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Technical Memorandum 33-581

Heat-Sterilized Silver Oxide-Zinc Cells: Cycle Life Studies

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PREFACE

The work described in this report was performed by the Guidance and Control Division of the Jet Propulsion Laboratory.

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ABSTRACT

A JPL study was conducted to evaluate the cell design parameters that contribute to the cycle life of sealed, heat-sterilized silver oxide-zinc cells. Test cells having a rated capacity of 4.2 A-h were fabricated using zinc oxide electrodes prepared by the sintered Teflon process developed at JPL, silver electrodes purchased from ESB, Inc., and separators produced by Southwest Research Institute under NASA contract. Two separator variations were evaluated, one having acrylic acid and the other methacrylic acid grafted to irradiated polyethylene film.

All cycle life tests were conducted at ambient temperature on a 24-h cycle consisting of 3 h of discharge through a fixed resistance, and 21 h of charge by a modified constant potential having a current limit. Cells were tested as 6-cell batteries. Depth of cycle was approximately 50% of nominal. (Nominal rating was based on the value of 0.25 A-h per gram of silver.)

Significant results of this study included the following: (1) cycle life in excess of 300 cycles was attained; (2) a zinc oxide/silver stoichiometric ratio of 1.5 resulted in greater cycle life than a ratio of 1.1, and similar cycle life to cells having a ratio of 2; (3) cells having methacrylic acid grafted separators suffered somewhat less in capacity loss due to zinc electrode shape change than cells having acrylic acid type; (4) use of acrylic acid grafted separators was slightly superior to the methacrylic acid type in respect to silver penetration; and (5) the inclusion of a layer of potassium titanate paper adjacent to the zinc electrodes resulted in cells that achieved higher cycle life before any of the group failed than that reached by cells of any other construction.

I. INTRODUCTION

The Heat Sterilizable Battery Program was designed to provide for the development of battery technology which is required for spacecraft controlled by sterilization requirements. The program comprised the developments for the soft-impact and hard-impact modes of primary batteries for the de-orbit and descent phases, and of secondary batteries for extended life on the surface.

This report summarizes the results of a JPL study to develop the technology of heat sterilizable silver oxide-zinc cells for maximum cycle life. This study paralleled one at ESB, Inc. (JPL Contract 951296). The JPL study differed in several areas from the ESB, Inc. study. Among the differences were: (1) evaluation of both acrylic acid and methacrylic acid grafted polyethylene film type separator rather than only the acrylic acid type; (2) extension of the KOH concentration of the electrolyte to a higher value; (3) evaluation of the use of absorbers adjacent to the zinc electrodes to extend cycle life by retarding zinc electrode shape change; and (4) the use of mercuric oxide instead of mercuric sulfide as the additive to the zinc electrode to retard hydrogen evolution. (The mercuric oxide substitution was permissible only because these cells had been electrically cycled prior to heat sterilization and the somewhat soluble mercuric oxide was not present as such during sterilization.)

II. EXPERIMENTAL

A. Cell Components

Silver electrodes for all cells were of the type manufactured by the dispersed plastic process and were purchased from ESB, Inc. Dimensions were 3.7 × 4.7 × 0.068 cm. Active material in each was 5.7 g. Zinc oxide electrodes were fabricated by a sintered Teflon process developed at JPL during an earlier phase of the heat-sterilized silver oxide-zinc cell development. The first step in this process is to mix powdered materials including zinc oxide (J. T. Baker Co., Reagent grade), powdered Teflon (DuPont No. 7), red mercuric oxide or mercuric sulfide, and, as noted in the tables, zinc sulfide. In all instances, 9% Teflon, 3% mercuric compound, and 88% zinc compound or compounds constituted the mixtures. Mixing was done in a Waring blender. The powdered mixture was pressed on to an expanded metal grid using a pressing mold. A force of 88,964 newtons resulted in an electrode having a pressed powder density of 3 g/cm^3. After pressing, the electrodes were placed between sheets of silver metal and sintered for one hour at 350°C. Electrode thickness was a function of the ZnO/Ag stoichiometric ratio which was a variable. For thinner outer electrodes, the thickness range was from 0.063 to 0.096 cm, and for the inner electrodes 0.096 to 0.183 cm. Grids were prepared from 5 Ag 15-2/0 expanded, distorted silver (Exmet Co.). The inner electrode had grids of two layers of expanded metal and the outer ones a single layer. All had the edges folded to reduce the possibility of metallic edge shorts.

Separation consisted of from 8 to 10 layers of polyethylene film irradiated and grafted with either acrylic or methacrylic acid, as noted on the tables. These films were prepared by Southwest Research Institute under JPL subcontract (Ref. 1). The absorber materials were of two types of polypropylene. One was EM476 (Kendall Co.) which had been irradiated by Radiation Applications, Inc., to improve post-sterilization wetting. The other type was FT2140 (Pellon Corp.). In addition, one group of three cells had potassium titanate material identified as LPM-174-67 (The Mead Corp.) adjacent to the zinc electrodes.

