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by Harvey J. Schwartz and Daniel G. Soltis
Lewis Research Center
Cleveland, Ohio

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by Harvey J. Schwartz and Daniel G. Soltis

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, U.S.A.

ABSTRACT

A new kind of silver-zinc cell has been developed and tested under NASA support which can withstand severe heat sterilization requirements and does not display the traditional life limiting aspect of sinc electrodes i.e. shape change. These cells could be used on planetary lander mission which require wet-stand periods of over a year, a modest number of cycles (400 to 500) and may require dry heat sterilization. The weight advantage of these cells over the traditional nickel-cadmium batteries also makes it an attractive alternative for synchronous orbit service where 400 to 500 cycles would be required over a 5 year period.

INTRODUCTION

In order to launch larger, more sophisticated, and more useful satellites and space probes, it is becoming increasingly important to make significant weight reductions in spacecraft systems to avoid overtaxing the lifting capability of available boosters. One primary candidate for weight savings is the spacecraft battery. In this respect, the silver oxide-zinc system has long been recognized as an attractive, but hitherto unsuccessful, alternative to the nickel oxide-cadmium battery.

During the past 5 years, a new kind of silver-zinc cell has been developed and tested under NASA support for use on planetary lander missions which may require dry heat sterilization followed by long wet-stand periods during interplanetary flight and several months of charge-discharge cycling. The key to this development is a chemically stable inorganic separator which has demonstrated long life in heat-sterilized, sealed 40 ampere-hour cells.

Since the combination of long wet-stand and modest numbers of cycles required for the planetary application is similar to the requirements for batteries in synchronous orbit satellites, a synchronous orbit test program has been initiated. Here the silver-zinc cell under development would weigh approximately one-third of the weight of nickel-cadmium cells presently used.

MISSION CHARACTERISTICS

The treatment of a battery, in terms of the manner in which it is used and the environment it sees, has a profound effect on life. Therefore, the characteristics of planetary and synchronous orbit missions as they effect the battery design will be briefly reviewed. We are concerned here primarily with missions to the near planets (Mars, Venus) for which solar cell-battery power systems are used. A hypothetical planetary orbit mission is shown on figure 1. Approximately 6 months elapse between the time cells are manufactured and the actual launch. During this period, cells are formed, matched for capacity, then assembled into batteries which undergo environmental testing and storage before finally being installed in the spacecraft. After launch the spacecraft follows its planned trajectory to the planet, a period of months during which the battery is used sparingly, if at all. Finally, the spacecraft is injected into orbit around the planet of interest and the battery is called upon to operate. Typically, a Venus mission might require a 12 month transit period after which the battery must undergo six charge-discharge cycles per day for 90 days, a total of 540 cycles. A Mars landing mission is shown on figure 2. For this mission, dry-heat sterilization of the lander and its systems is required prior to launch. In the case of the 1975 Viking mission, the sealed cells will undergo an acceptance sterilization of 60 hours at 125° C (398° K) after which the cells and batteries will see three additional sterilizations at 135° C (408° K) totaling 140 hours prior to launch. In general then, the planetary missions of interest require a battery with approximately 2 years wet-life and capable of delivering a modest number of charge-discharge cycles (hundreds) near the end of its wet-stand period.

An examination of the characteristics of earth-synchronous orbits (fig. 3) reveals similar requirements. The two nodal eclipse periods require the battery to deliver less than 100 cycles of varying depth of discharge in 1 year. For a useful life of 5 years, less than 450 cycles are required of the battery. While the battery delivers less than 1/10 of 1 percent of the total energy requirement (Dunlop et al. 1970), it currently accounts for 30 to 50 percent of the weight of the power system. Table I shows the weight breakdown for the Intelsat series (Billerbeck 1972).

Synchronous orbit satellites most frequently are of the facility-type rather than experimental vehicles. That is, they are launched to establish a continuing capability in a particular area (communications, weather forecasting, etc.). As a result, reductions in subsystem weights can be translated into increased capability, either through increasing the capacity (more data channels) or increasing the operating life by permitting greater redundancy of critical components. Therefore it is clear that the replacement of the presently used nickel-cadmium batteries with a lighter battery would represent a significant technology advancement.

