NASA CONTRACTOR REPORT

NASA CR-40

NASA CR-405

STUDY OF THE USE OF AUXILIARY ELECTRODES IN SILVER CELLS

by W. N. Carson, Jr., J. A. Consiglio, and J. W. Marr

Prepared under Contract No. NAS 5-3669 *by*
GENERAL ELECTRIC COMPANY
Schenectady, N. Y.
for Goddard Space Flight Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1966

STUDY OF THE USE OF AUXILIARY ELECTRODES IN SILVER CELLS

By W. N. Carson, Jr., J. A. Consiglio, and J. W. Marr

Prepared under Contract No. NAS 5-3669 by
GENERAL ELECTRIC COMPANY
Schenectady, N.Y.

for Goddard Space Flight Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – Price $0.60

ABSTRACT

This report covers the work done on the use of auxiliary electrodes in silver-zinc cells, the design and development of a hydrogen combination cell, and the testing of silver-cadmium cells with auxiliary electrodes. The results show that a cobalt-aluminate-spinel catalyzed auxiliary electrode can be used to recombine oxygen when connected to the zinc electrode through a suitable diode. Auxiliary electrodes using platinum catalysts can be used to recombine hydrogen when connected to the silver electrode through a 2-10 ohm resistance. The platinum catalyzed electrode can be used alone in the cell to control pressure as long as an excess of hydrogen over oxygen is generated.

A design for a hydrogen combination cell suitable for use in a satellite has been developed and tested. This cell can be used to remove hydrogen from the interior gas space of satellites powered by primary zinc cells; the hydrogen is evolved from the cells during operation.

The results of the testing of silver-cadmium cells with auxiliary electrodes confirm the work done in a previous contract (NAS 5-2817). The auxiliary electrode reduces the cell operating pressures and aids in maintaining uniform cell voltage.

SUMMARY

This report describes the work performed in the investigation of the use of auxiliary electrodes in silver-zinc cells for the recombination of hydrogen and oxygen evolved during cell operation, the work performed on the development of a hydrogen combination cell, and the results of tests made on silver-cadmium cells with auxiliary electrodes. The results of the work performed show that auxiliary electrodes made using a cobalt-aluminate-spinel catalyst on a silver substrate can be used to recombine oxygen when connected to the zinc electrode through a diode. In the absence of the diode, the connection of the auxiliary electrode to the zinc electrode induces a rapid self-discharge of the zinc electrode. Auxiliary electrodes made using a platinum catalyst on a silver substrate or on a nickel substrate can be used to recombine hydrogen when connected to the silver electrode through a low (2-10 ohm) resistance. The electrode with silver substrate is non-magnetic. The platinum catalyst on these electrodes promotes the direct combination of oxygen and hydrogen and the use of this electrode alone appears sufficient to control internal gas pressure in silver-zinc cells.

Results from the testing of silver-cadmium cells containing auxiliary electrodes confirm the work done in a previous contract (NAS 5-2817). A six cell battery charged at constant potential of 9.12 ± 0.06 volts maintained low pressure and uniform cell voltage over a period of seven months with the auxiliary electrode unconnected. Cycle tests show that cells can be charged and discharged without pressure rise and maintain capacity.

A design of a hydrogen combination cell suitable for use in satellites has been developed and tested. The design uses a hydrogen gas electrode, an alkaline electrolyte and a cupric oxide cathode. The cell will be used to remove hydrogen from the interior gas space of satellites powered by primary silver-zinc batteries. These batteries evolve substantial amounts of hydrogen during their operating life which must be removed to preserve the integrity of the battery and satellite. The hydrogen reacts at the hydrogen electrode and the cell reaction is the reduction of cupric oxide to free copper and water.

INTRODUCTION

Auxiliary Electrode Cells

Of primary concern in the application of auxiliary electrodes to silver-zinc cells is poisoning of the zinc electrode with platinum from the auxiliary electrode which catalyzes the self-discharge reaction of the zinc electrode:

$$Zn + 2\,KOH \longrightarrow K_2ZnO_2 + H_2$$

It is believed that the danger of platinum migration to the zinc electrode is small since, (1) the binder of the electrode has been very effective in holding the catalyst in place and has shown no deterioration in electrodes used for 10-14 months; (2) the platinum is in a highly insoluble form and has shown no tendency to go into solution when the electrode is used at current densities below 50ma/cm^2; (3) the barriers used in silver cells for blocking silver migration are equally effective for platinum, since platinum compounds are more easily reduced or absorbed than silver.

Although the auxiliary electrode has been used primarily as an oxygen electrode in silver-cadmium applications, there is no basic reason for an auxiliary electrode being operated only as an oxygen electrode. It can also be operated as a hydrogen electrode. For use as a hydrogen electrode, the auxiliary electrode would be connected to the positive (silver oxide) electrode in use, the recombination reactions being:

$$H_2 + 2OH^- \longrightarrow 2\,H_2O + 2\,e$$

$$Ag_2O + H_2O + 2\,e \longrightarrow 2\,Ag + 2OH^-$$

With this type of auxiliary electrode operation, the cell should be designed to be negative plate limiting, so that hydrogen is preferentially evolved on charging. The use of a hydrogen recombination system is desirable for silver-zinc cells, since there is an evolution of hydrogen during the cell stand and discharge that leads to pressure build-up in many applications.

The use of two auxiliary electrodes -- one for oxygen recombination which is attached to the negative electrode, and one for the recombination of hydrogen which is attached to the positive electrode -- is possible. The principal advantage of this dual system is that gassing of either hydrogen or oxygen would be taken care of. Also, the use of a platinum containing catalyst for the oxygen electrode is not needed, thus removing the possibility of zinc electrode degradation by coupling through the external circuit. This non-platinum containing type of electrode was originally proposed for use in silver-cadmium cells, but was abandoned in favor of the currently used one which can recombine small amounts of hydrogen directly, since this property was useful and presented no problems in use in silver-cadmium cells.

Another potential problem area is the possible poisoning of the auxiliary electrodes by interactions with both silver and zincate ions present in the electrolyte phase of these cells. At present, there is no evidence that either will degrade the electrode for oxygen or hydrogen recombination.

Hydrogen Combination Cells

The use of primary zinc - silver oxide cells as the power supply in satellites presents the basic design problem of how to dispose of the gases generated by these cells during stand and discharge (largely hydrogen with a small amount of oxygen). The amount of hydrogen given off is relatively large and hence the cells cannot be sealed without the use of very heavy cell cases and supports to withstand the pressure that would develop. Venting the cells to the outside of the satellite is not feasible since this would expose the cell electrolyte to space vacuum and all of the electrolyte water would boil off in a short time. The present practice is to vent the cells into the interior of the satellite which is gas-tight. This is satisfactory for short mission times, but for longer times the amount of gas given off by the cells is sufficient to pressurize the satellite to dangerous levels. Also the possibility exists of forming an explosive mixture of oxygen and hydrogen which can be ignited by the satellite electrical and electronic circuits. For these longer missions some additional means for disposing of the gases from the cells must be used. One possibility is to periodically vent the satellite to space in order to remove the accumulated gases; another is to chemically combine the hydrogen (and any oxygen) by some means. The work reported here is concerned with the latter approach.

EXPERIMENTAL

Silver-Cadmium Cell Studies

New test cells were constructed and put on test to obtain additional design and performance data. These cells are fabricated from Yardney YS-5 electrode packs consisting of four silver and five cadmium electrodes and the original separators. The auxiliary electrode was of the same material used previously, i. e. a nickel wire mesh coated with a thin layer of electrode catalyst containing platinum metals, plus a nickel powder electron collector and Teflon binder. The dimensions of the auxiliary electrode are the same as the dimensions of the YS-5 electrodes. The auxiliary electrode is placed against one of the two end cadmium electrodes with a Pellon 2505W Nylon separator between the two. The gas side of the auxiliary electrode is separated about 3/16 inch from the cell case by a piece of polyethylene grid (Vexar Plastic Netting, Vexar Division, E. I. du Pont de Nemours, Buffalo, N. Y., diamond pattern 4/4-30-90-PE-3). An additional 1/4 inch length of cell case has been provided to serve as electrolyte storage during cycling operation; wicks of Nylon separator were placed to extend from the bottom of original cell separators and the bottom of the reservoir. The test cells are potted in 1 inch of epoxy and are fitted with a pressure connection to either a pressure gauge or pressure transducer. A toggle valve is provided to permit connection of the gas system to external gas pumps or analysis equipment as desired.

The test cells were formed by filling the cell with 30 per cent potassium hydroxide to a level above the top of the electrode pack and allowing a 24 to 48 hour soak period to equilibrate the separators. The cells were then charged at 300 ma constant current for 20 hours, and the electrolyte level adjusted so that the bottom 3/8 inch of the cell (i. e. the 1/4 inch reservoir plus 1/8 inch of the electrode pack) was left filled with electrolyte. The cell was then discharged to a one volt cut off at 2.5 amperes. The electrolyte level at the end of discharge was about 1/8 inch deep in the reservoir. The excess electrolyte present assures that the separators in the electrode pack are completely wetted. Six of the cells were cycled three times at the forming rates to determine cell capacity before making the long term tests. The results are given in Table 1. The reason for the wide variation in capacity shown in the tests is not known; this variation in capacity either disappeared in the subsequent testing, or was an artifice of the test. In any case, coupling of cells as unbalanced as these appeared to be in series was a severe test of auxiliary electrode pressure control, since under constant potential charging conditions, the low capacity cells would be expected to gas severely on prolonged overcharge. After the capacity cycles were completed, the cells were connected in series and charged at 300 ma. for 20 hours. The charging was then changed to a constant potential mode of 9.12 ± 0.06 volts across the six cell battery (1.52 ± 0.01 volts per cell). The power source used was a Harrison Laboratories Model 865 B power source operating in the constant voltage mode. The voltage across the battery alone was controlled; this arrangement allowed the individual cell potentials to vary during the prolonged charging. The purpose of this test was to determine the behavior of the cells on continuous overcharge such as would be experienced in satellites in a polar orbit or in highly elliptical orbits. In the experiment, the auxiliary electrodes were not connected with either electrode in the cell; this was intended to test the hypothesis that only a gas recombination catalyst is needed to allow cell operation under constant voltage charging conditions to prevent excessive build-up of gas pressure or severe loss of cell balance.

TABLE 1

CAPACITY* TESTS OF SILVER-CADMIUM CELLS

Cycle	CELL					
	061501	061502	061503	061504	061505	061506
1	3.125	5.000	4.375	---	4.060	3.750
2	4.400	5.625	5.150	4.690	4.060	3.590
3	4.525	6.025	5.310	4.375	2.920	3.440

* 300 ma charge for 20 hours, discharge at 2.5 amperes to 1.0 volt cut off.