B. Cell Design

With the exception of one group of three cells, all had U-wrapped zinc oxide electrodes. The exceptional group had U-wrapped silver electrodes.

Some cells had negatives of greater area than positives (extended edges). To effect this change, the dimensions of the silver electrodes were reduced 0.25 cm in width and 0.25 cm in height.

The stoichiometric zinc oxide/silver ratio varied from 1.1 to 2.0.

Cell pack tightness varied from 0.0040 to 0.0077 cm per layer of acrylic acid grafted separator material, and from 0.0050 to 0.0083 cm for the methacrylic acid grafted type. (The calculations for pack tightness values were arrived at in the following manner. The total of the measured thickness of the electrodes and absorbers and the calculated thickness of the separator, using the thickness recorded in the tables under the column labeled "pack tightness allowance," was subtracted from the inside case thickness at a point half way between the top and bottom. Spacers having the thickness equal to the difference obtained above were selected. For these calculations, the value used as the thickness was 0.025 cm for FT2140 and 0.007 cm for EM476.)

C. Activation and Sterilization

After the cell elements and spacers had been inserted into the cell jars and the case-to-cover seals effected, threaded Teflon tubes were turned into the threaded fill hole openings. The cells were inserted into a beaker containing electrolyte of the desired KOH concentration and the beaker transferred to a vacuum chamber which was evacuated by mechanical pump to maximum vacuum attainable. Upon opening the chamber to the atmosphere, the free volume of the cells was completely filled with electrolyte. The quantity of electrolyte needed to fill the cells varied from 17 to 25 ml and depended on the construction. Those having the thickest absorber, the thickest electrodes, and the most separator layers absorbed the most electrolyte. Three milliliters of electrolyte were then removed from each cell using the vacuum technique. Empirically, it was found that removal of this quantity allowed sufficient free volume to accommodate the effect of temperature variations. The quantity of electrolyte retained was sufficient for operation of the cell. The technique lent itself to the activation of cells having widely varied internal design.

The next step was to convert electrochemically the mercuric compound. This was done at rates which varied from 3 to 16 hours as convenient. Subsequent cell performance was not affected by the rate selected for the conversion. This portion of the charge was terminated when the cell had accepted the theoretical ampere-hours needed to effect the conversion, or when the cell reached a closed-circuit voltage of 1.60 V, whichever occurred later. Following this, cells were placed in pressure vessels containing a small quantity of electrolyte of the same concentration as contained in the cells. Thus, the vapor pressure in the vessels and in the cells remained equal during the subsequent heat cycle and loss of cell electrolyte was minimized. The vessels containing the cells were transferred to an oven, the temperature of which was increased from 40 to 100°C in three 20-deg increments. The 100°C temperature was maintained for 4 h, after which the temperature was reduced to ambient. The purpose of this heat cycle was to cure the epoxy used in sealing the cell. (The fill holes retained the Teflon tubes during this time. To have subjected the unactivated cell to the 100°C temperature would have been detrimental to the separator. To have exposed the activated cell prior to conversion of the mercuric oxide would have resulted in some of that species having dissolved and migrated to the silver electrodes. The effect of this would have resulted in reducing the charge acceptance of those electrodes. If the mercuric compound were mercuric sulfide, the prior conversion would not have been needed, since its solubility is low, but the same procedure was used for all cells.)

After cooling, the cells were removed and weighed. Any adjustment in the quantity of electrolyte to restore it to its previously adjusted value was made. Cells underwent their formation charge after which the final seal was made by removing the Teflon tubes, inserting the threaded plugs into the fill holes, and overpotting the plugs with epoxy.

The formation charge was 0.100 A (0.8 mA/cm^2 of silver electrode area), which was the 60-h rate. The cells were then discharged at 1.8 A to a terminal load voltage of 1.20 and then at 0.36 A to the same voltage. Following this, the cells were discharged to 0.100 V using 50-Ω resistors. This was to assure oxidation of any remaining zinc.

The cells were then weighed, placed in restraining holders, and transferred to the sterilization oven. Approximately 30 min after power was supplied to the heating elements, the ovens had reached the sterilization temperature of 135°C. The normal period of sterilization was 72 h. After sterilization and cooling, the cells were removed from the oven, their supporting clamps removed, and their weights recorded. Normal weight loss was approximately 0.7 g. In separate tests for longer and shorter periods of sterilization, the weight loss was determined to be linear with time. The rate of loss was 0.01 g/h. The implication of this is that the weight loss resulted from water transfer through the case.