CELL DESCRIPTION

Early in the Viking program landing capsule weight restrictions required use of a heat-sterilizable silver-zinc battery. The Lewis Research Center undertook the development of such a battery, based on work being supported at McDonnell-Douglas Corporation on a long-life silver-zinc secondary cell using an inorganic separator. Changes in mission profile later permitted adoption of a more conservative approach for Viking based on a nickel-cadmium battery, but the successful development of a sealed, heat-serilizable 40 AH silver-zinc cell encouraged NASA to continue the development program in anticipation of future use. A full-size model of the 40 AH cell is shown on figure 4. Two aspects of the cell construction are worthy of comment; all other design features being in keeping with standard commercial practice.

Zinc Electrode

The zinc electrode used is prepared by pressing a mixture of 98 weight percent zinc oxide and 2 percent mercuric oxide onto a silver Distex[1] grid. A sheet of potassium titanate paper (Mead Corp. LPM 174-67, 0.020-0.026 Uncompressed) is pressed into each face. No contouring or teflonation is used.

Separator

The separator used is one of a class of "inorganic separators" which are covered by United States Patents issued to McDonnell-Douglas Corporation. Earlier test results have been reported (Moe and Arrance 1971). The particular material tested is described in U.S. Patent 3,625,770, issued December 7, 1971. The separator consists of a mixture of zirconium oxide and potassium titanate (KT) (18:1) which is bonded together by polyphenelene oxide (PPO) resin (5%). The mixture is deposited on a fuel cell grade asbestos substrate

[1]Registered Trademark, Exmet Corporation, Bridgeport, Conn.

which has previously been impregnated with a 13 percent solution of PPO dissolved in a suitable solvent. The film is applied by dip coating a layer of zirconia/KT/PPO slurry onto the surface of an electrode bag which is made by gluing two sheets of treated asbestos together along three edges. Prior to dipping, the pressed zinc plate is inserted into the bag through the fourth (unglued) edge.

The cell tested, designated 40-7 has six positive and five negative plates, each enclosed in a single bag of separator material. Assembly of the plate-pack is shown on figure 5. The plate-pack is inserted into a molded poly-phenylene oxide jar, made from glass fortified grade 534-801 natural PPO (Liquid Nitrogen Processing Corporation Product NF-1006, Natural). The case-to-cover joint is made by ultrasonic welding. After filling with 110 cc of 45 percent KOH, the fill-hole is closed with a molded PPO plug, and the case top is potted with a filled epoxy resin. Details of the cell design, construction, and materials are contained elsewhere (Himy 1971). Over 200 cells of this design have been built and tested. Total cell weight is 851 grams. A weight breakdown is shown on table II. For expediency, case molds, terminals and electrode and separator tooling which were available at the time were used. This resulted in excess weight in the cell, as indicated by the excessive head space above the plates in figure 4. A detailed weight analysis was made for an optimized cell design. An analysis of this model, designated the 40-10X, is also shown on table II. The total cell weight would be 650 grams. The design is basically the same as model 40-7, except for the use of nine plates instead of eleven. Though no cells of this type were built, a full-scale mockup was made to test assembly methods. The 40-7 and 40-10X models are shown together on figure 6.

ELECTRICAL PERFORMANCE OF MODEL 40-7 CELL

The electrical performance as a function of discharge rate and temperature was measured. Capacities were measured to a 1.0 volt cutoff at currents of 20, 40, 80, and 120 amperes and temperatures of 0° C, 25° C, and 50° C. Typical values are shown on table III. The energy density delivered, based on a cell weight of 851 grams is shown on figure 7 as a function of drain rate and temperature. At 25° C, the energy density approaches 40WH/lb for a full discharge at the low (2A) drain rates associated with the Viking mission. In synchronous orbit, assuming 60 percent depth of discharge for the peak 72 minute eclipse period, discharge would be at the 20 ampere rate, and an energy density of 17.7 WH/lb is delivered. For comparison, the power system and battery weights, and battery energy density for Intelsats 2, 3 and 4 are shown on table I. Based on these figures, the use of the 40-7 silver-zinc cell on a spacecraft like Intelsat 4 could result in a weight savings of about 60 pounds in the battery. Assuming equivalent electrical performances, the use of the 40-10X design could increase the savings to about 68 pounds since the expected energy density delivered would be 23.2 WH/lb. Therefore, a significant gain in payload capacity can be realized through use of the silver-zinc battery.

