GPO PRICE $ ____

OTS PRICE(S) $ ____

Hard copy (HC) 2.00

Microfiche (MF) .50

[redacted]

FACILITY FORM 602

N65 23061	
(ACCESSION NUMBER)	(THRU)
49	1
(PAGES)	(CODE)
CR 62486	06
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

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Research & Development of the Silver Oxide-Cadmium Electrochemical System

Report No. 1

Contract No. NAS 5-9106
First Quarterly Progress Report
10 November 1964 to 9 February 1965
National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

Yardney Electric Corporation
New York, N. Y.

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PURPOSE

The purpose of this program is to investigate electrode reactions which take place in a sealed silver oxide-cadmium cell. In addition, the scope of this work will include a study of methods for improving the performance characteristics and reliability of the system for spacecraft use.

INTRODUCTION

Several improvements in sealed cell construction were developed last year on NASA program NAS 5-3452. These include; (1) wet-proofed cadmium negatives to increase gas recombination, (2) low density positive electrodes with improved utilization on cycling, (3) cells which do not show evidence of hydrogen evolution because of lower extent of negative charge, and (4) a new separator wrap that gives 90% greater cycle life to silver shorting. Some insight into the mechanism of cell reaction was obtained in the areas of: the passivation of electrode surface by material leached from the separators; the irreversibility of the cadmium electrode after prolonged cycling; and the effect of separator debris on oxygen recombination.

As a result of these developments, a further investigation will be carried out this year under NASA sponsorship in these and associated areas, to assure reliable silver-cadmium cells for satellite missions. Specifically, the work for this year will encompass determination of the rates of gas evolution and recombination as a function of temperature, a study of the efficiencies of active materials, and an investigation of the passivation of electrodes and variation of cell characteristics with cycling. At the end of the contract 30 cells containing improvements in cell construction based on the above findings will be delivered to NASA for evaluation.

ABSTRACT

Two groups of cells were built to study the effects of various constructions on performance. These cells were cycled on the 100 minute and 24 hour orbital regimes. The short orbit cells were stopped after 1950 cycles because of a malfunction in the automatic scanning equipment. The equipment is presently being repaired. The long orbit cells were dissected because of poor performance after 230 cycles. "Dummy" cycling of the positive and negative electrodes showed that the observed poor capacity was a result of separator attack and passivation of the negatives. Some negative electrodes from the long orbit cells are being prepared for microscopic and surface area analysis to determine how low rate charging affects the area of the plate.

Two sealed cells which use a nylon-dynel interseparator in combination with 3 turns of Visking cellulose main separator have completed 1000 shallow cycles (35% DD) and are still operating at about 78% of original capacity. The control cells made with C19 are at 65% of original capacity.

A factorial experiment has been designed to study the main effects and interactions of negative plate construction-separator system-temperature-and cycling regime on cell performance. The cells for this study are presently being constructed.

The effect of temperature on voltage and capacity is being investigated over the range of +40 to -10°C on both silver and cadmium electrodes. Little differences in performance have been found above 10°C. At minus 10°C the discharge capacities for both electrodes decreased sharply by about 50%.

The effect of density on performance of the negative electrode does not appear to be significant at any temperature studied. However, some improvements in the rate of oxygen recombination have been observed with the lower density negatives.

An investigation to improve the material utilization of the negative electrode has been initiated. Parameters under study during this quarter included grid structure, powder surface area, and internal cell pack pressure. Data show that increasing the surface area of CdO powder from 1.5 to 4.5 m^2/g increases the cadmium utilization from 63% of theoretical to 75% during initial cycles. Increasing internal cell pack pressure decreased the cadmium utilization, while increasing the grid area had little effect on performance.

To study the effect of separator debris on performance, single negative electrodes are being "dummy" cycled in electrolyte containing the oxidized solubles of either C-19 or PVA, Initial cycle data indicate that about 15% less capacity is obtained in cells containing separator debris than in the cell containing "clean" electrolyte.

Several cells which feature supported cadmium electrodes in a silver matrix have been constructed. Results, after several deep cycles, show that their performance is comparable to standard cadmium impregnated nickel electrodes.

BODY OF THE REPORT

1. Phase 1

1.1 Cell Tests

In order to study the effect of electrode density, separator system, and electrolyte concentration on charges in cell performance with cycling, a series of 11 cells was constructed. The cycle period was 24 hours at room temperature, 23 hours charge at 87 ma (5 ma/in^2), and discharge to 70% of nominal capacity in one hour at 2.0 A (120 ma/in^2). The cells were stopped after 230 cycles because of poor performance, (i.e. failure to give 2.0 AH for one hour to 0.6 volts cut-off).

The units were dissected in the discharged condition to determine the effect of prolonged cycling on the cell components. Visual observations showed that penetration of the separator by silver, in most instances, was not too severe considering the fact that the cells had a wet-life of about 14 months. Deterioration of the separators, however, appeared to be most extensive in cells which contained PVA. It was noticed that the PVA had oxidized completely and had "caked" on the silver electrodes in numerous places. In some cells cadmium dendrites appeared prominent over the tops of the separators, causing shorts between the plates. Cadmium appeared to grow only when subjected to low rate constant current charges or prolonged periods of constant potential charging. Similar behavior of cadmium during constant potential charging has been reported by our laboratories, in work carried out under Nobs Contract 78420 for the Bureau of Ships. It is interesting to note here that cells which were cycled on the 100 minute orbit showed no evidence of cadmium creepage. The quantity of free electrolyte in the cells was too small to enable sampling.

One positive and one negative was removed from each cell. These electrodes were cycled between either two fresh cadmium electrodes or fresh silver electrodes in pure 42% KOH. The electrodes were then given three cycles at current densities equivalent to the 24 hour orbit. The results are presented in Table I. At the same time four negative electrodes were selected for surface area measurements from both reverse and normal wrapped cells. The normal wrapped cells had been constructed with either C19 or PVA. The object of these measurements was to determine if changes in construction effected the surface area of the electrodes during cycling. The apparatus used for the measurements was an Orr Surface Area-Pore Volume Analyzer, Model M1C-107 distributed by Numinco Instruments Inc. A photograph of the instrument is shown in Figure 1.

The electrodes were prepared for measurement by washing them free of alkali and air drying overnight at 60°C. Each electrode was cut into several pieces and placed in a glass sample holder and attached to the gas manifold of the instrument. The samples were "de-gassed" overnight at 150°C to a pressure of about 5 microns of mercury. The samples were then cooled with liquid nitrogen to 78°K and allowed to equilibrate for 30 minutes. Following preliminary measurements, an appropriate quantity of nitrogen was introduced through the manifold to the sample and the amount of nitrogen absorbed by the sample was recorded as $P_1 - P_2$, where P_1 is the manifold pressure and P_2 the final pressure after absorption. The actual surface area of the sample was calculated. The results of these measurements are also included in Table I.

The data in Table I show that average capacities for both positive and negative electrodes cycled in 42% KOH with C-19 separators were 1.06 ampere hours, while the capacities of electrodes cycled in the same electrolyte concentration but with PVA separators were 0.82 and 0.90 ampere hours respectively for the positive and negative. It can be seen that the surface areas of cadmium electrodes cycled in contact with PVA were about 2.5 times lower than the measured areas for cadmium electrodes cycled in contact with C-19, and about 60% lower than a freshly charged Cd electrode. It should be pointed out, however, that although it is evident that PVA solubles decrease the reversibility and the surface area of the individual electrodes to a greater extent than the C-19 solubles, the final capacities of the cells before dissection were about equal, due to the presence of a large excess of negative material.

A further study of the undesirable effect of oxidized separator debris on cadmium utilization is presently being made in single electrode "dummy" cells. Four cells were fabricated with standard CdO electrodes and cycled in pure 42% KOH, 42% KOH + 120 mg K_2CO_3/ml, 42% KOH containing oxidized C-19 separator debris, and 42% KOH containing oxidized PVA separator debris. The cells were initially formed to 75% of theoretical cadmium capacity. They were then given several deep cycles at 50, 100, and 200 ma/in^2 discharge rate; the charge rate was kept constant at 20 ma/in^2. Following these preliminary cycles the cells were sealed in polyethylene bags to prevent additional carbonation of electrolyte by air, and placed on the short orbit regime at 65 ma/in^2 charge and 100 ma/in^2 discharge. After 300 shallow cycles the cells were given several deep discharges at the above three rates, while the charge rate was again lowered to 20 ma/in^2. The results are given in Table II.

Initial cycle data indicated that the electrode in pure 42% KOH was delivering from 5-12% better capacity (depending on discharge rate) than the electrodes cycled in separator debris. It should be noted that the electrode cycled in saturated K_2CO_3 was initially quite poor in capacity and was discontinued after cycle 3. After 300 cycles the electrode cycled in C-19 separator debris was performing about 7% poorer than the control, while the electrode cycled in PVA separator debris gave about 17% poorer capacity than the control. Cognizance should be taken of the fact that although the absolute capacity values for the three electrodes are different, all the plates decreased about 25% from their respective initial capacities. The cells have since been put back on the rapid shallow cycle regime for further evaluation.