Table 2 gives the summary of the results of the first continuous overcharge tests. This table is in two parts,part A giving the pressure readings, and part B giving the voltage readings. The pressures and voltages of each cell were measured every working day, except for a two week period in late December 1964. After the first two weeks of the test period, only samples of the test data are given because of the slow change in readings with time. The voltage of the cadmium to auxiliary electrode was also measured daily; the sign and magnitude of this voltage allows a determination of whether the gas present in the cell is oxygen or hydrogen. Thus, with the auxiliary electrode positive to the cadmium electrode, by approximately one volt open circuit, the gas present in the cell is oxygen at a pressure of over 5 to 10 mm. Negative voltage would indicate hydrogen. In the test period, only oxygen was indicated.

The general behavior of all the cells can be summarized by stating that the cells show a pressure rise in the first few weeks of operation which is followed by a rapid drop in pressure to a low value. The cells then show a slow rise to a moderate pressure which does not exceed a few pounds gauge on the remainder of the cycling. This behavior can be explained by assuming that the initial gas pressure is due to gassing of the silver electrode on overcharge (shown by the fact that the gas is oxygen) followed by gassing of hydrogen from the cadmium electrode. This combines with the oxygen in the presence of the auxiliary electrode catalyst. An essentially balanced evolution of oxygen and hydrogen then takes place for the remainder of the overcharging period.

TABLE 2

SILVER-CADMIUM CELL CONTINUOUS OVERCHARGE TEST - I (1)

Part A - Pressure (2)

Cell #	061501	061502	061503	061504	061505	061506
Day						
7/20/64	30 in.	30 in.	25 in.	18 in.	4 psi	30 in.
7/21	30 in.	30 in.	15 in.	5 in.	10 psi	23 in.
7/22	25 in.	28 in.	5 psi	5 in.	20 psi	20 in.
7/23	5 in.	26 in.	12 psi	5 in.	23 psi	15 in.
7/24	3 psi	25 in.	9 psi	5 in.	23 psi	12 in.
7/27	8 psi	18 in.	6 psi	1 psi	17 psi	7 in.
7/28	9 psi	12 in.	8 psi	2 psi	15 psi	5 in.
7/29	11 psi	3 in.	5 psi	0 psi	14 psi	5 in.
7/30	12 psi	2 psi	4 psi	2 psi	14 psi	4 in.
7/31	13 psi	3 psi	2 psi	1 psi	12 psi	0 in.
8/3	14 psi	4 psi	3 psi	0 psi	8 psi	4 psi
8/7	17 psi	8 psi	3 psi	1 psi	7 psi	6 psi
8/13	18 psi	9 psi	2 psi	1 psi	5 psi	5 psi
8/19	15 psi	8 psi	2 psi	1 psi	2 psi	3 psi
8/25	10 psi	4 psi	0 psi	0 psi	0 psi	2 psi
9/3	1 psi	5 in.	6 in.	4 in.	8 in.	4 in.
9/10	7 in.	11 in.	12 in.	4 in.	9 in.	5 in.
9/16	16 in.	17 in.	13 in.	4 in.	9 in.	4 in.
9/22	21 in.	20 in.	12 in.	3 in.	7 in.	0 in.
9/28	22 in.	21 in.	12 in.	3 in.	5 in.	0 in.

(1) Constant voltage, 9.12 ± 0.06 volts on battery (1.52 ± 0.01 volt/cell avg). Started 8 a.m. 7/20/64, readings taken at 4 p.m. each day.

(2) Pressure in inches of mercury vacuum or gauge pressure.

TABLE 2 (cont.)

Part A - Pressure

Cell #	061501	061502	061503	061504	061505	061506
Day						
10/2/64	22 in.	21 in.	8 in.	2 in.	3 in.	0
10/8	20 in.	22 in.	8 in.	2 in.	1 in.	0
10/14	19 in.	20 in.	5 in.	1 in.	0	0
10/20	18 in.	20 in.	5 in.	1 in.	0	0
10/26	16 in.	20 in.	5 in.	0	0	0
10/30	16 in.	20 in.	5 in.	0	0	0
11/2	16 in.	20 in.	5 in.	0	0	0
11/9	15 in.	19 in.	5 in.	0	0	0
11/16	14 in.	18 in.	4 in.	0	0	0
11/23	13 in.	18 in.	4 in.	0	0	0
11/30	13 in.	18 in.	4 in.	0	0	0
12/7	12 in.	17 in.	3 in.	0	0	0
12/14	11 in.	16 in.	2 in.	0	0	0
1/5/65	12 in.	15 in.	2 in.	1 psi	0	0
1/12	10 in.	15 in.	2 in.	1 psi	0	0
1/19	10 in.	15 in.	2 in.	1 psi	0	0
1/26	10 in.	14 in.	2 in.	2 psi	0	0
2/1	10 in.	13 in.	2 in.	2 psi	1 psi	0

Part B - Voltage (3)

Cell #	061501	061502	061503	061504	061505	061506	Charge Current
Day							
7/20/64	1.48 v	1.50 v	1.50 v	1.51 v	1.72 v	1.50 v	60 ma
7/21	1.51	1.53	1.54	1.51	1.60	1.49	30
7/22	1.54	1.52	1.56	1.50	1.58	1.48	16
7/23	1.56	1.52	1.56	1.50	1.56	1.48	6
7/24	1.56	1.52	1.56	1.53	1.56	1.48	4

(3) Volts/cell using 1000 ohms/volt meter.

Part B - Voltage (cont.)

Cell #	061501	061502	061503	061504	061505	061506	Charge Current
Day							
7/27/64	1.54 v	1.54 v	1.54 v	1.54 v	1.55 v	1.49 v	3 ma
7/28	1.54	1.53	1.54	1.53	1.54	1.48	3
7/29	1.53	1.53	1.54	1.53	1.54	1.51	3
7/30	1.53	1.53	1.53	1.53	1.54	1.53	3
7/31	1.54	1.53	1.54	1.53	1.53	1.54	3
8/3	1.54	1.53	1.54	1.53	1.54	1.53	3
8/7	1.54	1.53	1.54	1.54	1.54	1.54	3
8/13	1.53	1.53	1.54	1.54	1.54	1.54	3
8/19	1.54	1.53	1.54	1.55	1.55	1.55	3
8/25	1.53	1.53	1.53	1.53	1.54	1.56	3
9/3	1.51	1.53	1.52	1.53	1.54	1.65	2
9/10	1.51	1.51	1.51	1.51	1.54	1.68	2
9/16	1.47	1.49	1.49	1.50	1.54	1.69	1.5
9/22	1.46	1.48	1.46	1.47	1.63	1.65	1
9/28	1.46	1.48	1.46	1.47	1.64	1.65	1
10/2	1.46	1.46	1.45	1.46	1.65	1.64	1
10/8	1.47	1.48	1.46	1.47	1.66	1.66	1
10/14	1.46	1.47	1.46	1.47	1.65	1.63	1
10/20	1.46	1.46	1.45	1.46	1.64	1.63	1
10/26	1.47	1.47	1.46	1.47	1.66	1.65	1
10/30	1.45	1.46	1.45	1.46	1.64	1.63	1
11/2	1.46	1.46	1.45	1.49	1.65	1.64	1
11/9	1.44	1.46	1.42	1.56	1.63	1.62	1
11/16	1.43	1.47	1.43	1.56	1.61	1.60	1
11/23	1.43	1.53	1.43	1.57	1.61	1.60	1
11/30	1.43	1.54	1.46	1.56	1.60	1.60	1
12/7	1.43	1.55	1.42	1.56	1.59	1.60	1
12/14	1.43	1.55	1.43	1.56	1.59	1.59	1

Part B - Voltage (cont.)

Cell #	061501	061502	061503	061504	061505	061506	Charge Current
Day							
1/5/65	1.44 v	1.56 v	1.43 v	1.57 v	1.57 v	1.59 v	1 ma
1/12	1.44	1.56	1.42	1.58	1.58	1.59	1
1/19	1.43	1.58	1.43	1.59	1.59	1.59	1
1/26	1.44	1.58	1.44	1.59	1.59	1.60	1
2/1	1.43	1.57	1.44	1.58	1.58	1.58	1

The cells were tested for capacity after removal from continuous overcharge. All cells showed capacities of over 6.7 ampere-hour. Seven cycles of charge at 300 ma for 20 hours followed by discharge at 2.5 amperes for 2 hours were run; all cells showed 5.0 ampere-hour capacity above the 1.0 cut-off point. (In these tests, no cell was run to cut off). The cells were then allowed to stand uncharged for 43 days. The cells were reconnected in series and the auxiliary electrodes connected to the cadmium electrodes by two ohm resistors.

An attempt was made to charge the battery by constant current charge of 330 ma for 20 hours. This failed because four of the six cells had the auxiliary electrodes shorted to the positive (silver) electrodes and thus did not charge. The auxiliaries were then disconnected and a second attempt made to charge the cells. This was successful and all cells gave good capacity of over six ampere-hours at a 2.5 ampere discharge to 0.6 volt cut off. The cells were then fully charged at 500 ma and placed on continuous overcharge at 9.12 ± 0.06 volts as before. Table 3 gives the results to June 1, the cut-off date for the report. These tests are continuing.

It has been found that the short circuits between the auxiliary electrodes and silver electrode are intermittent. Mere handling of the cells often sufficed to make or break the contact. This is suggestive of silver dendrite formation in the cell.

Five new silver-cadmium test cells were fabricated from Yardney YS-5 cell electrode packs as described previously. These cells were equilibrated with electrolyte for 48 hours, and then formed by cycling three times at 300 ma charge for 20 hours, followed by 2.5 ampere discharge to 1.0 volt cut off. Five cycles to determine capacity were then run, using the forming rates. The results are shown in Table 4. The cells were then connected individually to the cycling apparatus used previously for testing auxiliary electrode silver-cadmium

TABLE 3

SILVER-CADMIUM CELL CONTINUOUS OVERCHARGE TEST - II (1)

Part A - Pressure (2)

Cell # Date	061501	061502	061503	061504	061505	061506
5/6/65	28 in.	15 in.	28 in.	30 in.	8 psi	2 psi
5/7	28 in.	15 in.	28 in.	30 in.	32 psi	20 psi
5/10	22 in.	14 in.	2 psi	2 in.	12 psi	10 psi
5/11	3 psi	18 in.	10 psi	1 psi	5 psi	3 psi
5/12	4 psi	12 in.	9 psi	3 in.	1 psi	1 in.
5/13	4 psi	7 in.	8 psi	9 in.	5 in.	9 in.
5/14	3 psi	5 in.	9 psi	9 in.	10 in.	12 in.
5/17	0	3 psi	4 psi	15 in.	15 in.	15 in.
5/18	4 in.	2 psi	1 psi	18 in.	15 in.	15 in.
5/19	6 in.	1 psi	0	20 in.	15 in.	13 in.
5/20	8 in.	1 psi	4 in.	20 in.	13 in.	13 in.
5/21	12 in.	0	7 in.	22 in.	13 in.	13 in.
5/24	20 in.	8 in.	19 in.	25 in.	10 in.	8 in.
5/25	22 in.	9 in.	20 in.	25 in.	10 in.	8 in.
5/26	22 in.	9 in.	20 in.	25 in.	9 in.	5 in.
5/27	23 in.	10 in.	22 in.	25 in.	8 in.	5 in.
5/28	24 in.	10 in.	22 in.	25 in.	8 in.	5 in.
6/1	25 in.	11 in.	23 in.	26 in.	6 in.	4 in.