CELL TEST PROGRAMS

The longest duration tests were initiated to duplicate two versions of the Viking mission profile. More recently, cycling tests duplicating and relating to synchronous orbit have been undertaken.

Test Descriptions

(a) VK-1 - This is an early version of the Viking mission profile. It required the sealed cell to be heat sterilized for 200 hours at 135° C

(308° K), undergo 8 months wet-stand, and then to be discharged once each day for 2 hours to 10 percent depth of discharge (based on 40 AH nominal capacity). A minimum of 90 cycles was desired.

(b) VK-2 - A profile simulating the 1975 Viking mission. The wet stand period is extended to 21 months. At the end of this time, the cell is given two conditioning cycles and then discharged at 7 A for 3 hours, followed by a 12 A pulse for 40 seconds. The cell must deliver the 12 A pulse at or above 1.2 volts. It is then discharged twice each day to a cumulative total of 22.5 percent depth between once daily recharges. Again a 90 day life is desired.

(c) VK-3 - An accelerated life test under which the cell is sterilized, undergoes 8 months wet stand, and is discharged three times per day for two hours to 35 percent depth of discharge.

(d) Full Discharge - A few cells have been placed on wet-stand and discharged completely to a 1.0 volt cut-off at regular intervals.

(e) Synchronous Orbit - Cells manufactured, sealed, and heat sterilized in September-October 1970 were used to initiate a synchronous orbit test program at NASA-Lewis. The cells are cycled in accordance with the profile shown on figure 3. The maximum depth of discharge is 60 percent at the peak (72 minute) eclipse period. The first eclipse period was initiated in July, 1971 at which time the cells had already been stored for 9 to 10 months. The goal is to complete 10 eclipse periods over a 5 year period.

(f) 24 Hour Cycle - Since the average depth of discharge during the eclipse period of a synchronous orbit cycle test is near 40 percent, a qualitative accelerated test was started at the same time as the synchronous orbit tests under which cells are discharged to 40 percent depth of discharge in 72 minutes and then recharged. The cycle is repeated once each day. The same cells were used as in test (e) above. The goal is 450 cycles.

Failure is defined in all cases to be the inability of the cell to deliver the required capacity above a cutoff voltage of 1.0 volt for two consecutive cycles. Charging is performed at constant current, with the cutoff voltage controlled to 1.96 to 1.98 volts.

TESTS RESULTS

The status of all tests as of 1 March 1972 is shown on tables IV to VI. The results may be summarized as follows:

1. On the VK-1 cycle, 29 of 42 cells are still on test. The wet-lives of those cells still on test range from 30 to 40 months, and cycle lives from 664 to 814 cycles. Among the failed cells, the earliest appeared after 283 cycles and 16 months on test. The latest failure occurred after 33 months and 679 cycles.

2. Four cells were tested on the VK-2 cycle, but without the wet-stand and entry discharge cycles. These cells have undergone 1164, 1206, 1207 and 1207 cycles.

3. Under the VK-3 cycle, one heat-sterilized cell was cycled 1003 times over 513 day to failure. Fifteen nonheat sterilized cells were later tested under the same regime, but exhibited shorter lifetimes. Failures ranged from 265-497 cycles applied over 7-1/2 to 11 months total wet-life. These cells were different in that they represent a series of experiments which introduced epoxy resin, cured by several techniques, into the cell to anchor the plate-pack to the case bottom. The control cells (no epoxy)

exhibited the best life of the group (497 cycles-11 months), but still fell below expectations. The reason for this anomaly is not known.

4. A total of 17 cells have been cycled to 100 percent depth of discharge for extended periods. The cells are discharged at 9.0 A to 1.0 V, and then drained at 3.0 A to 1.0 V. Of 15 cells discharged once per month, 12 presently have 15-17 cycles over an average of 20 months wet-life. Three cells exploded when the automatic cycling panel failed and drove the cells in reverse. Two other cells have been fully discharged on an irregular basis. One failed after 136 cycles spread over 29 months. The other is still operating and has undergone 143 cycles with the total wet life nearing 3 years.

