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Life Capability of the Silver Electrode in Alkaline Electrochemical Cells

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16. Abstract

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The approach involved examination of aged (to 12 years) Ag-Zn and Ag-Cd cells. The capacities of the cells' silver electrodes were determined both in situ and in a specially designed bath with the use of zinc reference electrodes. Estimates of silver electrode degradation rates were made by comparing the recently measured capacities with the reported early life capacities. Chemical analyses were carried out to determine the extent of silver loss from the electrode and its distribution throughout the cell components.

The results established that the silver electrode is very stable when stored at reduced temperatures in the range of 0 to -51 C, in which it exhibits a permanent degradation in capacity of only about 0.5%/year. The results also indicated that the silver electrode is not quite so stable when operated and stored at room temperature, where it exhibits permanent degradation in the range of 3% to 14%/year. Appreciable amounts of silver were found throughout

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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

The investigation described in this report was concerned with establishing the life capability of silver electrodes in alkaline cells. The results were employed in predicting the life capability of the proposed new Ag-H_2 cell and also in assessing the merits of employing silver electrodes in long-life probe batteries.

The approach involved examination of aged (to 12 years) Ag-Zn and Ag-Cd cells. The capacities of the cells' silver electrodes were determined both in situ and in a specially designed bath with the use of zinc reference electrodes. Estimates of silver electrode degradation rates were made by comparing the recently measured capacities with the reported early life capacities. Chemical analyses were carried out to determine the extent of silver loss from the electrode and its distribution throughout the cell components.

The results established that the silver electrode is very stable when stored at reduced temperatures in the range of 0 to -51 C, in which it exhibits a permanent degradation in capacity of only about 0.5%/year. The results also indicated that the silver electrode is not quite so stable when operated and stored at room temperature, where it exhibits permanent degradation in the range of 3% to 14%/year. Appreciable amounts of silver were found throughout the cells operated at room temperature, including even small amounts in the negative electrode.

The significance of these findings is discussed in terms of the life capability of Ag-H_2 cells and the applicability of silver electrodes to probe batteries.

I. INTRODUCTION

The objective of this investigation was to establish the life capability of silver electrodes in alkaline silver electrochemical cells. The information derived from this effort will be useful in assessing the merits of current and proposed programs to develop new lightweight aerospace cells containing silver electrodes such as, for example, the proposed Ag-H_2 cell (Refs. 1,2).

In a prior report, JPL presented the results of initial findings on this subject (Ref. 3). One of these findings, based on reports from others in the field, was that the silver electrode should be at least capable of delivering the following outputs while on continuous cycling: (1) 270 cycles at 80% depth of discharge (DOD) to 6500 cycles at 20% DOD while being tested to a low earth orbit cycling regime and (2) 300 cycles at 50% DOD to 470 cycles at 30% DOD while being tested to a high earth orbit cycling regime. Other findings were derived from stand tests conducted on JPL cells by the Naval Weapons Support Center (NWSC). It was noted that the silver electrode exhibits a capacity loss of (1) no more than 1 to 3% per month while on room temperature charged stand (magnitude uncertain and perhaps below indicated limits) and (2) less than 10% over an 8-year period of intermittent use provided its temperature is maintained in the range of -7 to -13°C.

Also in the above report, a plan was outlined to gather additional data so as to be able to either confirm or perhaps modify the initial findings. The plan principally involved the conduct of failure analyses of a group of aged silver cells which had been on test at JPL, NASA Lewis Research Center (LeRC), and NWSC.

Since the onset of these follow-on activities, JPL completed in-house failure analyses on 17 such aged silver cells. Also JPL requested NWSC to conduct failure analyses on an additional group of seven aged silver cells which had been maintained on test at JPL. At this point, sufficient information has been collected to yield meaningful results. The intent of this document is to present these findings and their significance.

II. EXPERIMENTAL PROCEDURES

All of the cells employed in this investigation were secondary Ag-Zn or Ag-Cd units, and each was hermetically sealed in a plastic container. Table 1 gives a brief description of each cell and its pertinent history. Cells 1 through 9 were taken from a group that had been on charged stand at low temperatures at NWSC and were shipped to JPL in January 1976. Cells 1 through 7 were of the Ag-Zn type, and cells 8 and 9 were of the Ag-Cd type. Cells 10 through 14 were sent to JPL by NASA LeRC in March 1976, after having been subjected to an assortment of extended cycle tests at room temperature. Cell 15 was a special in-house-developed Ag-Zn cell that had been subjected to extensive room temperature cycling at JPL. Cell 16 was taken from a spare JPL Ranger battery which had been maintained in cold storage at JPL since 1964. Cell 17 was one of a group of Ag-Zn cells that was sent to JPL by LeRC in 1974. This particular cell had undergone extensive cycling at room temperature at JPL.

Table 2 gives a brief description and history of the Ag-Zn cells examined by NWSC. These cells were from the same group as cells 1 through 9; i.e., they had been on charged stand at low temperatures at NWSC. The only difference between the two groups of cells was that those shown in Table 1 were examined by JPL and those in Table 2 were examined by NWSC, as described at the end of this section.

The JPL-devised procedure for analyzing the cells consisted of the following steps:

(1) Open circuit voltage and impedance of the cells were measured in the "as received" condition.

(2) The cell was rinsed with distilled water and sprayed with phenolpthalein solution to determine the presence of leaks.

(3) The residual capacity of the cell was determined by placing it on constant current discharge to a 1.0-V cutoff in the case of the Ag-Zn cells and an 0.8-V cutoff in the case of the Ag-Cd cells. The discharge current was the same as that employed in prior characterization tests and was usually near 10 A. If no prior history was available, a current of 10 A was employed in the discharge.

