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Technical Memorandum 33-462

Battery Storage Optimization and Design Studies

R. S. Bogner R. E. Patterson

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JET PROPULSION LABORATORY CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

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Preface

The work described in this report was performed at the JPL Battery test Facility and at the Naval Ammunition Depot Crane Test Facility for the Guidance and Control Division of the Jet Propulsion Laboratory.

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Abstract

Sealed Ag–Zn cells with five different separator systems from four different vendors, and one group of Ag–Cd cells, were tested to evaluate their capability of maintaining a predictable output after long periods of inactivity. Electrolyte concentration was included as a variable in two of the cell designs. The cells were grouped into sets of three for storage at six different temperatures and four different time intervals. Extrapolation of rate capacity loss data at low temperature storage (0° to -20°C) indicates that after ten years of storage most of the cell designs would deliver 75% of their original capacity. Cells with the RAI-116 separator system showed the best charge retention. Cells of the one Ag–Cd design did not maintain charge retention as well as most of the Ag–Zn cells.

Battery Storage Optimization and Design Studies

I. Introduction

Although a great deal of data on various cells have been produced, the capabilities of different separator systems for alkaline battery systems for future planetary missions requiring flight durations of 3 to 5 years or longer have received little attention. During most of the flight time, spacecraft power is delivered from solar panels or radioisotope thermoelectric generators; however, certain events requiring peak power, such as launch and planet encounter maneuvers, call for the use of storage batteries. Various cycling requirements, if the spacecraft is put into planetary orbit, may also call for such a system. The problem, then, is how to provide a battery system that maintains a predictable output after long periods of inactivity.

Several approaches to the problem can be investigated. One approach is to use automatically activated drycharged batteries similar to the systems used in missiles and rockets. Another approach is to store charged primary batteries such as the mercury-cadmium system. A third approach is to store a charged secondary battery

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system at some reduced temperature, and then heat the battery to its operating temperature just before it is used. Other approaches are modifications of the third approach, in which the battery might be stored on a float charge or stored in the discharged state or even in the unformed state. An investigation of the third approach, in which cells having different separator systems were placed on stands in the charged condition, is discussed in this report. The silver-zinc system is the prime system for investigation at present because of its high-energy density. A secondary objective of the tests was to determine the feasibility of performing accelerated tests.

II. Description of Cells Tested

Ideally, all separator systems tested should have been in cells of the same basic design and produced by one manufacturer; however, the present tests cover five separator systems in four different cell designs by four manufacturers. Tables 1 and 2 show the construction features of the cells and the separator configuration for each. In addition, the concentration of electrolyte was included

 Table 1. Cell construction features

Cell manufacturer	Rated capacity, A-h	Weight, Ib	KOH concentration, %	Separator membrane
Delco	25	1.43	50	FSC
Delco	25	1.40	45	FSC
Delco	25	1.47	40	FSC
ESB	25	1.21	45	Cellophane
ESB	25	1.24	45	RAI-116
Whittaker	43	1.30	40	RA1-300
Yardney	25	1.02	45	C19-300
Yardney	25	1.00	35	C19-300
Yardney ^a	20	1.03	-	C19-300
^a Silver–Cadm	ium.	L	L	

Table 2. Separator configurations

Cell manufacturer	Positive electrode	Separator membrane	Negative electrode
Delco	Dynel 470, 1L	FSC, 4L	Viscon, 1L
ESB	Polypropylene 476, 1L	Cellophane, 6L	Viscon, 1L
ESB	Polypropylene 476, 1L	RAI-116, 6L	Viscon, 1L
Whittaker	_	RAI-300, 4L	Viscon, 1L
Yardney	Woven nylon, 1L	C19-300, 4L	Bag, PVA
Yardneya	Woven nylon, 2L	C19-300, 3L	Aldex, 1L
^a SilverCadı	nium.	-	

as a variable in the cell groups with FSC and C19-300 separators. Electrolytic concentration might have been a variable for each separator type, but it was thought that the effect of electrolyte concentration would be similar for each of the separator types tested. Figure 1 shows a picture of each type of cell tested. As can be noted from Tables 1 and 2 and Fig. 1, some of the cells, notably the Delco cells, are larger and heavier than the other cells although they have the same ampere-hour rating. No attempt is made in this discussion to account for the effects of this design parameter and other parameters, such as additives, to the cells.