5. Forty cells have been tested to the full VK-2 (Viking mission profile) regime. The results are shown on table V. In addition to life, the test was designed to determine the optimum conditions for maintaining the cells during the earth-to-planet transit period. One group of cells was held on open-circuit in the charged state at 10° C (283° K), room temperature, 32° C (305° K), and 42° C (315° K). A second group of cells was maintained on float-charge at a voltage of 1.86 volts. These were held at 10° C (283° K), room temperature, and 32° C (305° K). Seven additional cells were placed on stand in the discharged state at room temperature only.

The optimum stand condition was found to be the discharged state at room temperature. All seven cells met the entry cycle requirement and have now delivered 315 to 318 cycles for a total wet-life of 835 to 981 days. Virtually all of the cells on float charge or allowed to stand in the charged state above room temperature failed the entry test either due to low capacity or low voltage during the 12 A pulse. A greater proportion of cells held at

10° C (283° K) passed the entry test than those held at room temperature. However, the cycle life of the room-temperature cells appears better.

6. The synchronous orbit testing at NASA-Lewis was started in July 1971. The results are summarized in table VI. The second eclipse cycle was completed on January 17, 1972. All cells are still operating well. Ten additional cells are being cycled to 40 percent depth once each day. They have reached 252 cycles and 557 days wet-life with no failures. Total capacity measurements were made after 100 and 200 cycles. No loss in capacity has occurred up to that point.

FAILURE ANALYSIS

A detailed failure analysis program is presently underway and definitive results are not yet available. However, based on preliminary observations several qualitative conclusions have been reached.

1. Silver is slowly deposited in the separator bag surrounding the positive plate. X-ray diffraction shows the silver to be present as metal. Electron beam microprobe analysis indicates that the silver is distributed in such a way as to imply attack on the organic binder. Metallic silver is also found in the negative plate bag.

2. The predominant problem area is failure of the glued seam on the negative plate separator bag. All failed cells have split bag seams, and mossy zinc is usually observed to grow out of the opening and come into contact with the positive bag. It is not known whether the silver electrode separator bag must also contain enough metallic silver to provide a shorting path.

3. The most striking observation is that the classical zinc electrode failure mode (capacity loss due to "shape change" or "slumping") is absent. Figure 8 shows two typical zinc plates after heat sterilization, extensive wet life and cycling to 40 percent depth of discharge. Note that no obvious shape change has occurred. The material missing from the area near the tab in the upper photo was lost by adhering to the separator bag when it was removed. Considering that the zinc plates were not treated to delay or inhibit shape change through contouring or teflonation, this behavior is most unusual. Similar behavior has been reported in the literature for zinc plates in nickel-zinc cells which were wrapped in "inorganic" separators (Charkey 1969). These observations have lead to incorporation of the zinc plate/electrode combination into nickel-zinc cells in our laboratory with encouraging results (Schwartz 1971).

SUMMARY AND CONCLUSIONS

1. A long life sealed silver-zinc cell has been demonstrated which can be heat sterilized at 135° C for 200 hours, and has demonstrated a combination of wet-life and cycle life which make it suitable for use on spacecraft designed to orbit Venus or Mars, or for a sterilized Mars landing capsule.

2. This cell would offer a significant weight advantage over the nickel-cadmium for synchronous orbit use. Tests in this regime are underway.

3. Slumping or shape change of the zinc electrode is not observed. The reason for this is not known as yet. The electrode/separator combination looks attractive for use in other systems (i.e., Ni-Zn).

4. The preferred wet-stand condition is in the discharged state. For wet-stand under charged or float conditions, temperatures of room temperature or below are favored.

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TABLE I. - INTELSAT POWER SYSTEMS

Spacecraft	In-orbit weight, lb	Power System		Battery		D. C. Load, watts	Battery[a] energy density, wh/lb
		Total weight, lb	Percent spacecraft weight	Weight, lb	Percent power system weight		
Intelsat 2	169	59.9	35.3	25.1	42	76	3.63
Intelsat 3	293	65.2	22.7	22.7	34.8	120	6.4
Intelsat 4	1575	260.4	16.5	89	34.2	400	5.4

[a] Calculated for 72 minute eclipse period

TABLE II. - CELL WEIGHT ANALYSIS

Component	Weight, g	
	Model 40-7	Model 40-10X
Positive material	138.0	134
Grid and leads	11.5	8
Negative material	150.0	148
Grid and leads	25.0	16
Separator	107.0	72
Jar and cover	213.5	115
Terminals	46.5	29
Epoxy	8.5	8
Electrolyte	151.0	120
Total weight	851.0 (1.88 lb)	650 (1.43 lb)
Total positive capacity (AH)	68.5	66.5
Effective capacity (70 percent utilization) (AH)	48	46.5

TABLE III. - CAPACITY AND PLATEAU VOLTAGES FOR 40 AH CELLS.
[Data obtained after formation and heat sterilization, average values - 5 cell groups.]