(1) Constant voltage 9.12 ± 0.06 volts on battery. Readings taken 4:00 p.m. each day.

(2) Pressure in inches of mercury vacuum or in gauge pressure.

Part B - Voltage (3)

Cell # Date	061501	061502	061503	061504	061505	061506	Charge Current
5/6/65	1.53 v	1.53 v	1.52 v	1.53 v	1.53 v	1.53 v	200 ma
5/7	1.48	1.45	1.47	1.49	1.59	1.60	40
5/10	1.56	1.50	1.58	1.59	1.44	1.45	8
5/11	1.56	1.54	1.57	1.56	1.44	1.45	4
5/12	1.55	1.54	1.57	1.56	1.44	1.45	5

(3) Voltage of cell, taken with 1000 ohm/volt meter.

Part B - Voltage (cont.)

Cell # Date	061501	061502	061503	061504	061505	061506	Charge Current
5/13/65	1.55 v	1.56 v	1.56 v	1.56 v	1.44 v	1.45 v	4 ma
5/14	1.55	1.56	1.56	1.56	1.45	1.44	-
5/17	1.53	1.56	1.54	1.54	1.46	1.45	3
5/18	1.53	1.56	1.54	1.54	1.45	1.46	2
5/19	1.53	1.56	1.55	1.55	1.45	1.47	2
5/20	1.52	1.54	1.53	1.53	1.46	1.57	2
5/21	1.50	1.53	1.52	1.52	1.45	1.61	2
5/24	1.50	1.52	1.50	1.52	1.45	1.63	1
5/25	1.49	1.52	1.50	1.52	1.45	1.63	1
5/26	1.50	1.52	1.51	1.52	1.45	1.64	1
5/27	1.49	1.52	1.51	1.50	1.45	1.63	1
5/28	1.49	1.52	1.51	1.51	1.45	1.63	1
6/1	1.50	1.52	1.51	1.51	1.45	1.64	1

TABLE 4

INITIAL CAPACITY OF SILVER-CADMIUM CYCLE TEST CELLS (1)

Cell # Run	072401	072402	072403	072404	072405
1	4.38	4.38	4.38	4.68	4.68
2	4.38	4.38	4.38	4.68	4.83
3	4.38	4.05	4.38	4.53	5.00
4	4.38	4.05	4.38	---	4.38
5	4.05	4.05	4.38	5.00	4.53

(1) Charge 300 ma for 20 hours, discharge 2.5 A to 1.0 volt cut off of 2 hours. Auxiliary electrode connected to cadmium electrode through 5 ohms.

cells under contract NAS 5-2817. The apparatus was modified by incorporating a safety pressure cut-off system. Cell voltage, auxiliary electrode to cadmium voltage and pressure are monitored continuously. The cells were cycled from March 15, 1965 to May 15, 1965 as follows:

> Charge at 0.12 amperes for 11 1/2 hours. Discharge at 2.5 ampers for 1/2 hour or to a 1-0 volt cut-off. In the test, all cells had their auxiliary electrodes connected to the cadmium electrode through a

five ohm resistor. In the test period, all cells operated between ca. 28 in. to 10 in. vacuum, and all delivered the discharge current at voltages well above the 1.0 volt cut off.

Cycling tests were discontinued to allow extensive repair of the equipment.

The auxiliary electrode material used in these cells has been shown in previous work to be capable of sustaining currents at current densities up to 50 ma/cm^2 at oxygen pressures of 50-100 mm mercury or above. This current capacity is dependent upon temperature, circuit impedance, and cell construction. Both the nickel and the silver substrate electrodes have the same catalyst, and give the same overall performance in tests.

Silver-Zinc Cell Studies

These studies were concerned with obtaining design data on the suitability of various auxiliary electrode compositions for the recombination of hydrogen and oxygen. The major factors in evaluation were: rate of recombination of oxygen and hydrogen at various levels of gas pressure, the effect of the auxiliary electrode on the self-discharge of the silver and zinc electrodes and the operability in complete cells of single and double auxiliary electrode designs.

Several types of auxiliary electrodes were used in these experiments. For oxygen recombination, the following types were used:

Silver mesh - Expanded silver metal mesh (AG-079-2) manufactured by Designers Metal Corporation.

Silver powder - Handy and Harmon Silflake 131 silver powder pressed on a silver screen into sheets with Teflon as a waterproofing and binding agent.

Silver-spinel - Handy and Harmon Silflake 131 silver powder and a spinel structure cobalt aluminate pressed on a silver screen into sheets with Teflon as a waterproofing and binding agent.

For hydrogen recombination, the following types were used:

Conventional - A mixture of nickel and platinum pressed into sheets on a nickel mesh Teflon as a waterproofing and binding agent.

Silver-Modified Conventional - A mixture of silver and platinum pressed into sheets on a silver mesh with Teflon as a waterproofing and binding agent. This electrode is similar to the one described above except that the silver is used in place of nickel.

The auxiliary electrodes have been shown to have current carrying capacities as follows:

Silver mesh and silver powder - Close to 0 ma/cm^2 at low pressures of oxygen.

Silver-spinel - 3 ma/cm^2 at oxygen pressures above 100-150 mm mercury at room temperature.

Conventional and Silver-Modified Conventional - Up to 50 ma/cm^2 for oxygen at pressures above 50-100 mm mercury at room temperature; - up to 35 ma/cm^2 for hydrogen at pressures above 50-100 mm mercury at room temperature.

Self-discharge Studies

The composition of conventional auxiliary electrodes for oxygen recombination was found to be unsatisfactory for this function in silver-zinc cells. The platinum contained in these electrodes promotes a rapid discharge with the zinc electrode electrically connected through a load resistor. In one test a zinc electrode from a 3.0 amp-hour Yardney silver-zinc cell (Model PM-3) was completely discharged in approximately 8 hours when connected to an auxiliary electrode through a one ohm load. The dimensions of the auxiliary electrode were the same as the dimensions of the electrodes in the PM-3 cell pack (14. cm^2).

Auxiliary electrodes using platinum catalysts as for the conventional electrode but with different electron carriers and overall construction were found, as expected, to discharge zinc electrodes rapidly when connected to the zinc electrode. Connection of the conventional and special auxiliary electrodes containing platinum catalysts to the silver electrode does not induce evolution of oxygen from the silver electrode or hydrogen from the zinc electrode in the same cell. This behavior was as expected.

Silver mesh, silver powder, and silver-spinel electrodes (electrode area 14 cm^2) were connected to a zinc electrode from a three ampere-hour Yardney silver-zinc cell (Model PM-3) and the current through a 1 ohm load measured. The gas formed was collected at the same time in a gas buret. The data for the three types of electrodes is shown in Table 5. It was found that the silver mesh does not discharge the zinc electrodes. However, the silver powder and the silver-spinel electrodes when connected to the zinc electrode discharge it at a rapid rate.

The non-linear resistance of a diode may be used to block self-discharge current but permit the passage of the recombination current. Such a procedure is described in Patent No. 3, 080, 440 by P. Ruetschi of the Electric Storage Battery Company. By proper choice of diode, it should be possible to use an auxiliary electrode so that the self-discharge current will be in the micro-ampere range at the potential of half a volt, while the current would be in the ampere range to near a volt when the voltage climbed due to the recombination potential.

To overcome the self-discharge problem, the silver-spinel catalyzed electrode was connected to the zinc electrode through 1N457 and 1N198 diodes. The self-discharge data for these tests is shown in Table 5 also. The amount of gassing and self-discharge of the zinc electrode are drastically reduced. Upon admission of oxygen to the cell, substantial currents flow with the rise in auxiliary electrode voltage caused by depolarization with the oxygen. However, the use of diodes with platinum catalyzed auxiliary electrodes was not successful, due to the much higher couple voltage of the zinc-platinum couple in strong caustic solutions. The use of the spinel electrode is thus feasible, but the more efficient platinum electrode cannot be used coupled with the zinc electrode.

Oxygen recombination studies. - These were made with test cells composed of auxiliary electrodes of silver mesh, silver powder or silver plus spinel and either cadmium or nickel counter electrodes. During overcharging, the cadmium or nickel electrode generates oxygen which is reacted at the auxiliary electrode. This procedure simulates the effect of the oxygen cycle on cell overcharge.

In the test, electrodes of the same cross-section as the electrodes of the Yardney (Model PM-3) 3 ampere-hour silver-zinc cells are used (electrode area 14 cm^2). The electrodes were assembled in cells with Nylon separators, 40% KOH electrolyte added, the cells charged to complete the charge on the nickel hydroxide electrode, and purged with oxygen. The oxygen pressure was adjusted to 700, 100, 10 and 0 millimeters of mercury. The cells were then charged at 12. 5 milliamperes continuously for 48-72 hours. A current of 12. 5 milliamperes represents a C/20 charge rate. This procedure was repeated for 25 milliamperes and 50 milliamperes.

At 12. 5 milliamperes, electrodes of silver mesh and silver powder did not recombine oxygen at a rate rapid enough to keep the pressure in the system constant. The cell electrode voltage and pressure monitors indicated that the auxiliary electrodes were gassing; this was presumably hydrogen. Analysis of the cell gas after the experiment was terminated showed that this was the case since over 50% hydrogen was found. This behavior for silver electrodes is expected at lower pressures of oxygen since it is known that the reduction rate at oxygen electrodes made from ordinary silver metal is low. Undoubtedly,

TABLE 5

Self-Discharge of Zinc Electrodes (1)

Counter Electrode	Cell Load	Elapsed Time Minutes	Total Volume Gas Evolved CC	Current Micro-amperes	Voltage Volts
1. Silver Mesh	1Ω resistor		< 0.1cc	< 10	
			No measurable gas evolution and no measurable discharge current.		
2. Silver Powder	1Ω resistor	0	0	64,000	
		20	13	74,000	
		50	29	72,000	
		85	47	70,000	
		115	64	68,000	
3. Silver Spinel #1	1Ω resistor	0	0		
		20	9	66,000	
		40	17	60,000	
		60	26	45,000	
		75	32	40,000	
		105	39	30,000	
4. Silver Spinel #2	1Ω resistor	0	0	4,000	0.05
		5	2	1,400	0.0154
		40	4	800	0.0086
		65	6	620	0.0072
		125	7.6	550	0.0057
5. Silver Spinel #2	1N457 diode	0	0	60	0.58
		15	0	40	0.44
		30	0	40	0.42
		45	0.5	40	0.41
		60	0.6	40	0.40
6. Silver Spinel #2	1N198 diode	0	0	40	0.45
		7	0	40	0.44
		10	0	40	0.42
		20	0	40	0.42
		60	0	40	0.42

(1) Electrode Area 14 cm^2, Electrolyte 40% potassium hydroxide, room temperature

silver catalysts made in special ways could be made into useful auxiliary electrodes, but not without considerable development in fabrication and preparation of the catalysts. The spinel catalyzed electrode was developed previously for use in fuel cells using oxygen as the cathode depolarizer. This electrode showed constant pressure in the tests at the 12. 5 and 25 ma tests, but gave a slow rise in pressure at 50 ma. This pressure dropped during periods with no current passing, showing that some oxidation of the silver subtrate in the presence of the spinel catalysts might be taking place. No hydrogen was found in the atmosphere of the cell.

