Research and Development
of the
Silver Oxide-Cadmium
Electrochemical System

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Prepared by Allen Charkey
Allen Charkey
Project Engineer

Approved by
Dr. G.A. Dalin
Director of Research

Frank Solomon
Frank Solomon
Asst. Vice President

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ABSTRACT

Silver electrodes after "doping" with lead show improved utilizations at low temperatures. Moreover, no voltage dip is observed when these electrodes are discharged at moderately high rates at temperatures down to -10°C after a room temperature charge.

Cells have been fabricated with multi-layers of RAI 2.2XH separator material. Evaluation deep discharges at room and low temperature show good performance following a low rate charge. However, following a high rate charge the electrical efficiency drops to 82% compared to 94% which is obtained from cells with C-19 separators at the same charge rate.

Gas recombination data after 3000 short orbit cycles show that about 0.8 ma/in^2 is obtained at 60 psia for wet-proofed electrodes and about 0.2 ma/in^2 for untreated plates. The gas recombination rates at the start of cycling were about 5 and 2 ma/in^2 respectively.

A factorial experiment has been started to determine the optimum binder-wet proofing content.

Two 5-cell batteries with Pellon with no free electrolyte have been on constant potential charge for 260 days. Results show that voltage spread is still within 80 mv at a nominal float voltage of 7.75. Standard YS-5(S)-4 cells show a spread of as much as 0.3 volts after 150 days on float. Hydrogen evolution studies on single cells indicate that YS-5(S)-4 cells begin to evolve hydrogen below 1.65 volts while cells with non-woven absorbent separators show no hydrogen until 1.75 volts. Both types of cells were initially charged to 65% of theoretical Cd capacity.

BODY OF THE REPORT

1. PHASE 1. - Cell Tests

1.1 Effect of "Doping" of Positive Electrodes on Low Temperature Performance

An investigation of low temperature performance characteristics of the silver cadmium system was initiated during the second quarter of work. It showed that a 30-40 mv voltage dip (below the Ag_2O plateau) occured during discharge at 100 ma/in^2 at temperatures below 0°C. This dip was particularly pronounced when the discharge was preceded by a charge at room temperature. The discharge following a charge at low temperature, however, did not produce this phenomenon. The voltage dip observed at low temperatures may be attributed to a high concentration of Ag_2O adjacent to the grid. Electrodes charged at lower temperature probably contain a smaller quantity of Ag_2O since the AgO decomposition reaction

$$Ag + AgO \longrightarrow Ag_2O$$

proceeds at a much slower rate than at room temperature.

In the attempt to eliminate the voltage dip and to improve capacity of the silver electrode at low temperatures, three groups of positive electrodes were "doped" by several methods with lead. Silver electrodes which contained 5.4 g of Ag were plated with 1,5 and 10 percent by weight of lead from a 2N lead fluoborate solution at a current density of 250 ma/in^2. The plates were washed free of fluoborate and then dried. A second group of electrodes was electroplated in a similar manner, but after the "doping" the plates were heated at 400°C in hydrogen to cause diffusion of the lead into the silver lattice. A third group of electrodes was also prepared which contained 1,5 and 10% PbO powder mixed with the silver. The three groups of positive electrodes were wrapped with one turn of 6 mil Pellon and 5 turns of C-19, and assembled into 5 ampere-hour cells. The cells were then activated with 42% KOH. Following several formation cycles the cells were subjected to a series of deep cycles at 100,250,500, and 1000 ma/in^2. The purpose of this test was first to determine whether the utilization of Pb treated electrodes varied with the method of "doping" employed, and secondly, if doping improved overall electrode capacity. The data for these tests are illustrated in Figure 1.

The results show that at current densities below 500 ma/in^2 the method of lead doping is not significant. However, at 1000 ma/in^2 the utilization of the Pb-plated and Pb-"alloyed" electrodes were about 12-15% better than electrodes prepared by simple mixing of PgO and Ag powders. Moreover, the results illustrate that untreated silver electrodes exhibit from 9-23% poorer utilization than the doped electrodes over the current density range investigated.

The cells containing various percentages of lead were also tested over the temperature range of -10 to 25°C at a constant discharge rate of 100 ma/in^2. The results are shown in Figure 2. At the three temperatures tested the performance of the cells with 5% Pb treated silver appeared optimum. It was therefore decided to restrict the subsequent evaluations of lead treated silver to a concentration of 5%.

The effect of temperature on silver utilization for 5% plated, alloyed lead and the data for 5% PbO are illustrated in Figure 3. It can be seen that at room temperature there is little difference among the electrodes. However, at -10°C the lead plated silver plates gave .25 AH/g while the electrodes containing PbO gave .20 AH/g, and the untreated plates gave about .15 AH/g. At this temperature the Pb alloyed silvers were delivering about 12% poorer capacity than the plated electrodes. The poorer performance of the alloyed electrodes is not understood. It may be however, that the sintering temperature for the silver was lowered by the addition of lead, which resulted in a decrease in surface area.

The voltage characteristics for the cells containing lead "doped" electrodes were also determined at 0° and -10°C, at constant discharge rates of 2.0A (100 ma/in^2) and 10 A (500 ma/in^2). In all tests the charging was carried out at room temperature at 15 ma/in^2. The main objective was to establish whether the Ag_2O plateau of lead treated positive plates is free of initial "dip". The voltage-capacity data are plotted in Figure 4. The control cells at the 2.0A discharge rate at 0°C and -10°C showed voltage dips of 60 and 110 mv respectively. The lead treated cells showed a "normal" discharge voltage at both 0° and -10°C. At the 10A rate of discharge at -10°C both the treated and untreated cells exhibited voltage dips of about 50 mv below the plateau voltage. It can be seen, however, that the cells containing Pb gave a plateau voltage of 0.84 compared to 0.795 for the untreated cells.

It is evident from these curves that improvement of efficiency and suppression of the voltage dip have been accomplished by using lead "doped" silver electrodes. It is probable that the mechanism for the improved performance can be related to an increase in plate conductivity. Cahan has shown (U.S. Pat. 3,017,448) that the presence of lead compounds in the silver electrode decreases the resistance by about 50%. The suppression of the voltage dip can also be related to a decrease in plate IR drop.