The results at this time indicate that although the organic salts present in the electrolyte and on the plate decrease cadmium utilization, a more severe decrease in utilization occurs through "aging" of the cadmium metal by re-crystallization.

Additional studies are underway to determine if organic solubles from the separator are acting as crystal modifiers in the cadmium lattice. Several standard electrodes were cathodized at constant currents of 5, 20, and 80 ma/in^2. Electrolytes were pure KOH, KOH containing C-19 separator debris, or KOH containing PVA separator debris. After several cathodization cycles the electrodes were prepared for surface area and photomicrograph analyses. The results will be presented in the next quarterly report.

1.2 Effect of Temperature on Positive Electrode Performance

To evaluate the effect of temperature on performance of the silver electrode, cells were constructed with a central positive electrode. The silver electrodes were pressed to a density of 4.2 g/cc and wrapped in Pellon and several turns of Visking casing. In all cases the quantity of cadmium present in the 2 counter electrodes was well in excess of that required for a silver limited cell. The electrolyte was 42% KOH. All charges were carried out at room temperature at a current density of 65 ma/in^2. In order to simulate the short orbit regime, a constant discharge rate of 100 ma/in^2 was employed. The discharge temperature varied between +40 and -10°C. The cells were equilibrated at the desired temperature, and then discharged to 0.6 volts. The efficiencies (AHo/AHi) of the silver electrodes obtained from these measurements are shown in Figure 2.

It can be seen that the cathode attained maximum efficiencies between 15° and 40°C. Below 10°C the performance decreased sharply and at -10°C it had decreased by about 50%. The input capacity at room temperature for each electrode was about 1.9 ampere hours (to oxygen evolution). Since all the cells were given a complete charge, it must be assumed then that increased resistance was responsible for the poorer performance. A portion of the increase in IR was due to reduced mobility of OH^- ions in the KOH electrolyte and separator at low temperature. Other factors affecting the IR (e.g., lattice transfer) will be investigated. Improvement in the discharge performance of silver at low temperature may be achieved by "doping" of the electrode, or by using electrolyte mixtures such as KOH/LiOH or KOH/CsOH. It is interesting to note here that in carrying out this series of temperature runs, it was found that the polarization on the positive plate increased during discharge, while little increase in polarization was noted on the negative plate over the same temperature range. The polarization data for both electrodes are shown in Figure 3.

1.3 Effect of Separator System on Cell Performance

Four cells have been built with either C-19 or Visking casing main separators in order to study the effect of these materials on cell performance characteristics. The cells contained positive electrodes pressed to 4.2 g/cc, and standard CdO negatives. All cells were filled with a "normal" quantity of 42% KOH. To accelerate the evaluation the cells were cycled at rates equivalent to the short orbit regime. The cells were charged at 1.7 A to 1.65 volts and discharged at 3.0 A for 35 minutes on each cycle. The cells were given a deep discharge every 250 cycles to determine their capacities. The performance data for 1000 cycles are shown in Figure 4.

The results show that the cells fabricated with Visking are maintaining about 20% better capacity than the cells made with C-19. The reason for the superior performance may be attributed to the lower resistance of the multilayers of Visking compared to the layers of C-19. The Visking probably permits better diffusion of OH^- ions to the silver electrode during charge thus allowing the cells to charge more efficiently than cells fabricated with C19. However, since the paramount purpose here is to increase the life of sealed cells further cycle information must be garnered before any definite conclusions are made concerning the overall merits of Visking. After failure the cells will be dissected and all the components analyzed to establish the mode of failure for each design.

Two additional cells were built with (+) 1 Pellon - 6 mil 3 Visking/(-)/ 1 Pellon - 6 mil, and contained no free electrolyte. These cells have completed 250 cycles, the data is also presented in Figure 4. It should be noted here that several 5-cell batteries of the above designs along with 5-cell batteries containing wet-proofed cadmium electrodes have also been built. Additional cycling equipment is now being constructed and evaluation of these cells should begin during the next quarter. These batteries are presently undergoing pre-cycle tests at low and high temperature for performance and gas recombination. This data and evaluation cycle data will be presented in the next quarterly progress report.

1.4 Inert Separators

During the course of last year's separator investigation, it was found that when cells were built with one turn of RAI-XPE 40/50 (irradiated grafted polyethylene) positioned between turns of the main cellulosic separators, cycle life was over 90% greater than that of similar cells without XPE. It has further been found that the physical location of the "inert" film in the cell pack is an extremely important factor in determining the performance characteristics of the cell. For example; if the inert film is positioned either against the positive or the negative electrode the capacity of the cell will be quite poor. The low capacity may be attributed to electrolyte "starvation" of the electrodes. It is obvious that this "starvation" is caused in part by the films' inability to retain electrolyte (as compared with, for example, nylon or non-woven felts).

Since grafted polyethylene is frequently non-uniform, areas of the membrane cannot be easily "wet", which results in increased internal cell resistance. Because of this fact other inert materials such as polypropylene felt (Kendall Mills EM476), asbestos, (R-14), nylon, and Polypor WA were studied. The cells were similar in construction to those built with XPE in between the main separator, and designed to show quickly the effects of high temperature cycling (only 3 layers of separator were used). The cells were deep cycled at 50°C, at rates equivalent to the short orbit regime, and were left standing charged at frequent intervals to observe whether shorting had occurred. The results are presented in Figure 5.

It can be seen that EM-476 polypropylene and Polypor WA showed about a 20% better cycle life to shorting than the control, while nylon and asbestos cells gave the same cycle life as the control. However, the XPE 40/50 still exhibited the best capacity maintenance. It should be pointed out here that the "inert" separators, except for the XPE material were either woven or non-woven macro porous films. It may therefore be concluded that while polypropylene and impregnated nylon (Polypor WA) show some improvements over ordinary nylon which is degraded by silver, only inert semi-permeable membranes such as XPE will increase cell life by providing an essentially silver free section of the separator.

The performance of inert materials at room temperature and -10°C will also be investigated, since at these temperatures resistance of the films become a limiting factor in cell performance.

1.5 Factorial Cell Design

A factorial experiment has been designed to study the main effects as well as interactions of negative plate construction, separator system, temperature, and cycling regime on cell performance. The study is specifically aimed at improving the overall cell and negative electrode performance as well as gas recombination characteristics during prolonged cycling. It is anticipated that at the conclusion of this investigation enough information will be garnered to construct an "optimized" sealed cell for spacecraft use.

The following cell parameters will remain constant:

1. Positive plate density at 4.2 g Ag/cc
2. Cd: Ag ratio = 1.5
3. Pellon-6 on positive and negative
4. 42% KOH
5. No free electrolyte
6. Formation charge to 65% of theoretical Cd capacity.

The main effects as well as all possible interactions that can be determined are listed in the table below. Although cubic interactions are listed, they would be unlikely in view of the physical characteristics of the system.

If cubic effects and quadratic interactions become negligible, they will be added to the error term in order to improve the precision of the experiment.

Table III

Main Effects & Interactions for Design Experiment

Effect	Degrees of Freedom
Main Effects	
A_L	1
A_Q	1
A_C	1
B_L	1
B_Q	1
B_C	1
C_L	1
C_Q	1
C_C	1
D_L	1
D_Q	1
E_L	1
E_Q	1
F	1
Interactions	
$A_L \times B_L$	1
$A_Q \times B_Q$	1
$A_L \times B_Q$	1
$A_Q \times B_L$	1
$A_L \times D_L$	1
$A_Q \times D_Q$	1
$A_L \times D_Q$	1
$A_Q \times D_L$	1
$A_L \times E_L$	1
$A_Q \times E_Q$	1
$A_Q \times E_L$	1
$A_L \times E_Q$	1
$A_L \times F$	1
$A_Q \times F$	1
$A_C \times F$	1
$B_L \times E_L$	1
$B_Q \times E_Q$	1
$B_L \times E_Q$	1
$B_Q \times E_L$	1

Interactions (con'td)	Degrees of Freedom
$B_L x F$	1
$B_Q x F$	1
$B_C x F$	1
$C_L x E_L$	1
$C_Q x E_Q$	1
$C_L x E_Q$	1
$C_Q x E_L$	1
$C_L x F$	1
$C_Q x F$	1
$C_C x F$	1
$D_L x E_L$	1
$D_Q x E_Q$	1
$D_L x E_Q$	1
$D_Q x E_L$	1
$D_L x F$	1
$D_Q x F$	1
$E_L x F$	1
$E_Q x F$	1

No. of cells = 64
N-1 = 63 (total)
Error = (N-1) - sum of effects
Error = 63-51 = 12 (degrees of freedom for error)

Thirty-two cells which will cycle on the 100 minute orbit will be monitored on a specially designed scanner. The instrument is designed to scan one cell every 2 seconds on charge and remove a cell from the circuit when pre-set voltage (1.65 V) is reached. The long orbit cells do not require such precise monitoring because the current density is relatively low (i.e. 5 ma/in^2). These cells will be cut off charge and put on discharge by a simple voltage relay circuit. It should be noted here that the power supply is being constructed essentially A.C. ripple free to simulate the characteristics of solar-cell charging. The discharge portion of the cycle will be constant current.