(4) The as received capacity of the cell was determined by subjecting it to a complete charge and discharge cycle. The charge was carried out at constant current to a cutoff of 2.0 V in the case of the Ag-Zn cells and 1.60 V in the case of the Ag-Cd cells. Discharge was carried out at constant current to a 1.0-V cutoff in the case of the Ag-Zn cells and an 0.8-V cutoff in the case of the Ag-Cd cells. Charge and discharge currents were the same as those employed in prior characterization tests. If no prior history was available, charge was carried out at 1.0 A and discharge at 10 A. Cell voltages were recorded once each 15 min during charge and once each 2 min during discharge with a Non-Linear Systems Data Acquisition System.

(5) At this point, the cell was equipped with a reference electrode so as to be able to monitor its silver electrode performance in subsequent tests. The reference electrode consisted of a short segment, about 10 cm. of pure (0.9999) zinc wire with a diameter of 0.1 cm. This electrode was prepared and installed in the cell as shown in Fig. 1. Electrolytic contact with the

plate stack was provided by a segment of KOH-moistened separator fabric (Dynel Webril EM-310), which surrounded the wire and extended to the top of the plates. The wrapped wire was inserted in a teflon sleeve and the assembly secured in place by application of quick-set epoxy cement, as shown in Fig. 1.

(6) After the reference electrode was installed, the cell was subjected to an extended charge and discharge cycle so as to measure the "recoverable in situ" capacity of its positive electrode. The first step consisted of constant current charge for an extended period of time such that the cell's positive electrode reached the state of overcharge and was evolving oxygen. In most cases, this condition was attained by charging at 1.0 A for a period of 48 h. The second step consisted of constant current discharge for an extended period of time such that the cell's positive electrode reached the state of reversal and was evolving hydrogen. In most cases, this condition was attained by discharging at 10 A for 3 to 5 h. During this cycle, the cell terminal voltage as well as the reference to positive terminal voltage were recorded each 15 min during charge and each 2 min during discharge with the data acquisition system. The conditions of overcharge and reversal were ascertained by observing a sharp inflection in voltage of the positive versus reference electrodes after extended periods of charge and discharge, respectively.

(7) At this point, the cell was removed from test and placed in a bench vise for disassembly. The case was cut open carefully with a hacksaw, care being taken not to damage the plates. The electrode pack was then removed, and the plate tabs were cut near the terminals

to separate the plates. The individual plates were placed in order on a sheet of polyethylene, and visual observations were made regarding the condition of the plates and separators. Samples of the negative plate, positive and negative plate wraps, and separator were collected in plastic bags for chemical analysis.

(8) In order to confirm the above results on the positive electrode capacity, the positive plates were removed from the stack, and their combined capacity was measured independently in a specially designed bath. The bath consisted of a large cylindrical glass container filled with 30% KOH and equipped with an array of stainless steel counter electrodes which were connected in parallel electrically. The silver plates were sandwiched between the counter electrodes and also connected in parallel electrically. The plates were held in place with specially designed Lucite spacers and were wrapped loosely with separator fabric to avoid internal short circuits. The bath was equipped with a zinc reference electrode, which consisted merely of a segment of pure zinc wire as described above. With this arrangement, the silver electrode was then charged and discharged against the stainless steel counter electrode. Both charge and discharge were carried out at constant current in an identical manner to that described in step 6 above. The counter-to-silver-electrode voltage as well as the reference-to-silver-electrode voltages were recorded each 15 min during charge and each 2 min during discharge.

(9) At the completion of the capacity test, the silver electrodes were removed from the bath, leached with distilled water, dried overnight at 110°C, and then weighed.

Chemical analyses were performed on a few of the cells in order to carry out an overall silver balance, i.e., to determine how much silver remained in the positive plates and how much silver had accumulated in the various cell components consisting of the zinc electrode, plate wraps and separators, and the electrolyte. The amount of silver in the plates was determined gravimetrically as given by step 9. The amount of silver in the zinc was obtained by chemically determining the ratio of silver to zinc in a sample of the zinc and then multiplying by the known weight of zinc. The amount of silver in the wraps and separators was determined by measuring the silver content of known sample areas of these components and then multiplying by the ratio of total to sample area. The amount of silver in the electrolyte was deemed negligible on the basis of the known solubility of silver in KOH near 4×10^{-4} N (Ref. 4) and the fact that the cells contained less than 100 cm^3 of electrolyte. On this basis, no analysis was carried out on the silver content of the electrolyte. The silver contents of the various components were determined by first dissolving (in the case of the zinc) or leaching (in the case of the wraps and separators) the sample in a 1:1 solution of nitric acid. The various washings were then diluted to 1.0 ℓ. The concentration of silver (and zinc in the case of the zinc sample) in the diluted samples was then determined by atomic absorption using a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer. Calibration curves for silver and zinc were determined using standard solutions in the 5- to 20-μg metal/ml range. Sample solutions were diluted accordingly for this range.

The NWSC method of analysis (for the cells given in Table 2) was not quite so extensive as that employed by JPL. Briefly, the NWSC method consisted of (1) opening a cell, (2) removing the positive plates, (3) selecting one of the positive plates for capacity measurement in a bath similar to that described above, (4) measuring capacity in the bath, and finally (5) multiplying the single plate capacity by the number of positive plates to arrive at the total silver electrode capacity.

III. RESULTS

Figure 2 gives typical results obtained during one of the in situ capacity tests on the silver electrode of a silver-zinc cell. The voltage trace of the cell's silver electrode is shown versus the installed zinc reference electrode potential during the course of a constant current discharge at 10 A. The cell had previously been overcharged for 48 h at 10 A to insure that the silver electrode was fully charged at the start. Inspection of this curve reveals a sharp decline in voltage of the silver electrode after 225 min of discharge. The in situ capacity of the silver electrode is thus determined to be 225 min × 10 A × 1 h/60 min or 37.5 A-h. It should be pointed out that the cell voltage declined sharply and reversed (below 0 V) well before the decline in silver electrode voltage. In this particular case, the cell voltage fell below 0 V after only 100 min. On this basis, the calculated cell output is 100 min × 10 A × 1 h/60 min or 16.7 A-h, and it is apparent that this output corresponds to the capacity of the cell's zinc electrode.