Test temperature, °C	Discharge Current									
	7A		20A (c/2)		40A (c)		80A (2c)		120A (3c)	
	AH	V	AH	V	AH	V	AH	V	AH	V
0	---	---	33.3	1.27	30.4	1.22	28.6	1.15	26.4	1.11
25	43.7	151	40.0	1.38	38.0	1.31	37.6	1.20	32.4	1.14
50	---	---	41.3	1.47	38.6	1.38	34.6	1.27	31.9	1.25

TABLE IV. - 40 AH SILVER-ZINC CELL TESTS

Cycle regime	Duty cycle		Cycling			Failed		
	DOD(%)	Cycles	No. cells	Cycles	Wet-life	No. cells	Cycles	Wet-life
VK-1	10	1/day	29	664-814	898-1243	13	283-679	477-996
---	22.5(cum)	2/day	4	1164-1207	728-740	----	-------	-------
VK-3	40	3/day	---	--------	-------	1	1093	513
VK-3	35	3/day	---	--------	-------	[a,b]15	265-497	223-323
Full	100	1/mon	[a]12	15-17	577-611	[a,c]3	10-14	418-536
Full	100	Irregular	1	143	1030	1	136	884

[a]Not heat sterilized

[b]Epoxy plate-lock experiments

[c]Test equipment failure

TABLE V. - VIKING MISSION TEST RESULTS

Wet stand mode	Formation cycles after wet stand		VK-2 Regime - 27% DOD(cum) at 2 cycles/day					
			Cycling			Failed		
	Failed	Passed	No. cells	Cycles	Wet-life	No. cells	Cycles	Wet-life
10° C charged	0	5	2	414-416	964	3	99-209	795-861
R.T. charged	1	4	4	414-416	964	---	------	-------
32° C charged	5	0	---	-------	------	---	------	-------
42° C charged	2	0	---	-------	------	---	------	-------
10° C float	1	4	1	318	953	3	152-777	869-931
R.T. float	2	3	2	316-318	953	1	218	903
32° C float	5	1	---	-------	------	---	------	-------
R.T. discharged	0	7	7	315-318	835-981	---	------	-------

TABLE VI. - SYNCHRONOUS ORBIT TEST RESULTS.

Duty cycle		Test status[a]		
DOD, %	Cycles/day	No. cells	Total cycles	Wet-life, days
60 (max.)	synchronous orbit	10	86 (two eclipses)	557
40	1	10	252	557

[a]As of March 1, 1972

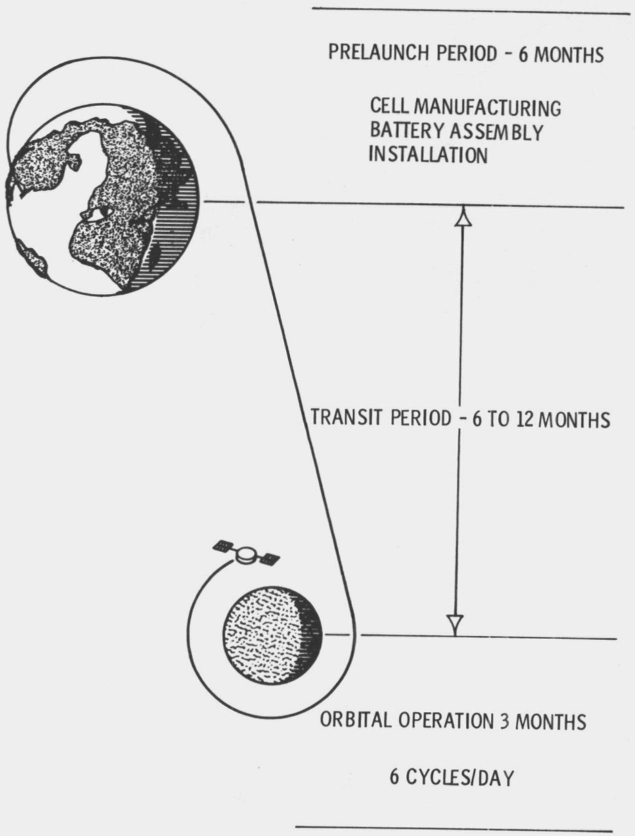

Figure 1. - Typical planetary orbit mission.