2. Phase 2 - Gas Recombination

2.1 Effect of Temperature on Oxygen Recombination

Because a satellite battery is on charge for most of the orbital period, it is necessary that it efficiently accept substantial overcharge at or above trickle rates. Therefore, an investigation is in progress to determine the rates of oxygen recombination in multi-cell batteries over the temperature range of -10°C to + 40°C. Four 5-cell batteries were constructed for this study; two contained partially wet-proofed negatives, and two contained standard sponge cadmium negatives. The main separator was either multi-layers of C-19 or Visking. One wrap of Pellon-6 was used on the positives and negatives in all of the cells. The cells were filled with 42% KOH. After two formation cycles, all the "free" electrolyte was removed from each cell. The cells were then assembled as 5-cell units, sealed in epoxy, and fitted with pressure gauges.

The oxygen recombination rate for each battery was measured at -10°C, 10°C RT, and 40°C. The batteries were overcharged at 65 ma/in^2 until the pressures reached 60 psia, the current was then shut off and the pressures were allowed to decay. Figure 6 shows pressure rise during overcharge as a function of time for each type of battery. The rate of oxygen recombination on stand was calculated by determining the values of log dP/dT versus log P. The values for log dP/dT at 60 and 15 psia are presented as a function of temperature in Figure 7. The data given are composite values for two runs at each temperature and an average of the five pressure readings for each battery.

Referring now to Figure 6, it can be seen that the batteries containing partially wet-proofed negatives give substantially better recombination rates during overcharge than sponge cadmium electrodes at all the temperatures tested. Figure 7 also shows that the recombination rate on stand for the treated electrodes is significantly better than the control. Comparison of the results in both figures shows that chemical recombination of oxygen (during stand) decreases at a faster rate with temperature than does electro-chemical (overcharge) recombination of oxygen. Specifically, it can be seen that the oxygen recombination rate decreased about 10 times when the ambient temperature was lowered from +40°C to -10°C. The electrochemical recombination rate of oxygen with cadmium during overcharge, however, was only 2 times lower for the sponge cadmium plates and about 35% lower for the wet-proofed electrodes. Additional tests will be conducted taking into account the cell temperature rather than the ambient temperature.

Furthermore, it has been found that the recombination rate on stand at 15 psia is inversely proportional to the viscosity of the electrolyte. The measured viscosity of 42% KOH at 20°C is about 5 cp, while at -10°C, it is about 15 cp, or an increase of about 3-fold. Over this temperature range the recombination rate decreased about 3 times from .03 psia/min to .009 psi/min. At 60 psia, however, the relationship of electrolyte viscosity to gas recombination is as yet not clear. Possibly at higher pressure the reaction rate is proportional to the activation energy for the transport per molecule of oxygen to cadmium.

The mechanism of recombination during overcharge, however, is somewhat different. As the electrode potential is made more negative during overcharge, the extent of chemical reaction decreases and is replaced by the electrochemical reaction. The equation for which is:

$$O_2 + H_2O + 4e^- \longrightarrow 4\ OH^-$$

Oxygen recombination during overcharge is dependent upon the transfer of electrons from the cadmium electrode to the oxygen molecules. This reaction rate in turn depends upon the electrode potential. During overcharge at high rates "fresh" surfaces of metallic cadmium are being exposed at faster rates than oxygen recombination is occurring, therefore the diffusion of oxygen through the oxide (or hydroxide) layer on the plate cannot be the rate limiting step, as is the case during chemical recombination. It follows then that the reaction of oxygen with cadmium during overcharge is kinetically limited. This work is still in a relatively early stage. The effects of high and low rate cycling, negative recrystallization and separator debris on recombination will also be studied during the next quarter. In addition, a study of the mechanism of recombination on individual cadmium electrodes containing silver, nickel, and iron catalysts is also planned. A new glass electrolytic cell containing a rotating disc - polarographic assembly has been fabricated for this purpose.

2.2 Effect of Cadmium Density on Oxygen Recombination

Preliminary work on recombination with single electrodes has been completed. For this study, four cadmium oxide electrodes were pressed to densities of 2.2, 2.6, 3.0, and 3.4 g Cd/cc. They were each assembled between 2 silver electrodes wrapped in C-19 and given two formation cycles. The negative plates were removed from their respective cell packs and wrapped in one Pellon "U". Each electrode was then placed in a cell case filled with just sufficient 42% KOH to wet the separator and electrode. The cells were then potted and fitted with pressure gauges. The cell cases were evacuated and filled with oxygen to a pressure of 60 psia. The rate of oxygen recombination was calculated by determining log dP/dT versus log P. Data shown in Figure 8 are plotted as a log function of dP/dT versus density at 15 psia and 60 psia.

The data indicate that at both 15 and 60 psia, negatives pressed to 2.2 g/cc showed about 20% better oxygen consumption than the electrodes which were pressed to 3.4 g/cc. These results are reasonable in view of the fact that less dense plates have more solid-liquid-gas reaction sites for oxygen recombination than do denser electrodes. Therefore, electrodes of various densities have been included as part of the study in the factorial cell design experiment.

Phase 3 - Investigation of Improving the Efficiency of the Negative Electrode

Both pasted and pressed CdO electrodes accept 85-96% of theoretical capacity on the first charge (depending on the current density) before gassing. However, only 60%-65% of the input is delivered on the subsequent discharge. This inefficiency may be due to: (1) the poor conductivity of the discharge products, (2) poor conductivity between the grid and active material, (3) lack of porosity and or real surface area of the CdO electrodes, which results in poor diffusion of OH^- ions in the plate during discharge, and/or (4) excessive internal pack pressure caused by unusual swelling of the separator-electrode assembly during initial wetting of the cell. These and related problem areas are presently being studied.

3.1 Effect of Internal Pack Pressure on Cadmium Efficiency

One of the problems encountered recently has been capacity decay of cells caused in part by excessive swelling of the electrode-separator assembly. To determine quantitatively how much swelling occurs during soaking and during the initial cycling, a cell pack was assembled in a special case with a movable side wall. On the other side of the movable wall, a rubber bladder was positioned and inflated to 1 psig. The cell was filled with 42% KOH and the expansion during soaking was recorded.

After soaking the cell was formed and given several cycles during which time changes in pack thickness were also measured. It should be noted here that the increase in pack thickness due to separator swelling is known, and was accounted for in the evaluation of the results.

It was found that during the initial period of soaking the cell pack thickness increased to .625" which is .035" thicker than the nominal pack thickness (i.e. .590"). Subtracting the thickness values obtained for the separators and positive plate, it was found that each negative plate had swelled by .007". After the formation charge, the pack thickness decreased to .610" and remained constant at this value during subsequent cycling.

The initial swelling of the negative is due to conversion of CdO to $Cd(OH)$, thus resulting in a volume change of about 11%. The reduction in thickness during the formation is caused by the reduction of most of the hydroxide to the metal.

In another test, partial cells designed to be negative limiting on charge and discharge were constructed. Each cell was then shimmed with lucite spacers so that the internal pack thickness varied from nominal to .050" less than nominal. The cells were then formed and cycled several times at 100, 200, 300, and 400 ma/in^2 rates of discharge. The data are shown in Figure 9.

The results show that at 100 ma/in^2 (about the current density of the 100 minute and 24 hour orbital regimes) the cell designed to have no internal pressure was performing only about 5% better than the standard design. However, as the discharge current density increased to a maximum (400 ma/in^2) the standard cells' performance decreased by 15% compared to the cell designed to 0.590 in. pack thickness.

It appears that while increasing the internal thickness is not a limiting factor at current densities below 100 ma/in^2, the performance of the anode is significantly affected at higher rates. This may be due, in part, to the quantity of electrolyte retained in the pores of the cadmium electrode. Probably as the cell pack is compressed, the resulting deficiency of electrolyte in the negative plate causes concentration polarization at the end of discharge.

Cells are now being fabricated which were designed very close to zero pressure, by removal of active material from the two end negative plates. This procedure will not damage cell performance since it was found that only about 50% of the CdO was working on the end plates.

3.2 Effect of Grid Structure

As part of this phase of the study, partial cells (1 negative and 2 positive plates) were constructed with CdO pressed on various silver exmet collectors, also included was one impregnated cadmium electrode in a porous nickel plaque. The exmets used ranged in increasing order of fineness from #1 to #4/0. The cells were initially given a formation charge at 15 ma/in^2

to hydrogen evolution. They were given several deep discharge cycles at 50, 100, 200, 300, 400, 500, and 600 ma/in^2. The charge rate was kept constant at 65 ma/in^2. The cells were then placed on the short orbit, shallow cycle regime and given 1200 cycles.