Figure 3 gives typical results of a capacity test on the individual silver electrode of the same cell as above in the specially designed bath. The figure shows the voltage trace of the silver electrode versus the potential of an installed zinc reference electrode during the course of constant current discharge at 10 A against counter stainless steel electrodes. As above, the silver electrode had been previously charged for 48 h at 1 A against the steel electrode to insure that it was fully charged at the start. Inspection of this curve reveals a sharp decline in voltage of the silver electrode after 240 min of discharge. On this basis the capacity of the silver electrode, as measured in this manner, is determined to be 240 min × 10 A × 1 h/60 min or 40.0 A-h.

Table 3 is a summary of the capacities of all cells tested at JPL. The first column gives the cell numbers, which correspond to those in Table 1. The second column presents a brief description and history of each cell as per Table 1. The third column gives the cell capacities as measured in their early stages of life. The fourth column lists the recent cell capacities after the indicated period of time and use and as measured in the usual manner to a fixed cutoff voltage. The fifth column contains the in situ silver electrode capacities as described above. Finally, the sixth column gives the capacities of the silver electrodes in the bath as described above.

Table 4 is a summary of the capacities of the cells tested at NWSC. The first three columns give identical information to that given in Table 3. The fourth column presents the most recent cell capacity as determined by NWSC during the course of the charged stand test, and the fifth column gives the silver electrode capacity as determined by the method discussed above.

Table 5 gives the results of one of the JPL chemical analyses on a cell that had been subjected to a low-temperature charged stand test. The table shows a breakdown of silver in the various components in terms of actual grams and also percent of total silver.

Table 6 presents the results of another of the JPL chemical analyses on a cell that had been subjected to extensive cycle and stand tests at room temperature. The table gives both actual weights and percentages of total silver.

IV. DISCUSSION

Inspection of Tables 3 and 4 reveals several significant points. First, it is noted that in all cases, regardless of type and history, the cells exhibit appreciable capacity degradation between the time of manufacture and the time of these tests. Also it is noted that the capacities of the silver electrodes are significantly higher than their corresponding cell capacities at the time of the tests. These results signify that the primary reason for capacity loss cannot be attributed to degradation of the silver electrodes. Rather, the loss is attributed either to the presence of internal short circuits (which were found in several cases) or degradation in capacity of the negative electrodes (which was found in other cases, as per the voltage traces of the in situ capacity tests).

Next, it can be shown that some of the silver electrodes exhibit little if any degradation in capacity throughout their lives. The capacities of some, especially those maintained at low temperatures, were even noted to increase during the course of their lives. Demonstration of this point is made by comparing the early life capacities (which are actually the capacities of the silver electrodes since the cells are positive-limited in early life) with either the in situ or "in bath" capacities of the silver electrodes during this test period. For example, the capacity of the electrode in cell 1 is noted to be 31.3 A-h in early life and 24.0 to 46.6 after 7 years of stand at low temperatures, depending on the method of measurement. Also the capacity of the electrode in cell 2 is noted to be 31.7 A-h in early life and 33.3 to 35.8 A-h after 7 years of stand at low temperatures. Similar results are noted for the electrodes in cells 3 through 7, which were also maintained for 7 years at low temperatures as well as the electrode in cell 16, which was maintained for 12 years at low temperature and for cells 20, 22, 23, and 24, which were stored for 8 years at low temperatures.

It is apparent that not all the silver electrodes are immune to degradative processes. In particular, it is noted that those operated and stored at room temperature did show some signs of capacity loss. The electrode of cell 10, for example, had a capacity near 40 A-h in early life and 27.5 A-h in the recent bath test after 6 years of operation and stand at room temperature. Similar results are noted for cells 11, 12, 13, and 14, which were operated and stored at room temperature for 6 years, and also for the electrodes of cell 15, which was operated and stored for 4 years at room temperature. One exception was the electrode of cell 17, which exhibited an increase in capacity after operation at room temperature. It should be noted, however, that cell 17 was operated for only slightly over 1 year.

Further evidence that the silver electrodes exhibit degradation at room temperature was presented in a report from NWSC in 1973, as given in Appendix A. Therein the performance of a Delco cell is described which was of the same type as cells 1 through 7 but had been on stand at room temperature rather than low temperatures. The results indicated an initial cell (and silver electrode) capacity near 25 A-h and a final silver electrode capacity of slightly over 3 A-h after 6 years of stand at room temperature. This amounts to a loss of about 14% per year for the charged stand condition at room temperature (assuming a linear degradation rate with time).

The results of the chemical analyses, summarized in Tables 4 and 5, are generally in agreement with those of the capacity measurements. Table 4, for example, shows that most (about 83%) of the initial silver content remains in the positive plates of cell 1, which was stored at low temperature. The amount retained, 98.2 g, is adequate to account for the observed capacity on the basis of the known practical yield of about 0.35 A-h/g of silver. Table 5, on the other hand, indicates some loss of silver from the electrode of cell 10, which was operated at room temperature. In this case, the electrode retained only about 58% of its initial silver content. The amount retained, 82.0 g, is in accord with the observed capacity on the basis of the above-mentioned yield of 0.35 A-h/g of silver.

