SECOND QUARTERLY REPORT

OPTIMIZATION OF DESIGN PARAMETERS FOR SPACECRAFT NICKEL-CADMium CELLS CONTAINING RECOMBINATION AND CONTROL ELECTRODES

by

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Goddard Space Flight Center
Greenbelt, Maryland

General Electric Company
Battery Business Section
Gainesville, Florida
A decrease in signal electrode sensitivity has been observed after 40°C exposure. At this time, the loss in output appears to be stabilized after two characterization cycles each of approximately twelve hours duration including temperature stabilization time.
# TABLE OF CONTENTS

1.0 INTRODUCTION AND SUMMARY

1.1 Background and Objectives 1

1.2 Description of Program Tasks 2-3

   1.2.1 Task I - Assembly of Cells and Test Equipment

   1.2.2 Task II - Auxiliary Electrode Stability

   1.2.3 Task III - Optimization of Recombination Load Resistance and Negative Precharge Level

   1.2.4 Task IV - Cycling of Cells with Optimized Precharge and Recombination Load Resistance

   1.2.5 Task V - Other Cell Characteristics

   1.2.6 Task VI - Post-cycle Teardown Analysis

1.3 Summary 4-5

2.0 TECHNICAL DISCUSSION

2.1 Task II - Recombination and Signal Electrode Stability during 40°C-25% DOD Cycling 6-8

2.2 Task III - Optimization of Recombination Load Resistance and Negative Precharge Level 8-10

2.3 Task IV - Cycling under Optimized Negative Precharge Level and Recombination Load Resistance 10-11

2.4 Task V - Other Cell Characteristics 11

2.5 Task VI - Post-cycle Teardown Analysis 11

3.0 WORK PLANNED FOR NEXT QUARTER 11-12

4.0 REFERENCES
LIST OF ILLUSTRATIONS


Figures 8-10: Task II Cells - Recombination electrode response (1.0 ohm load) at -20°C.

Figure 11: Task II Cells - Average data illustrating cell voltage, signal electrode response and cell pressure cycling to a 25% depth-of-discharge at 40°C. Negative precharge level (excess) set at 40%.


Figures 17,18,19: Task III Cells - Average data illustrating point to point tracking of signal and recombination electrode with cell pressure during charge-discharge cycle number 22.

**LIST OF TABLES**

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Task II - Cycle Data vs Negative Precharge Level and Recombination Load Resistance</td>
<td>14</td>
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<tr>
<td>II</td>
<td>Tasks II, III, and IV - Capacity (Ah) to 1.00V at 3.0A Discharge Rate</td>
<td>15</td>
</tr>
<tr>
<td>III</td>
<td>Task II - 48 Hour Overcharge Pressures (Recombination Electrode Disconnected)</td>
<td>16</td>
</tr>
<tr>
<td>IV</td>
<td>Tasks III and IV Cells - 48 Hour Overcharge Pressures (Recombination Electrode Disconnected)</td>
<td>17</td>
</tr>
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</table>
1.0 INTRODUCTION AND SUMMARY

1.1 Background and Objectives

A recently completed study entitled, "Characterization of Recombination and Control Electrodes for Spacecraft Nickel-Cadmium Cells," Contract NAS 5-10261, established that cells containing recombination and signal electrodes are capable of prolonged cycling under regimes which were too severe for cells of conventional design.

The recombination electrode serves several functions:

1. It maintains safe oxygen pressures during charge and overcharge.

2. It functions to reduce oxygen pressure to a sufficiently low level during discharge to prevent premature response from the signal electrode.

3. It provides a catalytic surface for the reaction between hydrogen and oxygen. This function permits the use of a high level of negative precharge thereby minimizing fading. Any hydrogen generated as a result is thereby oxidized to water.

The objective of this program is to determine the long-term mechanical and electrical stability of these electrodes and lead to the optimization of the design parameters for spacecraft nickel-cadmium cells containing recombination and signal electrodes.
1.2 Description of Program Tasks

1.2.1 Task I - Assembly of Cells and Test Equipment.

The objective of this task is to assemble all cells and cycling equipment required for carrying out the remaining tasks.

