic at 27 3 V)

latter cycles have contributed to memory effect which, coupled with the two weaker batteries operating at higher temperatures, have caused the battery terminal voltages to be depressed. Parasitic shorting has been evident, indicating the probability of cadmium migration into the separator material. With the higher operating temperatures and depressed terminal voltages, the

TABLE 6

VL-1 battery C degradation and reconditioning history [4]

Period	UTC date (Year/ day)	Discharge duration (h)	Average discharge voltage (V)	Discharge ampere hours (A h)	Discharge temperature °F (°C approx)	End discharge voltage (V)
CRUISE	76/117	6 0	30 0	8 7	79 6 - 89 5 (26 5 - 32)	27 3
SOL 227	77/069	5 6	29 2	8 1	43 5 - 53 4 (6 5 - 12)	27 3
SOL 308	77/152	5 5	29 4	8 0	43 5 - 48 5 (6 5 - 9)	27 3
SOL 837	78/331	5 0	29 4	7 43	51 8 - 68 1 (11 - 16 5)	27 3
SOL 1655	81/075	0 7	28 2	0 96	57 5 - 57 5 (14)	27 3
SOL 1951	82/015	0 5	28 5	0 75	63 2 - 64 1 (17 5 - 18)	27 3
SOL 2001	82/066	0 6	28 8	0 86	56 7 - 56 7 (13 5)	27 3
		7 0	14 5	5 21	56 7 - 57 5 (13 5 - 14)	4 1
SOL 2016	82/081	2 3	28 9	3 32	56 7 - 57 5 (13 5 - 14)	27 3
		7 0	20 4	7 22	56 7 - 60 0 (13 5 - 15 5)	8 9
SOL 2024	82/097	No data	Data lost due to DSN station problem.			
SOL 2053	82/126	4 0	28 9	5 81	59 2 - 60 0 (15 - 15 5)	27 3
		7 0	24 5	8 83	59 2 - 64 1 (15 - 18)	8 3
SOL 2142	82/211	1 1	28 5	1 62	68.9 - 72 2 (20.5 - 22)	27 3
		7 0	18 4	6 52	50 1 - 72.2 (10 - 22)	5 2

TABLE 7

VL-1 battery D degradation and reconditioning history [4]

Period	UTC date (Year/ day)	Discharge duration (h)	Average discharge voltage (V)	Discharge ampere hours (A h)	Discharge temperature °F (°C approx)	End discharge voltage (V)
CRUISE	76/128	6 25	30 1	9 10	79 8 - 89.3 (26 5 - 32)	27 3
SOL 795	78/288	4 9	29 3	7 47	64 0 - 66 5 (18 - 19)	27 3
SOL 1433	80/213	2 47	29 0	3 62	69 7 - 73 0 (21 - 23)	27 3
SOL 1729	81/152	0 55	30 0	0 74	56 7 - 57.5 (13 5 - 14)	27 3
SOL 1877	81/304	0 7	29 3	1 00	55 1 - 55 9 (13 - 13 5)	27 3
SOL 1957	82/021	2 2	29 6	3 30	62 4 - 73 0 (17 - 23)	27 3
		7 0	20 8	7 40	62 4 - 73 0 (17 - 23)	8 3
SOL 1971	82/035	4 7	29 7	7 01	60 8 - 69 7 (16 - 21)	27 3
		7 0	26 7	9 35	60 8 - 72 2 (16 - 22 5)	10 5
SOL 1994	82/059	4 9	29 4	7.80	61 6 - 70 5 (16 5 - 21 5)	27 3
		7 0	26 5	9 41	61 6 - 72 2 (16 5 - 22 5)	9 6
SOL 2099	82/165	1 0	28 3	1 49	68 1 - 72 2 (20 - 22 5)	27 3
		7 0	17 6	6 38	63 2 - 72 2 (17 5 - 22 5)	6 8
SOL 2127	82/195	3 3	29 3	4 95	59 2 - 62 4 (15 - 17)	27 3
		7 0	24 6	8 96	59 2 - 69 7 (15 - 21)	11 9
SOL 2210	82/280	2 0	28 2	2 86	51 8 - 55 4 (11 - 13)	27.3
		7 0	21 7	7 76	51 8 - 60 3 (11 - 16)	7 4

charge control logic has been ineffective in determining full charge on any of the batteries and has caused significant overcharge of the batteries, further heating them and depressing their terminal voltages even further.

An attempt on SOL 2208 to change the charging regime from one hour on charge and three hours off charge on each battery to one on and seven off to reduce the amount of overcharge was initially very successful. The batteries were being discharged by only 0.5 - 1.0 A h each week; however, the one hour on charge and three hours off charge regime was, in fact, stressing the batteries The new charging regime resulted in lowered operating temperatures and elevated terminal operating voltages. While the terminal voltage maxima increased by 0 5 - 1 0 V and appeared to be maintaining that level, the minima had an initial gain that diminished over the course of a week.

A second regime of one hour on charge and eleven hours off charge was attempted A drop of both the maxima and the minima was experienced and a return to the one on and seven off was attempted. It was observed that even cooler operation of the batteries occurred.

A sequencing problem terminated the mission on SOL 2245, which terminated the reconditioning investigations as well

Computer modeling

A model of each component of the power system was developed on an IBM 370/158 computer at Martin Marietta Corporation and was delivered to the Jet Propulsion Laboratory to be run on the IBM 360/75 computers The PCDA, RTGs, batteries, cabling losses, conversion efficiencies, thermal effects, and special hardware internal sequences and power profiles were completely modeled. Battery charge and discharge efficiencies, states of charge and discharge, charge and discharge rates, temperature effects, charge and discharge voltages and currents, and state of charge were modeled. Battery charger efficiency at various charge rates, and temperature effects on conversion efficiency were modeled

The program that used these models was called Lander Load Profile and Power Management (LPWR) It received inputs in the form of sequences of events, accessed a database and output a load profile, which when run through a thermal analysis computer program would provide the thermal data required for a second run of LPWR which performed the energy balance analysis The printed output was a detailed sequence of events that indicated RTG output power, state of charge of each Lander battery, PCDA power loads, individual subsystem loads and cabling losses. A plot of the output was also an available option.

Analysis of the data received from the Landers enabled the battery, RTG, and individual equipment models to be constantly modified as necessary *via* database modifications to improve the accuracy of the program The program became accurate enough to be trusted when predicting periods in excess of two weeks with no indications that the batteries would be fully charged

Additional observations

A reduction in the frequency of charging was the proper approach to reducing stress due to overcharge. Significant reductions in battery operating temperatures were observed. Battery terminal and equipment bus voltages were elevated, making more energy available above the minimum equipment bus voltage.

An opening and inspection of a comparable cell in the ground simulation from the original flight lot which had not, however, been exposed to the greater than 13 000 cycles of less than 10% DOD, showed no physical evidence of dendritic growth. The cell was clean. The separator was found to be adhering to the negative plate however

Had the mission not been terminated so abruptly, an additional plan was to discharge the batteries even deeper to enable all cells to be completely discharged. It was noted, however, that with the increased frequency of deep discharges the ability of the battery to maintain achieved levels of increased energy storage capacity was enhanced for shorter durations More and more frequent deep discharge reconditioning was required.

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