The results of the chemical analyses raise a potential area of concern for the new Ag-H_2 cell. The concern is possible contamination of the cell's hydrogen electrode catalyst by silver and is based on the observation of the presence of silver throughout the cell, including even small amounts in the negative electrodes. One developer of Ag-H_2 cells explains that some redistribution of silver is to be expected on the basis of the known solubility of Ag_2O in the KOH electrolyte. He points out, however, that small amounts of silver, such as we observed, may not necessarily be deleterious to the performance of the hydrogen electrode (Ref. 6). Another developer acknowledges the potential problem area and suggests that it be examined in detail (Ref 7). The technical monitor of a developmental Ag-H_2 cell program is also aware of the potential problem but is not seriously concerned in that he maintains that the silver can be contained by the use of new inorganic separators (Ref. 8).

Having established the point that the silver electrodes undergo degradation, we must now address the problem of determining the magnitude of their degradation rates. Also it would be desirable to ascertain how these rates are affected by both electrode constructional features and operational modes. In this manner, we can then proceed to project the life capability of silver electrodes.

Had these issues been raised some 10 years ago, we might be in a better position to answer them, in that we would undoubtedly have undertaken a largescale statistically designed experiment on a variety of silver electrodes under a variety of operational modes. Since such a program was not performed, we are left to work with the limited results obtained to this point. On this basis, we will proceed to extract the most information available from existing results.

One point that can be made without reservation is that there are several silver electrode configurations that are extremely stable when maintained in the charged state at low temperatures in the range of 0 to -51°C. Under these conditions, the electrodes can be cycled a few times a year and deliver essentially 100% of their original capacity for periods of at least 12 years. Based on the results of tests on cell 16, it can be stated that the silver electrode degradation rate under these conditions is only about 0.5% per year (based on the difference of early life capacity and in situ capacity in 1976 and assuming a linear rate of degradation with time).

A second point that can be made is that there is at least one silver electrode configuration that is quite stable at room temperature for a period of 1 year. Under these conditions, the electrode can be operated continuously for at least 6 months and deliver 100% of its original capacity after a period of 1 year. Based on results of tests on cell 17, it can be stated that the silver electrode degradation rate of this particular cell is 0.0% per year for the first year.

Further analysis of the data indicates that most types of silver electrodes are not entirely stable at room temperature after periods of 4 to 6 years. Under these conditions, the electrodes can be operated over an assortment of cycle regimes and periods of stand and deliver an appreciable output but not 100% of their initial capacities. Based on the results of tests on cells 10 through 15, it would appear that the electrodes degrade at a rate of about

3 to 8% per year (assuming a linear rate of degradation with time) when operated part time over a 6-year period. Based on the NWSC report presented in Appendix A, it would appear that electrodes stored in the charged state may degrade faster at rates up to 14% per year (again assuming a linear degradation rate). This latter result, incidentally, suggests that the life of the electrode may be longer when it is in operation (on a cycle regime) than when it is merely left on charged stand.

Insufficient data has been obtained to isolate the effects of separator type, KOH concentration, type of anode, and cycle regime on room temperature degradation rate. About all that can be said here is that these parameters can and probably do account for the spread in degradation rates from 3 to 14% per year in that each could conceivably exert some influence on solubility and transport of Ag_2O, which is believed to be the cause for degradation. Further it is conceivable that the degradation rate may be reduced below 3% per year by judicious selection of optimum parameters.

V. CONCLUDING REMARKS

(1) The silver electrode is extremely stable when stored at reduced temperatures of 0 to -51°C. Under these conditions, the electrodes exhibit a degradation rate of about 0.5% per year (assuming a linear rate of degradation with time).

(2) The silver electrode does not appear to be quite so stable when stored and/or operated at room temperature. Under these conditions, the electrodes exhibit degradation rates of from 3 to 14% per year (assuming a linear rate of degradation with time).

(3) The findings regarding the excellent low-temperature storage capability of the silver electrode is significant for development of probe batteries which require long periods of stand. The results suggest that it should be possible to develop a 12 year, limited-cycle probe supply by combining the silver electrode with a suitably inert anode (other than zinc) and storing the assembly at reduced temperatures.

(4) The findings regarding the room temperature degradation rates of the silver electrode are useful in projecting the life capability of the proposed new Ag-H_2 cell. Under the best conditions (with the lowest observed silver electrode degradation rate of 3% per year and an assumed degradation rate of 0% per year for the hydrogen electrode) one could expect the following lives at the indicated depths of discharge; 17 years at 50% DOD, 10 years at 70% DOD, and 3 years at 90% DOD.

(5) The finding regarding the presence of silver throughout the cell, even within the negative electrodes, should not be taken lightly. The reason for this is possible contamination of the hydrogen electrode catalyst with silver. If such contamination does occur, then the assumption

regarding no degradation of the hydrogen electrode may be in error as the electrode may indeed degrade with time. Accordingly, the life capability estimates may be somewhat optimistic for the Ag-H_2 cell. To resolve this issue, some attention should be devoted to the effect of silver contamination on the catalyzed H_2 electrodes.

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Table 1. Description and history of silver cells examined by JPL