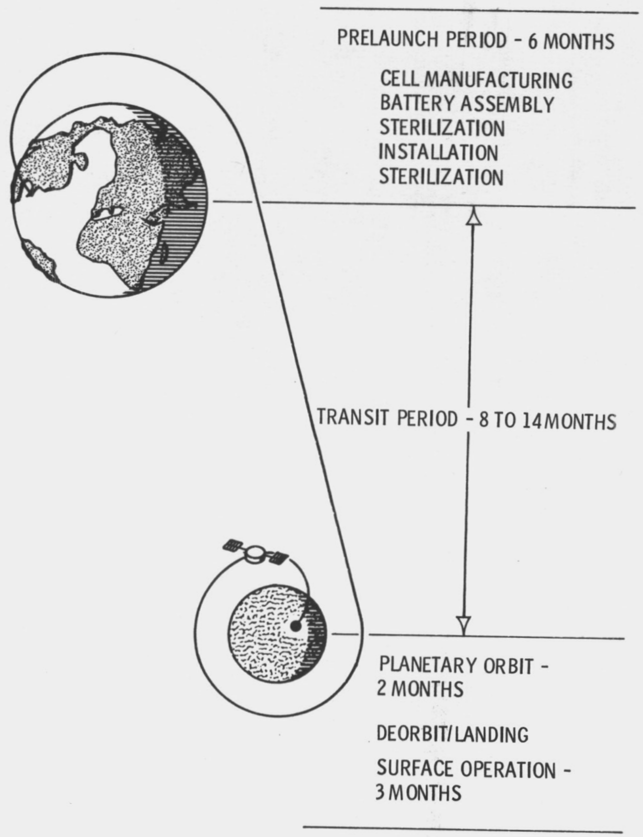

Figure 2. - Typical Mars lander mission.

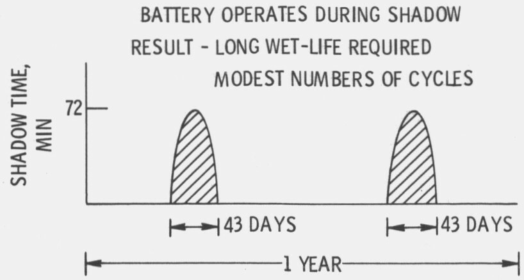

Figure 3. - Characteristics of synchronous orbit.

Figure 4. - Sealed 40 AH silver-zinc cell.

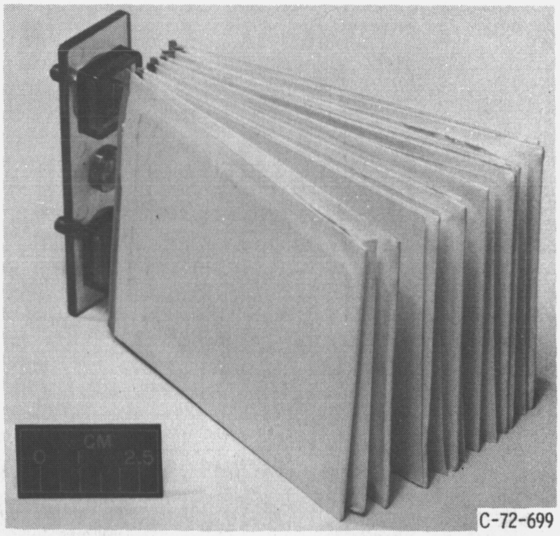

Figure 5. - Silver-zinc cell plate pack.

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MODEL 40-10X MODEL 40-7

Figure 6. - Silver-zinc cell designs.

