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RADIATION EFFECTS ON SILVER AND ZINC BATTERY ELECTRODES. V

Interim Report

April 1966 to July 1966

Prepared for

Jet Propulsion Laboratory

Under Contract No. 951109

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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By

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CONTENTS

FIGURES

TABLES

I. SUMMARY

The investigation of gamma radiation effects on silver electrodes at 60% and 30% states of charge was continued during this report period. Net capacity increases averaging 5% have been observed during recent irradiations at the 60% level with a total dose of 7×10^7 rads (H_2O). At 30%, net losses of 4% and 15% were found in the two runs, respectively. When these results are considered with those of earlier runs,[2] it appears that the losses at 30% may be significant, while the changes at 60% are essentially within the uncertainty of the measurements.

Hydrogen was again evolved during the irradiation of silver-cadmium cells. In one run two silver electrodes were cycled one against the other in the absence of cadmium. Hydrogen and oxygen were then produced in a mole ratio of 1.7:1.

Work with zinc electrodes was concentrated on the development of a reproducible procedure for determination of discharge capacity. This was partially accomplished by the use of cellophane-wrapped zinc electrodes in starved-electrolyte cells. With that construction, the capacity will offer at least a semiquantitative criterion for the evaluation of radiation effects.

II. INTRODUCTION

Batteries in space vehicles must be able to withstand exposure to cosmic rays and the more intense Van Allen radiation field. This work was undertaken to establish the nature and magnitude of comparable effects induced in battery electrode systems by Co^{60} gamma radiation. Earlier phases of the program have emphasized the study of commercial silver electrodes in experimental cells containing cadmium counter electrodes and 40% potassium hydroxide electrolyte.[1-4] During this report period, the investigation of silver electrodes was continued at lower states of charge, and procedures were developed for the electrochemical testing of zinc electrodes in a modified regime.

III. EXPERIMENTAL

A. CELLS AND ELECTRODES

The silver-cadmium cells containing 40% potassium hydroxide were constructed with three-compartment polystyrene liners and stainless steel outer cases, as described in the preceding report on this program.[4] The cadmium counter electrodes were the Eveready R-2 type.

Experimental silver-zinc cells were investigated in both flooded and starved-electrolyte conditions. The flooded cells were prepared in polystyrene containers similar to those used for the silver-cadmium runs, except that the quartz frits were attached directly to the zinc electrode assembly, rather than to the polystyrene partitions. This construction gave rigidity to the zinc plate, which had been found in earlier work to disintegrate after several charge-discharge cycles.[2] In the starved-electrolyte cells, the inner container was a polystyrene or polystyrene-lined rectangular box. A sketch of such a cell, showing details of the zinc electrode assembly, is given in Figure 1.

The zinc electrodes were from Yardney Electric Corporation, with the exception of that in Cell A of Run ZG-7, which was from the Electric Storage Battery Company. The Yardney zinc electrodes had a relatively heavy layer of porous zinc mounted on each side of a copper foil backing. The Electric Storage Battery type had a smaller amount of zinc powder per unit area pressed onto an exposed double grid consisting of zinc and silver screens. The Yardney type was preferred for its mechanical