Cell No.	Description	Rated capacity, A-h	Wet life, yr	History
1	Ag-Zn cell from Delco; SN 68-27; pos.: 1L Dynel 470; sep.: 4L FSC; neg.: 1L Viscon; 40% KOH	25	7+	7 yr on charged stand test at NWSC, 12 full 100% DOD cycles during course of stand at 0°C.
2	Ag-Zn cell from Delco; SN 68-39; pos.: 1L Dynel 470; sep.: 4L FSC; neg.: 1L Viscon; 40% KOH	25	7+	7 yr on charged stand test at NWSC, 18 full 100% DOD cycles during course of -35°C.
3	Ag-Zn cell from Delco; SN 68-40; pos.: 1L Dynel 470; sep.: 4L FSC; neg.: 1L Viscon; 40% KOH	25	7+	7 yr on charged stand test at NWSC, 18 full 100% DOD cycles during course of stand at -35°C.
4	Ag-Zn cell from Delco; SN 68-55; pos.: 1L Dynel 470; sep.: 4L FSC; neg.: 1L Viscon; 40% KOH	25	7+	7 yr on charged stand test at NWSC, 18 full 100% DOD cycles during course of stand at -51[illegible].
5	Ag-Zn cell from Delco; SN 68-56; pos.: 1L Dynal 470; sep.: 4L FSC; neg.: 1L Viscon; 40% KOH	25	7+	7 yr on charged stand test at NWSC, 18 full 100% DOD cycles during course of stand at -51°C.
6	Ag-Zn cell from Delco; SN 68-57; pos.: 1L Dynel 470; sep.: 4L FSC; neg.: 1L Viscon; 40% KOH	25	7+	7 yr on charged stand test at NWSC, 18 full 100% DOD cycles during course of stand at -51°C.
7	Ag-Zn cell from Delco; SN 68-63; pos.: 1L Dynel 470; sep.: 4L FSC; neg.: 1L Viscon; 40% KOH	25	7+	7 yr on charged stand test at NWSC, 12 full 100% DOD cycles during course of stand at -51°C.

Table 1. (contd)

Cell No.	Description	Rated capacity, A-h	Wet life, yr	History
8	Ag-CD cell from Yardney; SN × 35; pos.: 2L woven nylon; sep.: 3L C-19-300; neg.: 1L Aldex	20	8	8 yr on charged stand test at NWSC, 15 full 100% DOD cycles during course of stand at -51°C.
9	Ag-Cd cell from Yardney; SN × 36; pos.: 2L woven nylon; sep.: 3L C-1a-300; neg.: 1L Aldex	20	8	8 yr on charged stand test at NWSC, 15 full 100% DOD cycles during course of stand at -51°C.
10	Ag-Zn cell from LeRC; SN HS 66-4; inorganic sep. bag on both pos. and neg. plates	40	6+	878 cycles over an 878-day period at 10% DOD, remainder on stand at room temp.
11	Ag-Zn cell from LeRC; SN HS 66-6; inorganic sep bag on both pos and neg. plates	40	6+	933 cycles over a 933-day period at 10% DOD, remainder on stand at room temp.
12	Ag-Zn cell from LeRC; SN HS-66-12; inorganic sep. bag on both pos and neg. plates	40	6+	891 cycles over an 891-day period at 10% DOD, remainder on stand at room temp.
13	Ag-Zn cell from LeRC; SN NHS-114-27, inorganic sep. bag on both pos. and neg. plates	40	5+	22 cycles over a 791-day period at 100% DOD, remainder on stand at room temp.
14	Ag-Zn cell from LeRC; SN HS 86-3, inorganic sep. bag on both pos. and neg. plates	40	5+	1630 cycles over a 954-day period at 7.5 to 15% DOD, remainder on stand at room temp.
15	Ag-Zn cell developed at JPL; SN 84-14; methyl acrylic acid grafted sep.; 45% KOH	5-6	4+	360 cycles over a 1-year period on 24-h regime at 30% DOD at room temp., remainder on stand at room temp.

Table 1. (contd)

Cell No.	Description	Rated capacity, A-h	Wet life, yr	History
16	Ag-Zn cell from Ranger Battery; SN 376; pos.: 1L Dynel EM470, 1L Polypore AA; sep.: 4L Pudo Cel; neg.: 1L Rayon EM310	45	12	Stored in charged condition for 12 yr at -7 to -13°C.
17	Ag-Zn cell from LeRC; SN 2-1-003; inorganic sep. bag on both pos. and neg. plates	40	1+	180 cycles over a 6-month period on 24-h regime at 50% DOD at room temp. remainder on stand at room temp.

Table 2. Description and history of silver cells examined by Naval Weapons Support Center

Cell No.	Description	Rated capacity, A-h	Wet life, yr	History
18	Ag-Zn cell from Whittaker; SN-36; neg.: 1L Viscon; sep.: 4L RAI-300; 40% KOH	43	8	8 yr on charged stand test at NWSC, 12 full 100% DOD cycles during course of stand at 0°C.
19	Ag-Zn cell from Whittaker; SN-48; neg.: 1L Viscon; sep.: 4L RAI-300; 40% KOH	43	8	8 yr on charged stand test at NWSC, 15 full 100% DOD cycles during course of stand at -51°C.
20	Ag-Zn cell from Delco; SN-28; pos.: 1L Dynel 470; neg.: 1L Viscon; sep.: 4L FSC; 40% KOH	25	8	8 yr on charged stand test at NWSC, 12 full 100% DOD cycles during course of stand at 0°C.
21	Ag-Zn cell from Delco; SN-38; pos.: 1L Dynel 470; neg.: 1L Viscon; sep.: 4L FSC; 40% KOH	25	8	8 yr on charged stand test at NWSC, 18 full 100% DOD cycles during course of stand at -35°C.
22	Ag-Zn cell from Delco; SN-40; pos.: 1L Dynel 470; neg.: 1L Viscon; sep.: 4L FSC; 40% KOH	25	8	8+ yr on charged stand test at NWSC, 15 full 100% DOD cycles during course of stand at 0°C.
23	Ag-Zn cell from Delco; SN-58; pos.: 1L Dynel 470; neg.: 1L Viscon; sep.: 4L FSC; 40% KOH	25	8	8 yr on charged stand test at NWSC, 15 full 100% DOD cycles during course of stand at -51°C.
24	Ag-Zn cell from Delco; SN-59; pos.: 1L Dynel 470; neg.: 1L Viscon; sep.: 4L FSC; 40% KOH	25	8	8 yr on charged stand test at NWSC, 15 full 100% DOD cycles during course of stand at -51°C.