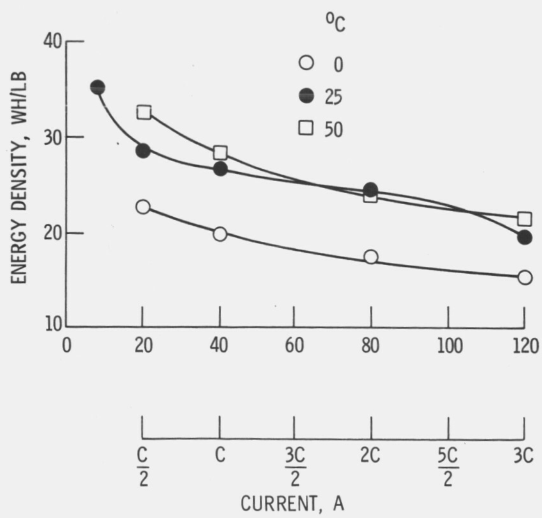
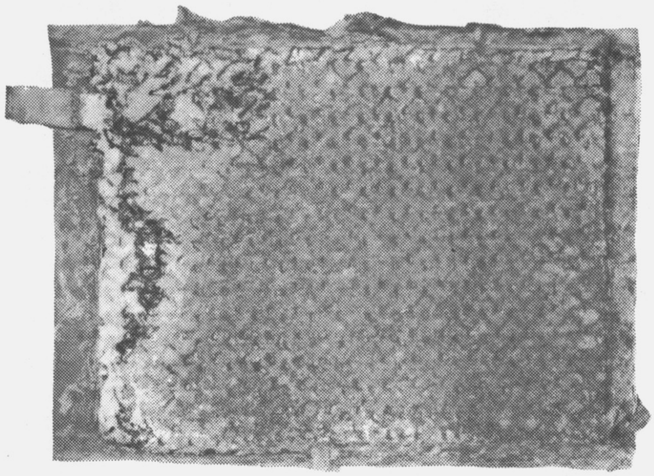
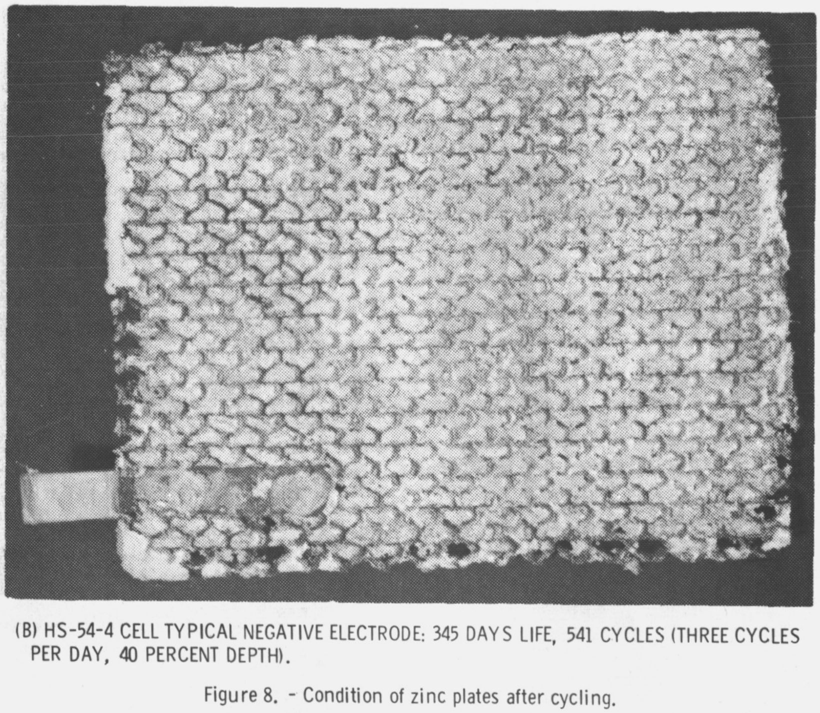


Figure 7. - Energy density of model 40-7 cell.



(A) HS-51-6 CELL TYPICAL ELECTRODE: 517 DAYS WET LIFE, 1 093 CYCLES (THREE CYCLES PER DAY, 40 PERCENT DEPTH).



(B) HS-54-4 CELL TYPICAL NEGATIVE ELECTRODE: 345 DAYS LIFE, 541 CYCLES (THREE CYCLES PER DAY, 40 PERCENT DEPTH).

Figure 8. - Condition of zinc plates after cycling.