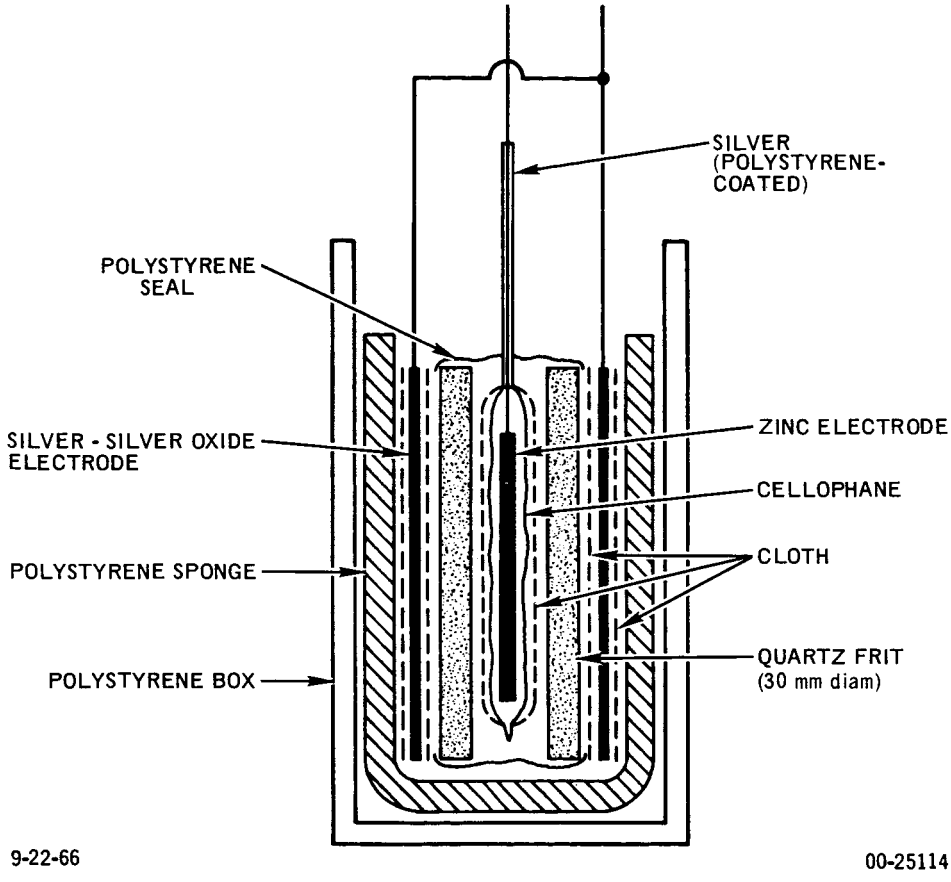


FIGURE 1. STARVED-ELECTROLYTE SILVER-ZINC CELL

stability when handled in the small sections that were needed for the experimental cells.

To retard the growth of zinc dendrites, the zinc electrode was sealed into an envelope of Pudo 193 battery grade glycerine-free cellophane. Then, as shown in Figure 1, the cellophane-sealed plate was cemented into position between cloth-lined quartz frits by the application of a polystyrene-carbon tetrachloride solution around the perimeter of the frits. The cloth padding was that removed from the R-2 cells. In the starved cells, similar cloth layers were placed against the silver electrodes, and additional electrolyte was contained in the polystyrene sponge that lined the cell container. In the flooded cells, the silver electrodes were placed, without wrapping, in the outer cell compartments, and the entire cell liner was filled with electrolyte. In all of the zinc cells, the electrolyte was 40% potassium hydroxide that had been previously saturated with zinc oxide.

Mercury-mercuric oxide reference electrodes were used in some of the zinc cells. With the starved-electrolyte design, the reference half-cell was placed in a corner of the rectangular container. Adequate electrical contact occurred through the wet padding material.

B. ELECTRICAL CIRCUITS

The equipment for automatic cycling and measurement of discharge capacity was described, with modifications, in the preceding report.[4] No changes were made in the instrumentation during this report period.

C. GAMMA RADIATION SOURCES

Irradiations were performed in the 10^6 rad (H_2O)/hr Co^{60} source at the North American Aviation Science Center. Subsequent work in the larger gamma source located at Atomics International will be described in the final report.

D. PROCEDURES

Procedures for the preconditioning and testing of silver-cadmium cells with discharge capacity limited by the silver electrode have been described in detail previously.[4] Conditions employed in this report period are summarized in Table I. Runs CG-31, CG-32, and CG-34 were made in the same way, with cycling at 90 $\rightleftharpoons$ 95% in the preconditioning stage.

Run CG-33 involved two silver electrodes which were prepared and characterized with respect to discharge capacity by measurement in separate cells, following the usual sequence. The two silver electrodes were then removed and placed in a single cell for cycling one against the other during the irradiation stage. Following irradiation, they were returned to the separate cells containing cadmium counter electrodes for the measurement of post-irradiation capacity. This experiment was performed primarily to determine which gases were evolved in the absence of an active metal anode such as cadmium.