The incorporation of lead probably decreases the resistance of Ag_2O by formation of silver plumbate or an interstitial alloy of silver and lead. It may also be possible to suppress the voltage dip by simple plating of the silver exmet with lead. Several cells which feature electrodes so treated are presently being fabricated and will be evaluated at low temperature. The cells will also be tested on extended float regimes where the dip problem has been shown to be serious.

1.2 Effect of Separator System on Cell Performance

The use of non-cellulosic membranes as battery separators has been studied extensively at the Delco-Remy Laboratories and at the Yardney Laboratories over the past two years. Specifically, the researchers at Delco have found that radiation acrylic-grafted low density polyethylene (prepared by Radiation Applications Inc. and coded 2.2XH) gives about 2-3 times the cycle life of reinforced Visking casing. Results in the Yardney Laboratory have been only moderately encouraging due to the fact that the material as received here was non-uniform. Also, the test regime was more severe.

Such improvements in performance as were noted in both laboratories can probably be related to the ability of the grafted membrane to stop silver and prevent the formation of continuous metallic silver "trails" which eventually cause cell failure by shorting. It should be pointed out however, that the RAI material was evaluated in silver-zinc cells both at Delco-Remy and at Yardney. The results obtained therefore may not be directly relatable to expected performance in sealed silver-cadmium cells.

To study performance in silver-cadmium cells, fourteen cells were built. These had one wrap of Pellon on the positive and negative and 4 wraps of RAI X2.2H main separator. The cells contained positive electrodes pressed to a density of 4.2g Ag/cc and "reinforced" CdO negatives. Seven cells were activated with 40% KOH and seven with 31% KOH. Following several formation cycles the cells were fitted with pressure gauges and sealed in epoxy. They were then discharged at -10°,RT, and 40°C at current densities of 100,250,500, and 1000 ma/in^2. The cells were charged at constant current at either 15 or 65 ma/in^2 at room temperature. The deep discharge at each current density and temperature are plotted in Figure 5. The charge acceptance performance following discharges at 100 ma/in^2 are shown in Figure 6. for both charge rates.

The results in Figure 5. indicate that at discharge rates below 500ma/in^2 the capacities at -10°C and room temperature are equivalent to the performance of cells fabricated with either C-19 or Visking.(see Second Quarterly Report) At 40°C the capacities of the cells with RAI X2.2H are about 10% better than cells fabricated with cellulosic separators.

The seven cells which were filled with 31% KOH exhibited somewhat better capacity than the cells with 40% KOH. This is probably due in part to the lower resistivity of 31% KOH . Referring now to Figure 6, it can be seen that charge acceptance following discharges at 100 ma/in^2 (which gave 8.1 ampere-hours) is very close to 100% efficient at 15 ma/in^2. However, at 65 ma/in^2 the charge efficiency dropped to 82% as compared to 94% which was obtained with cells fabricated with C-19 separators.(represented by a dash line in Figure 6). Following the evaluation cycles 10 cells with either

31 or 40% KOH were assembled into 5 cell batteries and placed on the 100 minute orbit regime. The remaining four cells are presently being subjected to overcharge studies to determine if the RAI separator impedes the diffusion of oxygen to the cadmium electrode. They will then be placed on the 100 minute orbit regime at -10°C and 40°C each pair will include one cell with 31 and 40% KOH.

2. PHASE 2.- Gas Recombination

Effect of Prolonged Cycling on Oxygen Recombination

Data obtained during last year's work has shown that organic separator debris when added to fresh cadmium electrodes lowered oxygen recombination by a factor of 2.5. The conditions chosen for this experiment were particularly severe, since it would be unlikely that the large abount of separator debris which was introduced into the test cell could accumulate in a cell during prolonged cycling. To make a more realistic determination of the extent of decrease in oxygen recombination as cells cycle, data were obtained on cells of various designs at intervals of 500 cycles. Specifically, the designs of the cells were one Pellon on the positive and negative with either multi-layers of C-19 or reinforced Visking casing main separators. The negatives were either mold pressed CdO or wet-proofed CdO. All cells were initially filled with 42% KOH. Following evaluation cycles and recombination experiments the cells were placed on the 100 minute orbital regime. The recombinations rates after 500,1000,1500,2000,2500 and 3000 cycles are given in Figure 7.

The data show that the cells containing wet-proofed CdO after 500 shallow cycles exhibited about a 2.5 times greater recombination rate than the cells with untreated electrodes.

It can further be seen that although the rates of recombination for both sets of cells decreased markedly with cycling, the wet-proofed set showed a rate of recombination of 0.8 ma/in^2 after 3000 cycles while the untreated set gave 0.2 ma/in^2. The differences between Visking and C-19 as far as oxygen recombination is concerned are negligible.

After 3000 cycles the cells were again placed on the short orbit regime and to date have completed 3220 cycles. The cells will eventually be dissected and the components analyzed to determine physical and chemical changes which occured on both electrodes.

3. PHASE 3.

Development of a "Ruggedized" Cadmium Electrode

The test cells discussed in previous reports contained 2.5% of wet-proofing and a small quantity of fibers to reinforce the electrode. However, the wet-proofing additive at this concentration necessitated the use of extremely high pressures (i.e. 18 tons/in^2) when fabricating the electrode. It was therefore necessary to reduce the concentration of wet-proofing to 1% at which value the fabrication pressure could be dropped to 6 tons/in^2. Since it is not known how this reduction in binder will affect the performance characteristics of the plate, a factorial cell experiment was designed with different levels of wet-proofing in the negative ranging from 0 to 2.5%. These cells have just begun their preliminary evaluation cycles.

Phase 4.

Prolonged Constant Potential Charging

The problems of oxygen and hydrogen evolution which arise from cell unbalance in a multi-cell battery during long periods of float are under investigation in this phase of the program. In addition, the capacity maintenance of a battery on float is also being studied as a function of time.

At present 5-cell batteries have been on constant potential charge for 260 days. All batteries were charged to 65% of theoretical negative capacity on the first charge. The cells in two batteries (Batteries E and F) were designed with enough Pellon interseparators so that all "free" electrolyte could be removed without damaging cell performance. Two additional batteries (Batteries G and H) contained woven nylon interseparators and normal quantities of electrolyte and have been on float for 180 days. In effect the last two batteries were standard 5 ampere hour models designated YS-5(S)-4. Every 30 days the batteries were given a deep discharge and then returned to float. When pressure increases became significant, gas analyses were also performed. The pressure, voltage, and capacity data for all four batteries are presented in Table I.