D. Electrical Cycling

Cells were cycled individually four times using a procedure similar to the formation cycle. For cells containing mercuric sulfide in the zinc electrodes instead of mercuric oxide, a partial cycle of 20% depth discharge followed by recharge was run as part of each recharge for these cycles. The effect of this was to increase the subsequent discharge capacity by approximately 10%. This partial cycle had little effect on cells containing mercuric oxide and was generally eliminated for such cells.

After completion of the above cycles, cells were transferred to an automatic cycle regime where they underwent daily cycles as 6-cell batteries of 3 h of discharge and 21 h of charge. Discharge was through a constant resistance load. Recharge was by modified constant potential with a current limit of 0.2 A and the power supply open-circuit voltage set a 1.96 V/cell. No voltage limits on an individual cell basis were used. In only a few instances did this result in loss of cells due to overcharge on them when one of the other cells of the battery developed an internal shorting path. This was true even though some cells reached potentials greater than 2 V and sustained that value for several hours.

Cycle depth was in the 50 to 60% of nominal range and is noted on each table. The nominal rating was based on the value of 0.25 A-h per gram of silver, which is the theoretical value for oxidation of silver to argentous oxide. For cells having silver electrodes reduced in size (extended negative electrodes), the depth was calculated on the basis of the amount of silver they would have contained if the electrodes had not been reduced in size.

E. Failure Analysis

Tests to determine the cause of a cell's failure were of two types. The first of these included observations of its voltage behavior under open-circuit and charging conditions. Also, a cell's capacity during discharge was sometimes helpful. (Open-circuit measurements following a stand period can often indicate whether internal shorting resulted from an isolated zinc "tree" or penetration by silver species through all layers of separation. In the case of a zinc "tree" short, the cell's voltage during constant current charging is generally erratic within the range of 1.82 to 1.952. Immediately on discontinuance of charge, the open-circuit voltage decays to a value below the normal 1.862, but after a short interval returns to normal as the material of the zinc path becomes oxidized. If silver species penetration were the cause of the shorting path, charge voltage is below normal and, as charging continues, decays further. Another test that is helpful in verifying that shorting has indeed occurred is to compare the amount of charge with that of discharge. In a cell which has been cycled several times, these should be equal. If charge exceeds discharge by any significant amount, the implication is that internal shorting is the cause.)

After completion of the above bench tests, cells were dissected. Identification of shorting paths by visual means was more difficult in cells having mercuric sulfide in the negative electrodes. In such cells, the presence of silver sulfide, being black, made location of zinc penetration more difficult. In cells having mercuric oxide in the negative electrodes, silver species deposits were not black, but might be more correctly described as gray or brownish gray.

III. DISCUSSION OF RESULTS

The accompanying tables show pertinent construction details for the cells tested. Also included are the numbers of cycles attained prior to failure, and, under the column entitled "Remarks," the reason for failure. For cells failing because of inadequate capacity, there was no difficulty in assigning a reason. For some cells, behavior during bench tests as well as observations during dissection provide conclusive evidence that zinc penetration caused failure. For many, it was not possible to say for certain whether either silver or zinc penetration was the cause of shorting, or whether, as is most likely, penetrating zinc met areas penetrated by the silver species and the resultant shorting path formed. In nearly all cells, large amounts of zinc had penetrated several layers of separation. Likewise, visual evidence of the presence of silver was found through many layers, its intensity diminishing as the number of layers removed from the silver electrodes increased.

A. Effects of Design Variations on Cycle Life

Table 1 presents data for six sets of cells in triplicate. The cycle life achieved by these cells varied more widely among similar cells than did that of any other group. This is attributed to the low zinc oxide/silver stoichiometric ratio. The lower the value of this ratio, the less uncharged zinc oxide remains in the electrode as the cell approaches a fully charged state. Zinc penetration is most likely to occur when the zinc electrode approaches a fully charged state. Of the cells which failed after fewer than 100 cycles, only in the instance of cell 40-3 was failure attributed to silver penetration of the separator, failure of the other such cells having resulted from zinc penetration. No significant difference in number of cycles was observed in cells having mercuric sulfide in the zinc electrodes rather than mercuric oxide. Cells having methacrylic acid grafted separator yielded not only the highest number of cycles, but also the lowest number of cycles. On the other hand, cells 50-1, 50-2, and 50-3 having acrylic acid grafted separator as a group reached more cycles before any failure. All of these cells failed because of low capacity and none developed internal shorting paths. No cycle life improvement was observed when zinc sulfide was included in the negative mix.

From the study of this group of cells, it was apparent that two design changes were needed to improve cycle life. One of these was to increase the zinc oxide/silver stoichiometric ratio, and the other to increase the number of separator layers. Preliminary data in separate studies indicated the desirability of increasing the potassium hydroxide concentration of the electrolyte also.