The silver-zinc cells were examined in most instances by application of a constant current density of approximately 7.2 ma/cm^2 on the zinc electrode. This is the value that has been used in recent silver electrode studies in this program.[3,4] Cycling times up to 24 hours were employed

in efforts to establish a reproducible procedure for testing purposes. It was found that automatic capacity measurement with extended overcharge was not applicable to zinc electrodes because of damage to the cellophane envelopes that occurred on hydrogen evolution. The charge and discharge currents were therefore applied by manual switching immediately after the corresponding transitions were observed. With the sealed construction, it would not be feasible to determine material losses for the zinc electrodes. Experimental conditions for the zinc runs are indicated in Table VII.

IV. RESULTS AND DISCUSSION

A. SILVER ELECTRODES

Capacity data for silver electrodes in irradiated and control cells at 30% and 60% states of charge are given in Table II. Table III summarizes these and other recent runs on silver electrodes. The cells irradiated at 60% showed an average net capacity gain of 5%, while the two cells at 30% lost 4% and 15%, respectively. Cells irradiated at 30% in earlier work on this program lost an average of 17% in capacity, while those irradiated at 60% showed a loss of 5%. Most of the losses at 30% are great enough to be outside the uncertainty of measurement and may indicate a significant radiation effect associated with the lower oxide. Since Run CG-33 involved the transfer of silver electrodes to a new cell for the irradiation step, the capacity changes are not directly comparable to those of other 60% runs.

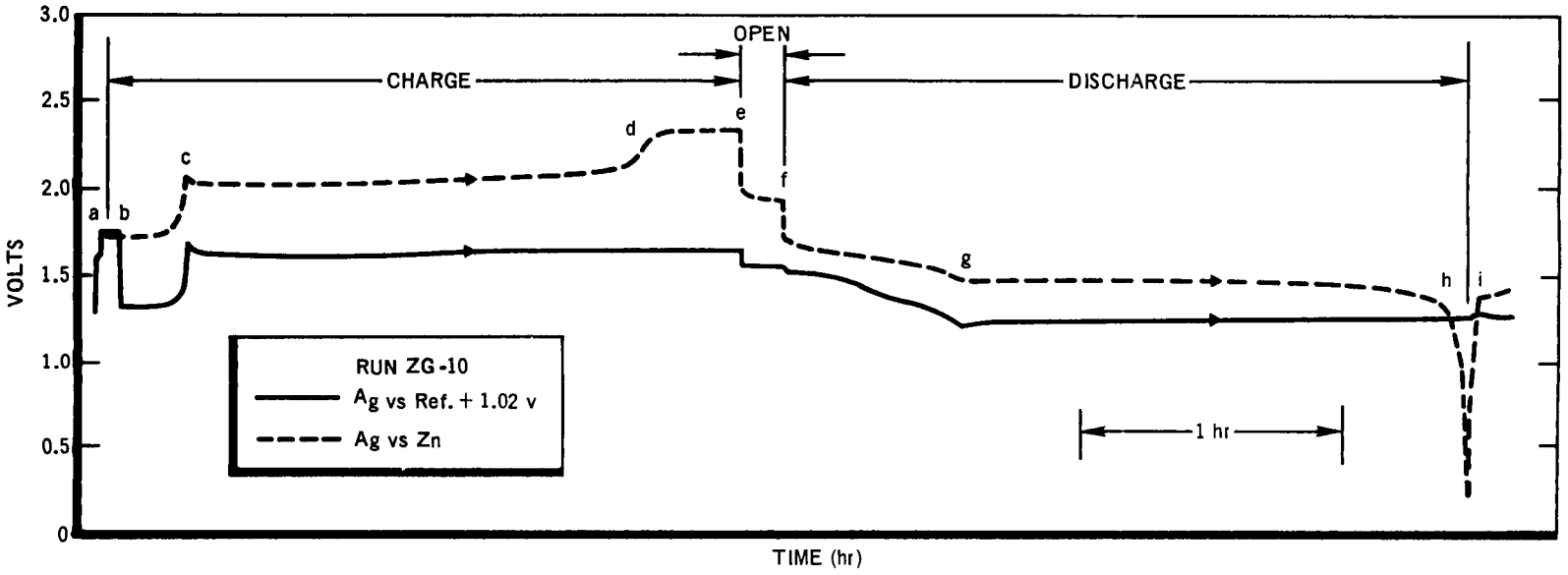
Gas analyses, reported in Table IV, again showed substantial amounts of hydrogen in the irradiated cells, with the exception of that in Run CG-31. The reason for inversion of hydrogen and oxygen percentages in this run is not obvious. The irradiated cell in Run CG-33, which had two silver electrodes but no cadmium, contained hydrogen and oxygen in a mole ratio of 1.7:1. This is a higher proportion of oxygen than has usually been found in silver-cadmium cells. Such a result might be expected when no active metal such as cadmium is present to reduce the hydroxyl radicals formed by radiolysis of water.[2]