Results after 8 months on float from Batteries E and F show that voltage variation is still within 80 mv at a nominal float voltage of 7.75. The results obtained from Batteries G and H which are of standard construction show a voltage spread of as much as 0.30 volts after about 5 months on float. Most important is the fact that Batteries E and F showed very little pressure rise after day 150. In fact it can be seen that the cells in Battery E are all in deep vacuum.

It is significant that pressure fluctuation and decay in Batteries G and H occured almost exclusively in cells 3 and 4 of Battery G and cell 1 in Battery H. Note that in all three cells the voltages were above 1.65. Gas analyses showed that cells 3 and 4 contained 19% hydrogen, and cell 1 of Battery H contained 11% hydrogen. The remainder of the cells in both batteries contained only oxygen.

In another experiment individual cells similar in design to Batteries E and G (with and without Pellon) initially charged to a low extent of cadmium formation, are being floated at potentials between 1.5 and 1.9 volts. The cells were fitted with reference electrodes in order to determine the exact cadmium potential at which hydrogen is evolved. Specifically, the float voltage for each cell was varied by 50 mv increments between 1.5 and 1.9 volts. Gas analyses were then taken after four days of stabilization at each voltage. The data are shown in Figure 8.

The results show that the standard cell began to evolve hydrogen at about 1.65 volts, while the cell with Pellon showed no hydrogen evolution until 1.75 volts. It appears from these data that the Pellon allows access to the interior of the negative plate by oxygen, keeping its state of charge relatively low. The cells with nylon however, may contain dry spots which result in increased polarization on the negative plates due to an increase in IR at the dry spot. This would then cause hydrogen evolution to begin sooner even though the state of charge of the negative is the same as in the cell with Pellon.

Similar studies will also be carried out in cells where the extent of negative charge is higher than 65 %.

PROGRAM FOR FOURTH QUARTER

Phase 1

Finish the study of lead treated positive electrodes, during prolonged cycling on both orbital and float regimes, to determine if beneficial effects remain. Fabricate cells with lead alloyed silver grids to establish whether this treatment eliminates voltage dip as well as when lead doping the plates is employed. Evaluate RAI X2.2H separators to establish rates of oxygen recombination at various temperatures and current densities of overcharge. Start life cycling of these cells on long and short orbit.

Deliver sealed cells incorporating various design improvements to NASA.

Phase 2

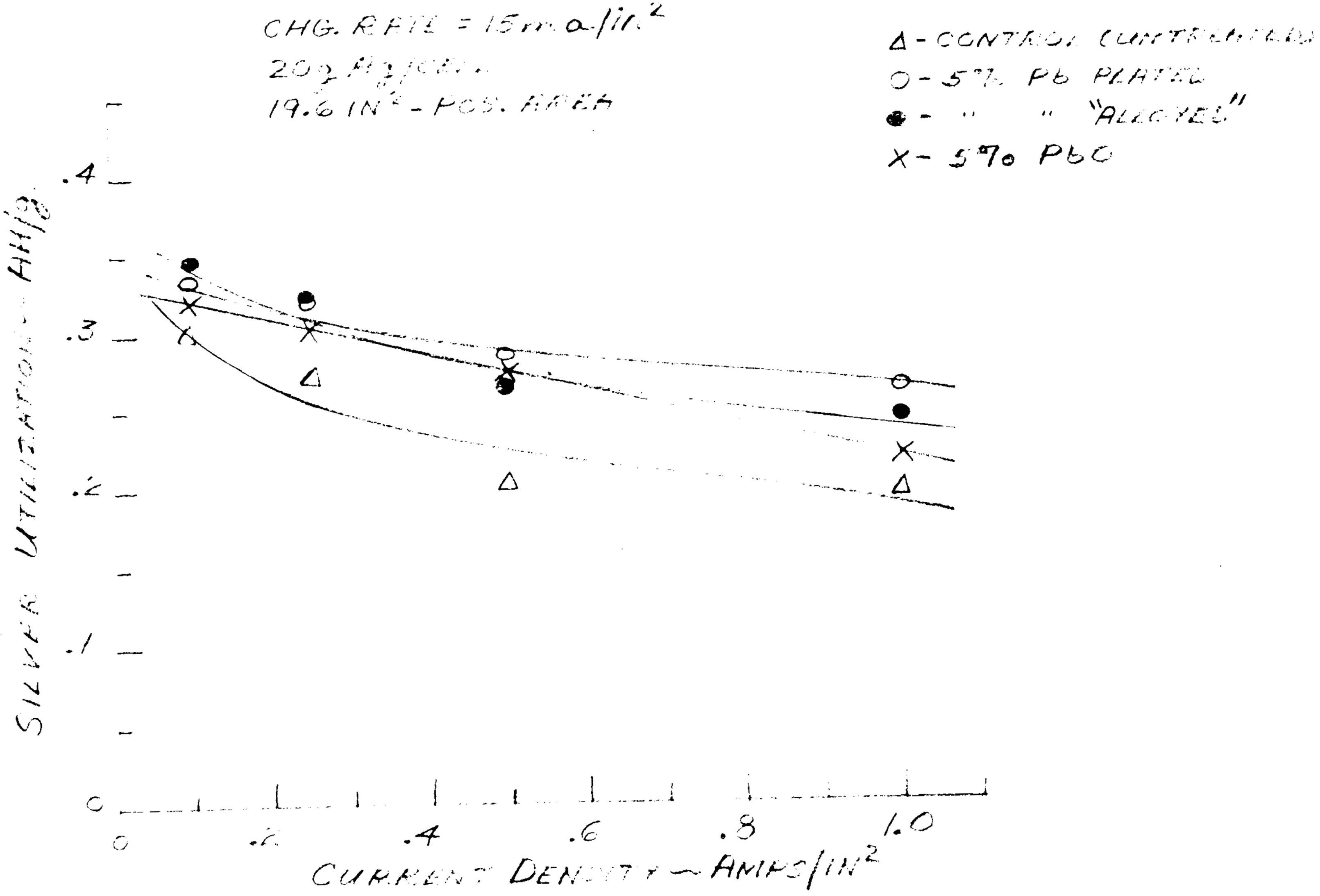
Finish the investigation of effect of prolonged cycling on recombination rates.

Phase 3

Optimize fabrication parameters for construction of "ruggedized" CdO electrodes.