B. Effects of Float on Cycle Life

The data in Tables 2 and 3 are for a group of five batteries of six cells each, four of which had been floated at 11.40 V (1.90 V/cell) for 14 mo subsequent to the initial few cycles and prior to their being placed on the automatic cycle regime. The fifth (the 17 group) was on open circuit for 2 mo after the initial cycles, and before initiation of the life cycle tests. This group (17) achieved the most cycles of any group. After 148 cycles, at which time their capacity had decreased to a value of 50% of nominal, the cycle depth was decreased to 30%. At that level, an additional 93 cycles were attained before their capacities dropped below the demand cycle. None of this group had developed internal shorts. No other group reached 148 cycles before at least two cells of the group had become shorted. The conclusion follows that cell cycle lives had been reduced as a result of the 14-mo float.

Also, as shown on Table 3, the cells that had been floated delivered less capacity after float than before. This result was not anticipated. A group of heat-sterilized cells in an earlier phase of the investigation had not demonstrated a decrease in their post-float capacities compared with those obtained prior to float. There were two differences between the two experiments that could have been significant. The cell elements in the first experiment had been sterilized as cell packs, then placed in cell jars and sealed. (These were fabricated before sterilizable cell cases were available.) Also, the earlier cells had been floated, in parallel, at 1.952 V. The data on Table 3 supports the additional observation that during a second post-float cycle the capacities did not reach those of the pre-float cycle, and in most cases were not greater than the first cycle after float.

Cycling of these cells was terminated after two cells of each battery had failed. Cell failures (the 17 group excepted) resulted from silver penetration of the separation. The first ones to fail were those of the 16 group, one cell failing after 112 cycles and the second after 115. The 19 group was similar in construction except that cells in this group had absorber adjacent to the silver electrodes while the 16 group did not; first cell failure occurred after 135 cycles. The results of this comparison, plus the observed condition of the separator during dissection, indicated that the pressure of the absorber was beneficial to separator life. The three groups of cells 15, 18, and 19 differed from each other in the percentage of zinc sulfide in the negative mix. The number of cycles before failure for these cells was least in the cells having the highest percentage of zinc sulfide (18 group), and most in those having the lowest percentage (15 group). These data suggest that the presence of that additive was detrimental to cycle life.

C. Effects of Separator Configuration on Cycle Life

The group of cells included on Table 4 were designed to investigate the effects on cycle life of increased pack tightness, of absorbers next to the zinc electrodes, and of increased number of layers of separator. Whether or not all voltages and capacities of some of these designs would be at unacceptable levels had not been established. These cell constructions were preliminary designs to obtain cell performance information, and, for this reason, were not evaluated in triplicate. From information obtained during initial cycles, it was planned that the most promising designs would be more extensively evaluated.

Six of the cells had the methacrylic acid grafted separator type with three pack tightness values. One of each pair of cells had an FT2140 polypropylene (Pellon Corp.) adjacent to the negative electrodes, with 8 layers of the grafted separator, and the other had 10 layers of the grafted material. All had FT2140 polypropylene at the positive electrodes.

Six cells, the data for which are in the lower part of Table 4, had acrylic acid grafted separator and FT2140 polypropylene adjacent to both sets of electrodes.

The zinc oxide/silver stoichiometric ratio was 1.5 and the KOH electrolyte concentration 45% by weight into which 120 g of zinc oxide per liter had been dissolved.

All had the same negative mix except for cell 60-1. This cell had been constructed to replace 40-2, which had been lost during initial cycling due to equipment failure. Inadvertently, in haste to replace it, so as not to delay the start of the automatic cycling of the others, electrodes having the negative mix containing 5% zinc sulfide were used. In prior tests of cells, those included in Table 2, inclusion of ZnS resulted in reduced cycle life of cells. In this test, this particular cell reached the highest number of cycles for cells having methacrylic acid grafted separator.

Of the six cell groups with methacrylic acid grafted separator, cells 34-1 and 34-2 were discontinued when cell leakage became excessive. (The epoxy used for sealing these differed from that used for the others.) Since these had the loosest cell packs, and accumulating data indicated tighter packs to be more advantageous to cycle life, no attempt was made to restore them. With the exception of cell 60-1 (233 cycles), cycle life varied from 179 to 210.

Of the cells of Table 4 having acrylic acid grafted separator, cycle life varied from 192 to 273. Cell 46-2, similar in construction to 46-1, failed due to zinc penetration of the separator after 199 cycles.