The results in Figure 10 show that during initial cycles at each current density little difference was noted in cadmium utilization. Deep discharge performance after 1200 cycles, however, clearly showed that the supported cadmium electrode (in a nickel matrix) was performing about 15% better on the basis of active material utilisation than pressed electrodes on any silver exmet. It should be noted, however, that the utilizations based on total plate weight was slightly better for the pressed than for the impregnated electrode.

The results to date have been very promising with impregnated electrodes, since it appears that they retain their activity longer than do sponge electrodes. However, because many NASA space missions require non-magnetic components on board the satellite, nickel plaques, of course, cannot be used. To eliminate the undesirable effect of nickel, cells were constructed with negative electrodes in which the active material is impregnated into a highly porous silver matrix. Silver plaques which were 85% porous were impregnated by standard techniques with a $Cd(NO_3)_2$ solution. The final impregnated weight corresponded to about 45% of the void volume in the silver plaque.

Early deep cycle data indicate that the performance of these cells are comparable to standard impregnated cadmium electrodes. Improvement in oxygen recombination over pressed electrodes can also be expected, since there is a copious quantity of free silver available which is known to catalyze the reaction. The cells have been sealed and were placed on a rapid cycling regime to obtain data on life perfomance characteristics.

3.3 Effect of Cadmium Density on Negative Electrode Performance

The effect of cadmium density on negative plate performance is being investigated over the temperature range of +40 to -10°C. For this study a single negative electrode pressed to one of four densities (2.2, 2.6, 3.0, and 3.3 g Cd/cc) was positioned between 2 silver electrodes. The electrolyte was 42% KOH for all cells. The charging was done at room temperature at a current density of 65 ma/in^2. The discharge rate was kept constant at 100 ma/in^2. The utilizations for the electrodes at each temperature are shown in Figure 11.

It can be seen that at all temperatures there was little difference in performance among the electrodes of various densities. The material utilization of the electrodes at -10°C was about 46% of theoretical, while at room temperature it was about 65%. These results indicate that at low temperature the rate controlling process during discharge appears to be dependent on the resistivity of the electrolyte. However, during prolonged cycling which will be evaluated shortly the effects of electrode density may become more noticeable as far as recrystallization and dimensionable stability of the electrodes are concerned.

3.4 Effect of Initial CdO Surface Area on Negative Plate Performance

A parameter that is known to affect cell performance is the actual surface area of the active material. It would be of interest therefore to determine whether or not the surface area of the active cadmium metal is related to the surface area of the oxide.

To study the effects of surface area on negative electrode performance special CdO of various particle size were synthesized. The powders used in this experiment were prepared essentially by four methods; (1) sieving of standard CdO powder through 200 mesh screen, (2) precipitation of $Cd(OH)_2$ from the nitrate salt in cold 31% KOH and subsequent thermal decomposition to the oxide, (3) same as in two only precipitation was carried out in hot alkali, and (4) thermal decomposition of cadmium acetate. The surface areas of the powders were then measured using the Numinco Surface Area-Pore Analyzer. The values are given below:

Sample	Surface Area m^2/g
standard CdO	1.5
method (1)	1.75
" (2)	3.5
" (3)	4.5
" (4)	8.0

The powders were pressed into electrodes to a density of 2.8 g Cd/cc. They were then assembled into individual cells so that the negative electrode limited the charge and discharge. Following a formation cycle the cells were charged at 15 ma/in^2 and discharged at 100 ma/in^2. The utilizations obtained for the discharges are plotted as a function of surface area in Figure 12.

The results clearly show a linear relationship between material utilization and surface area in the range 1.5 to 4.5 m^2/g. Specifically, the cadmium utilization improved from 63% of theoretical at 1.5 m^2/g to 75% of theoretical at 4.5 m^2/g during the initial cycles. It is of interest to note here that a decrease in performance was obtained with the electrode made from CdO which had a surface area of 8.0 m^2/g. The reason for this is not completely understood at present, but it may be due in part to the extremely high pressure which was needed to press the electrode to its correct apparent density. This may result in a lamination of the plate with an extremely dense surface and a more porous interior. As a result, of this study, full size 5 ampere hour cells have been designed and are being fabricated with CdO of the various surface areas. Orbital cycling of these cells will commence during the next quarter. It will be of particular interest to learn how these high surface area electrodes behave during prolonged cycling.

Phase 4 - Prolonged Constant Potential Charging of Batteries

NASA had reported some data indicating that gas evolution in freshly charged sealed silver-cadmium batteries during initial periods of "float" is excessive. It was further reported that when these batteries were given 40-50 cycles prior to floating, a hydrogen pressure was also noted on float but was followed by a pressure decay during the trickle portion of constant potential charge. In order to study this phenomenon in greater depth, two 5-cell batteries were constructed and instrumented with reference electrodes and pressure gauges. The design of each battery was such that all free electrolyte was removed without affecting cell performance. The batteries were initially given a formation charge to 65% of theoretical negative capacity. The extent of negative charge was kept low, because it was found that during prolonged shallow cycling (of single cells) the surplus of uncharged material precludes the evolution of hydrogen. (Charkey & Dalin Research and Development of the Silver-Cadmium Couple - NAS5-3452, Final Report 1964). The batteries were then given five evaluation deep cycles and placed on constant potential charge at 7.75 volts (1.55 V/cell). Where pressure increases in the cells became significant, gas analyses were performed. The history of two of the most erratic cells in one battery during a three month float period is shown in Figure 13.

It can be seen that it is difficult to establish any relationship between the pressure rise and subsequent decay with cell voltage. However, it should be noted that little if any hydrogen was evolved in all the cells during the entire three month period of constant potential charging. This must be due to the presence of a large excess of CdO. In order to ensure that this is indeed the case, cells with a minimum excess of CdO will be assembled as 13-cell batteries and placed on a constant potential charge. The battery will be instrumented to allow for periodic sampling of the gas. The results also indicate the erratic pressure variations in the cells had practically disappeared following a two-ampere deep discharge after 30 days of float.

One battery is presently being dissected. Physical and chemical measurements will be made on the positive electrodes to determine if their properties differ from freshly charged electrodes. In another test single cells have been placed on float at 1.55 volts and will be periodically removed from the charging circuit for analysis. It is anticipated that changes on the positive electrode which affect recombination of gases will occur during the early part of the float period rather than after 3 months.

PROGRAM FOR SECOND QUARTER

Phase 1

Determine the mechanisms by which cadmium ages and the effect of rate of charge and discharge on these mechanisms. Relate changes in surface area of cadmium during cycling with the decrease in the utilization of active material. Determine the solubility of CdO, and $Cd(OH)_2$ polaragraphically in various concentrations of KOH, over the temperature range of $-10^{\circ}C$ to $+40^{\circ}C$. Study cycled cadmium electrodes by means of the electron microscope to determine how cycling affects the crystal structure of the active electrode material. Continue investigation of the effects of separator debris on the crystal habit of cadmium. Investigate improvements in positive electrode utilization at low temperature, either by means of "doping" or with additives to the electrolyte. Study means of decreasing the diffusion rate of soluble silver oxide species through various separators by use of "diffusion barriers". Start cycling of cells built for the factorial design experiment.

Phase 2

Study the mechanisms of oxygen and hydrogen recombination in a special glass electrolytic cell, which includes a rotating disc-polarographic assembly, with particular emphasis on the effects of catalyst, KOH concentration, and separator debris. Determine the long term effects of cycling, electrolyte quantity, and cadmium recrystallization on gas recombination. Study gas recombination in cells fabricated with cadmium impregnated silver plaques.

Phase 3

Study the effects of initial surface area and density on performance and gas recombination of the negative electrode during extended cycling. Determine if cadmium recrystallization and efficiency is more affected by charge current density than by discharge current density. Study the performance of cadmium electrodes which incorporate various conductive and non-conductive "expanders" and corrosion inhibitors, with special emphasis on improving material utilization and dimensional stability of the electrode. Investigate the performance characteristics of cadmium impregnated silver plaques, with reference to retention of activity, and improvements in oxygen recombination.

Phase 4

Continue the study of conditions leading to evolution of hydrogen during constant potential charging, with particular reference to initial formation of the negative electrodes, electrode overpotential, and the effect of adsorbed organic material. Examine positive and negative electrodes after different float periods and analyze positive plates for AgO, Ag_2O, and Ag. Study the mechanism of hydrogen "scavenging" by the silver electrode as a function of potential.