1.2.2 Task II - Auxiliary Electrode Stability.

The objective of this task is to determine the long-term mechanical and electrical stability of both the oxygen recombination and oxygen sensing electrodes. This task will be accomplished by subjecting the cells to prolonged cycling to a 50% depth-of-discharge in a 40°C ambient, and then periodically recharacterizing the test electrodes under fixed conditions. Changes in signal and recombination electrode characteristics will thereby be determined.

1.2.3 Task III - Optimization of Recombination Load Resistance and Negative Precharge Level.

The objectives of this task are to determine the effects of recombination-to-negative load resistance and negative precharge level upon deep cycle capability and internal pressure characteristics. The factorial experiment for this task has been designed for evaluation of optimum levels and interactions.
1.2.4 Task IV - Cycling of Cells with Optimized Precharge and Recombination Load Resistance.

This task is a continuation of Task III. The purpose is to evaluate the characteristics of cells and control electrodes which have been optimized per the results of Task III. The cells are to be subjected to the following cycling regimes, i.e., 40°C-50% DOD and 25°C-75% DOD. These cycles will determine the extent of cycle life improvement and control electrode stability under severe conditions.

1.2.5 Task V - Other Cell Characteristics.

Under this task are included test programs to determine the performance of cells on continuous overcharge, the hydrogen recombination ability and performance during reversal, and to determine the maintenance of negative precharge.

1.2.6 Task VI - Post-cycle Teardown Analysis.

The objective of this task is to evaluate the extent to which the various cycle regimes employed in the above tasks result in physical damage to the plates, separators and the auxiliary electrodes.

Additional such data will be accumulated under Task VI since one cell from each temperature regime presently undergoing life testing (cells submitted to NASA under previous Contract NAS 5-10261) will also be subjected to teardown analysis.
1.3 Summary

The data obtained from signal electrode pre-cycle characterization tests revealed that the signal electrode outputs versus temperature were uniform from task to task. Several cells yielded maverick data which indicates that the signal electrodes are internally shorted to the recombination electrodes. This will be confirmed by teardown analysis. The pre-cycle characterization tests of signal electrodes indicated that a period of stabilization is required for uniform behavior of this electrode. In tasks II, III, and IV the two 40°C characterizations, which were approximately 12 hours each, appeared to yield stability. The following two observations regarding the signal electrode characteristics were also noted during pre-cycle tests:

1. The spread in signal electrode millivolt response between different cells in a group increases with internal cell pressure. The region between 10 and 30 psia yields the minimum signal range.

2. The signal output spread between cells in a group is temperature dependent, being greatest at 40°C and least at -20°C.

The cycling regimes of 40°C-25% DOD, 40°C-50% DOD and 25°C-75% DOD utilized for Tasks II and III cells revealed the requirement for higher than previously investigated negative precharge levels for cells cycling under these types of regimes. Thus far it appears that such precharge levels must be in the 125-140% of positive capacity range.
The Task III cycle tests also revealed that negative-to-recombination electrode load resistances below 1.0 ohm lead to rapid fading of the cell end of discharge voltages. The two ohm load has yielded the best cycle life data to date.
2.0 TECHNICAL DISCUSSION

2.1 Task II - Recombination and Signal Electrode Stability During 40°C-25% DOD Cycling.

Individual cell capacities and steady-state overcharge pressures were reported in the First Quarterly Report. The cells have since completed all pre-cycle signal electrode and recombination electrode characterization tests. The signal electrode cells were subjected to seven characterization tests (10 ohm load) in the following order of ambient exposures: 25°C, 40°C, 40°C, 25°C, -20°C, 25°C, and 25°C. Cells were temperature-stabilized for 4 hours, then charged at the C/2 rate and discharged at the C/2 rate in the required ambient. Figures 1-7 illustrate the signal output responses at various test temperatures. The signal levels yielded on the second 25°C test were lower than expected. This shift occurred after the cells were returned to 25°C following two 40°C exposure periods. The reduction observed appears to be stable thus far. Exposures to the 40°C environment were of short duration during pre-cycle characterization tests. The determination of whether the electrode characteristics undergo further changes as a result of prolonged cycling at 40°C is the objective of this task.