Solids losses for the silver and cadmium electrode compartments are reported in Tables V and VI, respectively. The silver compartment losses at 30% and 60% were much smaller than those observed in earlier irradiations at 90%[4] (disregarding accidental mechanical losses in Run CG-33). Earlier silver losses at 60% were slightly higher than those found here. The present cadmium electrode losses of 6 to 8 mg are within the range previously observed for R-2 electrodes. Material loss data will be treated more fully in the final report.

B. ZINC ELECTRODES

The work with zinc electrodes was done to establish a reproducible electrochemical criterion as a preliminary to the investigation of radiation effects. Earlier experiments had shown the instability of unwrapped zinc electrodes in flooded cells on repeated cycling.[1] The present series of runs was therefore made with wrapped electrodes of the constructions described in the Experimental section.

Some qualitative observations are noted in Table VII. No overcharge transition was observed in the flooded condition, despite the cellophane wrapping. On prolonged charging, the deposition of zinc from excess zincate ion in the electrolyte continued until the seal between the frits was broken. More satisfactory results were obtained in the starved cells of Runs ZG-8 to ZG-10. A representative pair of charging curves is shown in Figure 2, where it is clearly demonstrated that the transition at position (d) is a characteristic of the zinc electrode system and not the silver. This rise in potential signals the onset of hydrogen evolution that occurs upon depletion of the zincate ion in the vicinity of the electrode. At position



(a) BEGINNING OF CHARGE AT 36 ma
(b) REFERENCE SYSTEM SWITCHED IN
(c) Ag_2O/AgO TRANSITION
(d) Zn OVERCHARGE; EVOLUTION OF H_2
(e) OPEN CIRCUIT
(f) BEGINNING OF DISCHARE AT 36 ma
(g) AgO/Ag_2O TRANSITION
(h) END OF Zn DISCHARGE
(i) OPEN CIRCUIT

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FIGURE 2. POTENTIAL-TIME CURVES FOR SILVER-ZINC CELL

(h), a well-defined discharge transition for the depletion of usable zinc metal is seen. With this behavior, it was feasible to apply a series of complete charge-discharge cycles for the purpose of capacity measurements.

Discharge capacity data for three zinc electrodes are given in Table VIII. Within the sets of consecutive cycles, the reproducibility is ± 2 to $\pm 6\%$. Preliminary cycles yielding very low capacities, such as Cycle 1 in Run ZG-10, were disregarded in evaluating the averages. This initial low capacity, which disappeared after several hours, apparently was caused by slow passage of the electrolyte through the cellophane envelope. Changes of the order of 10 to 20% occurred while the cells stood on open circuit, as between Cycles 2 and 3 of Run ZG-10. A more pronounced capacity change was observed after 24-hour cycling at $90 \rightleftharpoons 95\%$ in Run ZG-8. The zinc electrode capacity decreased 28% in this instance. On the basis of these results, the zinc discharge capacity is expected to yield information on radiation effects which will be of somewhat lower precision than that in recent work on silver electrodes.

V. PLANS FOR FUTURE WORK

Future work will be concentrated on the irradiation of zinc electrode systems and on the study of silver electrode behavior at higher radiation doses and dose rates.