TABLE I
SINGLE ELECTRODE DATA – LONG ORBIT CYCLING
(AFTER 230 CYCLES)

CELL NO	① CAPACITY AHO	* POSITIVE AHO	POSITIVE g/AH	NEGATIVE AHO	NEGATIVE g/AH	SURFACE AREA m^2/g	CONSTRUCTION
1	1.75	.94	3.05	1.12	5.30	—	4.8g Ag/cc (+)2NY/6C[illegible] 2.8g Cd/cc
3	1.95	1.0	3.25	1.17	5.15	—	" "
5	1.86	1.06	3.30	1.05	5.75	8.95	" "
15	1.75	1.03	3.28	.88	6.15	—	4.3g Ag/cc 2.3g Cd/cc "
31	1.90	.91	3.45	.85	6.20	—	4.8g Ag/cc " 2.8g Cd/cc + 2% SHAW[illegible]
33	1.98	.98	3.51	1.0	5.30	—	" (+)2NY/6C19 " + 2% GRAPHITE
35	1.82	1.06	3.20	1.07	5.69	—	" (+)2NY/6C19 " + 5% FRAG
37	1.91	1.10	3.35	.93	5.95	5.70	" (−)2NY/6C19 " REVERSE WRAP
69	1.71	.83	3.81	.88	6.15	—	" (+)2PVA/3C19 "
71	1.65	.81	4.10	.91	6.0	3.45	" (+)2NY/3PVA "
73	1.74	.73	3.75	.97	5.70	3.86	" " " "

1 - CAPACITY OF CELL PRIOR TO DISSECTION

CHG. = 5 ma/in²
DISCHG. = 120 ma/in²

FRESH Ag ELECTRODE CAPACITY = 1.25 AH
" Cd " " = 1.55 AH
" " SURFACE AREA = 6.4 m²/g
Pos. [illegible] 3 [illegible]

* SILVER UTILIZATIONS (g/AH) ARE BASED ON FINAL WT. OF ACTIVE MA

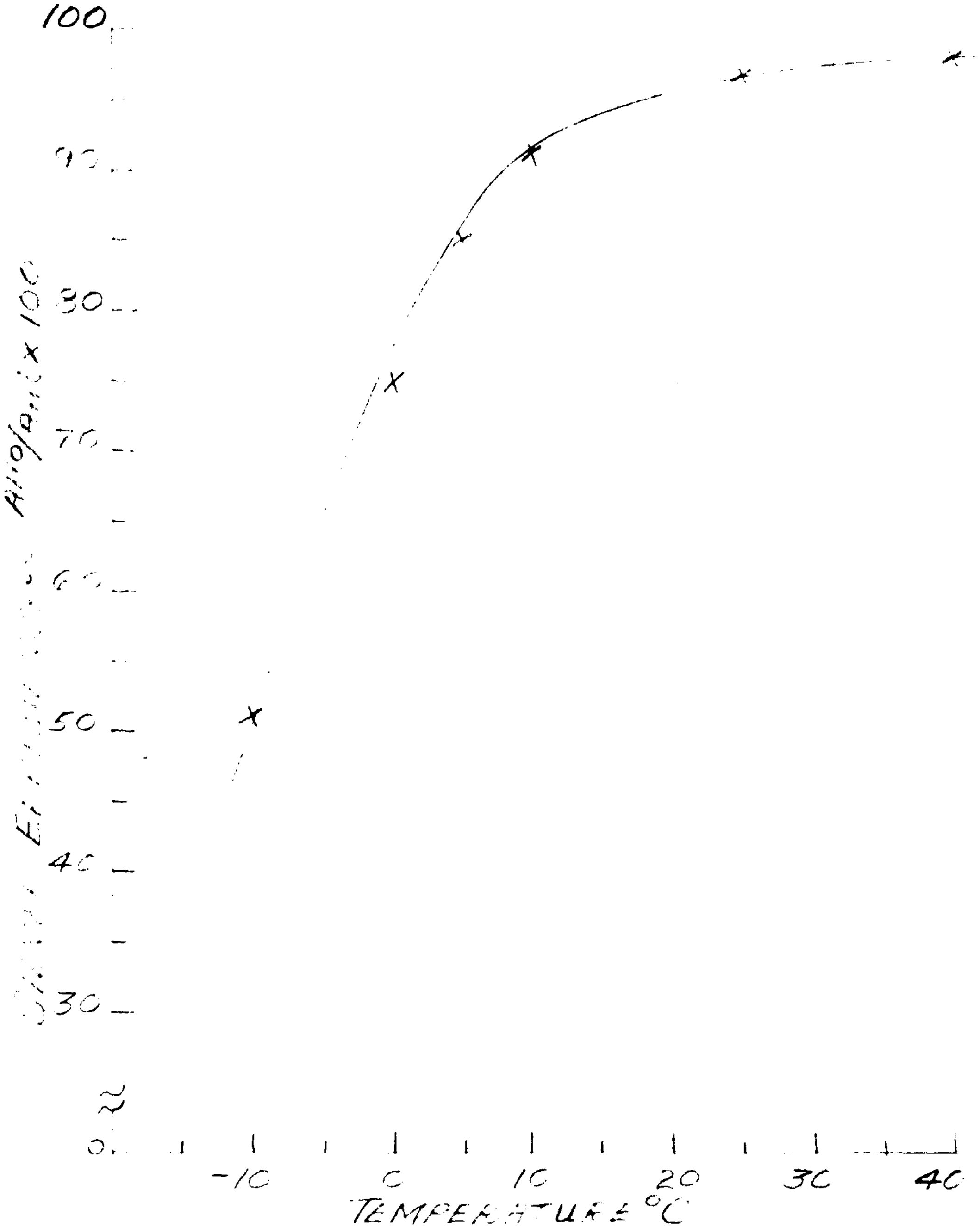
TABLE II
EFFECT OF SEPARATOR DEBRIS ON NEGATIVE ELECTRODE PERFORMANCE

ELECTROLYTE	INITIAL CAPACITIES			CAPACITIES AFTER 300 CYCLES		
	50ma/in²	100ma/in²	200ma/in²	50ma/in²	100ma/in²	200ma/in²
PURE 42% KOH	1.45 AH	1.40 AH	1.32 AH	1.15 AH	1.08 AH	0.95 AH
* 42% KOH + 120mg/ml K_2CO_3	0.82 "	0.75 "	0.68 "	DISCONTINUED AFTER 3 CYCLES		
42% KOH + C-19 DEBRIS	1.46 "	1.33 "	1.18 "	1.07 AH	1.00 AH	0.89 AH
42% KOH + PVA DEBRIS	1.37 "	1.24 "	1.13 "	0.95 "	0.85 "	0.77 "

WT. OF CADMIUM = 4.75 g/PLT.
DENSITY = 2.3 g/cc
AREA = 4.9 in²
Ic = 20 ma/in²
* SATURATED K_2CO_3