Table 3. Capacities of cells and their silver electrodes as determined at JPL

Cell No.	Cell type and history	Cell capacity in early life, A-h	Cell capacity (1976), A-h	Silver electrode capacity in situ (1976), A-h	Silver electrode capacity in bath (1976), A-h
1	Ag-Zn, low-temp. charged stand, 7 yr	31.3	13.7	24.0	43.0
2	Same as No. 1	31.7	6.0	33.3	35.9
3	Same as No. 1	36.0	12.7	37.5	40.0
4	Same as No. 1	23.0	4.3	30.0	37.5
5	Same as No. 1	29.8	4.5	26.7	37.5
6	Same as No. 1	22.5	3.8	29.3	41.7
7	Same as No. 1	35.0	5.7	31.6	39.3
8	Ag-Cd, low-temp. charged stand, 8 yr	20.0	3.5	13.3	13.2
9	Same as No. 8	20.0	11.0	24.1	15.3
10	Ag-Zn, room temp. cycling and stand, 6+ yr	~40.0[a]	1.0	shorted	27.5
11	Same as No. 10	~40.0[a]	0.0	shorted	26.7
12	Same as No. 10	~40.0[a]	0.0	shorted	21.2
13	Same as No. 10	~40.0[a]	8.2	shorted	29.5
14	Same as No. 10	~40.0[a]	8.7	shorted	23.3
15	Ag-Zn, room temp. cycling and stand, 4+ yr	6.7	3.3	5.7	4.9

[a] Reference 5.

Table 3. (contd)

Cell No.	Cell type and history	Cell capacity in early life, A-h	Cell capacity (1976), A-h	Silver electrode capacity in situ (1976), A-h	Silver electrode capacity in bath (1976), A-h
16	Ag-Zn, low-temp. charged stand, 12 yr	65.0	0.0	60.7	45.0
17	Ag-Zn, room temp. cycling and stand, 1+ yr	42.3	11.0	56.2	46.7

Table 4. Capacities of cells and their silver electrodes as determined at NWSC

Cell No.	Cell type and history	Cell capacity in early life, A-h	Cell capacity (1975), A-h	Silver electrode capacity (1976), A-h
18	Ag-Zn, low-temp. charged stand, 8 yr	38.5	0.3	16.3
19	Same as No. 18	49.4	0.0	18.1
20	Same as No. 18	30.5	13.0	43.6
21	Same as No. 18	29.3	6.3	10.8
22	Same as No. 18	27.7	10.0	42.0
23	Same as No. 18	28.0	11.8	47.9
24	Same as No. 18	28.2	15.3	47.3

Table 5. Distribution of silver in cell 1 (Delco SN 68-27)

Component	Silver content, g	Total silver, %
Positive plates[a]	98.2	82.69
Negative plates[a]	0.1	0.08
Positive dynel wrap	0.4	0.33
FSC separator	20.0	16.90
Total	118.5	100.00

[a] Does not include silver in grids.

Table 6. Distribution of silver in cell 10 (LeRC SN HS-66-4)

Component	Silver content, g	Total silver, %
Positive plates[a]	82.0	57.87
Negative plates[a]	2.3	1.62
Positive bags	27.8	19.63
Negative bags	29.6	20.88
Total	141.7	100.00

[a] Does not include silver in grids.

APPENDIX A

NWSC Letter Report on Delco Cell Performance

DEPARTMENT OF THE NAVY
NAVAL AMMUNITION DEPOT
CRANE, INDIANA 47522

IN REPLY REFER TO:
3053-DEM:mvm
8900

19 JUL 1973

From: Commanding Officer, Naval Ammunition Depot, Crane, Indiana
To: Jet Propulsion Laboratory, California Institute of Technology
(Mr. R. S. Bogner), 4800 Oak Grove Drive, Pasadena, CA 91003

Subj: Plate Capacity of Delco 25 AH Silver-Zinc Cell

1. During the annual capacity test of the Ag-Zn cells that had been on open-circuit stand, it was determined that the capacities of the cells stored at room ambient were less than 5.0 AH. In order to determine which plate was limiting the capacity, one cell was opened and the capacities of the positive and negative plates were determined.

2. A Delco, Ag-Zn cell, serial number 14, having a 50% concentration level of KOH was opened and electrical tests were performed to measure the individual plate capacities of one positive and one negative plate (plate #4 in each case) from the center of the cell. This Delco cell was rated at 25 ampere-hours; contained FSC separator; had been stored at 20° - 29°C; and started test 19 October 1967.

3. Dissection revealed that the cell contained eight positive (Ag) and seven negative (Zn) plates. Based on this information, the charge and discharge rates for the plates were determined as follows:

25 AH/7 plates = 3.571 AH/plate

C/10 = 0.357 amperes
C/2 = 1.79 amperes

4. The plates were charged at 0.357 amperes for 22 hours and discharged at 1.79 amperes. The positive and negative plates were charged and discharged against two "dummy" stainless steel electrodes. The following summarizes the results:

	End of Charge Voltage	End of Discharge Voltage	Capacity	Calculated Battery Capacity
Positive (Ag)	1.56V	-1.57V	0.469 AH	3.283 AH
Negative (Zn)	1.54V	-2.50V	9.02 AH	63.14 AH

3053-DEM:mwm
8900

5. Based on the results of the plate capacity test, the positive plate was limiting the cell capacity. This also agrees with the 3.2 ampere-hour capacity of the battery from capacity test #5.