An additional three cells included in Table 4, 63-1, 63-2, and 67-1, were similar in construction to 60-1, but with slight variation in the negative electrode mix. The first two of this group had 10% instead of the 5% ZnS and the third had none. (There is one difference between these cells containing zinc sulfide and those of Table 2. That is, these had mercuric oxide instead of the mercuric sulfide as in the former ones.) In this group of cells, electrolyte having a KOH concentration of 50% with 150 g of ZnO/liter was used for activating. Cell 67-1 failed after 181 cycles. Upon dissection, zinc was found to have penetrated seven layers of separation. As a result of the failure of 67-1, cells 63-1 and 63-2 both received excessive overcharge and leaked. Because these were the only cells having 50% KOH electrolyte and had good discharge capacities during bench tests, they were resealed by overpotting. Electrolyte was added and cycling resumed. (Additional cycles on cells which have been overcharged and have leaked cannot be considered equivalent to those of cells which have not leaked, because the relative states of charge have been altered. Due to the escape of gas, the zinc electrode reaches a higher state of charge. The likely result of this is that subsequent capacity would be greater than that which would have been available if the cell had not leaked.)

D. Effects of Extended Negatives and Additives on Cycle Life

Table 5 shows two groups of cells, one having acrylic acid grafted separator and the other methacrylic. Three cells of each group had positives reduced in size (extended negatives). Depth of cycle was 50% of nominal based on the amount of silver in those having the standard size silver electrodes. The stoichiometric ZnO/Ag ratio was 2. If the ratio calculations were based on the total ZnO in those having the extended negatives, the ratio would be 2.4. For the 66 group, having methacrylic acid grafted separator, the extended negative cells had the longest cycle life, failure resulting from loss of capacity. The others failed by shorting except for 66-2, which burst due to overcharge. Of the 72 group having acrylic acid grafted separator, the three having extended negatives failed first due to loss in capacity. The other three of the 72 group reached 211 cycles before the first cell was removed due to loss in capacity. In this test, the use of extended negatives did not result in delaying the shape change of the zinc electrodes.

Of the cells on Table 6, the 74 group was similar in construction to the 66 group of Table 5 except that mercuric oxide replaced mercuric sulfide as the additive in the zinc electrodes. Cells 74-4 and 74-6 achieved higher cycle life than the other three, which had extended negatives. (Cell 74-5 was not tested since it demonstrated behavior during initial cycles which varied from the others of the group. This could have resulted from improper wetting of all components of the cell.) Since the failure mode of these cells was by shorting, any effect of the extended negative electrodes in delaying erosion of the zinc electrodes was not seen.

The other cells of Table 6 differed from cells 74-4 and 74-6 in that three had FT2140 polypropylene (Pellon Corp.) adjacent to the negative electrodes and the others had potassium titanate paper, LPM-174-67 (The Mead Corp.). All had 9 layers of separator instead of 10 as in the 74 cells. Comparing cells 78-1, 78-2, and 78-3 with cells 74-4 and 74-6, no advantage is seen to have resulted from the inclusion of the polypropylene at the negatives. The cells having the potassium titanate paper adjacent to the zinc electrodes, however, reached the highest number of cycles before any failure than any other group. Also, their voltages at the end of load during the automatic cycles has shown less decay from the initial values, indicating that active material erosion of the zinc electrodes has been less. It should be pointed out, however, that the potassium titanate paper used was 0.060 cm thick and occupied considerable space. The consequent reduction in active material of larger cells would seriously reduce their specific energy compared with cells not using the potassium titanate paper.

IV. CONCLUSIONS

The data included in this report, and observations made during failure analysis studies, support the following statements:

(1) Cycle life in excess of 300 cycles, at 50% depth, has been demonstrated for heat-sterilized cells.

(2) Two types of separators were evaluated. Deterioration in capacity due to negative electrode shape change was generally the mode of failure of cells having acrylic acid grafted separator. Internal shorting by zinc and/or silver penetration was more prevalent in cells having the methacrylic acid type. Load voltages for cells having methacrylic acid grafted type separator were approximately 40 mV higher at the 3-h rate than for cells having acrylic acid grafted type.

(3) No beneficial effect on cycle life was obtained from cells in which mercuric sulfide replaced mercuric oxide in the zinc electrode.

(4) No beneficial effect on cycle life was obtained in one group of cells which had zinc sulfide additive to the negative electrode. Another group of three cells containing the zinc sulfide additive achieved more cycles than similarly designed cells without it.

(5) Cells having a zinc oxide/silver stoichiometric ratio of active materials of 1.1 achieved fewer cycles than those having a ratio of 1.5. Cells having a zinc oxide/silver ratio of 2.0 did not achieve more cycles than those with 1.5.

(6) The use of extended negative electrodes did not result in improved cycle life compared with similar cells having positive and negative electrodes of the same size.

(7) Within the range tested, an allowance per layer of separator of 0.0055 cm for methacrylic acid type, and of 0.0040 cm for acrylic acid type, resulted in slightly higher cycle life than more loosely or more tightly packed cells.

(8) No improvement in cycle life was attained by inclusion of a polypropylene absorber adjacent to the negative electrode. However, the highest cycle life of any group prior to failure of any cell occurred in cells having potassium titanate paper adjacent to the zinc electrode. (Because of the space occupied by this material, batteries of cells containing potassium titanate paper would operate at lower specific energy values than similar cells without it.)