EFFECT OF DISCHARGE TEMPERATURE ON SILVER EFFICIENCY

SILVER DENSITY = 4.2 g/cc
DISCH. = [illegible] ma/in²
CHG. = 65 ma/in²
42% KOH



NOTE:
ALL CHARGES CARRIED OUT AT ROOM TEMPERATURE
100% AHE = 1.9

Fig. 2

EFFECT OF TEMPERATURE ON VOLTAGE

42% KOH

CHARGE = 65 ma/in² AT R.T.
DISCHARGE 100 ma/in²

SILVER DENSITY = 4.2 g/cc
CADMIUM DENSITY = 2.8 g/cc

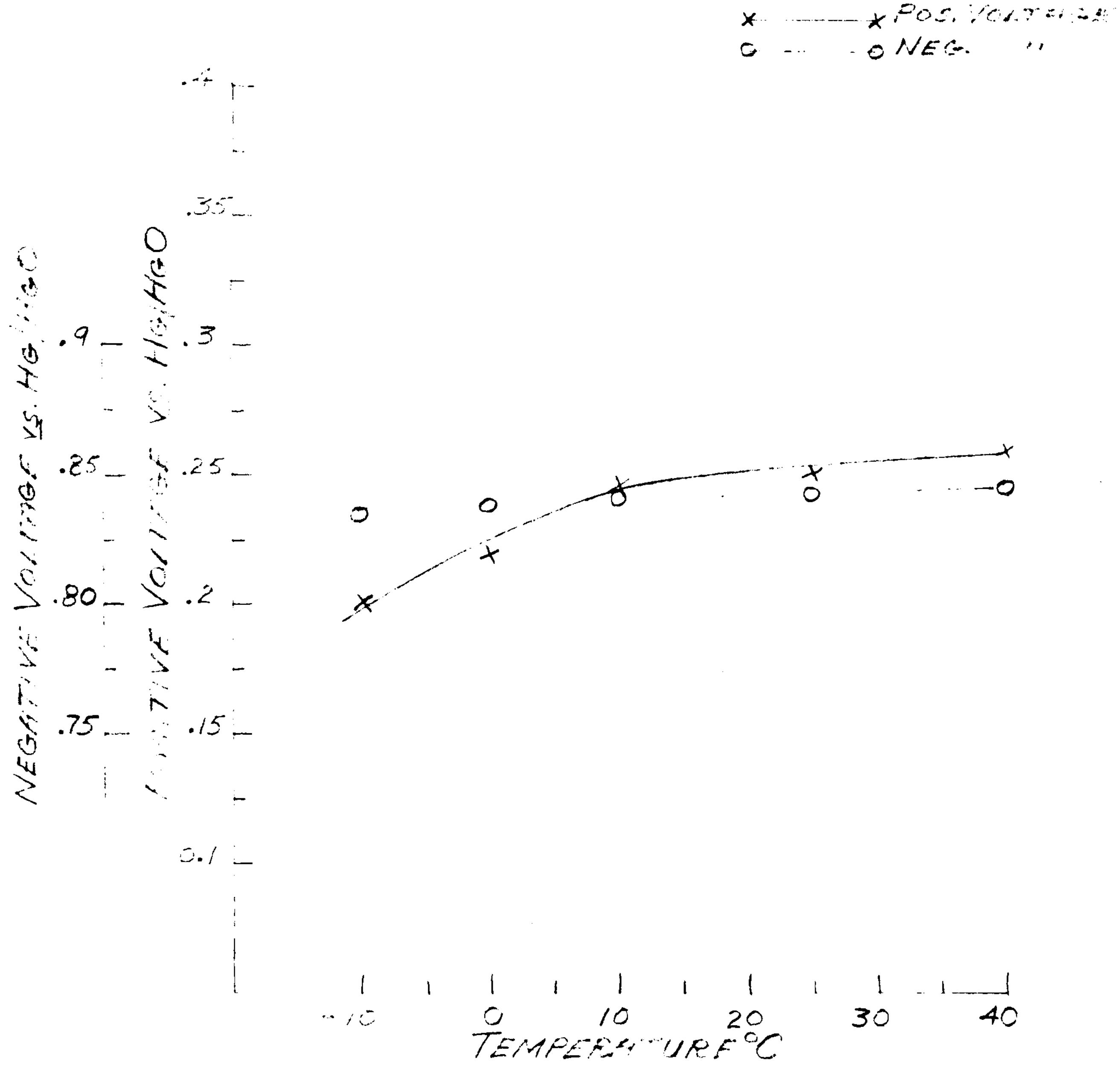


Fig. 3

DEEP DISCHARGE PERFORMANCE DATA ~ SHORT ORBIT

CHARGE = 1.7A
DISCHG. = 3.0A
42% KOH

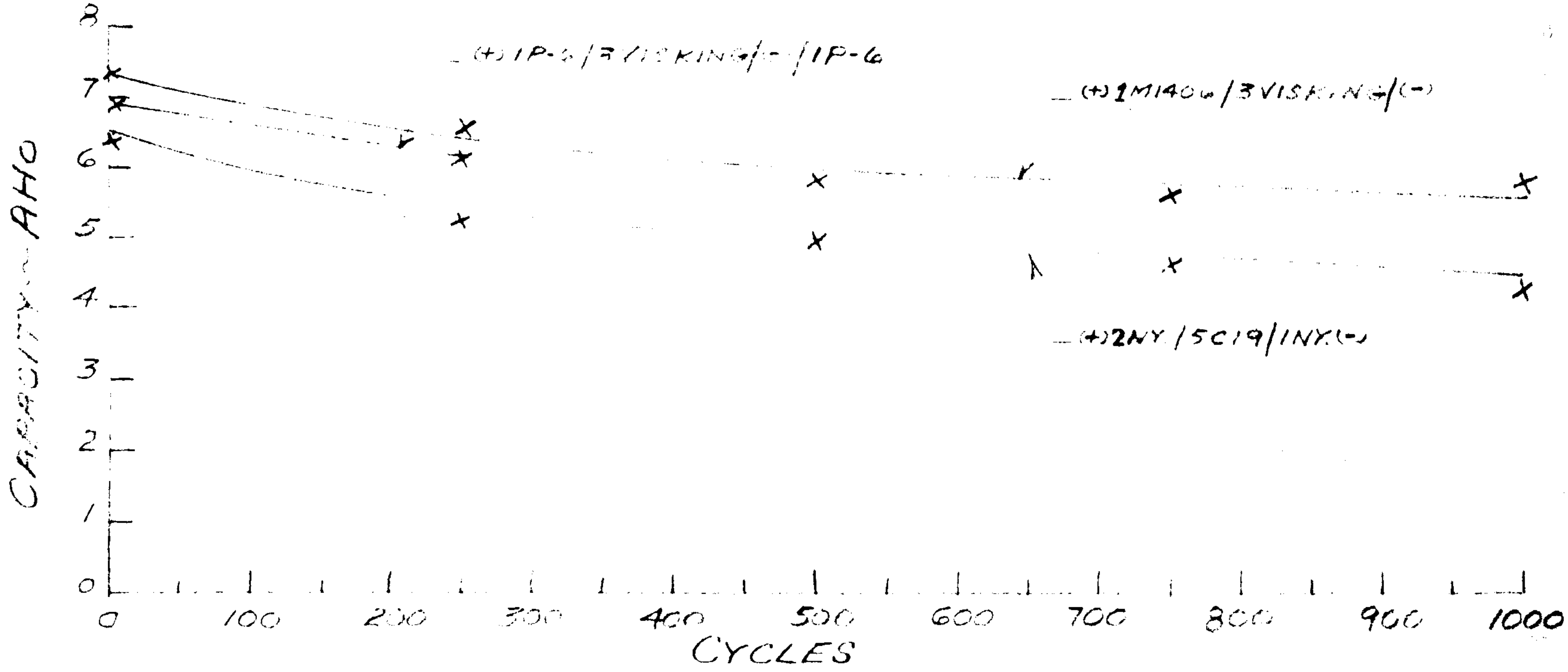


Fig. 4

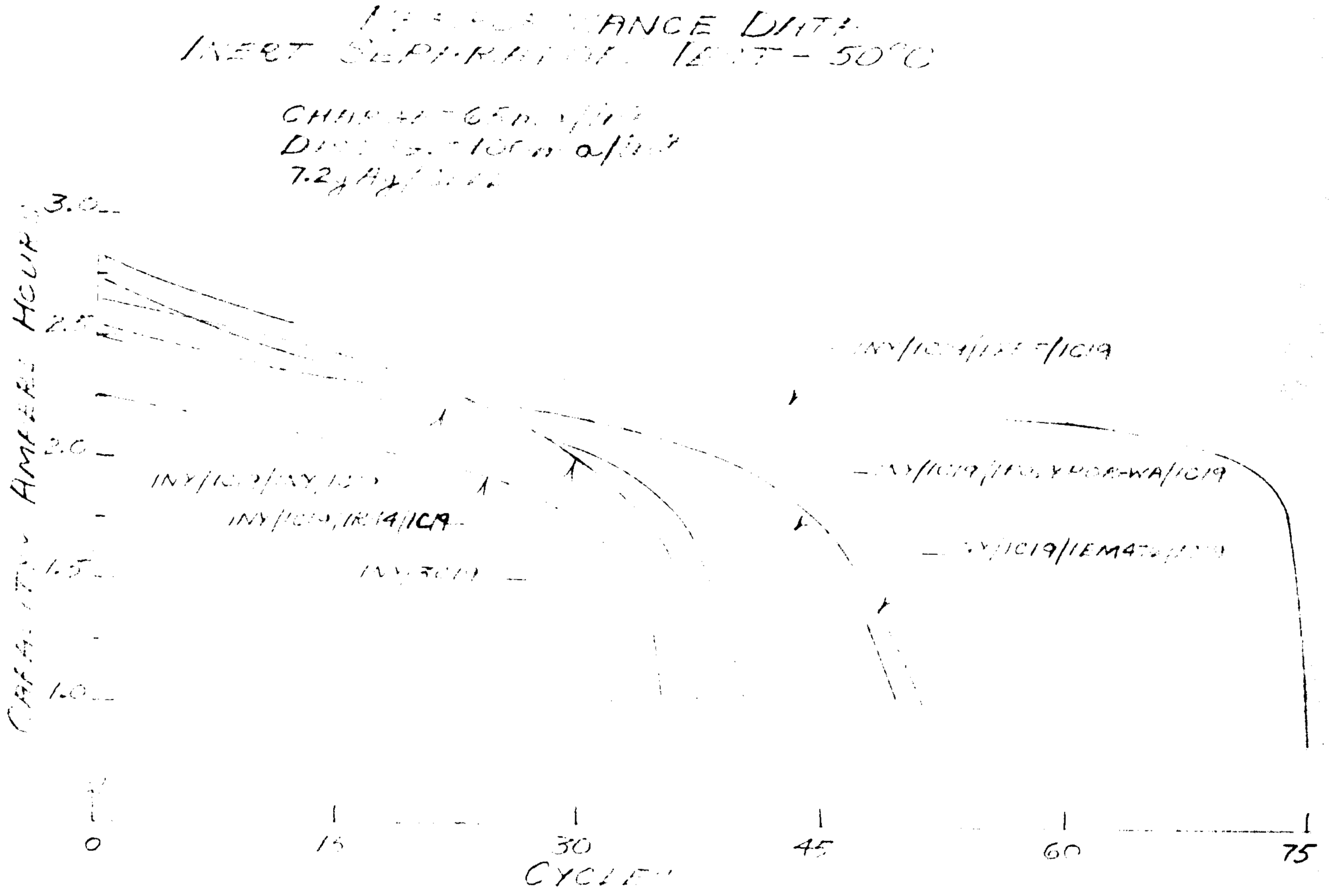
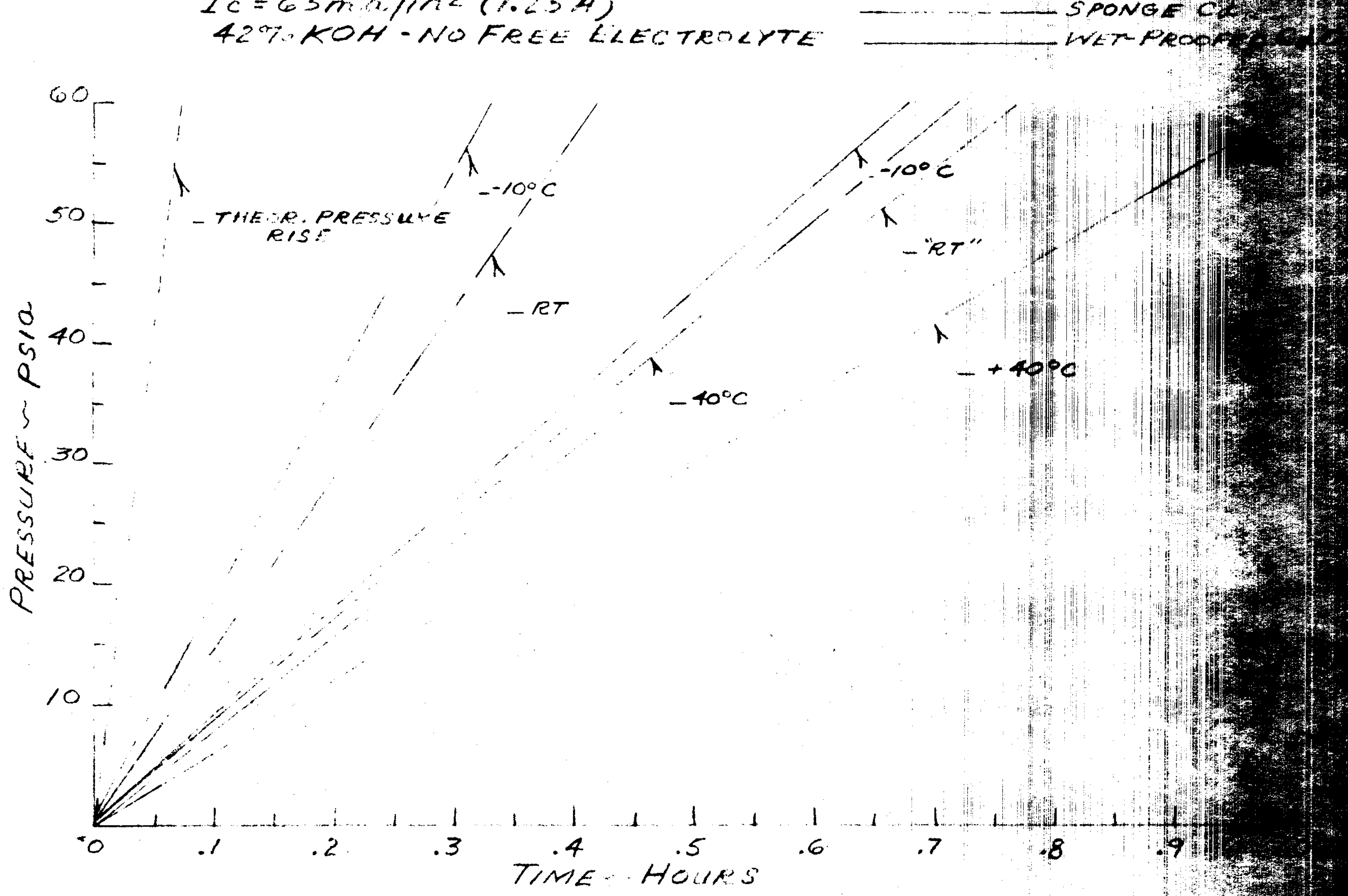
