General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

FIRST QUARTERLY REPORT

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

by

I. B. Weinstock and G. Rampel

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

October, 1968

CONTRACT NAS 5-11547

Goddard Space Flight Center
Greenbelt, Maryland

General Electric Company
Battery Business Section
Gainesville, Florida

ABSTRACT

This report presents detailed plans for an investigation, in depth, of the factors which contribute to the cycle capability of cells built with oxygen recombination and oxygen sensing control electrodes. The purpose of this program is to optimize the design parameters for such cells, and extend their usefulness for spacecraft applications.

Included is a description of the cells and equipment to be used in the program, as well as the detailed test plans. Preliminary cell performance characteristics are also reported.

TABLE OF CONTENTS

LIST OF TABLES

1.0 INTRODUCTION AND SUMMARY

1.1 Background and Objective

Results obtained in a recently completed study, "Characterization of Recombination and Control Electrodes for Spacecraft Nickel-Cadmium Cells", Contract NAS 5-10261, indicate that cells containing recombination and control electrodes are capable of prolonged cycling under regimes which could not be met by cells of conventional design. Prototype cells were cycled over the -20°C to 40°C temperature range at depths-of-discharge up to 75% on a 90 minute orbit.

The improvements in cycle capability demonstrated by these cells are the result of two interacting factors: the recombination electrode and the high percentage of the excess negative capacity in the charged state.

The recombination electrode has as its primary function the maintenance of safe pressure levels within the cell by recombining the oxygen generated by the positive plates during charge. It also returns the pressure to a low level during open circuit and discharge portions of the cycle, insuring that the subsequent charge will not be terminated by a premature signal from the oxygen-sensing control electrode on account of residual oxygen pressure. This electrode also provides a catalyst which can promote the reaction between hydrogen and oxygen. In this manner it also prevents excessive pressures due to accumulation of hydrogen in the cell. This mechanism for the safe removal of any hydrogen generated allows cells to be constructed with a high percentage of the excess negative capacity in the charged state. Cells so constructed are designed to minimize or eliminate negative fading thereby insuring that the positive electrode remains limiting.

This program is directed at optimizing the design parameters for spacecraft nickel-cadmium cells containing recombination and control electrodes. The objective is to increase the deep cycle capability of such cells and to further extend their usefulness for spacecraft applications.

To provide program visibility for reporting and monitoring purposes, the program has been broken down into six tasks, as follows:

1.2 Task I - Assembly of Cells and Test Equipment

The objective of this task was to assemble the cells and cycle equipment required for carrying out the remaining tasks. During the first quarter, 93 cells to carry out the experimental program and for delivery to NASA/GSFC upon completion of the program were assembled. Automatic cycle equipment, which is capable of cycling the 6 AH test cells at depths-of-discharge to 75% on 90 minute orbits, was also assembled.

1.3 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 control electrodes. This will be accomplished by subjecting the test cells to prolonged cycling at elevated temperatures, and periodically comparing the performance of the individual electrodes, under fixed conditions, to their performance measured under these same conditions prior to cycling.

1.4 Task III - Optimize Recombination Load Impedance, and Task IV - Optimize Precharge Level

The objectives of these tasks are to determine the effect of the recombination-to-cadmium load impedance and the level of negative precharge on a) deep cycle capability and b) pressure behavior of cells. The experiments for these tasks will be run together, so that the effect of any interactions between the factors can be evaluated, and the optimum levels of the factors can be determined.

1.5 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 the negative precharge.

1.6 Task VI - Post-Cycle Tear-Down Analyses

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, or the auxiliary electrodes.

Additional 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 tear-down analysis.

2.0 TECHNICAL DISCUSSION

2.1 Task I - Assembly of Cells and Test Equipment

2.1.1 Cell Design and Assembly

Cells for experimental purposes and for delivery to Goddard Space Flight Center were built according to the design developed under Contract NAS 5-10261(1). The cells, of six ampere-hour nominal capacity, were all built from the same lots of both negative and positive plates, thus eliminating any variations due to lot-by-lot differences in the plates.

The plate pack consists of 11 negative and 10 positive plates and non-woven nylon separator. The recombination electrode (R-4 type - 5.00 mg/cm^2 catalyst and 1.20 mg/cm^2 TFE) consists of two pieces, each 1.5X5.0 cm located along the narrow edge of the pack. The oxygen-sensing control electrode (#1 in Ref. 1, page 12), of 10 cm^2 area, is located on one broad face of the pack. Descriptions of the recombination and control electrodes used in these cells may be found in Reference 1.

Electrical connection to the recombination electrode is made via the cell case, to which these electrodes are welded. The electrical connection to the control electrode is through a special terminal located on the cover. This electrode configuration allows for the variation of the resistance between the negative plates and both auxiliary electrodes.