(9) Cells having methacrylic acid grafted separator displayed load voltages at a current density of 16 mA/cm^2, which were approximately 40 mV higher than for cells having the same number of layers of acrylic acid grafted material.

V. FUTURE WORK

Any future work on the heat-sterilized silver-zinc cell should more extensively study the effect on cycle life of: the inclusion of potassium titanate paper adjacent to the zinc electrode, and electrolyte containing 50% potassium hydroxide. Additional testing of cells having zinc sulfide, but not mercuric sulfide, in the zinc electrode should be done.

REFERENCE

1. Adams, L. W., and Harlowe, W. W., Development of Battery Separator Materials, Final Report, Southwest Research Institute, San Antonio, Tex., Apr. 1970.

Table 1. Construction and cycle life data on sterilized Ag-Zn cells

Cell number series 179-	Separator	Thickness/ separator layer, cm	Negative mix	Cycles to failure	Remarks
31-2	8MA	0.0083	15	195	Capacity loss
31-3				146	Zinc short
31-4				191	Zinc short
40-1	8MA	0.0083	15	98	Zinc short
40-2				192	Capacity loss
40-3				63	Silver short
41-1	8AA	0.0077	15	140	Capacity loss
41-2				125	Silver short
41-3				127	Silver short
45-1	8AA	0.0070	17	124	Silver short
45-2				95	Zinc short
45-3				125	Silver short
50-1	8AA	0.0070	15	154	Capacity loss
50-2				154	Capacity loss
50-3				154	Capacity loss
55-1	8AA	0.0083	17	185	Silver short
55-2				185	Capacity loss
55-3				84	Zinc short

Notes:

1. All cells had U-wrap negative construction except for the 40 group, which had U-wrap positive.
2. All cells had U-fold polypropylene absorbers at the silver electrodes (EM476, Kendall Co.).
3. All cells contained 43% KOH into which 105 g of ZnO/liter had been dissolved.
4. Cycle depth 55% of nominal (based on 0.25 A-h per gram of silver).
5. ZnO/Ag stoichiometric ratio, 1.1.
6. Negative mix 15 contained 78% ZnO, 10% ZnS, 3% HgO, 9% Teflon. Negative mix 17 contained 88% ZnO, 3% HgO, 9% Teflon.

Table 2. Construction and cycle life data

Cell number series 123-	Separator	Pack tightness, cm	Negative mix	Cycles to failure	Remarks
15-1	8AA	0.007	1A	142	
15-2				142	Ag short
15-3				142	
15-4				142	
15-5				123	Ag short
15-6				142	
16-1	8AA	0.007	4A	115	Ag short
16-2				118	Ag short
16-3				118	
16-4				118	
16-5				112	Ag short
16-6				118	Ag short
18-1	8AA	0.007	9A	120	Ag short
18-2				122	Ag short
18-3				123	
18-4				123	
18-5				123	
18-6				123	
17-1	8AA	0.0070	4A	148, 241	Capacity loss
17-2				148, 241	Capacity loss
17-3				148, 241	Capacity loss
17-4				148, 241	Capacity loss
17-5				148, 241	Capacity loss
17-6				148, 241	Capacity loss
19-1	8AA	0.0070	4A	136	
19-2				136	Ag short
19-3				135	Ag short
19-4				136	
19-5				136	Ag short
19-6				136	

Table 2 (contd)

Notes:

1. Electrolyte for all cells, 44% KOH, in which 110 g of ZnO/liter had been dissolved.

2. Absorber for 15, 17, 18, 19 series, EM476 (Polypropylene, Kendall Co.) irradiated by RAI.

3. After failure due to capacity loss at 50% depth, cycling continued at 30% depth for 17 series only.

4. ZnO (and ZnS when included)/Ag ratio, 1.7 stoichiometric.

5. Series 15, 16, 18, 19 had been floated as batteries of six cells each at 1.90 V/cell for 14 mo prior to cycling. For series 17, cycling began 2 mo after sterilization.

6. Negative mix 1A contained 88% ZnO, 3% HgS, 9% Teflon powder; Negative mix 4A contained 81% ZnO, 3% HgS, 7% ZnS, 9% Teflon powder; Negative mix 9A contained 76% ZnO, 3% HgS, 12% ZnS, 9% Teflon powder.