REFERENCES

1. Atomics International, "Radiation Effects on Silver and Zinc Battery Electrodes," AI-65-158, Interim Report I, Jet Propulsion Laboratory Contract 951109, April 1965 to July 1965

2. Atomics International, "Radiation Effects on Silver and Zinc Battery Electrodes," AI-65-264, Interim Report II, Jet Propulsion Laboratory Contract 951109, July 1965 to October 1965

3. Atomics International, "Radiation Effects on Silver and Zinc Battery Electrodes," AI-66-33, Interim Report III, Jet Propulsion Laboratory Contract 951109, October 1965 to January 1966

4. Atomics International, "Radiation Effects on Silver and Zinc Battery Electrodes," AI-66-83, Interim Report IV, Jet Propulsion Laboratory Contract 951109, January 1966 to April 1966.

TABLE I. CONDITIONS FOR SILVER ELECTRODE RUNS[a,b]

Run	Initial State of Charge %	Silver Electrode Weight[c] g	Silver Electrode Area[d] cm^2	Capacity Measurements Total Current ma	Capacity Measurements Current Density ma/cm^2	Irradiation Cycling Current[e] ma
CG-31	60					
Irradiated Cell		1.43	14.8	107	7.2	90
Control Cell		1.44	14.6	107	7.3	93
CG-32	30					
Irradiated Cell		1.46	14.2	103	7.2	92
Control Cell		1.43	14.2	103	7.2	91
CG-33[f]	60					
Electrode A (60⇌65%)		1.5	12.8	91	7.1	95
Electrode B (60⇌55%)		1.6	12.6	91	7.2	95
CG-34	30					
Irradiated Cell		1.44	14.2	103	7.3	95
Control Cell		1.43	14.2	103	7.3	93

[a] All irradiations were at 0.98×10^6 rads (H_2O)/hr dose rate, 7×10^7 rads (H_2O) total dose

[b] Preconditioned 90⇌95%, 24 hrs, 45°

[c] Corrected for weight of leads, but including embedded silver grid

[d] Total projected area, including both sides

[e] Selected for 5% cycle depth in 15 minutes

[f] Silver electrodes cycled 90⇌95% in separate cells in pre-irradiation stage; cycled silver vs. silver in a single cell during irradiation: 60⇌65% and 60⇌55%

TABLE II. SILVER ELECTRODE CAPACITY IN IRRADIATION RUNS

Run	Initial State of Charge %	Cycle	Irradiated Cell[a] Pre-Test Capacity amp hrs	Δ[b]	Irradiated Cell[a] Post-Test Capacity amp hrs	Δ[b]	Control Cell Pre-Test Capacity amp hrs	Δ[b]	Control Cell Post-Test Capacity amp hrs	Δ[b]
CG-31	60	1	0.453	0.000	0.540	+0.006	0.464	-0.002	0.502	+0.008
		2	0.451	-0.002	0.537	+0.003	0.466	0.000	0.504	+0.010
		3	0.455	+0.002	---[c]	---	0.467	+0.001	---[c]	---
		4	---	---	0.528	-0.006	---	---	0.475	-0.019
		Average	0.453	±0.001	0.534	±0.005	0.466	±0.001	0.494	±0.012
		Change		+18% (±1%)				+6% (±3%)		
CG-32	30	1	0.447	-0.012	0.392	-0.021	0.451	-0.006	0.401	-0.027
		2	0.457	-0.002	0.417	+0.004	0.457	0.000	0.437	+0.009
		3	0.475	+0.016	0.433	+0.020	0.461	+0.004	0.449	+0.021
		Average	0.459	±0.010	0.413	±0.015	0.457	±0.003	0.428	±0.019
		Change		-10% (±5%)				-6% (±5%)		
CG-33[c] Electrode A (60⇌65%)	60	1	0.465	-0.008	0.376	+0.030				
		2	0.482	+0.009	0.334	-0.012				
		3	---	---	0.316	-0.030				
		Average	0.473	±0.009	0.346	±0.024				
		Change		-27% (±7%)						
Electrode B (60⇌55%)		1	0.473	-0.001	0.414	-0.022				
		2	0.477	+0.003	0.445	+0.009				
		3	---	---	0.447	+0.011				
		Average	0.474	±0.002	0.436	±0.014				
		Change		-8% (±3%)						