Cells for use in the experimental program were filled with 34% KOH electrolyte, and subjected to manual screening cycles prior to conducting the various pre-cycle characterization tests outlined below for the specific tasks. Cells for later delivery to Goddard Space Flight Center are being stored without electrolyte, and will be filled and the state of charge adjusted to the optimized value determined from this contract, only immediately prior to the pre-shipment testing.

The manual cycles consisted of charging at 600 mA (C/10) for 16 hours, followed by a discharge at 3.0A. All cells tested had capacities in excess of 5.8 AH, the overall capacity being about 6.2 AH. Table II lists the individual cell capacities obtained at the 3.0A discharge rate to a 1.00 volt end point at 75°F.

2.1.2 Test Equipment

Two basic units for cycling and monitoring cells have been assembled. The first of these, designed primarily for Task II cycle requirements, has the capability of cycling cells at any rate to 10 amperes. Charging is done to a fixed percentage return, but inclusion of a transistorized charge control circuit would permit termination of the charge from a control electrode signal. Equipment for continuously monitoring and recording cell and control electrode voltages is also included.

The second basic unit is capable of cycling cells on up to nine different regimes simultaneously, using three different cycle rates and three different percentages overcharge. Facilities for monitoring and recording cell and auxiliary electrode voltages for the cells cycled by this equipment is also available.

In general, all cycle tests will be conducted with the charge and discharge rate the same. The percentage overcharge will be varied by adjusting the length of the recharge. Cells after completing charge will rest at open circuit during any unused portion of the one-hour "daylight" period, with no trickle charges employed. Recharge will be done to fixed percentages, although all cycle units can be quickly modified to provide for charge termination from a control electrode signal.

2.2 Task II - Auxiliary Electrode Stability

2.2.1 Experimental Approach

The long-term mechanical and electrical stability of both the recombination and control electrodes may be determined by comparing their characteristics after periods of cycling to their characteristics as determined prior to cycling. Cycling will be carried out at elevated temperatures (using an extended overcharge) so as to accelerate any degradation processes which may occur. A detailed plan for carrying out this task is outlined below:

A. Pre-cycle Characterizations:

1. Cell capacity, 3 cycles
2. Steady-state overcharge pressures at -20°C, 25°C, 40°C.

3. Control electrode response at C/2 at -20°C, 25°C, 40°C.

4. Recombination electrode polarization at -20°C.

B. Cycle:

1. 40°C, 25% DOD, 150% charge return.

2. Monitor cell voltage, pressure, control electrode voltage, and recombination electrode current.

C. Periodic Re-characterization:

1. Remove cells from cycling at regular intervals.

2. Re-determine the following cell and electrode characteristics:

a. Cell capacity

b. Overcharge pressure at -20°C

c. Control electrode response at -20°C

d. Recombination electrode polarization at -20°C.

2.2.2 Results and Discussion

During the first quarter, the cells required for this task were subjected to a limited number of the pre-cycle characterization steps. All cells were given two capacity cycles, and the average capacity for the six cells set aside for this task was 6.2 AH. Forty-eight hour overcharge pressures at 40°C, -20°C and 25°C at rates of C/8 (0.75A) and C/10 (0.6A), (with the recombination electrodes not connected to the negative plates) are recorded in Table I. The pressures obtained were slightly higher than found in cells of conventional design. However, cells with recombination and control electrodes contain more electrolyte than cells of conventional design, and this would result in higher overcharge pressures when the recombination electrodes are not utilized.

Characterization of the recombination and control electrodes, as outlined in Section 2.2.1, has been started. Results of these tests will be presented in the next report.

2.3 Task III - Optimize Recombination Load Impedance, and Task IV - Optimize Precharge Level

The impedance between the recombination electrode and the negative plates is a critical factor in operation of cells containing both recombination and control electrodes. It must be selected so as to limit the recombination of oxygen to a fraction of that generated during overcharge. In that manner, a pressure rise, suitable for detection by the control electrode, is obtained. The rate of recombination may also affect the cycle capability of cells by altering the reserve of charged cadmium present during the discharge. The extent to which this occurs will be determined in this task.

Another factor known to increase cycle capability, especially on deep discharge and at elevated temperatures, is the presence of a large reserve of charged negative capacity. While the amount required approaches all the excess negative available, the optimum amount has not been established. This will also be accomplished in this task.

The experiments planned for these two tasks are being conducted together. In this way interactions between these two factors can be determined, and design parameters for cells containing both recombination and control electrodes may be set. The experiments, outlined below, have been designed to facilitate the analysis of the results using regression techniques.