H. L. Forston
H. L. FORSTON
By direction

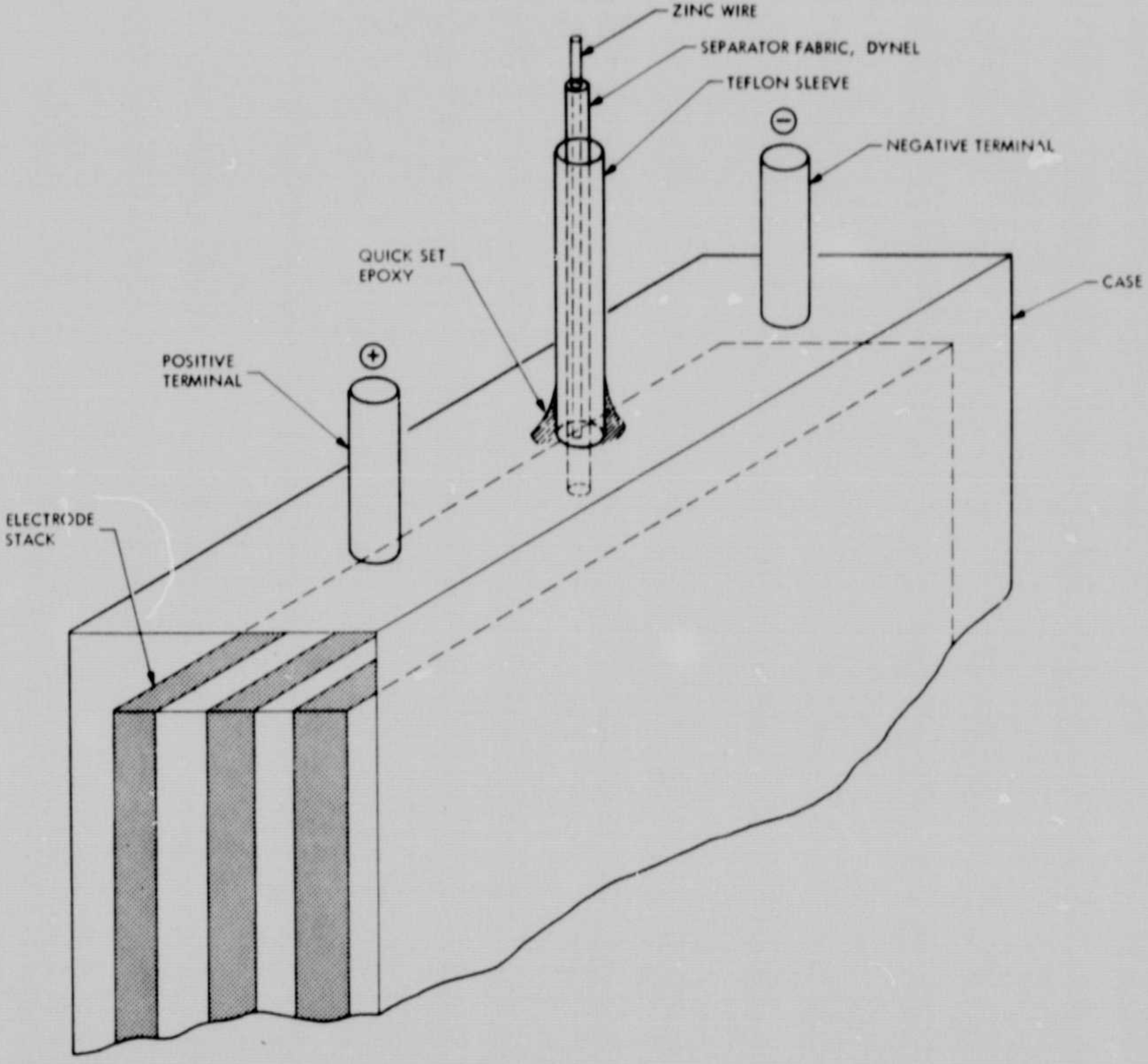

Fig. 1. Schematic diagram of reference electrode installation in silver cells

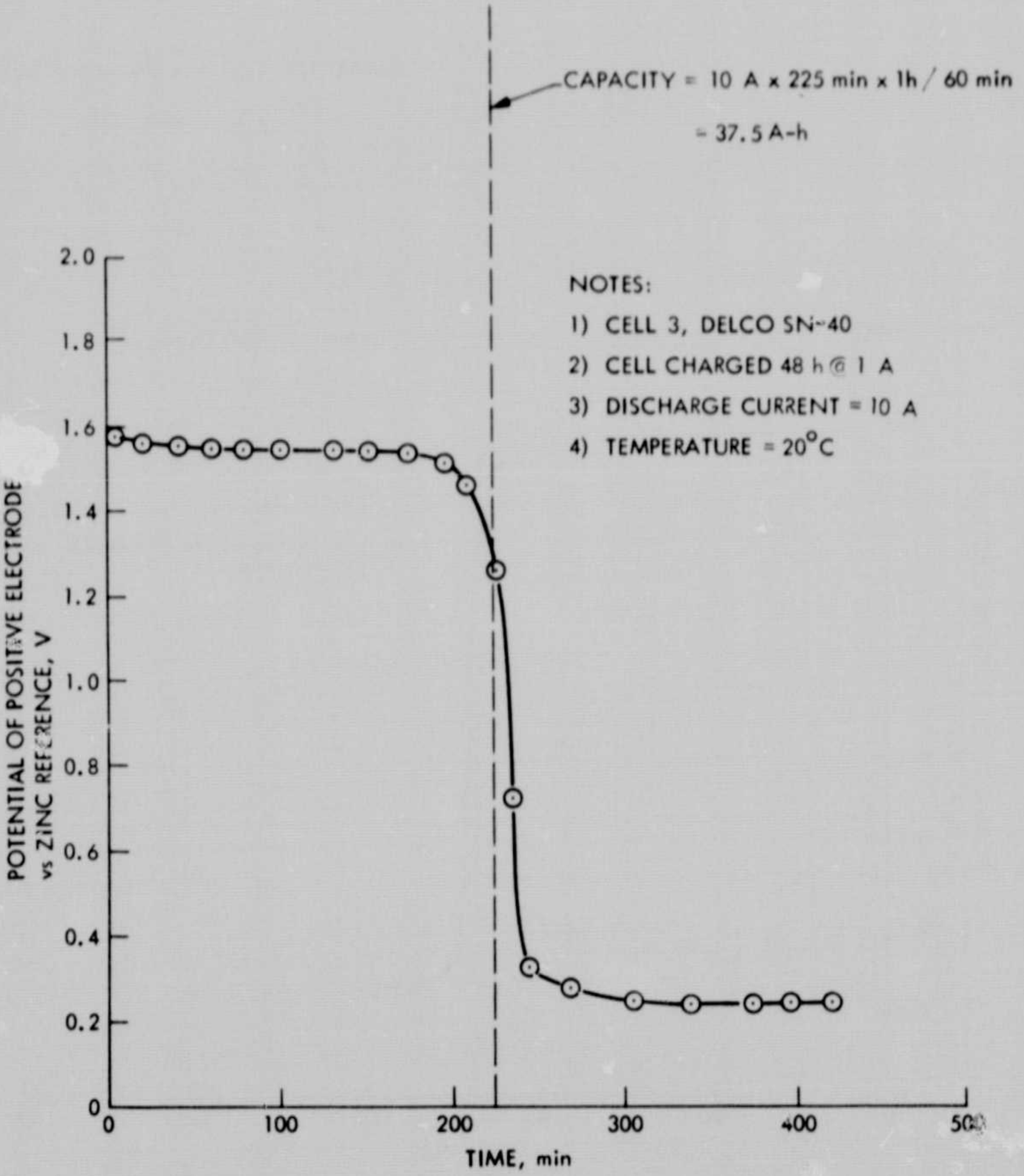