7. Pack tightness in allowance per separator layer using 0.0075 cm per layer of EM476 absorber.

8. AA refers to acrylic acid grafted separator.

Table 3. Capacities of Ag-Zn cells before and after 14-mo float

	1	2	3	4	5	6	1	2	3	4	5	6
	15 Series						16 Series					
Pre-float cycle, A-h												
At 60 mA/cm^2	3.46	4.17	4.71	4.38	3.93	3.93	3.57	1.80	4.44	3.66	3.51	3.87
At 12 mA/cm^2	1.18	0.90	0.60	0.82	1.50	0.87	1.72	2.40	0.81	1.33	1.33	1.18
Total	5.14	5.07	5.31	5.20	5.43	4.80	5.29	4.20	5.25	4.99	4.84	5.05
First post-float cycle, A-h												
At 60 mA/cm^2	2.70	1.85	3.25	2.70	2.52	2.52	3.25	3.25	3.45	3.45	2.95	3.25
At 12 mA/cm^2	0.66	1.45	0.28	0.82	1.18	1.00	1.02	0.76	0.63	0.45	0.71	0.50
Total	3.36	3.30	3.53	3.52	3.70	3.52	4.27	4.01	4.58	3.90	3.66	3.75
Second post-float cycle, A-h												
At 60 mA/cm^2	2.88	2.97	3.25	3.33	3.15	3.15	3.18	3.48	3.33	3.21	2.37	3.03
At 12 mA/cm^2	0.54	0.50	0.32	0.25	0.46	0.28	0.80	0.40	0.65	0.65	1.26	0.52
Total	3.42	3.43	3.57	3.58	3.61	3.43	3.48	3.88	3.98	3.85	3.63	3.55
	18 Series						19 Series					
Pre-float cycle, A-h												
At 60 mA/cm^2	4.53	4.38	4.14	4.44	3.39	4.56	4.95	4.62	5.01	4.68	4.44	5.00
At 12 mA/cm^2	0.90	0.84	1.20	0.88	1.74	0.78	0.45	0.76	0.72	0.64	0.91	0.62
Total	5.43	5.22	5.34	5.32	5.13	5.34	5.40	5.38	5.73	5.32	5.35	5.62
First post-float cycle, A-h												
At 60 mA/cm^2	3.25	2.90	2.90	3.42	2.40	3.42	4.00	3.25	3.95	3.65	3.02	3.25
At 12 mA/cm^2	0.65	0.93	1.00	0.57	1.05	0.54	0.28	0.56	0.43	0.43	0.98	0.55
Total	3.90	3.83	3.90	3.99	3.45	3.96	4.28	3.81	4.38	4.08	4.00	3.80
Second post-float cycle, A-h												
At 60 mA/cm^2	3.09	2.91	3.21	3.72	2.79	3.15	3.72	3.33	3.47	3.66	3.69	3.60
At 12 mA/cm^2	0.64	0.67	0.57	0.21	0.74	0.67	0.40	0.43	0.26	0.33	0.39	0.42
Total	3.73	3.58	3.78	3.93	3.58	3.82	4.12	3.76	4.23	3.99	4.08	4.02

Table 4. Construction and cycle life data on Ag-Zn cells

Cell number series 189-	Separator	Separator allowance/layer, cm	Negative electrode mix	Absorber	Cycles to failure	Remarks
34-1	8MA	0.00625	1A	Both	155	Leak
34-2	10MA	0.00625	1A	Positive	162	Leak
40-1	8MA	0.0055	1A	Both	210	Short
60-1	10MA	0.0055	26	Positive	233	Short
44-1	8MA	0.0050	1A	Both	179	Zn short
44-2	10MA	0.0050	1A	Positive	193	Short
63-1	10MA	0.0055	15	Positive	323	Capacity loss
63-2	10MA	0.0055	15	Positive	272	Short
67-1	10MA	0.0055	17	Positive	181	Zn short
41-1	8AA	0.0050	1A	Both	203	Capacity loss
41-2	8AA	0.0050	1A	Both	192	Capacity loss
42-1	8AA	0.0040	1A	Both	211	Capacity loss
42-2	8AA	0.0040	1A	Both	213	Capacity loss
46-1	10AA	0.0040	1A	Both	273	Short
46-2	10AA	0.0040	1A	Both	199	Zn short

Notes:

1. Electrolyte KOH concentration for 63-1, 63-2, and 67-1, 50% into which 150 g of ZnO/liter had been dissolved. For all others, 45% into which 120 g of ZnO/liter had been dissolved.
2. ZnO/Ag stoichiometric ratio, 1.5.
3. MA refers to methacrylic acid grafted separator; AA to acrylic acid.
4. Negative mix compositions: 1A (88% ZnO, 3% HgS, 9% Teflon); 15 (78% ZnO, 10% ZnS, 3% HgO, 9% Teflon); 17 (88% ZnO, 3% HgO, 9% Teflon); 26 (83% ZnO, 5% ZnS, 3% HgO, 9% Teflon).
5. Cycle depth 50% of nominal.