Phase 4

Complete investigation of conditions leading to hydrogen evolution during float. Analyze Cd electrodes after prolonged periods of float and determine composition of plate at various locations.



EFFECT OF DISCHARGE CURRENT DENSITY ON SILVER UTILIZATION
Pb TREATED ELECTRODES
42% KOH-ROOM TEMP.
CHG. RATE = 15 ma/in²
20 g Ag/CELL
19.6 IN² - POS. AREA

Fig. 1

LEAD PLATED SILVER ELECTRODES
PERFORMANCE DATA
LEAD ADDITIVES

ID = 100 ma/in²
Ic = 15 " "
42% KOH
20g Ag/cell
11.6 in² - POS. AREA

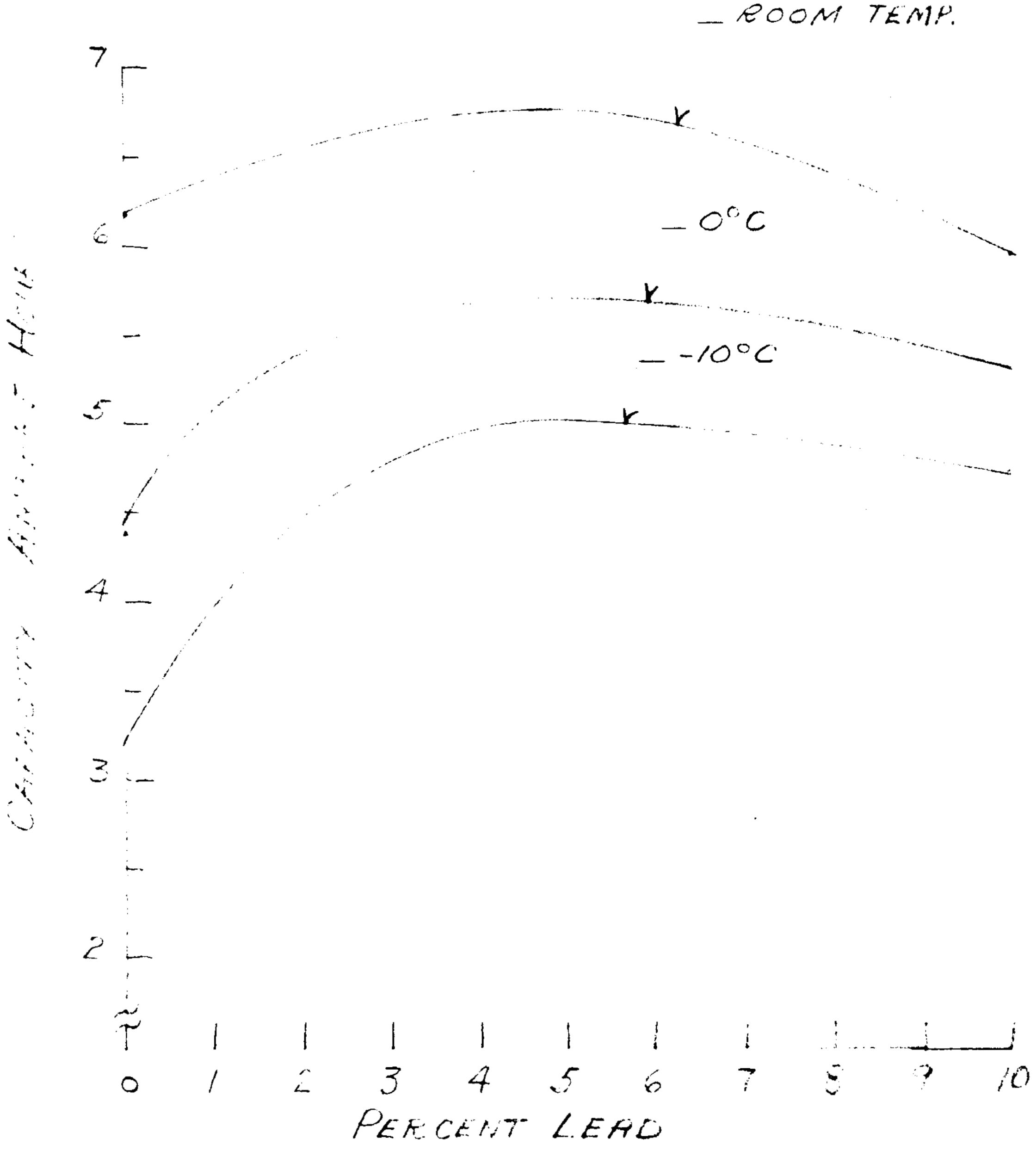


Fig. 2

EFFECT OF TEMPERATURE ON SILVER UTILIZATION (Pb TREATED ELECTRODES)