III. Description of Tests

Most of the cells were purchased about 2½ years ago and they are just now approaching 24 months of opencircuit stand; therefore, only data to 16- or 18-months stand are presented here. Figure 2 depicts the test plan for each cell group of each type. Six cells of each group were randomly selected for control cells, and the remaining cells were grouped into sets of 12 for storage in the charged state at ambient temperatures of 49, 25, 0, -20, -35, and -51° C. The sets of 12 were further split into sets of three cells for testing at four different time intervals at the various storage temperatures. The cells were stored in forced-air environmental chambers and were clamped in retainers for support. Each cell contained monitoring leads connected to a terminal board, located on the outside of the chamber for the purpose of taking periodic open-circuit readings.

All cells were given checks for initial capacity at the start of the test, at room temperature. The cells were charged at a C/25-ampere rate* to an end voltage of 1.95 to 1.98 V/cell followed by a C/2.5-ampere discharge to 1.30 V/cell. All subsequent capacity checks were performed the same way. Table 3 shows the spread and average capacity input and output of each of the cell groups. Problems were encountered with some of the cells containing the RAI-116 separators, in that four of the cells had very low capacities (0 to 10 A–h). These low-capacity cells were cycled a couple of times at low rates and, at the suggestion of the manufacturer, additional electrolyte was added to the 0-capacity cell. The cell capacity increased to 10 A–h.

After the initial capacity checks, the cells were put on their given test regime. The control cells were placed on cycle test at room temperature. The cycle tests consisted of a 21-h charge at C/12.5 to 1.97 V/cell, with the tapering off of the current followed by a 3-h discharge at C/5 to a 60% depth of discharge of the manufacturer's rated capacity. The stored cells were removed from storage at the appropriate intervals of time and checked at room temperature for discharge capacity. They were charged and given a second capacity (restorable capacity) check, and were then placed on the cycle-life test regime as already described.

Most of the data were recorded on punched paper tape and transferred to magnetic tape for computer printout. Cell voltages and charge and discharge currents were recorded every five minutes; therefore, the amperehour in and out on each cycle can be readily integrated by the computer, and any given charge or discharge curve can be plotted by the computer. If deemed appropriate

C =ampere-hour rating of the cell; for example, a C/25 for a 25 A-h cell would be a one-ampere rate.



Fig. 1. Cell types tested



Fig. 2. Cell grouping

Cell type	н	ligh	L	ow	Av	erage
and KOH	Charge	Discharge	Charge	Discharge	Charge	Discharge
FSC, 40%	43	38	27	17	36	30
FSC, 45%	48	34	36	25	40	29
FSC, 50%	45	35	30	26	37	30
Cellophane, 45%	34	35	28	28	31	30
RAI-116, 45%	38	38	1	o	30	30
C19-300, 45%	33	32	28	27	31	28
C19-300, 35%	35	37	29	29	31	31
RAI-300, 40%	61	54	25	15	51	46
AgCd,	23	23	18	18	21	21

Table 3. Room temperature charge and discharge capacities, in ampere-hours

at the conclusion of the test, programs can be written to statistically analyze the data on the computer; however, no statistical analysis is attempted in this report.

IV. Results and Discussion

Each three-cell group tested was averaged for analyzing the data. This can lead to some anomalies. For example, the worst cell in the group might fail at 50 cycles, while the best cell might fail at 250 cycles; and if batteries were being tested, the battery would have to be considered a failure when the first cell failed. In some instances, the failure of one cell induced the failure of other cells in the circuit.

The cells containing the RAI-300 have shown such poor performance during stand and cycling that they will not be considered further. The results of testing these cells are summarized in Table 4. Several of the cells shorted an open-circuit stand even at reduced temperatures. Part of the problem was that these cells had only four layers of separator.

Figure 3 shows a summary of the stand data at 49°C for seven of the silver-zinc cell groups. The RAI-300 cells and the silver-cadmium cells are not shown because most of the cells failed this test. Both the residual and recoverable capacities are plotted. During the first month of stand, most of the cell capacity is recoverable after the initial discharge; however, the recoverable capacity generally follows a slope similar to the residual capacity and there is a permanent loss in capacity. Perhaps additional cycling would have reconditioned the cells, but this was not attempted. The numbers across the top show how each group is ranked just at this test condition, considering both residual and recoverable capacities.