Two more sets of silver-spinel electrodes were made and tested in the same manner. The first set did not recombine oxygen under any current conditions, and was most likely of faulty construction. The second set of electrodes allowed the cell to equilibrate to approximately one atmosphere pressure at current rates up to 50 milliamperes per plate (14 cm^2). At 50 milliamperes, a slow pressure rise was observed. Spinel catalyzed electrodes thus allow recombination of oxygen at rates in the vicinity of C/10 with an auxiliary electrode area equal to the cell electrode area. Continuous overcharge at these rates is not likely in practice because of the damage done to the silver electrode.

Hydrogen recombination studies. - These studies were made with test cells composed of an auxiliary electrode and either a zinc or a cadmium electrode. During overcharging, the zinc or cadmium electrode evolves hydrogen which is reacted at the auxiliary electrode, in effect setting up the hydrogen cycle for cell overcharge. It has been found useless to use catalysts that do not use platinum metals for hydrogen recombination in cells, since the non-platinum catalysts such as Raney nickel are rapidly destroyed by oxygen, and thus cannot be subjected to oxygen during their life. This oxygen attack precludes their use in cells that may at times have oxygen evolved from the electrodes.

Conventional auxiliary electrodes employ a nickel mesh, a nickel powder electron collector mixed with platinum black powder as catalysts, and a Teflon binder. This structure is magnetic. Since there is considerable interest in a non-magnetic structure, we explored the use of silver mesh and silver flake powder in place of the magnetic nickel in hydrogen recombination electrodes. The pasting behavior of the non-magnetic material is poorer than for the nickel substrate, and the initial batches of electrodes were inferior in behavior to the conventional electrodes. However, with experience and added trials, silver substrate electrodes have been prepared that compare favorably with the conventional electrode.

In the test, electrodes of the same cross-section as the electrodes in Yardney 3, ampere-hour silver-zinc cells were used. The electrodes were assembled in the cells with Nylon separators, electrolyte added and the cells charged at 50 milliamperes to charge up the negative electrode completely. Gas space behind the auxiliary electrode was free of electrolyte and ample gas passage between the working electrode and the auxiliary electrode was provided. The cells were provided with pressure connectors for monitoring pressure with a pressure transducer and taking gas samples. Initially, four each of cadmium and zinc cells with silver substrate auxiliary electrodes were made. These cells were purged after charging by evacuation and filling with hydrogen; then the cells were adjusted to various initial pressures of 700, 100 and 10 and zero millimeters of hydrogen absolute and sealed. The voltages of the electrodes, auxiliary to reference, was in the vicinity of 0.3 to 0.4 of a volt at this stage. The cells were then subjected to charging at 12.5 milliamperes and the pressure and auxiliary to reference voltage monitored. The cells showed negligible pressure rise or change in voltage at this charging rate over 48 to 72 hours of continuous charging. The charging rate was then increased to 25 milliamperes and the cells with 700 and 100 millimeter initial pressure of the cadmium series showed pressure rise with the auxiliary electrode, reference to voltage rising to over 1.5 volts. Gas analysis showed the presence of oxygen in substantial amounts indicating that the platinum catalyst in the auxiliary electrode had failed. This indication was confirmed in later tests on these cells and electrodes. At 50 milliampere charging rate, all the cells gave pressure rises and all of the auxiliary electrodes appeared to fail by oxidation. All the electrodes rose to about 1.5 volts with respect to the reference. An analysis of the gas in the cells shows substantial amounts of oxygen as well as hydrogen, indicating again the failure of the auxiliary electrode catalyst.

The initial cell tests were made using the first attempts to make non-magnetic auxiliary electrodes. New tests were made on improved non-magnetic electrodes and showed that operation at 50 milliamperes can be obtained without signs of oxygen evolution or other indication of failure for hydrogen pressures as low as 0 and 10 mm initial cell pressure, and operation at higher hydrogen pressures is better than low hydrogen pressure. These tests confirm the conclusion that satisfactory non-magnetic auxiliary electrode material can be made with the proven high performance of the conventional electrodes.

Tests with complete silver-zinc cells. - Six cells were made up to test auxiliary recombination electrodes developed in the program. The cells used Yardney PM-3 cell electrode packs with appropriate auxiliary electrodes and were potted in epoxy to provide a pressure container. The cells were equipped with pressure transducers. The cells were not formed prior to the tests reported here. The auxiliary electrode had an area of 14 cm^2 and the electrolyte used was 40% potassium hydroxide. In all cells, sufficient electrolyte was present to completely wet the Yardney cell separators, but the access to the auxiliary electrode was free of electrolyte.

Two of the silver-zinc test cells were built using single silver-spinel auxiliary electrodes. These were evacuated to 30 inches of mercury vacuum, and charged continuously at 12.5 ma. with the spinel electrode connected to the zinc electrode through a diode. After the cell became charged, the gas pressure rose continuously; the cell voltage was 1.97-1.98 volts. Analysis of the gas showed that it was pure hydrogen, indicating that all of the oxygen evolved was recombined, but that the use of the spinel catalyzed electrode alone is not satisfactory because of build up of hydrogen.

Two of the silver-zinc cells were built using conventional auxiliary electrode material. The cells were evacuated to 30 inches of vacuum and subjected to overcharge at 12.5, 25, and 50 ma. without connecting the auxiliary electrode to either cell electrode. The cell voltages were 1.85 volts, and there was no pressure rise in the cells during the tests. This indicates that hydrogen and oxygen were being evolved in stoichiometric proportions during the overcharging period; this balance was accidental since no attempt to make the balance had been made. With stoichiometric evolution of the two gases, the auxiliary electrode acts as a carrier for the recombination catalyst, and is not used as an electrode. This type of behavior is well known.

The two remaining silver-zinc test cells were built with both a conventional and a silver-spinel auxiliary electrode. These cells were evacuated to 30 inches of mercury vacuum, and charged at 12.5, 25, and 50 ma. with the electrodes unconnected. In one of the cells, the pressure did not rise and the cell stayed at a constant potential of 1.82 volts during the charging. The pressure in the other cell rose on charging at 12.5 ma. The conventional auxiliary electrode was then connected to the silver electrode and the cell pressure dropped to vacuum. Upon charging at 25 and 50 ma, the auxiliary electrode current was approximately the charging current, and the cell pressure remained below atmospheric. Toward the end of the tests a short developed in the cell and the test was stopped.

Modification of Silver-Zinc Cells

Fifty Yardney HR 10 DC 2 silver-zinc cells have been fitted with non-magnetic auxiliary electrodes. In the modification, the original cell pack is kept intact, and the auxiliary electrode placed at one edge of the pack. The lead for the auxiliary electrode is a silver wire which is passed through a hole in the cell top and cemented in place. The original cell case is used. About one-quarter of the cells were fitted out with two of the auxiliaries, since the current carrying capacity of a single electrode is limited and it is of interest to have some cells with higher capacity. These cells will be used in tests set up by Goddard Space Flight Center.

Hydrogen Combination Cell Studies

These cells were developed to remove hydrogen from a surrounding atmosphere. The cell is a galvanic cell designed to use hydrogen as the anode, oxygen or a metal oxide for the cathode depolarizer, and an alkaline electrolyte. The cells discussed here employ a metal oxide as the depolarizer and the cell reaction is oxidation of the hydrogen to water:

$$MO + H_2 \longrightarrow M + H_2O$$

where MO is the metal oxide used as the cathode depolarizer. This type of depolarizer is most useful for applications in which the total amount of hydrogen evolved is relatively small and thus does not justify the weight and complexity of a bottled or cryogenic oxygen supply. However, because of its favorable weight, oxygen should be used for cases in which large amounts of hydrogen are to be combined, or for cases in which the oxygen needed can be "piggy-backed" on an oxygen supply needed for another purpose in the satellite.

Theoretically, power can be obtained from the combination cell system. Practically, the amount of power will be quite small for small systems, and tend to be erratic since the supply of hydrogen will not be constant. For larger systems, the use of this combination system to supply power should be investigated, although it is unlikely that the extra complexity will be justified in most cases.

The choice of the metal oxide or hydroxide to use is dictated primarily by the weight of material needed to adsorb a given quantity of hydrogen. If power is not to be obtained from the cells, then cell voltage is not critical and more materials can be considered. Table 6 shows data on possible materials for use in the cell, assuming a caustic electrolyte and no power output. On the basis of minimum weight, copper oxide is the obvious choice. In addition to the weight advantage, copper oxide is satisfactory with respect to cell voltage and electrode fabrication techniques.

The obvious selection of copper oxide for the cathode depolarizer is fortunate in that copper oxide electrodes are available commercially. Our electrodes were obtained from Thomas A. Edison Industries, Inc., Battery Division, East Orange, N. J. This company produces them for use in their renewable copper oxide - zinc cell, but the electrodes can be obtained as separate items. The electrodes are sintered, porous copper oxide, superficially coated with a reduced layer of copper serving as the electron collector. The density of the electrode is about 50% of theoretical. The electrodes

TABLE 6

METAL OXIDE PARAMETERS

Metal Oxide	Expected Utilization	Weight Needed to Adsorb 10,000 cc (1) Hydrogen	Volume of Hydrogen Adsorbed Per Pound	Notes
	%	Pounds	Liters	
Cadmium Oxide CdO	90	0.161	62.3	2
Copper Oxide CuO	90	0.071	143.0	2
Ferric Oxide Fe_2O_3	80	0.199	50.3	3
Lead Dioxide PbO_2	80	0.297	33.8	4
Manganese Dioxide MnO_2	80	0.172	47.2	5
Mercuric Oxide HgO	90	0.214	47.0	2
Nickelic Hydroxide $NiOOH$	80	0.227	44.2	6
Palladium Oxide PdO	90	0.121	74.5	2
Platinum Dioxide PtO_2	90	0.249	40.1	2
Silver (II) Oxide AgO	90	0.136	73.5	2

Notes
(1) At STP Conditions.
(2) Reduction to metal.
(3) Reduction to ferrous oxide, FeO.
(4) Reduction to plumbous oxide, PbO.
(5) Reduction to manganic oxide, Mn_2O_3.
(6) Reduction to nickelous hydroxide $Ni(OH)_2$.

purchased for this program were about 1/2 inch thick; thinner electrodes used in some of the tests were readily prepared by machining the thick electrodes (copper oxide is brittle, relatively soft, and machines smoothly) to size; thicker electrodes were prepared by cementing the thinner electrodes with conductive epoxy cement. The copper coating can be placed on cut surfaces by flaming with a torch whose flame has been adjusted to be slightly reducing.