Analysis of the data plotted in Figures 1-7 indicates the following patterns:
1. The spread in signal output between cells increases with internal cell pressure at all test temperatures.

2. The signal output spread between cells is temperature dependent, being greatest at 40°C and least at -20°C where sensitivity is low.

3. The short-term exposure to a 40°C ambient appears to stabilize the signal electrode sensitivity at a lower level. Higher outputs can, however, be obtained by utilizing a greater load resistance than 10 ohms.

The pre-cycle characterization of the oxygen recombination electrode response at -20°C was also completed during this report period. The -20°C ambient was chosen for this study as a result of poor sensitivity at this temperature. If degradation in recombination performance were to result during the stress cycling, it should appear as loss of sensitivity during periodic -20°C recharacterizations. Typical data is illustrated by curves 8, 9, and 10. The recombination load resistance used was 1.0 ohms; therefore, the vertical axis represents either millivolts or milliamperes. It should be noted that saturation of the electrode starts to occur very rapidly at -20°C, i.e., between 20 and 40 psia.

Once pre-cycle characterizations were completed, the cells in the group were placed on a cycling regime comprised of a 25% depth-of-discharge in a 40°C ambient. The orbit
period was 90 minutes and the recharge coefficient was set at 150%. The negative-to-recombination load resistance is 1.0 ohm. The cells failed to meet the minimum discharge voltage of 0.5 by cycle number 163. The state of negative precharge was then adjusted from the factory imposed level during plate processing to a level of 120% of the positive capacity. Cycling was resumed. The cells have achieved another two hundred cycles thus far. Figure 11 illustrates the effect of this cycling regime upon the cells in the 1.20 negative/positive precharge condition. The data plotted in Figure 11 indicates the following trends:

1. The signal electrode sensitivity is increasing with cycling in this group.

2. The 1.0 ohm recombination electrode load resistance is capable of maintaining uniform low pressures.

3. The cell capacities are fading at the 1.20 negative/positive precharge level indicating the necessity of introduction of a higher level.

2.2 Task III - Optimization of Recombination Electrode Load Resistance and Negative Precharge Level.

Pre-cycle characterization studies of signal electrode and recombination electrode responses have been completed on all cells. (Tables II and IV list pre-cycle capacity, overcharge pressure and void volume data.) The order of exposure to the various ambient temperatures was the same as used for Task II. The data obtained was averaged and plotted in Figures 12-16. Task III data essentially agrees with that
obtained from Task II; however, in two instances, different charge rates were utilized. This permits a direct comparison of signal electrode output level versus charge rate. A comparison of Figures 2 and 14 indicate an increase of approximately 91 millivolts (over most of the curve) at 40°C at the "C" rate of charge versus the "C/2" rate. Similarly, Figures 4 and 15 may be compared for the difference in output at 25°C between a "C/2" and a "1.5C" charge rate. In this case, the increase in output was approximately 28 millivolts.

Eighteen cells were selected from this group and were quantitatively treated to introduce three levels of excess negative precharge into the three 6-cell subgroups; i.e., 1.25, 1.375, and 1.50 negative/positive precharge. These levels represent a departure from the original test plan requirements of 1.40-1.45. The original proposed levels were changed in order to achieve a greater spread in evaluating gross differences. The cells are presently being cycled under two different regimes as follows:

1. 40°C ambient; 50% depth-of-discharge and 135% charge return.

2. 25°C ambient; 75% depth-of-discharge and 120% charge return.

In addition, the various subgroups have been further divided to include the effect of different recombination-to-negative
electrode load resistances at values of 0.1, 1.0 and 2.0 ohms. Previous work had not selectively determined this effect. The data obtained is illustrated by Table I. The trends are clear, thus far. The cells containing an excess precharge level of 1.50 and a 2.0 ohm negative load resistance are performing best. The figures in parenthesis represent the end-of-discharge voltage levels for the 25°C group prior to a malfunction in the cycling equipment. None of the cells were damaged and cycling has been resumed.