I_D = 100 ma/in²
I_C = 15 " "
42% KOH
20g Ag/CELL
19.6 IN² - POS. AREA

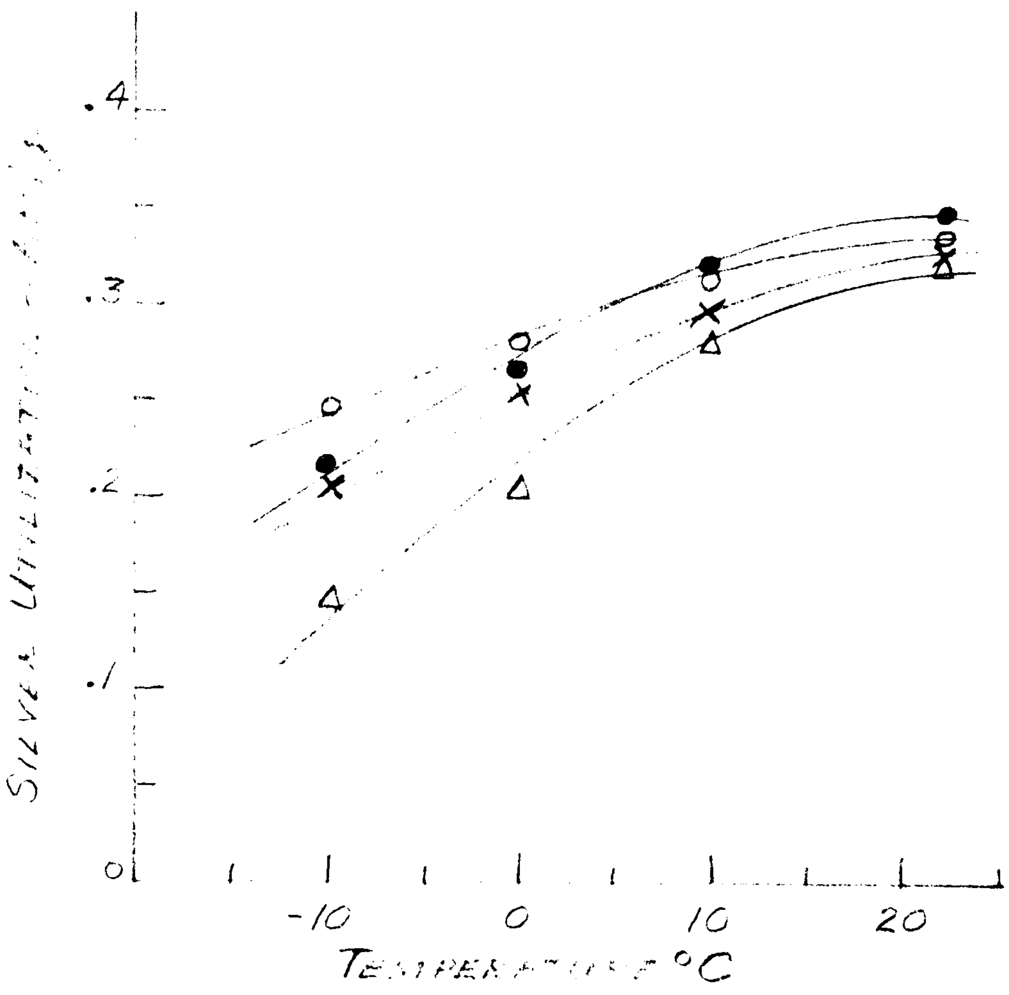
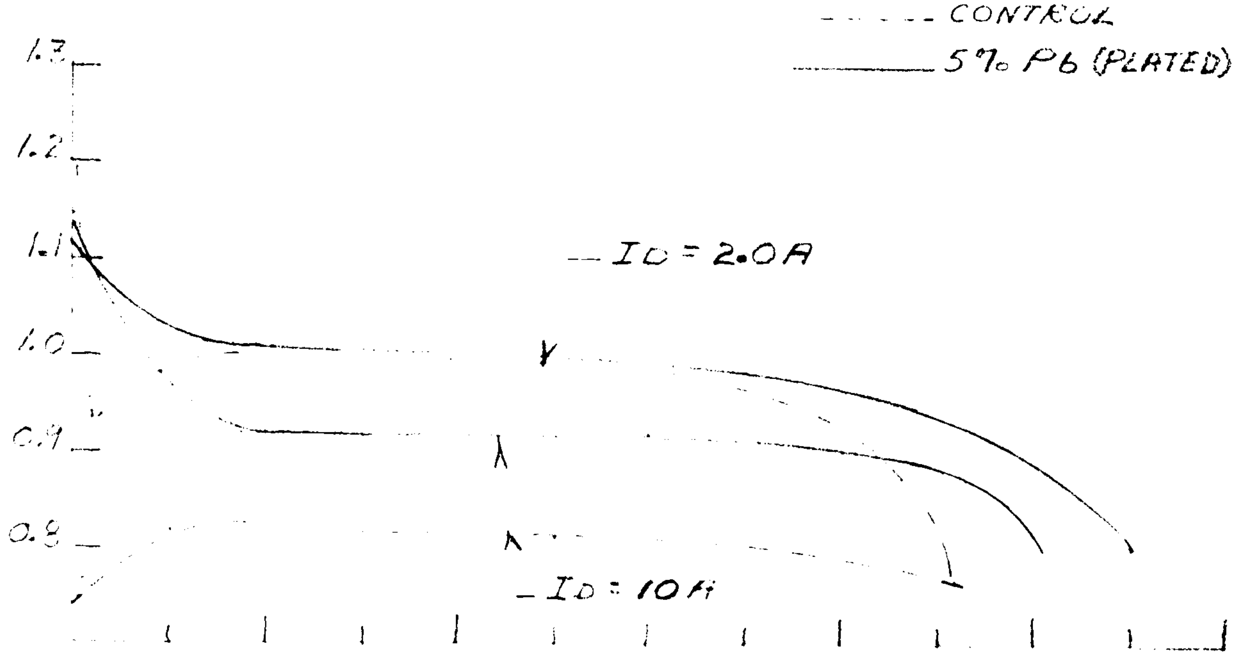


Fig. 3

LOW TEMPERATURE DISCHARGE PERFORMANCE DATA

42% KOH
20g Ag/CELL
19.6 IN² - POS. AREA
ALL CHARGING @ 15 ma/in² @ "RT"