The same basic design was used in all cells and is shown schematically in Figure 1. The hydrogen electrode uses a platinum catalyst waterproofed with Teflon. The mixture of catalyst and Teflon is placed as a thin layer on a nickel collector screen that also serves to provide mechanical support. The same type of electrode has been used as the auxiliary electrode in sealed auxiliary-electrode, silver-cadmium and nickel-cadmium cells. The cell electrolyte is held in the Nylon separator placed between the hydrogen and copper oxide electrodes. A water reservoir is placed behind the copper oxide electrode; this is used to take up the water formed in the cell reaction.

The cell terminals are 8-32 stainless steel machine screws. These are cemented into the wall of the cell body, and secured mechanically with a hex nut. Internal connection to these terminals is by a nickel wire welded to the head of the screw; this wire is welded in one case to the nickel screen of the hydrogen electrode, and cemented with conductive epoxy to the copper oxide electrode copper collector. Stainless steel screws are used to provide resistance to the alkali electrolyte; pure nickel or nickel plated terminals could also be used. A shorting bar is provided with each cell to short the cell output during combination. This must be left in the open position after the cell is activated until the cell is placed in service, since otherwise the copper collector will oxidize from an air reaction.

The cell electrolyte is 45 percent potassium hydroxide initially. This will be diluted to about 17 percent at the end of the cell life by the water formed in the cell reaction. About 100 milliliters of the 45 percent electrolyte is needed for the two-inch thick 4.5 inch x 4.5 inch cell; a large amount of this is electrolyte absorbed by the porous copper oxide electrode. A minimum amount of initial electrolyte is desired to allow more volume for the water formed in the cell reaction; however, enough electrolyte must be added to give good cell performance initially. The electrolyte is added to the cell after completion of the assembly by boring a small hole in the back and adding the electrolyte by a hypodermic syringe and resealing the hole with flexible epoxy cement. The electrolyte is usually added as late as possible prior to installation or test. The polyethylene film placed in front of the hydrogen electrode is used to prevent water that seeps through the hydrogen electrode during operation from being lost to the interior of the satellite; this seepage water results from the electrode reaction and the water is adsorbed into the interior of the cell through the electrode after a time. Hydrogen readily diffuses through this polyethylene film to the electrode surface.

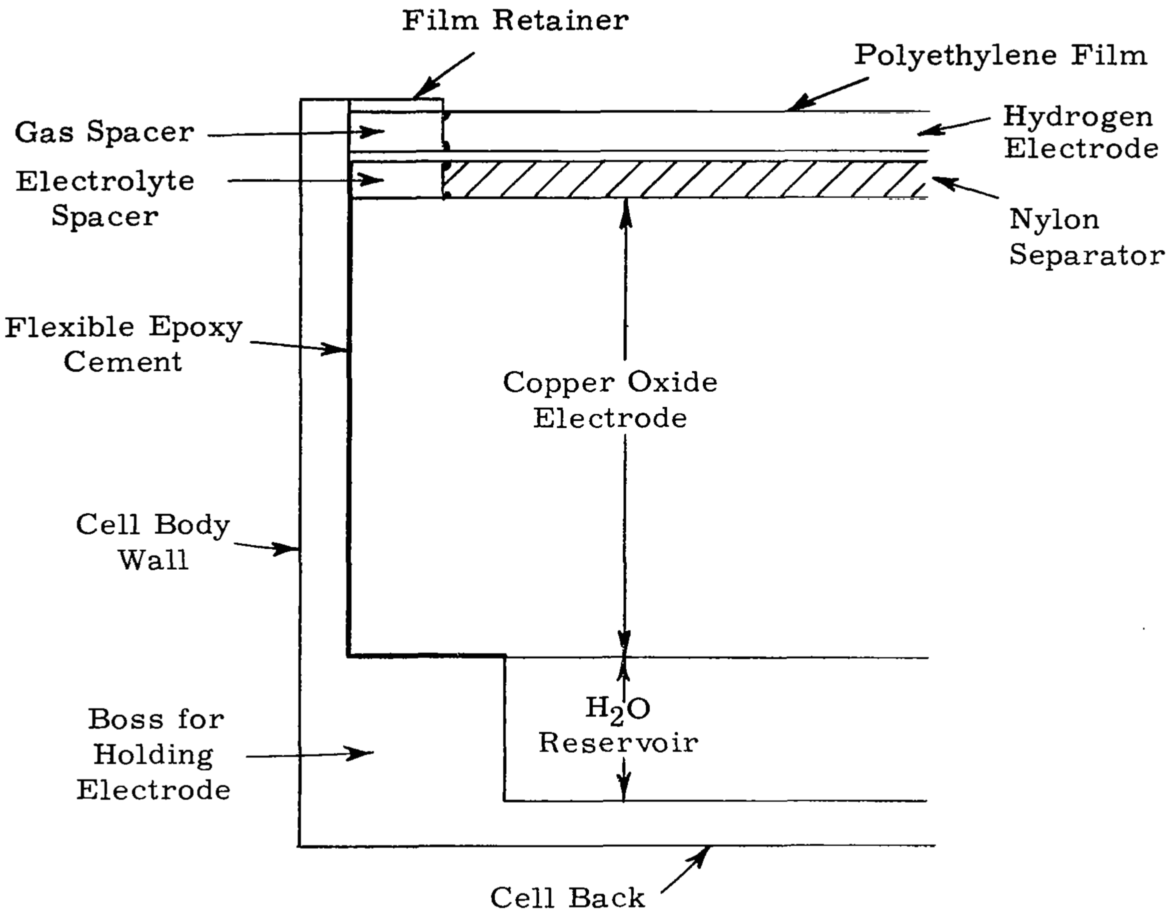


Figure 1. Hydrogen Combination Cell Schematic

Figure 2 shows a photograph of the completed unit ready for installation. The later versions have shorter terminals than shown in this photograph, and smaller mounting holes in the corners. Otherwise the appearance is the same. The surface of the hydrogen electrode can be seen through the polyethylene film cover.

The typical performance of the combination cell is shown in Figure 3, which is a polarization curve taken immediately after assembly of the complete unit and activating with electrolyte. The open circuit voltage of the cell in hydrogen is 0.55 to 0.60 volts. The cell internal impedance is high at the beginning of its service because of the limited amount of electrolyte present; as the cell is used, the water formed in the cell reaction dilutes the original electrolyte and the performance improves as better wetting of the electrodes is obtained. The copper oxide electrode impedance decreases with use of the cell because of the formation of free copper. The test conditions for the curve shown in Figure 3 were: the cell was placed in an enclosure of about 3 times the volume of the cell; this enclosure was filled with hydrogen at 18 psia during the test. After the initial burn-off of oxygen trapped in the cell gas space between the film and electrode, the data for the curve were taken and the gas flow into the enclosure shut off. The cell was placed on 50 ohm load (gives 9-11 ma. initially at 0.45 volt) and allowed to discharge overnight. At the end of 16 hours, the enclosure hydrogen pressure was below 5 psia, showing that the cell will operate with partial pressures of hydrogen below one atmosphere. This polarization test was run with all cells before shipping, and has been run on several test cells repeatedly over a period of several months. No cell has been run to exhaustion of the copper oxide electrode due to lack of time. Continuous operation for several weeks has been readily obtained with a very flat voltage curve.

The catalyst in the hydrogen electrode promotes the direct combination of hydrogen and oxygen to form water:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

The direct reaction occurs at rates much higher than the cell reaction rate; hence oxygen is always consumed if an excess of hydrogen is present as is the usual case. The converse is also true, in that hydrogen is always consumed if there is an excess of oxygen present. If the amount of oxygen present in the gas is below the explosive limit (95% hydrogen, 5% oxygen) the combination proceeds smoothly. The small amounts of oxygen given off during the stand and discharge of the silver oxide-zinc cells are thus readily removed from the satellite gas space. However, if the electrode is exposed to an explosive mixture of hydrogen and oxygen, there is a high probability that the direct combination at the surface will ignite the mixture. The formation of such explosive mixtures is unlikely if the oxygen and hydrogen from the primary cells are not allowed to accumulate in the satellite gas space.