Curves 17, 18 and 19 are composite curves for cycle number 22 which illustrate the relationships between internal cell pressure, signal electrode output (millivolts across 10 ohms) and recombination electrode output at the three levels of load resistance. The curves follow the anticipated pattern; i.e., the lowest value of recombination load resistance (0.1 ohm) maintains the lowest internal cell pressure and, therefore, the lowest signal output. The signal electrode peak and the internal cell pressure peak correspond within the limits of accuracy of the pressure gages.

2.3 Task IV - Cycling Under Optimized Negative Precharge Level and Recombination Load Resistance.

The six new cells allocated for this task have been subjected to the same pre-cycle characterization tests as groups II and III with one difference. The order of ambient exposures during signal electrode tests was 25°C, -20°C, and 40°C.
Table II lists the capacity data for these cells and Table IV lists steady state overcharge pressures at 25°C at the C/2 rate and sample cell void volumes. The curves (Figures 20-23) reveal that the signal electrode output drops between the first and second 25°C characterization test, but to a lesser degree than was seen after the second (40°C) exposure in Tasks II and III. There is apparently a "normalizing" break-in required prior to establishment of base line data for the signal electrode. Further signal electrode characterization tests will be conducted on this group of cells at 25°C and -20°C at the C/2 rate for comparison data. The cells will then be held aside until the best six cells are selected from the Task III study. The complete group of twelve cells will then be cycled until end-of-discharge voltages fall below 0.50 volt. The cells will then be subjected to recharacterization tests in order to ascertain the degree of change in signal and recombination electrode characteristics.

2.4 Task V - Other Cell Characteristics.

This work is scheduled for the fourth quarter of the contract.

2.5 Task VI - Post-Cycle Teardown Analysis

None of the cells are available for teardown analysis to date.

3.0 WORK PLANNED FOR NEXT QUARTER

Task II - A higher negative precharge level will be introduced into Task II cells which are in a 40°C ambient and cycling will be resumed.

Task III - Task III cells will continue cycling until the best combination of negative precharge level and recombination load resistance is finalized.
Task IV - Cycling will be started during the Third Quarter.

Task V - This work is scheduled for the Fourth Quarter.

Task VI - Teardown analysis of discarded cells from Task III will be initiated.
REFERENCES

4.0 FINAL REPORT, CHARACTERIZATION OF RECOMBINATION AND CONTROL ELECTRODES FOR SPACECRAFT NICKEL-Cadmium CELLS, W. N. Carson, Jr., G. Rampel, and I. B. Weinstock, prepared for NATIONAL AERONAUTICS AND SPACE ADMINISTRATION, January 1968, CONTRACT NAS 5-10261, Goddard Space Flight Center, Greenbelt, Maryland.
**Task III - Cycle Data versus Negative Precharge Level and Recombination Load Resistance.**

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<thead>
<tr>
<th>TABLE I</th>
<th>Pos/Neg Prechg Ratio</th>
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<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Failed /L 18</td>
<td>Failed /L 194</td>
</tr>
<tr>
<td>Failed /L 18</td>
<td>Failed /L 67</td>
</tr>
<tr>
<td>Failed /L 13</td>
<td>Failed /L 52</td>
</tr>
<tr>
<td>~/ 250 (1.07V)</td>
<td>~/ 250 (1.09V)</td>
</tr>
<tr>
<td>~/ 250 (0.72V)</td>
<td>~/ 250 (1.04)</td>
</tr>
<tr>
<td>Failed /L 33</td>
<td>~/ 250 (1.03)</td>
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* NOTES: EQUIPMENT FAILURE ON CYCLE 250.

THE NUMBER IN PARENTHESIS INDICATES THE END-OF-DISCHARGE VOLTAGE AT THE CYCLE BEFORE EQUIPMENT FAILURE.
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<tr>
<td></td>
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<td>6.14</td>
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<td>6.58</td>
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<td></td>
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<td>6.37</td>
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<td></td>
<td>6</td>
<td>6.37</td>
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TABLE II

Capacity (AHR) to 1,000V at 3.0A Discharge Rate
# TABLE III

Task II Cells  
48 Hour Overcharge Pressures*  
(*Recombination Electrode Disconnected)