ANCE DATA
INERT SEPARATOR TEST - 50°C
CHARGE - 65 m a/in²
DIS - 100 m a/in²
7.2 g Ag
3.0
2.5
2.0
1.5
1.0
CAPACITY AMPERE HOURS
0
15
30
45
60
75
CYCLES
INY/IC19/
INY/IC19/IRI4/IC19
INY/IC19
INY/IC19/ /IC19
INY/IC19/ XPOR-WA/IC19
INY/IC19/IEM4 /IC19

Fig. 5

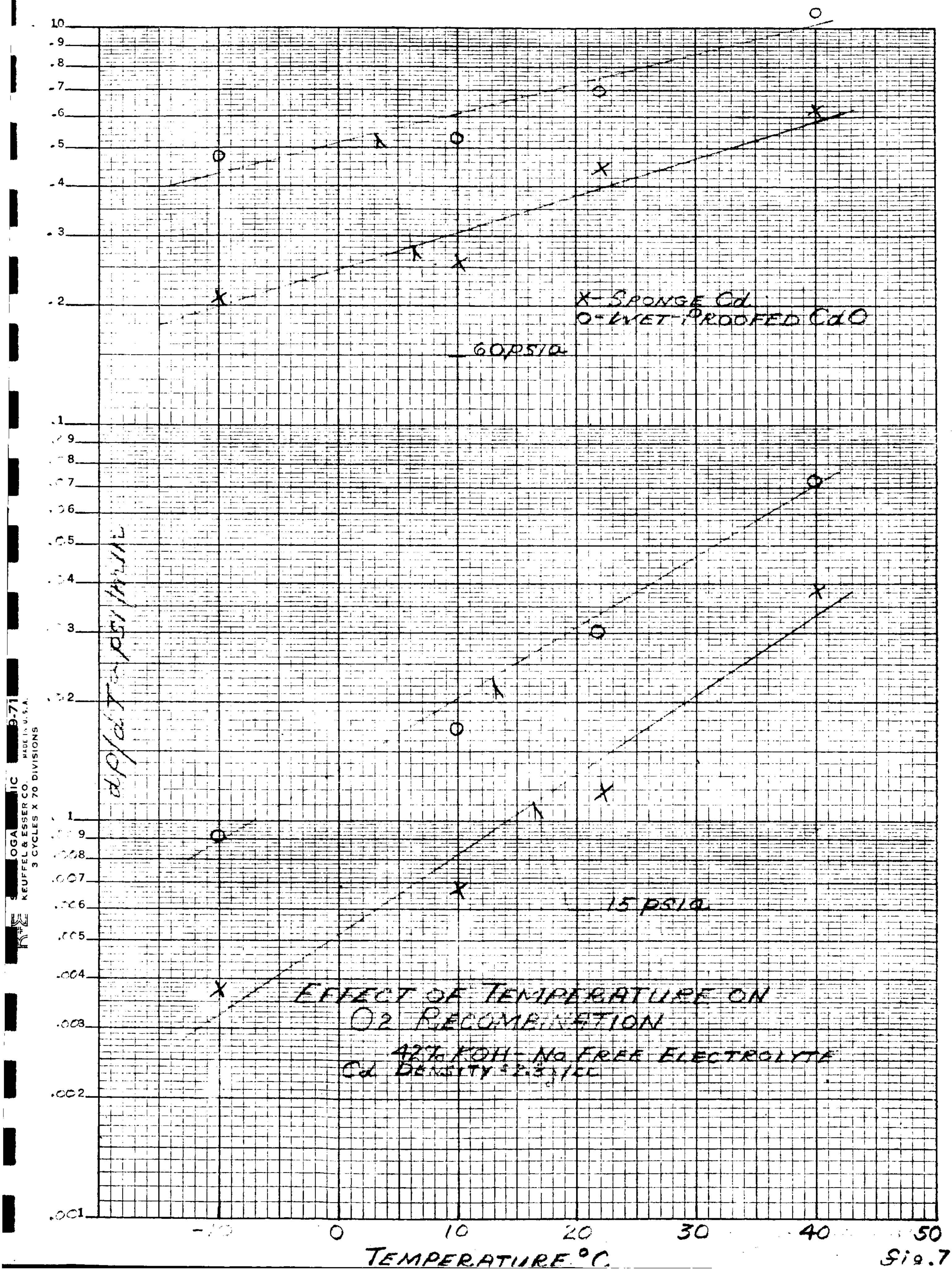
PRESSURE BUILD-UP DURING OVERCHARGE

$I_c = 65$ ma/in² (1.25A)
42% KOH - NO FREE ELECTROLYTE



*O = BEGINNING OF OVERCHARGE - FROM 1.58 V/CELL

Fig. 6



EFFECT OF TEMPERATURE ON O2 RECOMBINATION

42% KOH - No FREE ELECTROLYTE
Cd DENSITY 2.3 g/cc

Fig. 7

EFFECT OF CADMIUM DENSITY
ON OXYGEN RECOMBINATION
(420 AH)