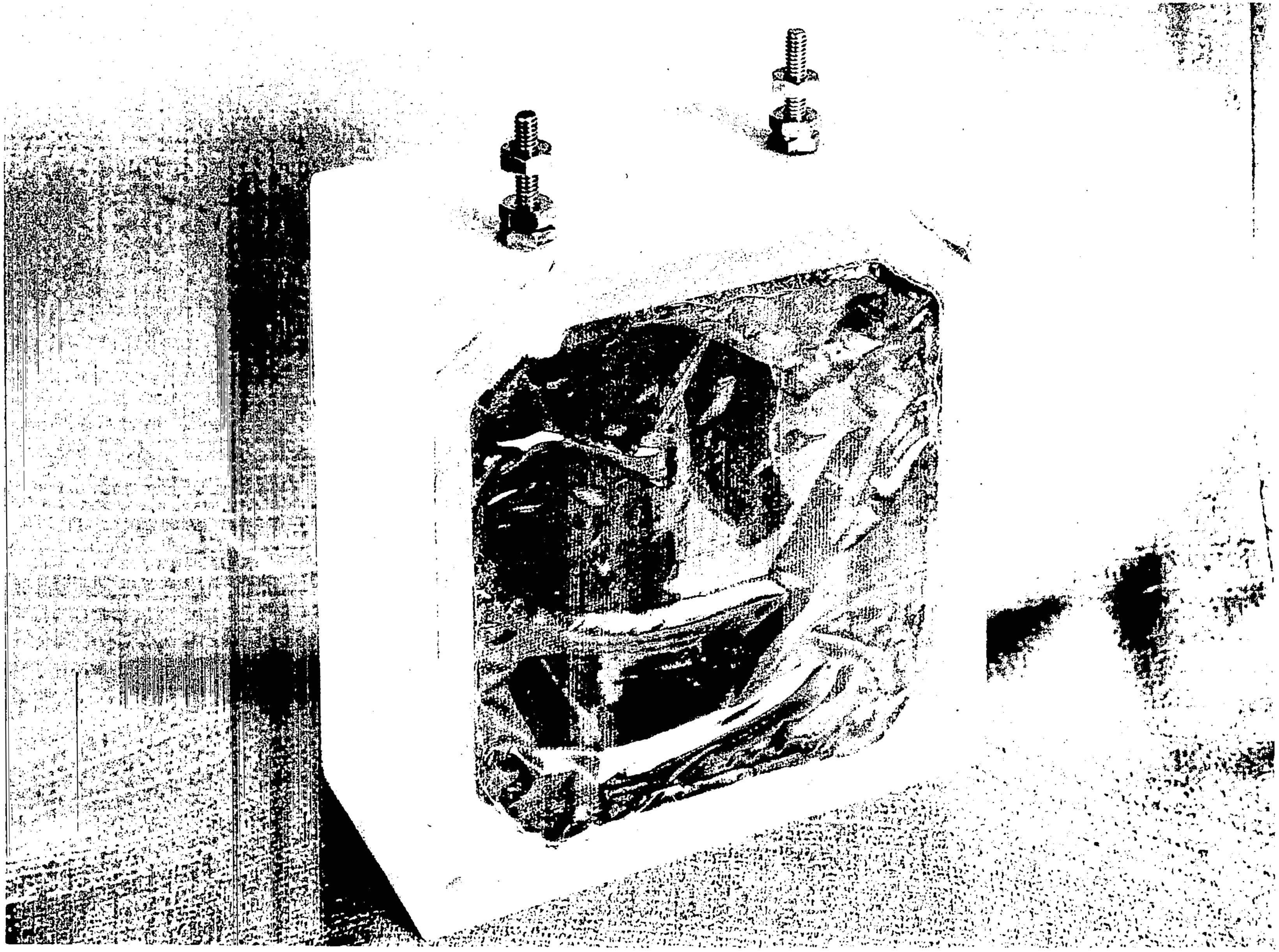


Figure 2. Satellite Combination Cell

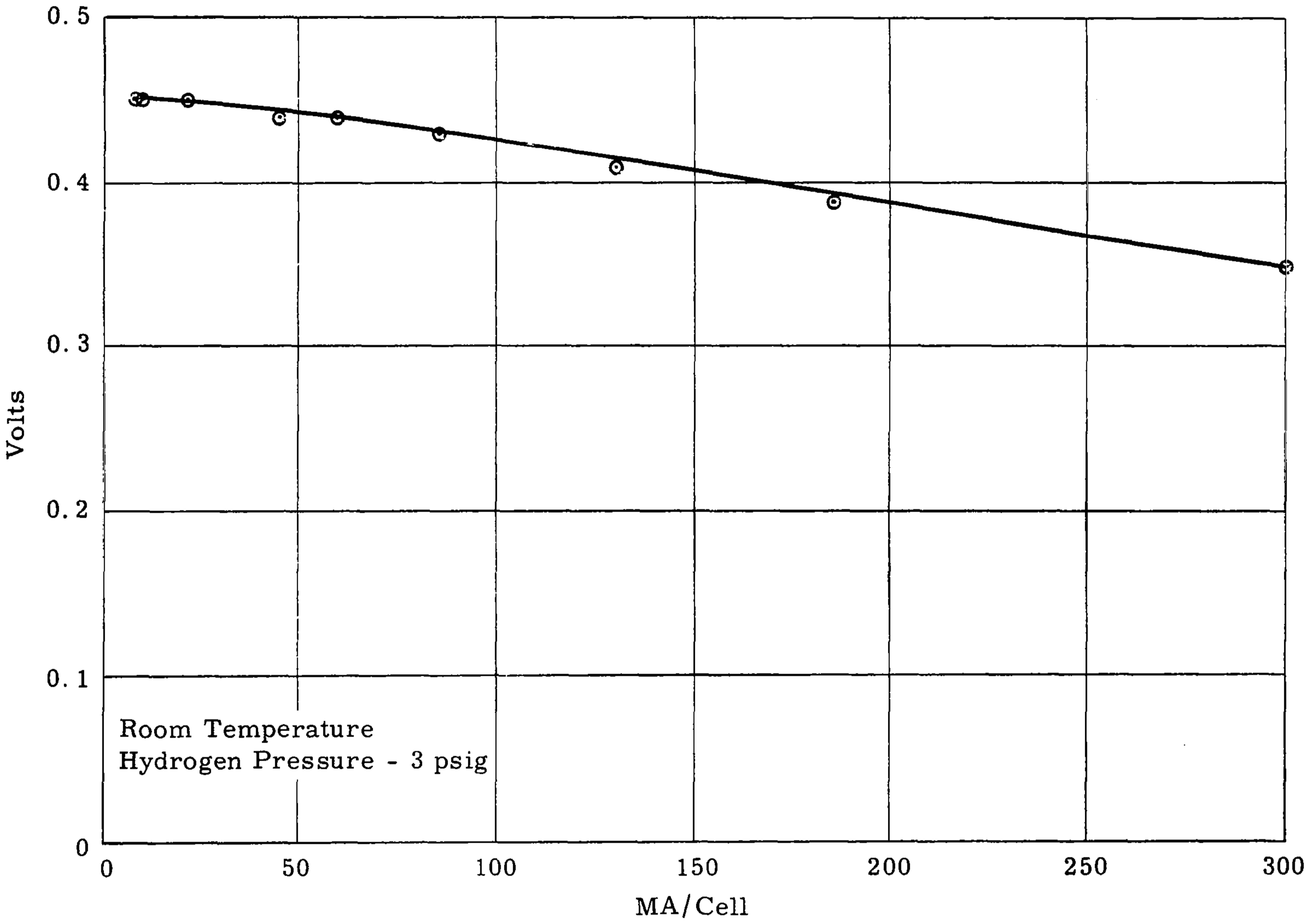


Figure 3. Polarization of Hydrogen Combination Cell

An unexpected bonus of the combination cell design comes from the ability of the hydrogen electrode to also act as an oxygen electrode, if no hydrogen is present. Operation with air or oxygen reverses the sign of the cell potential, and the cell reaction is the oxidation copper:

$$2\ Cu + O_2 \longrightarrow 2\ CuO$$

This reaction occurs at a potential about one-half that for operating on hydrogen. The existence of this reaction has helped in checking out the cell and associated circuits since these are readily done in air and there is no need to use hydrogen. The existence of this reaction means, however, that the user must not connect up the cell for long periods of time after it has been activated to a load in the presence of air in order to avoid loss of the copper current collector of the copper oxide electrode.

The specific design of the combination cell requires consideration of the size of the cells to be used, the combining rate needed, and the total amount of hydrogen to be combined over the lifetime of the satellite. Because of space limitations in the satellite designs, it was decided at a conference at NASA-Goddard with AE-B Satellite design engineers that the best approach would be to design the cell with a fixed cross-section of 4.5 inches by 4.5 inches and to vary the combining rate capability by varying the number of cells used, and to vary the total combining capacity by varying the individual cell capacity. The capacity of the cell is determined by the amount of copper oxide, which in fixed cross-section cells varies with the thickness of the electrode used. With the exception of the water reservoir, the remainder of the cell design parameters are fixed; these are given in Table 7. Most of these fixed parameters have been arbitrarily assigned, and can be varied as necessary in the design. The parameters shown are the ones used in the reported work.

The ratio of the total thickness of the water reservoir plus the thickness of the copper oxide electrode to the thickness of the copper oxide electrode alone is critical in the design, since this sets an upper limit on the amount of copper oxide that can be put into a cell with a fixed thickness. This ratio was calculated as follows: Assuming a 1 cm^2 area electrode of 1 cm thickness, the total volume of copper oxide in this volume of electrode is 0.5 cc since the density of the electrode is only 50% of the theoretical. This volume of copper oxide has a weight of 3.2 grams; thus, assuming that 90% utilization is obtained, this weight of copper oxide will give 0.65 cc of water. The initial volume of electrolyte per cubic centimeter of electrode is 0.25 cc. The total occupied volume is thus 0.5 + 0.65 + 0.25 or 1.40 cc. This gives the ratio of total volume to volume of electrode as 1.4.

The total weight, combining capacity, and other data on combination cells of 4.5 by 4.5 inch cross-section have been calculated and are shown in Table 8.

TABLE 7

Combination Cell Design Parameters

PARAMETER	DIMENSION
Cell Cross Section:	4.5" x 4.5" (130 cm^2)
Effective Electrode:	3.75" x 3.75" (90 cm^2)
Fixed Spacings:	
Film Retainer	0.020 inches
Film	0.001 inches
Gas Spacer	0.130 inches
Hydrogen Electrode	0.015 inches
Electrolyte Spacer	0.050 inches
Cell Back	0.110 inches
TOTAL	0.326 inches
Ratio: Copper oxide electrode plus water reservoir thickness to electrode thickness	1.4

TABLE 8

Combination Cell Calculations

Total Cell Thickness Inches	1		1.5		2.0		Units	Notes
Net Thickness	0.675		1.125		1.675		inches	1
Copper Oxide Electrode Thickness	1.36		2.22		3.18		cm	2
Copper Oxide Electrode Weight	475		290		1,100		g	2
Combination Capacity Weight Hydrogen	10.7		17.8		25.0		g	
Combination Capacity Volume Hydrogen	120,000		198,000		280,000		cc	3
Capacity Ratio 1" Cell = 100	100		166		234			4
Cell Weight (Approximate)	1.6-1.7		2.2-2.3		3.3-3.4		lbs.	
Operation Data Lifetime	$\frac{\text{cc}}{\text{hr.}}$	ma	$\frac{\text{cc}}{\text{hr.}}$	ma	$\frac{\text{cc}}{\text{hr.}}$	ma		5
6 months	28	67	46	110	64	153		
4 months	41	98	68	163	96	230		
3 months	55	132	91	220	128	306		
2 months	82	198	136	325	192	460		
1 month	165	396	272	650	384	920		

Notes:

(1) After making allowance for hydrogen electrode, etc.

(2) Maximum allowed, using 40% allowance for water reservoir.

(3) Gas at STP conditions.

(4) Shows effect of increasing cell thickness.

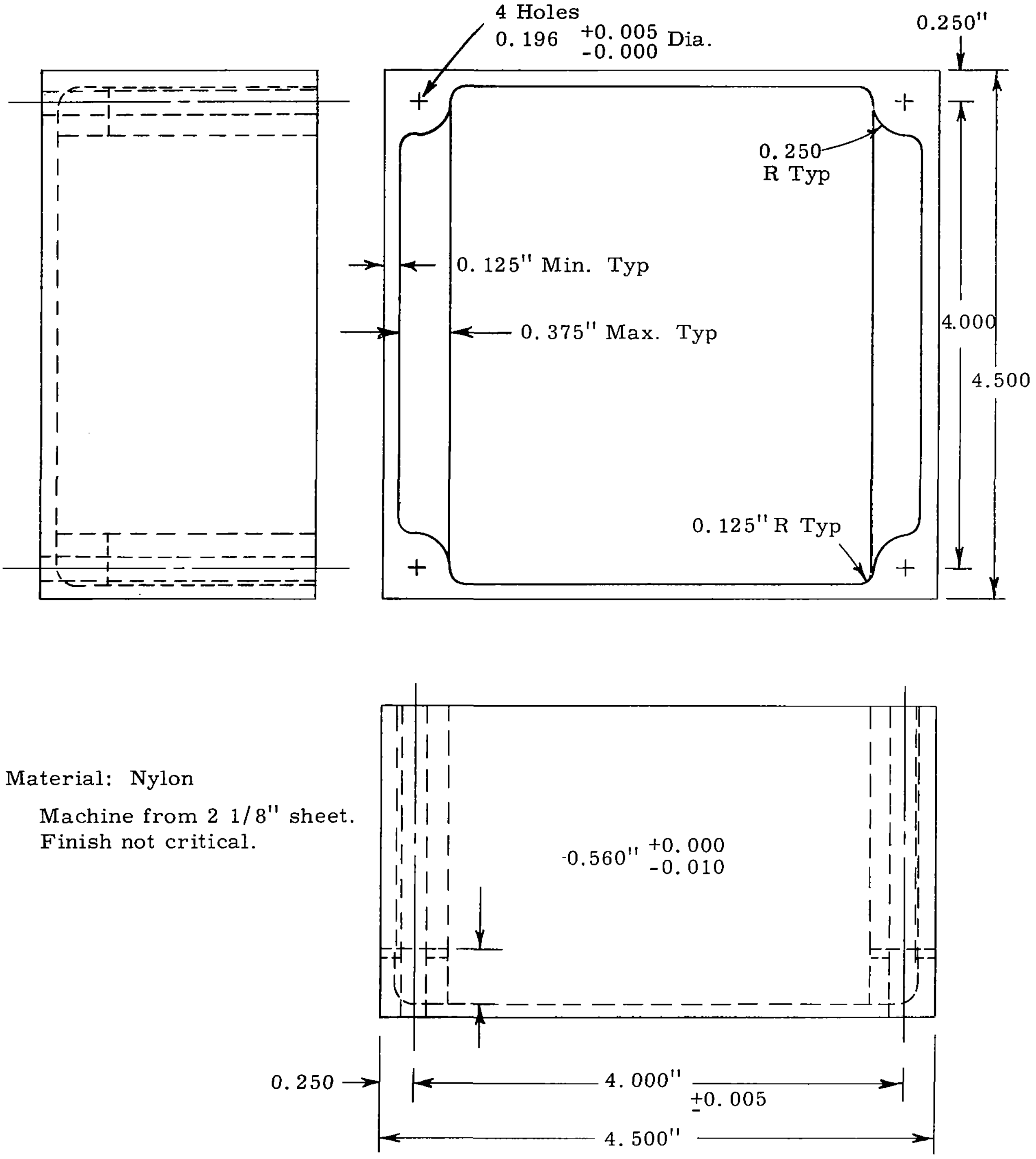
(5) For single cell. cc/hr. gives amount of hydrogen at STP combined at steady-state; ma gives current for the combination of hydrogen at steady-state. Lifetime is operating life of cell.