Table 5. Construction and cycle life data on Ag-Zn cell groups 66 and 72

Cell number series 189-	Separator	Separator allowance/ layer, cm	Negative electrode mix	Extended negatives	Cycles to failure	Remarks
66-1	10MA	0.0055	1A		180	Short
66-2	10MA	0.0055	1A		188	Leak
66-3	10MA	0.0055	1A		171	Short
66-4	10MA	0.0055	1A	X	212	Capacity loss
66-5	10MA	0.0055	1A	X	212	Capacity loss
66-6	10MA	0.0055	1A	X	212	Capacity loss
72-1	10AA	0.0050	1A	X	144	Capacity loss
72-2	10AA	0.0050	1A	X	147	Capacity loss
72-3	10AA	0.0050	1A	X	147	Capacity loss
72-4	10AA	0.0050	1A		211	Capacity loss
72-5	10AA	0.0050	1A		211	Short
72-6	10AA	0.0050	1A		211	Capacity loss

Notes:

1. Potassium hydroxide concentration for all cells, 45% (120 g of ZnO/liter).
2. Absorber adjacent positive electrodes for all cells (FT2140, Pellon).
3. Stoichiometric ratio, ZnO/Ag, 2.0. (For cells having extended negatives, value of ratio is 2.4 if total amount of ZnO is used for calculations.)
4. Negative mix 1A contained 88% ZnO, 3% HgS, 9% Teflon.
5. MA refers to methacrylic acid types; AA to acrylic acid.

Table 6. Construction and cycle life data on Ag-Zn cells

Cell number series 189-	Separator	Separator allowance/ layer, cm	Negative mix	Extended negatives	Cycles to failure	Remarks
74-1	10MA	0.0055	17	X	177	Short
74-2	10MA	0.0055	17	X	136	Short
74-3	10MA	0.0055	17	X	182	Short
74-4	10MA	0.0055	17		222	Short
74-6	10MA	0.0055	17		267	Short
78-1	9MA	0.0055	17		198	Short
78-2	9MA	0.0055	17		206	Burst
78-3	9MA	0.0055	17		145	Short
78-4	9MA	0.0055	17		311	Capacity loss
78-5	9MA	0.0055	17		325	Stopped cycling
78-6	9MA	0.0055	17		325	Stopped cycling

Notes:

1. Electrolyte, 45% KOH into which 120 g of ZnO/liter had been dissolved.
2. Zinc oxide/silver stoichiometric ratio 2.0.
3. FT2140 polypropylene absorber adjacent all silver electrodes and to zinc electrodes of 78-1, 78-2, and 78-3.
4. Potassium titanate adjacent zinc electrodes of cells 78-4, 78-5, and 78-6.
5. MA refers to methacrylic acid separator types.
6. Negative mix 17 contained 88% ZnO, 3% HgO, 9% Teflon.

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TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No. 33-581	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle HEAT-STERILIZED SILVER OXIDE-ZINC CELLS: CYCLE LIFE STUDIES		5. Report Date January 1, 1973 6. Performing Organization Code
7. Author(s) J. T. Arms		8. Performing Organization Report No.
9. Performing Organization Name and Address JET PROPULSION LABORATORY California Institute of Technology 4800 Oak Grove Drive Pasadena, California 91103		10. Work Unit No. 11. Contract or Grant No. NAS 7-100 13. Type of Report and Period Covered Technical Memorandum
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15. Supplementary Notes		

16. Abstract

A JPL study was conducted to evaluate the cell design parameters that contribute to the cycle life of sealed, heat-sterilized silver oxide-zinc cells. Test cells having a rated capacity of 4.2 A-h were fabricated using zinc oxide electrodes prepared by the sintered Teflon process developed at JPL, silver electrodes purchased from ESB, Inc., and separators produced by Southwest Research Institute under NASA contract. Two separator variations were evaluated, one having acrylic acid and the other methacrylic acid grafted to irradiated polyethylene film.

All cycle life tests were conducted at ambient temperature on a 24-h cycle consisting of 3 h of discharge through a fixed resistance, and 21 h of charge by a modified constant potential having a current limit. Cells were tested as 6-cell batteries. Depth of cycle was approximately 50% of nominal. (Nominal rating was based on the value of 0.25 A-h per gram of silver.)

Significant results of this study included the following: (1) cycle life in excess of 300 cycles was attained; (2) a zinc oxide/silver stoichiometric ratio of 1.5 resulted in greater cycle life than a ratio of 1.1, and similar cycle life to cells having a ratio of 2; (3) cells having methacrylic acid grafted

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16. Abstract

separators suffered somewhat less in capacity loss due to zinc electrode shape change than cells having acrylic acid type; (4) use of acrylic acid grafted separators was slightly superior to the methacrylic acid type in respect to silver penetration; and (5) the inclusion of a layer of potassium titanate paper adjacent to the zinc electrodes resulted in cells that achieved higher cycle life before any of the group failed than that reached by cells of any other construction.

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