Fig. 3. Charge retention on storage at 49°C

Table 4. Cells with RAI-300 and 40% KOH concentration

Initial	Stora	ge	Capacity, %	of Initial:	Cualas
A-h	Months	°C	Residual	Repeat	Cycles
52.4	0	25	Cont	rol	49
53.3	6	25	29.2	63.4	26
45.5	12	25	0	34.6	0
47.2	16	0	o	91.4	13
44.9	16	-51	36.5	98.1	10
47	1.5	49	30.3	31.4	5
54.6	2	49	23.3	37.4	5
48.3	2.5	49	18.8	28.2	0

Figure 4 shows the summary of the stand data at 25° C. The recoverable capacity followed the same general trend as at 49° C. The reason for unusually high results on cellophane is not readily explainable. It may be that the full capacity of the cells had not been attained on just one cycle; however, all cells were given the same treatment. In most instances, the data fall in a nearly straight line. Interestingly, five of the cell groups fall fairly close to one another with nearly the same slope. The silver–cadmium cells were considerably worse than the silver–zinc cells.

Figure 5 shows a summary of the results at 0° and -51° C. A couple of the curves are anomalous in that the longer the time the better the charge retention.



Fig. 4. Charge retention on storage at 25°C

Figure 6 is an Arrhenius-type plot of data in which the log of the rate of capacity loss per month is plotted as a function of the inverse of temperature for the different separator groups and cell groups. These data were obtained from the slopes of the curves shown in Figs. 3, 4, and 5. When the data are plotted in this form, most of the separator systems fall in a narrow band. The RAI-116 separator is slightly better (Fig. 6) than the others. The scatter of the data at -51° C is not readily explainable; however, it is possible that some other reaction mechanism might be taking place, possibly because of phase



Fig. 5. Charge retention on storage at 0° and -51 °C

Table 5. Cycle-life data

Storage temperature	+25°C	-5	1°C	0°	с	+2	25°C	+4	9°C
Storage time	(Control)	8 mo	16 mo	8 mo	16 mo	8 mo	12 mo	2 mo	4 mo
Cell type				Cy	cle-life averag	le			
FSC, 50%	198	248 ^a	126 ^a	188	80	230	115 (18)	216	0
FSC, 45%	141	96	77	143	92	167	81 (18)	173	27
FSC, 40%	85	-	-	—	_			199	23
C19-300, 45%	14	226	-	243		176 (6)	155	71	82 (3)
C19-300, 35%	90	127	115	137	—	121	89	0	o
Cellophane, 45%	24	24	29	100	96	90 (6)	130	105	79
RAI-116, 45%	58	55	-	126	89	90 (6)	19	98	20
RAI-300, 40%	49		11		13	40	0	0	o
Ag-Cd, C19-300	231	41	194	_	-	69	o	0	0
^a At —35°C. ^b Numbers in parenthese	s indicate storaç	ge time, if diff	erent from that	shown in colun	ın heading.		····		



Fig. 6. Effect of temperature on rate of capacity loss

changes in the electrolyte. Figure 6 shows that the optimum storage temperature lies between 0° and -20°C. There is little difference between the cells with the 45% electrolyte and those with 50%; however, there is considerable difference between the cells containing 45% electrolyte and those with 35%.

From the rate loss at low temperatures $(0^{\circ} \text{ to } -20^{\circ}\text{C})$, it is estimated that after 10 years of storage, most of the cell designs would deliver 75% of their original capacity. The poor performance of the silver-cadmium cells was unexpected; however, in comparing their separator system with the silver-zinc cells, it is not too surprising. These results suggest that the failure mechanism of the silver-zinc and silver-cadmium cells on open-circuit stand is primarily caused by reactions of the cathode with the separator, and is not appreciably affected by the anode.

Table 5 shows a summary of the cycle-life test results. As is usual with silver-zinc cells, the cycle data are quite varied. No relationship between storage time and cycle life is apparent except at 4 months at 49°C. The low results obtained on some of the control groups might be due to the premature failure of a single cell, which could have resulted in over-charging the rest of the cells; however, the cycle data have not yet been examined in depth.

V. Conclusions

The results of the tests present the following conclusions:

- (1) The optimum storage temperature is around 0° to -20° C. If present trends are followed, the majority of cells stored at these temperatures will deliver 75% of their original capacity after 10 years of storage.
- (2) Since the rate data are a linear function of the temperature, accelerated testing should be feasible.

- (3) The RAI-116 separator system produced the best charge retention.
- (4) Thus far, storage time has shown practically no relationship to cycle life.
- (5) Electrolyte concentration (40% to 50%) does not appear to be a critical factor in charge retention.
- (6) The silver-cadmium cells did not maintain charge retention as well as most of the silver-zinc cells. The results suggest that the failure mechanism "on stand" is primarily associated with the reaction between the cathode and the separator material.

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