In the Table, the operation data have been calculated as a function of the lifetime of operation up to six months. Thus, if a cell of 1 inch thickness is to be used for a period of one month, the rate of hydrogen that should be combined is 165 cm^3 per hour, corresponding to a cell current of 396 ma. The highest rate shown in Table 8 (384 cm^3/hr or 920 ma) is well within the electrical capacity of the hydrogen electrode, which is 4.5 amperes (20,000 cm^3/hr of hydrogen) for maximum continuous operation (50 ma/cm^2). The use of the polyethylene film covering limits the maximum combining rate possible to about 2,000 cm^3 of hydrogen per hour, since the governing factor is the diffusion rate of hydrogen through the film which is comparatively slow. If higher rates must be obtained, the use of this film must be abandoned in the design, and other means for retaining the weepage of the electrolyte employed.

The exact total weight of the cell is not calculable in advance with high accuracy due to the variation in the weight of the copper oxide electrode and cementing materials used. The copper oxide electrode is made up of sheets of copper oxide obtained from Thomas A. Edison Industries, Inc.; the ones used for the most part in the work reported here were the replacement electrodes for 500 ampere-hour cells. As would be expected for materials not made to tight specifications, the weight of the electrodes varies about 7 - 8% for the same volume. The variation in the cementing is somewhat under better control, but the overall variation in weight can be as much as 10% as shown in the Table.

The detailed design of the two-inch thick cell is given in the Figures 4, 5, and 6. The body is machined out of a block of Nylon: this is satisfactory for a few units, but a molded body should be considered in larger scale production. The earlier models had separate supports for the copper oxide electrode; these were machined in the body in the later units fabricated.

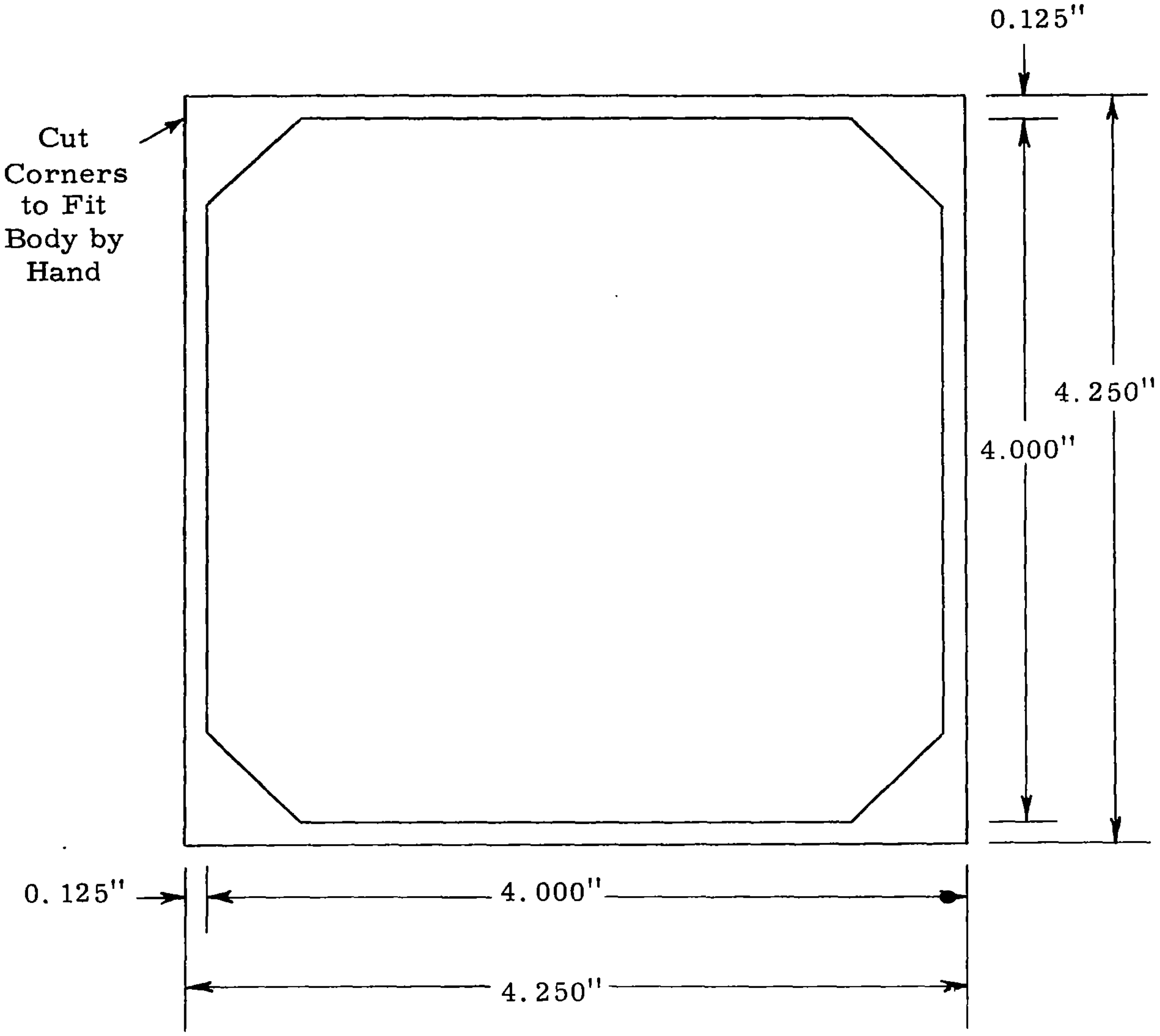
The hydrogen combination cells described in this report were developed specifically for use in the AE-B (Atmospheric Exploratory-II) satellite which will be launched in summer, 1965. The general usefulness of the combination cell concept extends beyond this application however. Thus, the satellite design, with minor modifications such as size and case construction, could be useful for removing hydrogen from other sealed spaces on a one-shot or short term basis. A modified design in which oxygen was used in place of the metal oxide used in the satellite design would be useful for longer term applications and for applications in which large amounts of hydrogen would have to be combined. Some of the applications would be: emergency battery power supply enclosures, enclosures for process equipment using hydrogen as part of the process, enclosures in which hydrogen tanks are stored, and enclosures with equipment in which hydrogen is generated, such as electrolysis cells giving off by-product hydrogen. The use of combination cells in these applications might make possible a drastic reduction in ventilation air requirements, and might allow tight enclosure of the space to aid in controlling or protecting the process being carried out.



Material: Nylon

Machine from 2 1/8" sheet.
Finish not critical.

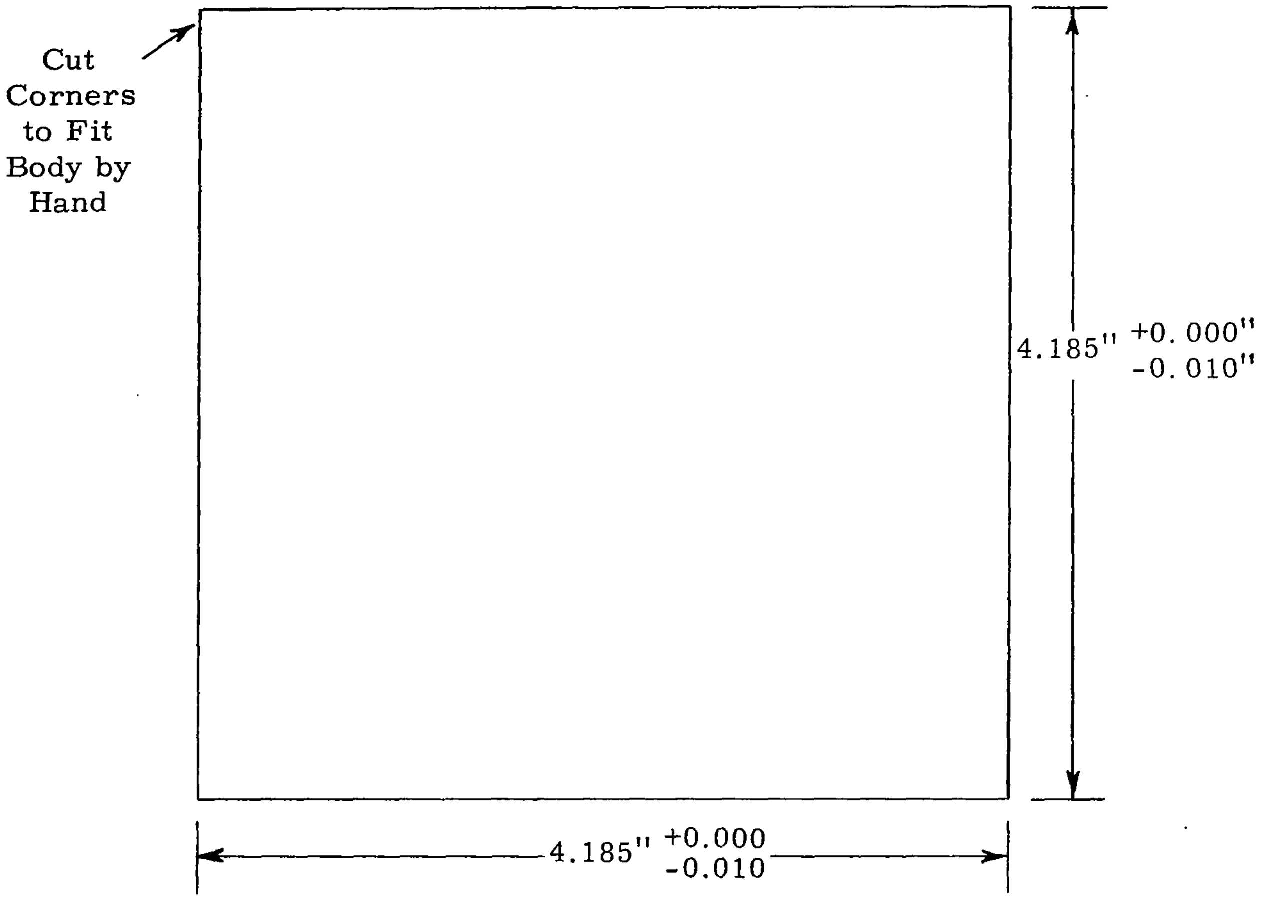
Figure 4. Cell Body



Material: Nylon

1 Piece - 0. 020" thick (Film retainer)
1 Piece - 0. 130" thick (Gas spacer)
1 Piece - 0. 050" thick (Electrolyte spacer)