DISCHARGE @ 0°C



DISCHARGE @ -10°C

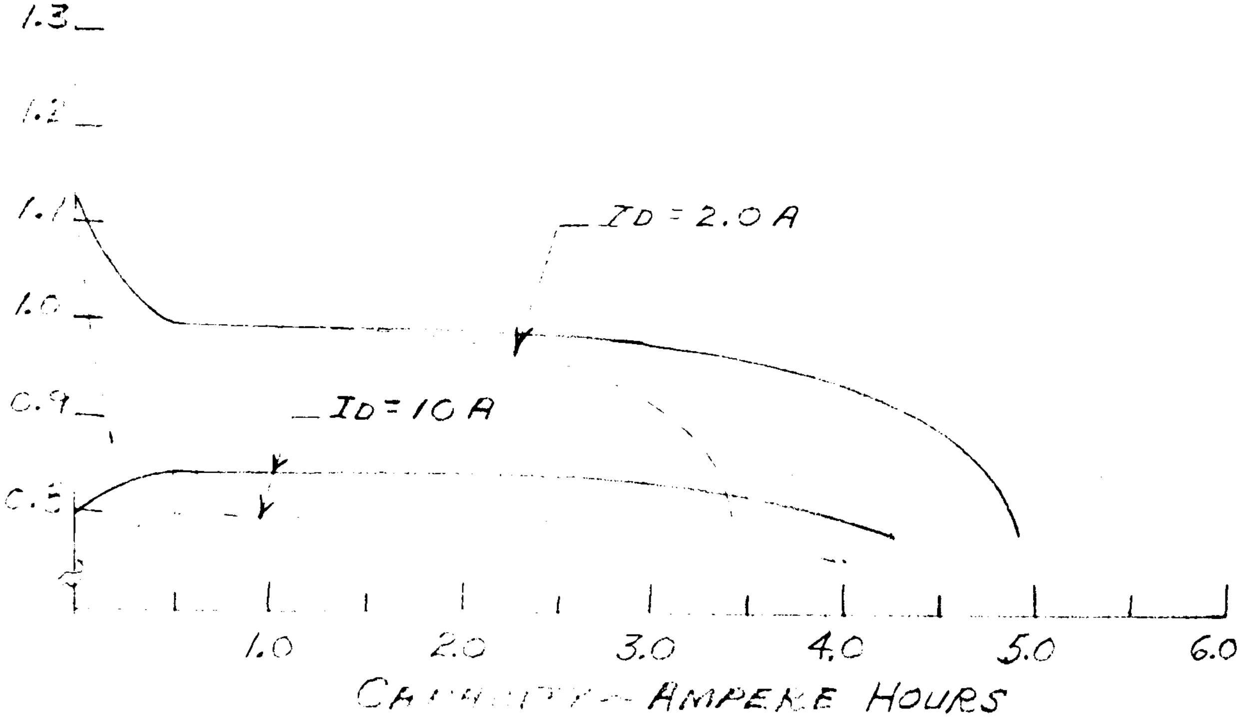


Fig. 4

PERFORMANCE DATA - INITIAL CYCLES

SEPARATOR SYSTEM - 1PELLON / 4X2.2H / 1PELLON
40% KOH
24 g Ag/cell
AREA = 24.5 in²

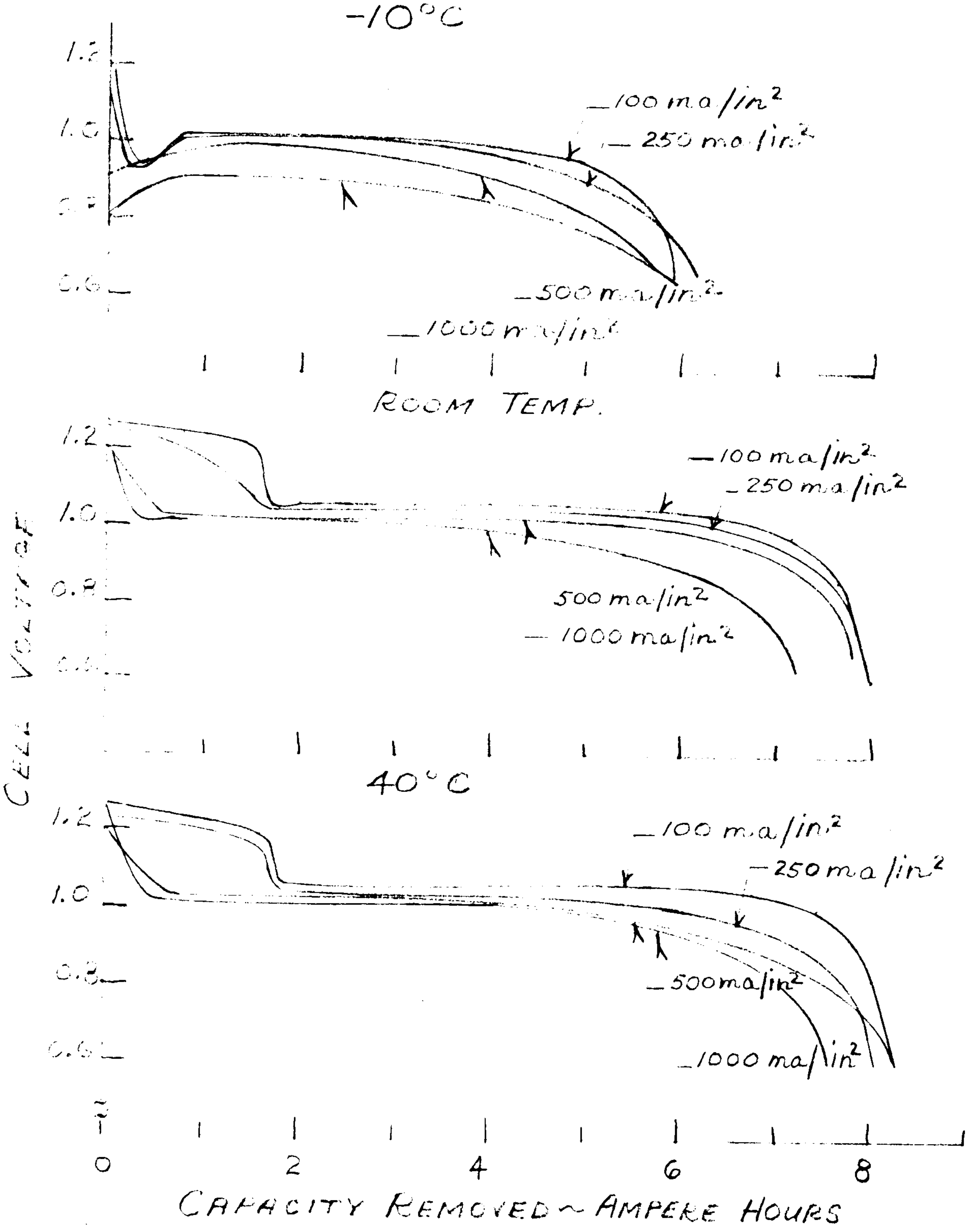


Fig. 5

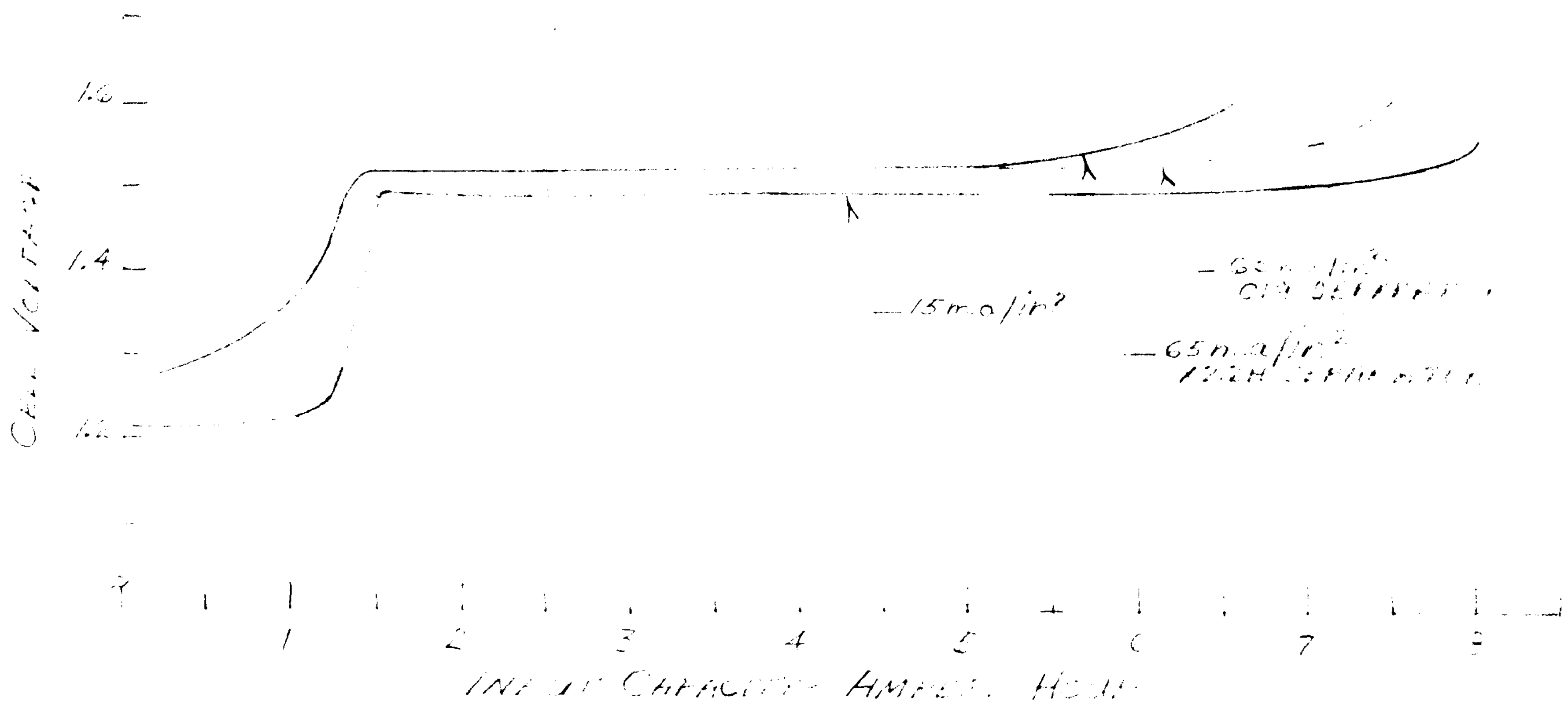