A. Pre-cycle characterizations:

   1. Cell capacity, 3 cycles.

2. Cell free volume. This value must be known to accurately adjust and/or measure the level of negative precharge.

3. Steady state overcharge pressure at cycle conditions.

4. Control electrode response at cycle conditions.

B. Precharge and Recombination Load:

Select 3 levels of precharge, (80%, 90%, and 100%) and three levels of recombination load, (0.1, 1.0, and 2.0 ohms) and set-up in a full factorial array:

LOAD	PRECHARGE LEVEL		
	80%	90%	100%
0.1 ohm	X	X	X
1.0 ohm	X	X	X
2.0 ohm	X	X	X

(Each X represents 2 cells)

C. Cycle:

1. Nine cells at 40° C to 50% DOD, nine cells at 25°C to 75% DOD.

2. Monitor cell voltage and pressure, control electrode voltage, and recombination current.

3. Cycle until end-of-discharge voltage falls below 0.50 volt.

4. Redetermine cell and auxiliary electrode characteristics.

5. Analyze cycle data and determine the optimum values of the parameters evaluated.

D. Test at optimum conditions:

1. Precharge cells to optimum level, as determined above.
2. Connect optimum recombination load, as determined above.
3. Subject to cycling at both 40°C to 50% DOD and 25°C to 75% DOD.

2.4 Task V - Other Cell Characteristics

2.4.1 Performance on Continuous Overcharge

The performance of conventional cells during continuous overcharge, at low rates, is well known. In this task, the performance of cells with recombination and control electrodes during overcharge at rates not compatible with cells of conventional design, will be determined. The test program will be straight-forward, and will include overcharging at temperatures between -20°C and 40°C, at rates of C/5, C/2, and, where possible, C.

2.4.2 Hydrogen Recombination and Cell Reversal

It is known that the recombination electrodes incorporated in these cells contain a catalyst capable of promoting the combination of hydrogen and oxygen in the cell. The effectiveness of this catalyst to electrochemically recombine hydrogen, or to recombine both gasses when large amounts of hydrogen are present, as following a reversal of the cell, will be determined in this task.

The hydrogen recombination ability of the recombination electrode will be determined by backfilling test cells with an atmosphere of pure hydrogen and monitoring the recombination current and the pressure decay. These tests will be conducted over the -20°C to 40°C temperature range.

The ability of the recombination electrodes to remove the hydrogen generated when cells are overdischarge (reversed) will be determined by overdischarging cells, which have been precharged and have recombination loads as determined in Section 2.3, and observing cell voltage, pressure, and auxiliary electrode behavior. The cells will then be returned to normal cycling to determine whether there is any accumulation of hydrogen, and whether the reversal has had any permanent effect on the cell or the auxiliary electrodes.

2.4.3 Maintenance of Negative Precharge

The relative states-of-charge of the plates in a sealed cell should not change during cycling, unless there is a net flow of oxygen into or out of the cell. The amount of charged excess negative capacity after cycling should be the same as before. Corrections may have to be applied to account for the capacity stored as gas in the cell, but as cells generally return to very near zero pressure after cycling, this is usually only a trivial amount.

In order to demonstrate this, cells with known amounts of negative precharge will be cycled, and cells periodically removed from cycling and the amount of excess negative capacity remaining determined. This determination can be made by fully discharging the cell and then adding oxygen. The amount of excess charged negative is directly proportional to the amount of oxygen consumed and can thus be readily determined.

2.5 Task VI - Post-Cycle Tear Down Analyses

Selected cells, after cycling, will be torn down and examined for physical damage to the plates, auxiliary electrodes, and for separator. The extent, if any, of migration of the catalyst from the recombination electrodes will also be determined.

Other tests and examinations, not outlined in the above tasks, may, from time-to-time be added as results of the tests indicate. Similarly, results may eliminate the need to perform certain of these tests.

3.0 WORK PLANNED FOR NEXT QUARTER

The cells required for Task II should be completely characterized, and cycling at 40°C underway. Results showing any changes in the auxiliary electrode behavior as a result of short-term 40°C cycling should be available.

Cells for the remaining tasks should also be fully characterized. Cycling for Tasks III and IV may be initiated.

TABLE I

48 Hour Overcharge Pressures*
(Recombination Electrode Disconnected)

	-20°C	25°C	40°C
C/8		83 psig	50 psig
		92 psig	61 psig
		118 psig	68 psig
		78 psig	49 psig
		123 psig	75 psig
			45 psig
C/10		56 psig	20 psig
		70 psig	24 psig
		84 psig	35 psig
		75 psig	24 psig
		92 psig	42 psig
		55 psig	20 psig
C/20	66 psig		
	76 psig		
	99 psig		
	102 psig		
	94 psig		
	71 psig		

*The design level of electrolyte is 20% greater in this type cell.

TABLE II

Capacity (AH) to 1.00V @ 3.0A Discharge Rate

Task II:

Cell #	Capacity (AH)
1	6.45
2	6.08
3	6.50
4	6.49
5	6.49
6	6.37

Task IV:

Cell #	Capacity (AH)
1	6.43
2	6.29
3	6.51
4	6.33
5	6.31
6	6.19

Task III:

Cell #	Capacity (AH)
1	6.25
2	6.20
3	6.55
4	6.14
5	6.23
6	6.58
7	5.95
8	6.51
9	6.30
10	6.14
11	5.99
12	6.19
13	6.54
14	5.97
15	5.83
16	6.03
17	6.12
18	6.09

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.