Figure 5. Spacers



Material:

1. Hydrogen - 0.015" thick - special
2. Copper Oxide - 1.25" thick
   (Assemble from copper oxide sheet)

Figure 6. Electrodes

The use of combination cells or auxiliary electrodes permits the construction of sealed silver-zinc battery systems without the danger of excessive build-up of gas pressure. The choice of which approach to use depends upon the type of silver-zinc battery and the total amount of hydrogen to be combined. For secondary cells, the best approach is to use auxiliary electrodes, since no net consumption of materials is required, and the cell material balance is maintained. For primary cells, the use of auxiliary electrodes is limited to the cases where only a small amount of hydrogen is to be combined. Combination cells are more economical in weight for larger amounts of hydrogen.

The critical value for the amount of hydrogen is the value for which the weight of silver oxide consumed using the auxiliary electrode approach is equal to the weight of the combination cell. In effect, although cupric oxide or oxygen is lighter than the equivalent amount of silver oxide, the use of cupric oxide or oxygen requires additional weight in the form of cell structure, piping, etc. Only when this weight is amortized by consumption of the critical amount of hydrogen can the combination cell weight be less than silver oxide weight. In making the calculations for the critical amount of hydrogen, the costs rather than weights can be used if desired.

The equation for the critical value of hydrogen can be derived as follows:

Let X = critical weight of hydrogen in grams

Then, weight of silver oxide = $AgO/_2 \cdot X$ grams

$$\text{weight of cupric oxide combination cell} = CuO/_2 \cdot X + Q_1 + Z_1 \cdot \frac{CuO}{2} \cdot X \text{ grams}$$

$$\text{weight of oxygen combination cell} = O_2/4X + Q_2 + Z_2 \cdot \frac{O_2}{4} \cdot X \text{ grams}$$

where: AgO, CuO, O_2 represent the molecular weight of silver oxide, copper oxide, or oxygen respectively; and

Q_1 and Q_2 are the minimum cell weights for the respective combination cells, i. e. no depolarizer present; and

Z_1 and Z_2 are the proportional cell and container weights for cupric oxide and oxygen respectively, i. e. the fraction of depolarizer weight that must be added to make up the final cell system.

For the critical amount of hydrogen, the weight of silver oxide and the combination cell are equal by definition. Therefore, for the cupric oxide depolarized combination cell:

$$\frac{AgO}{2}\,X = \frac{CuO}{2} \cdot X + Q_1 + Z_1 \frac{CuO}{2}\,X$$

$$X = \frac{Q_1}{\frac{AgO}{2} - \frac{CuO}{2} - Z_1 \cdot \frac{CuO}{2}}$$

Similarly, for the oxygen depolarized combination cell.

$$X = \frac{Q_2}{\frac{AgO}{2} - \frac{O_2}{4} - Z_2 \frac{O_2}{4}}$$

The value of X using the present cupric oxide depolarized cell design can be calculated as follows:

$AgO/2$ = 61.94 grams

$CuO/2$ = 39.77 grams

Z_1 = 0.25 grams/equivalent

$\frac{CuO}{2} Z_1$ = 9.94 grams (weight of electrolyte, and case material per gram of hydrogen)

Q_1 = 120 grams (weight of hydrogen electrode, spaces, back of cell, terminals, etc.)

$X = \frac{120}{61.94 - 39.77 - 9.94} = 9.8$ grams

The 1" cell design(Table 8) is thus close to the critical value for the cupric oxide depolarized cell.

Since the constants for the oxygen cell are not known from actual cell data, only an estimate can be given. This is as follows:

Q_2 = 150 grams (oxygen-hydrogen cell plus piping)

$O_2/4$ = 8 grams

Z_2 = 6 for bottled oxygen supplied solely for combination cell use. This value is not constant over a wide range of X.

Z_2' = 4 for bottled oxygen supplied by "piggy-back" from another source.

Cryogenic oxygen would have a Z_2 value much lower than these figures.

$$X = \frac{150}{62 - 8 - 48} = 25 \text{ grams}$$

$$X' = \frac{150}{62 - 8 - 32} = 6.8 \text{ grams}$$

CONCLUSIONS

Silver-Cadmium Cell Studies

Auxiliary electrodes with platinum catalysts can be used in silver-cadmium cells to recombine gases evolved during continuous overcharge at constant potential without being connected to either cell electrode. Cell voltage balance is improved. Limited cyclic tests with silver-cadmium cells constructed with auxiliary electrodes show that low pressure operation is obtained. These tests confirm the early work done on these cells under contract NAS 5-2817.

The auxiliary electrodes used can recombine oxygen when connected to the cadmium electrode at rates up to 50 ma/cm^2 of surface area. The auxiliary electrodes also catalyze the combination of oxygen and hydrogen.

Silver-Zinc Cell Studies

Auxiliary electrodes using a cobalt-aluminate-spinel catalyst and silver substrate can be used in silver-zinc cells to recombine oxygen if they are attached through diodes to the zinc electrode. These electrodes will recombine only oxygen even if hydrogen is present. Direct connection causes evolution of hydrogen from the zinc electrode. The recombination rate is partially dependent upon oxygen pressure, and rates up to 3 ma/cm^2 can be handled at atmospheric pressure.

Conventional platinum catalyzed auxiliary electrodes can be used to recombine hydrogen when attached directly to the silver electrode. No enhancement of oxygen evolution from the silver electrode or hydrogen from the zinc electrode is observed with this mode of operation. Recombination of oxygen with the hydrogen occurs preferentially at the electrode surface. The use of a platinum catalyzed auxiliary electrode in the cell attached to the silver electrode is adequate for pressure control if the cell is negative-electrode limited so that an excess of hydrogen over oxygen is generated upon overcharging the cell. The addition of oxygen recombination auxiliary electrodes attached to the zinc electrode is not necessary under these conditions.

The auxiliary electrode may be constructed of magnetic or non-magnetic materials, and will recombine hydrogen at rates up to 35 ma/cm^2 for hydrogen pressures of 200 mm. Recombination at lower pressures is also feasible with some loss in performance.

The use of auxiliary electrodes in silver-zinc cells permits the sealing of the cell without danger of marked pressure rise on charging or stand. Recombination of hydrogen on stand consumes silver oxide.

Hydrogen Combination Cell Studies

A practical electrochemical method has been developed using a galvanic cell made with a platinum catalyzed hydrogen electrode, a cupric oxide cathode, and an alkaline electrolyte. This cell will remove hydrogen from a surrounding atmosphere and will also remove oxygen either by promoting the reaction of hydrogen with oxygen, or by a cell reaction in the absence of hydrogen. It should be a useful device for use with primary silver-zinc cells where these cells must be vented to an enclosed space during stand and use. The combination cell can remove hydrogen at rates up to 21 $cc/hr/cm^2$ of hydrogen electrode surface. This corresponds to a current of 50 ma/cm^2. The rate is decreased if a cover is placed over the electrode through which hydrogen must diffuse. This rate is 2 $cc/hr/cm^2$ (5 ma/cm^2) for a polyethylene sheet 0.001 inch thick.

APPENDIX

FORMULATIONS OF EPOXY CEMENTS USED IN PROGRAM

Flexible Epoxy Cement. - This cement is adherent to treated Nylon surfaces and is used to cement Nylon parts to each other or to other materials. The formulation is:

50 parts by weight	EPON 820	(1)
50 parts by weight	VERSAMID 125	(2)

Heat to 80°C to reduce viscosity and mix thoroughly. Deaerate under vacuum to remove gases and apply hot.

Nylon parts should be cleaned to remove traces of molding agents or grease, sanded to remove glossy surfaces, and wetted thoroughly with molten phenol before cementing.

This cement will cure, after heating, at room temperature in 6-12 hours, and at 80°C in about 1 hour.

Clay-Filled Epoxy. - This material is used to seal around leads, tubing, and to fill wide cracks in experimental cells. It is not suitable for use with Nylon, but can be used with Lucite or other acrylic resin. The formulation is in two parts:

Part A

100 parts by weight	EPON 820	(1)
100 parts by weight	CLAY #33	(3)
15 parts by weight	BENTONE 34	(4)

This mixture can be mixed and stored for long periods in closed containers. The final mixture is made by adding 4-8 parts of DETA (5) to 100 parts of A. Cure at room temperature overnight or at 60°C for 1-2 hours.

Silver Conductive Epoxy Cement. - This cement is used to attach parts together electrically when hot solder or other means are unusable. The conductivity of the cured resin is high, about 80% that of silver. However, the adherence is poor and the cement should not be used as the sole or principal bonding element. The formulation is in two parts:

Part A

20 parts by weight	EPON 815	(1)
80 parts by weight	SILFLAKE 131	(6)

Mix thoroughly and store in air-tight containers. Refrigerate if stored more than 1-2 days to avoid air-catalyzed cure.

Final mixture is made by adding 2-3 parts by weight of DETA to 100 parts of Part A. Cure at room temperature overnight or at 60°C for 1-2 hours. Use only thin layers on roughened surfaces for best adherence.

Transparent Potting Epoxy. - This material is used in the laboratory for potting experimental cells made with Lucite cases to provide pressure containment. The transparent epoxy permits observation of the interior of the cell. The formulation is:

100 parts by volume	Resin 332	(7)
8 parts by volume	DETA	(5)

Evacuate to remove gas after mixing, and cure 18 hours in refrigerator at 40°F, followed by post cure of 6 hours at room temperature. This procedure prevents damage to test cell contents from overheating during the curing exotherm.

Sources of Materials. -

(1)	Shell Chemical Company	(EPONS)
(2)	General Mills	(VERSAMIDS)
(3)	Whitacre, Clark & Daniels	(CLAYS)
(4)	National Lead Company	(BENTONE)
(5)	DETA is diethylenetriamine and is manufactured by several companies. This material must be handled with care as it is highly irritating.	
(6)	Handy and Harmon	(SILFLAKE)
(7)	Dow Chemical Company	(EPOXY RESINS)

NASA-Langley, 1966 CR-405