CHARGE PERFORMANCE DATA - INITIAL CYCLES
SEPARATOR SYSTEM - 1PELLON/4X2.2H/1PELLON
40% KOH
24g Ag/CELL
AREA = 24.5 IN²

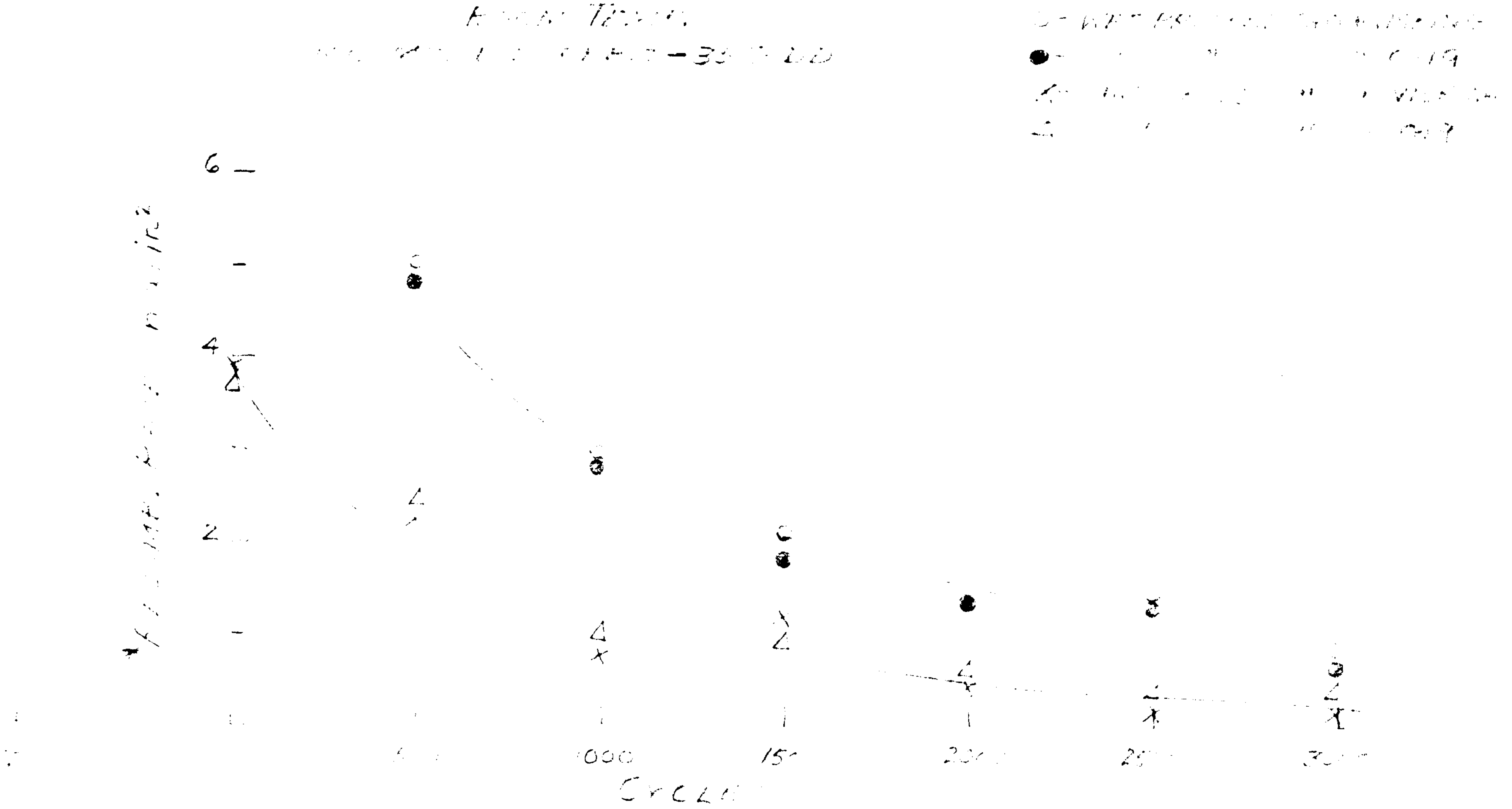
Fig. [illegible]

EFFECT OF PROLONGED CYCLING ON RATE OF O2 RECOMBINATION

4[illegible] F[illegible]

[illegible] TEMP.