<table>
<thead>
<tr>
<th></th>
<th>-20°C</th>
<th>25°C</th>
<th>40°C</th>
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<tbody>
<tr>
<td>C/8</td>
<td>83 psig</td>
<td>50 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>92 psig</td>
<td>61 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>118 psig</td>
<td>68 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>78 psig</td>
<td>49 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>123 psig</td>
<td>75 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>45 psig</td>
<td></td>
</tr>
<tr>
<td>C/10</td>
<td>56 psig</td>
<td>20 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70 psig</td>
<td>24 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>84 psig</td>
<td>35 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75 psig</td>
<td>24 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>92 psig</td>
<td>42 psig</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55 psig</td>
<td>20 psig</td>
<td></td>
</tr>
<tr>
<td>C/20</td>
<td>66 psig</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76 psig</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>99 psig</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>102 psig</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>94 psig</td>
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</tr>
<tr>
<td></td>
<td>71 psig</td>
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The design level of electrolyte in this cell is 20% greater than the amount used in conventional or standard cells.
<table>
<thead>
<tr>
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<th>Pressure (psig)</th>
<th>Void Volume (c.c.)</th>
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<td>73</td>
<td>32.0</td>
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<tr>
<td>2</td>
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<td>32.8</td>
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<td>5</td>
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<td>6</td>
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(Task IV)

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<td>5</td>
<td>155</td>
</tr>
<tr>
<td>6</td>
<td>45</td>
</tr>
</tbody>
</table>

The design level of electrolyte in this cell is 20% greater than the amount used in conventional or standard cells.
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 25°C, NO. 1
8-30-68
RL = 10-A
(TASK II CELLS)

FIGURE 1
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 40°C, No. 1
9-17-68
Rl = 10
(TASK 1I CELLS)
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 40°C, No. 2
9-19-68
RL = 10 Ω
(TASK II CELLS)

FIGURE 3
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 25°C, No. 2
9-23-68
RL = 10
(TASK 11 CELLS)

SYM | CELL
--- | ---
• | 1
• | 2
△ | 3
▽ | 5
□ | 6

SIGNAL, mV

PRESSURE - PSIA

FIGURE 4
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, -20°C,
10-28-68
RL = 10
(Task II Cells)

SYM

CELL

1
2
3
5
6

PRESSURE - PSIA

FIGURE 5
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 25°C, No. 3
9-30-68
RL = 10 Ω
(TASK II CELLS)

**Figure 6**

- **SYM**
  - ○: 1
  - △: 2
  - ●: 3
  - ▽: 5
  - □: 6

- **CELL**
  - 1
  - 2
  - 3
  - 5
  - 6

**PRESSURE, PSIA**

**SIGNAL, MV**
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 25°C, No. 4
10-1-68
RL = 10
(TASK 11 CELLS)

FIGURE 7
25% DOD-40°C-40% PRECHARGE
AVERAGE 5 CELL DATA

E.O.C. - PRESSURE

E.O.D. - PRESSURE

E.O.C. SIGNAL - mV (10Ω LOAD)

E.O.C. VOLTAGE (CELL)

E.O.D. VOLTAGE (CELL)

CYCLE NUMBER

FIGURE 11
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 25°C, No. 1
9-24-68
RL = 10  Ω
(Task 111 Cells)

Figure 12
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 40°C, No. 1
9-27-68
RL = 10Ω
(TASK III CELLS)

FIGURE 13
SIGNAL ELECTRODE RESPONSE
"C" CHARGE, 40°C, No. 1
10-18-68
RL = 10
(TASK III CELLS)
SIGNAL ELECTRODE RESPONSE
1.5C CHARGE, 25°C
10-23-68
RL = 10
(TASK 111 CELLS)

Figure 15
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, -20°C
10-28-68
R_L = 10
(TASK III CELLS)
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 25°C, No. 1
10-16-68
RL = 10 Ω
(TASK IV)

FIGURE 20
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 25°C, No. 2
10-17-68
RL = 10 -Ω
(TASK IV)

FIGURE 21
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, -20°C, No. 1
10-30-68
RL = 10
(TASK IV)

FIGURE 22
SIGNAL ELECTRODE RESPONSE
C/2 CHARGE, 40°C, No. 1
10-31-68
R_L = 10
(TASK IV)

FIGURE 23