TABLE II (continued)

Run	Initial State of Charge %	Cycle	Irradiated Cell[a] Pre-Test Capacity amp hrs	Δ[b]	Irradiated Cell[a] Post-Test Capacity amp hrs	Δ[b]	Control Cell Pre-Test Capacity amp hrs	Δ[b]	Control Cell Post-Test Capacity amp hrs	Δ[b]
CG-34	30	1	0.483	+0.004	0.357	-0.025	0.458	-0.007	0.427	-0.014
		2	0.477	-0.002	0.389	+0.007	0.463	-0.002	0.444	+0.003
		3	0.477	-0.002	0.399	+0.017	0.475	+0.010	0.450	+0.009
		Average	0.479	±0.003	0.382	±0.016	0.065	±0.006	0.441	±0.009
		Change		-20% (±4%)				-5% (±3%)		

[a] Total dose 7 x 10^7 rads (H_2O)

[b] Deviation from average

[c] Cycled Ag vs. Ag in a single cell during irradiation

TABLE III. SUMMARY OF RECENT RESULTS OF SILVER ELECTRODES AT 60% and 30% STATES OF CHARGE

Run	Initial State of Charge %	Preconditioning[a] Cycling %	Preconditioning[a] Temp. °C	Capacity Increase Irradiated Cell %	Capacity Increase Control Cell %	Net Change[b] %
CG-26[c]	60	60⇌65	~25	+3 (±4)	+7 (±4)	-4
CG-27[c]	60	60⇌65	~25	+17 (±6)	+11 (±3)	+6
CG-30[c]	60	90⇌95	45	+15 (±3)	+8 (±3)	+7
CG-31	60	90⇌95	45	+18 (±1)	+6 (±3)	+12
CG-33[d]	60					
Electrode A (60⇌65%)		90⇌95	45	-27 (±7)	---	---
Electrode B (60⇌55%)		90⇌95	45	-8 (±3)	---	---
CG-32	30	90⇌95	45	-10 (±5)	-6 (±5)	-4
CG-34	30	90⇌95	45	-20 (±3)	-5 (±3)	-15

[a] Preconditioning time 24 hrs.

[b] Increase in irradiated cell minus increase in control cell

[c] Data from Interim Report IV

[d] Cycled Ag vs. Ag in a single cell during irradiation

TABLE IV. ANALYSES[a] OF GASES IN SILVER-CADMIUM CELLS AFTER IRRADIATION STAGE

Run	Initial State of Charge %	Gas Volume ml	Total Pressure mm Hg	Volume Percent						
				O_2	N_2	Ar	H_2O	CH_4	CO_2	H_2
CG-31	60									
Irradiated Cell		30.1	860	20.30	74.80	1.00	3.33	0.11	0.07	0.43
Control Cell		47.9	772	2.18	95.00	0.77	2.09	0.41	0.09	0.15
CG-32	30									
Irradiated Cell		46.5	880	0	81.22	0.03	0.85	0.12	0.01	17.76
Control Cell		43.4	830	0	97.02	0.08	2.80	0	0.07	0.02
CG-33[b]	60									
Irradiated Cell		---[c]	---[c]	5.85	82.21	0.64	1.49	0.02	0.07	9.81
CG-34	30									
Irradiated Cell		35.3	1120	0.25	82.70	0.08	1.38	0.15	0.12	15.33
Control Cell		40.8	892	2.06	95.12	0.08	2.55	0.04	0.16	0

[a] Mass spectroscopy

[b] Cycled Ag vs. Ag in a single cell during irradiation

[c] Leak prevented pressure and volume determinations

TABLE V. ANALYSES OF SOLIDS RECOVERED FROM SILVER ELECTRODE COMPARTMENT

Run	Initial State of Charge %	Total Wt. mg	Wt. % SiO_2 [a]	Net Wt. mg	Identified [b]	Wt. Cd/Wt. Ag [c]
CG-31	60					
Irradiated Cell		5.4	6	5.1	Ag	0.021
Control Cell		5.6	---[d]	5	Ag	0.030
CG-32	30					
Irradiated Cell		9.7	6	9.1	Ag	0
Control Cell		5.5	43	3.1	Ag	0.024
CG-33	60					
Electrode A (60⇌65%)		91.0[e]	1	---	Ag, AgO	0
Electrode B (60⇌55%)		26.1[e]	4	---	Ag	0
CG-34	30					
Irradiated Cell		3.5	11	3.1	Ag	0.006
Control Cell		5.1	21	4.0	Ag, $Cd(OH)_2$	0.026