[illegible] —35[illegible]



* [illegible]

[illegible] [illegible] ON FLIGHT

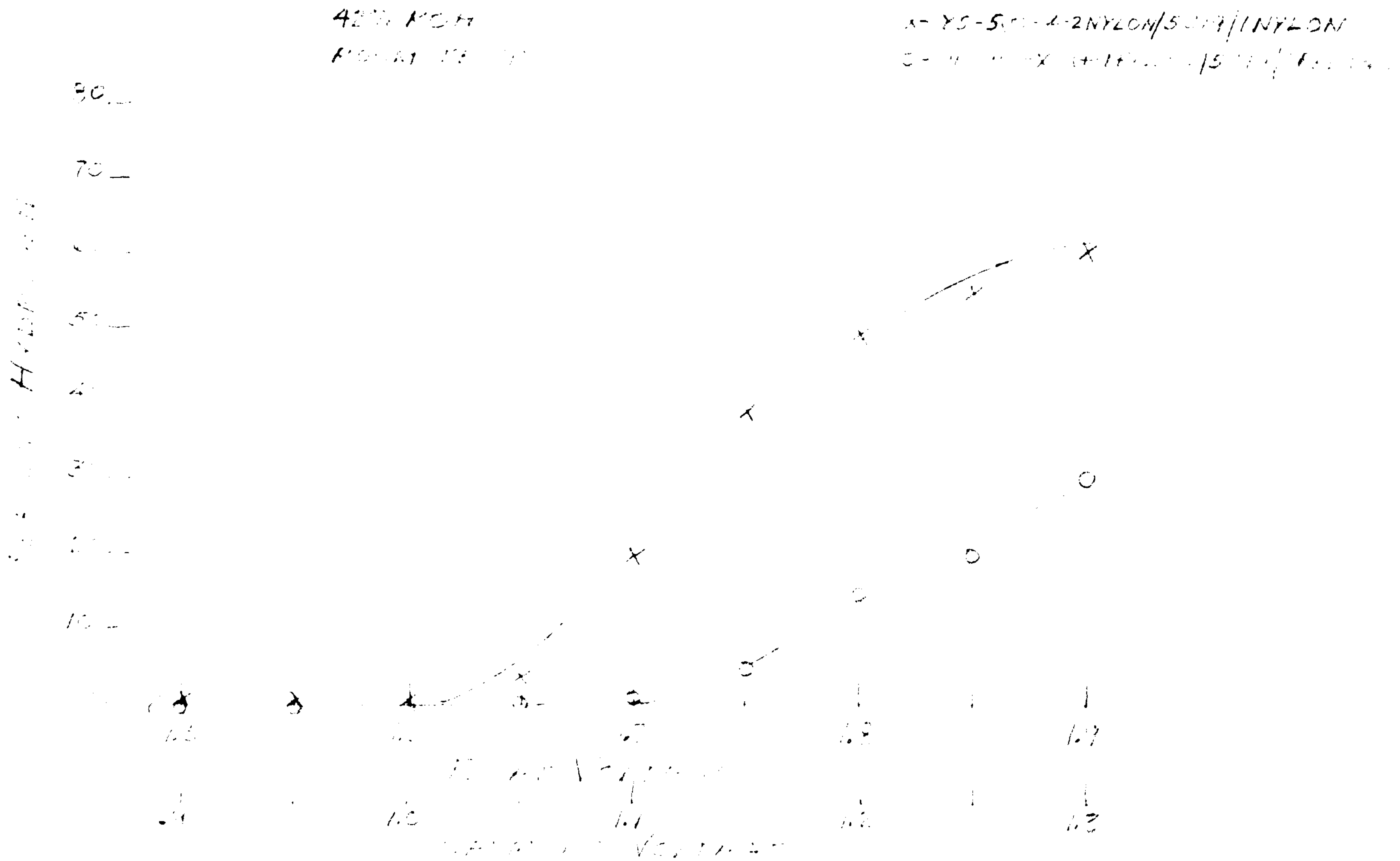


TABLE I
CONSTANT POTENTIAL CHARGING
FLOAT VOLTAGE = 7.75 (1.55 V/CELL)

	AFTER 150 DAY FLOAT					AFTER 210 DAY FLOAT					AFTER 240 DAY FLOAT				
BATTERY E	CELL 1	CELL 2	CELL 3	CELL 4	CELL 5	CELL 1	CELL 2	CELL 3	CELL 4	CELL 5	CELL 1	CELL 2	CELL 3	CELL 4	CELL 5
PSIG	11	8	-2	-7	-20	-7	-20	0	1	5	-22	-20	-20	-11	-23
VOLT	1.51	1.56	1.57	1.56	1.56	1.52	1.51	1.58	1.48	1.61	1.57	1.51	1.54	1.55	1.51
AHS	< 6.40 >					< 6.0 >					< 6.60 >				
BATTERY F															
PSIG	14	3	-5	-11	-24	12	0	1	-5	7	0	6	-5	7	-12
VOLT	1.58	1.54	1.51	[illegible]	1.55	1.54	1.56	1.54	1.55	[illegible]	1.58	1.54	1.53	1.66	1.54
AHS	< 6.15 >					< 5.85 >					< 5.90 >				
BATTERY G															
PSIG	14	6	50	47	55										
VOLT	1.52	1.41	[illegible]	1.71	1.41										
AHS	< 6.35 >														
BATTERY H															
PSIG	45	2	15	3	19										
VOLT	1.65	1.54	1.42	1.52	1.51										
AHS	< 6.50 >														

[illegible] DIS[illegible]
[illegible] IN INCHES OF Hg.