Fig. 2. Typical results of in situ capacity measurements on silver electrodes

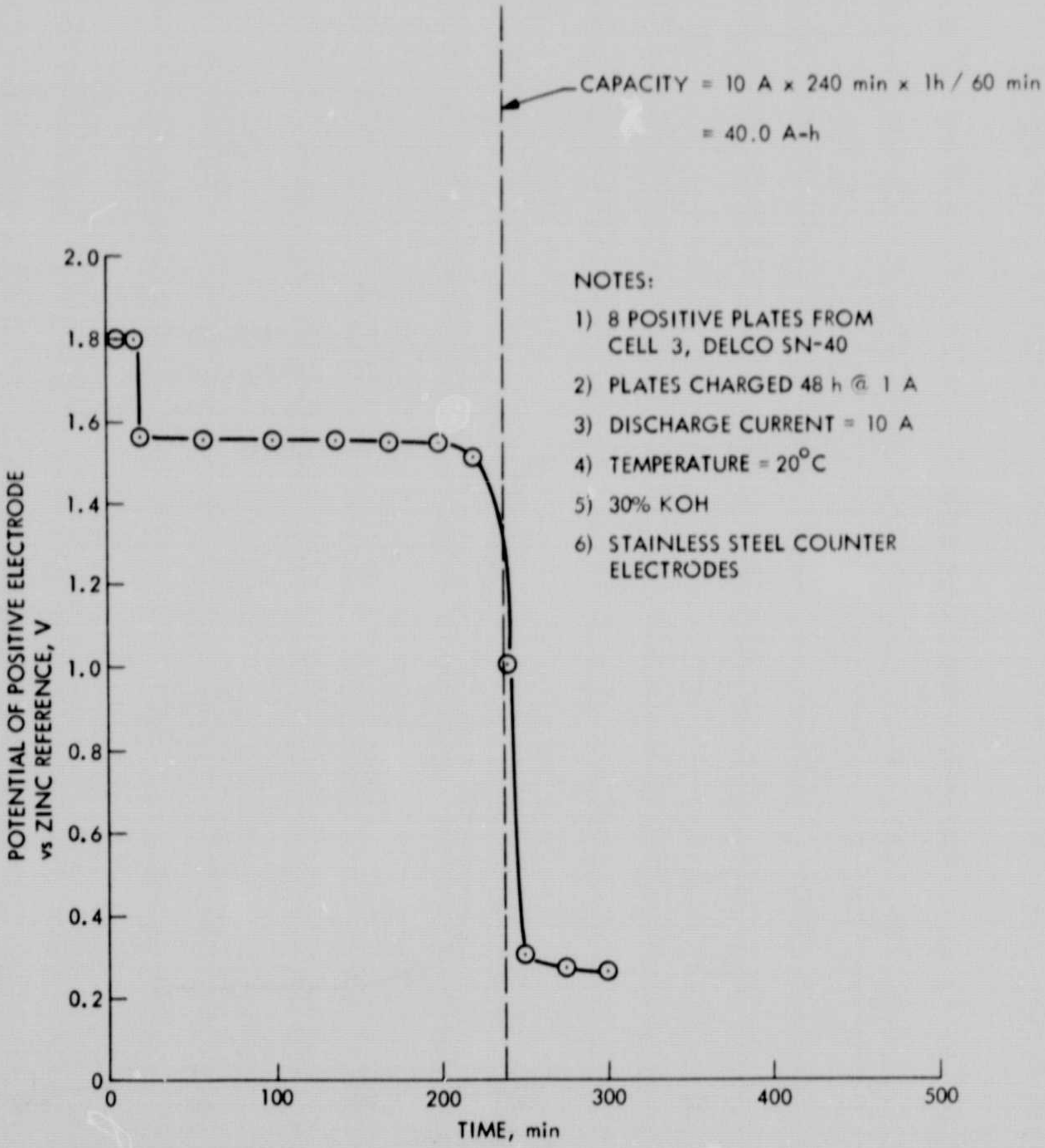

Fig. 3. Typical results of capacity measurements on silver electrode plates in KOH bath

NASA — JPL — Coml., L.A., Calif.