[a] Emission spectroscopy

[b] X-ray diffraction

[c] X-ray fluorescence

[d] Insufficient sample

[e] Includes fragment mechanically broken from electrode

TABLE VI. ANALYSES OF SOLIDS RECOVERED FROM CADMIUM ELECTRODE COMPARTMENTS

Run	Initial State of Charge %	Total Wt. mg	Wt. % SiO_2 [a]	Net Wt. mg	Identified [b]	Wt. Cd/Wt. Ag [c]
CG-31	60					
Irradiated Cell		8.2	---[d]	8	Ag, $Cd(OH)_2$	0.77
Control Cell		7.1	---[d]	7	Ag, $Cd(OH)_2$	1.2
CG-32	30					
Irradiated Cell		8.1	6	7.1	Ag, $Cd(OH)_2$	1.2
Control Cell		7.8	6	7.3	Ag, $Cd(OH)_2$	1.6
CG-34	30					
Irradiated Cell		9.3	1.1	9.2	Ag, $Cd(OH)_2$	2.2
Control Cell		6.4	6	6.0	Ag, $Cd(OH)_2$	3.4

[a] Emission spectroscopy

[b] X-ray diffraction

[c] X-ray fluorescence

[d] Insufficient sample

TABLE VII. CONDITIONS FOR ZINC ELECTRODE RUNS

Run	Wt. Zinc g	Electrochemical Treatment: Pre-Cycling Capacity Meas. No. of Discharges	Cycling Conditions	Post-Cycling Capacity Meas. No. of Discharges	Observations
ZG-7					
Flooded Cell A[a]	0.24	---	---	---	No overcharge transition; zinc grew into frits
Flooded Cell B	0.44	---	---	---	Similar to Cell A
ZG-8					
Flooded Cell	0.60	~6	---	---	Similar to ZG-7, Cell A
Starved Cell	0.40	4	90⇌95% 24 hrs; 25°	3	Overcharge observed; zinc retained in cellophane
ZG-9					
Starved Cell[b]	0.32	3	90⇌95% ~16 hrs; 25°	---	Capacity appeared zinc-limited; current off control in cycling
ZG-10					
Starved Cell[b]	0.30	7	---	---	Zinc-limited capacity clearly demonstrated; automatic measurement of capacity not feasible

[a] Electric storage battery zinc electrode with exposed grid

[b] Contained Hg/HgO reference electrode

TABLE VIII. ZINC ELECTRODE CAPACITY

Run	Cycle	Pre-Cycling Capacity		Post-Cycling Capacity[b]	
		amp hrs	Δ	amp hrs	Δ
ZG-8[c]	1	0.201	+0.009	0.134	-0.005
	2	0.189	-0.003	0.145	+0.006
	3	0.194	+0.002	0.137	-0.002
	4	0.191	-0.001	---	
	Average	0.192	±0.004	0.139	±0.004
ZG-9[c]	1	0.098	-0.007		
	2	0.109	+0.004		
	3	0.108	+0.003		
	Average	0.105	±0.004		
ZG-10[c]	1	~0.012[d]	---		
	2	0.103	-0.009		
	3[e]	0.122	+0.010		
	4[f]	0.110	-0.002		
	Average	0.112	±0.007		

[a] Cells were not irradiated

[b] Cycled 90 ⇌ 95%, 24 hrs, 25°

[c] Starved cell

[d] Low due to incomplete wetting of zinc; omitted from average

[e] Cell stood on open circuit 3 days (discharged) between Cycles 2 and 3

[f] Later cycles with automatic programming yielded erratic results