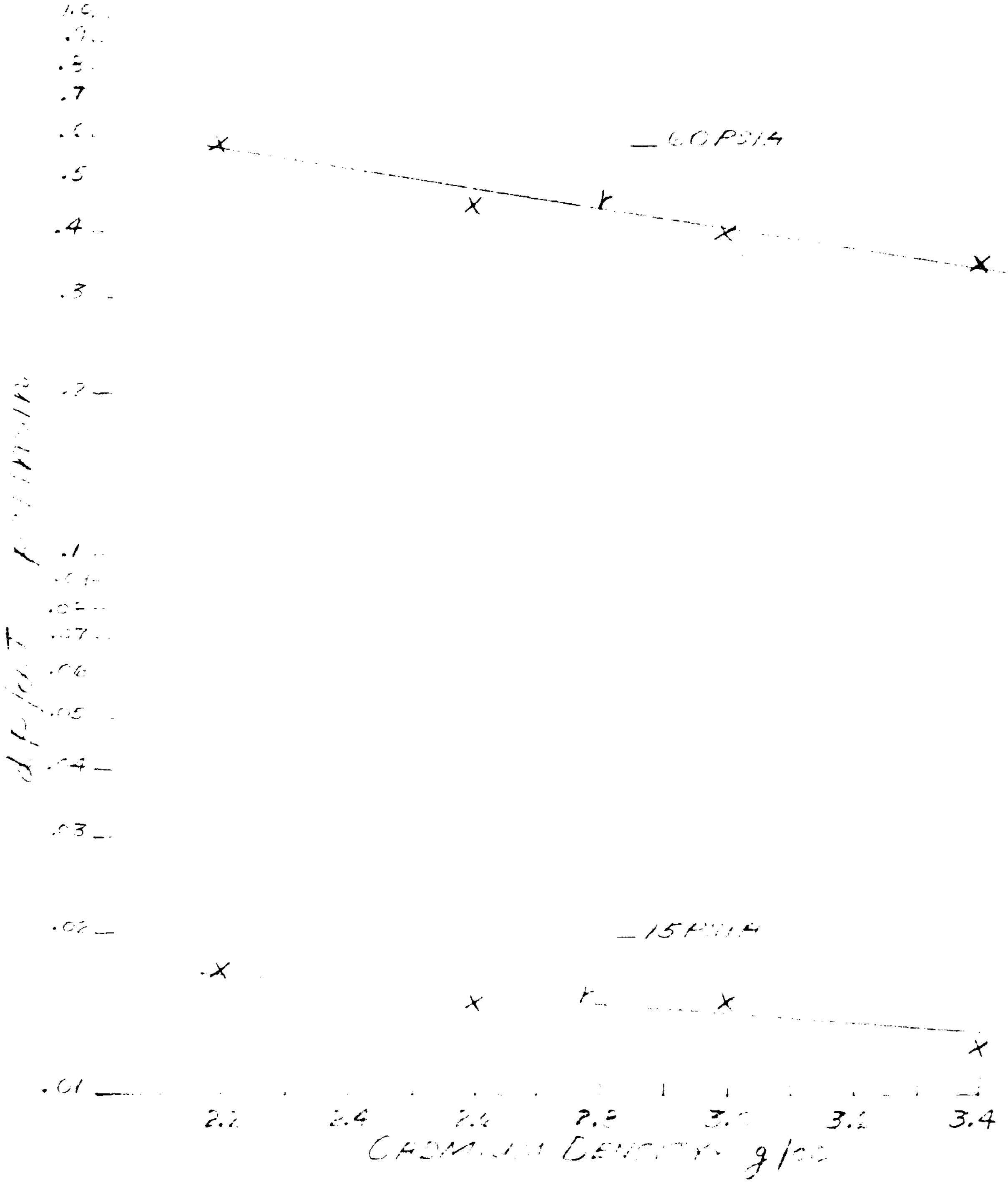


Fig. 8

EFFECT OF INTERNAL CELL PRESSURE ON CADMIUM EFFICIENCY

PRESSED CdO
DENSITY - 2.8 g Cd/cc
AREA = 4.9 IN²
I. D. CASE = .590" (NOMINAL)
I c = 65 ma/in²

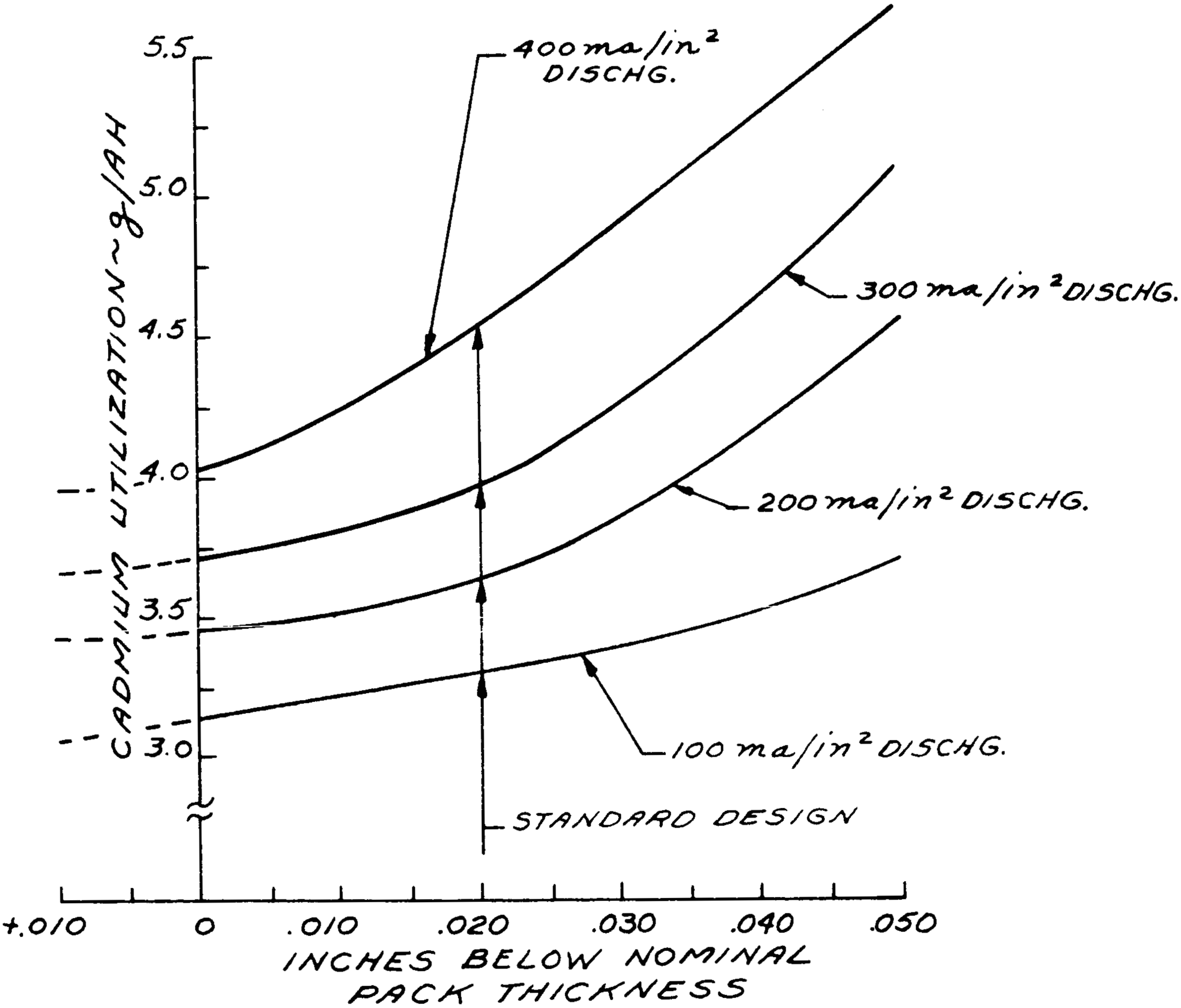


Fig. 9

EFFECT OF GRID STRUCTURE ON CADMIUM UTILIZATION

PRESSED CdO

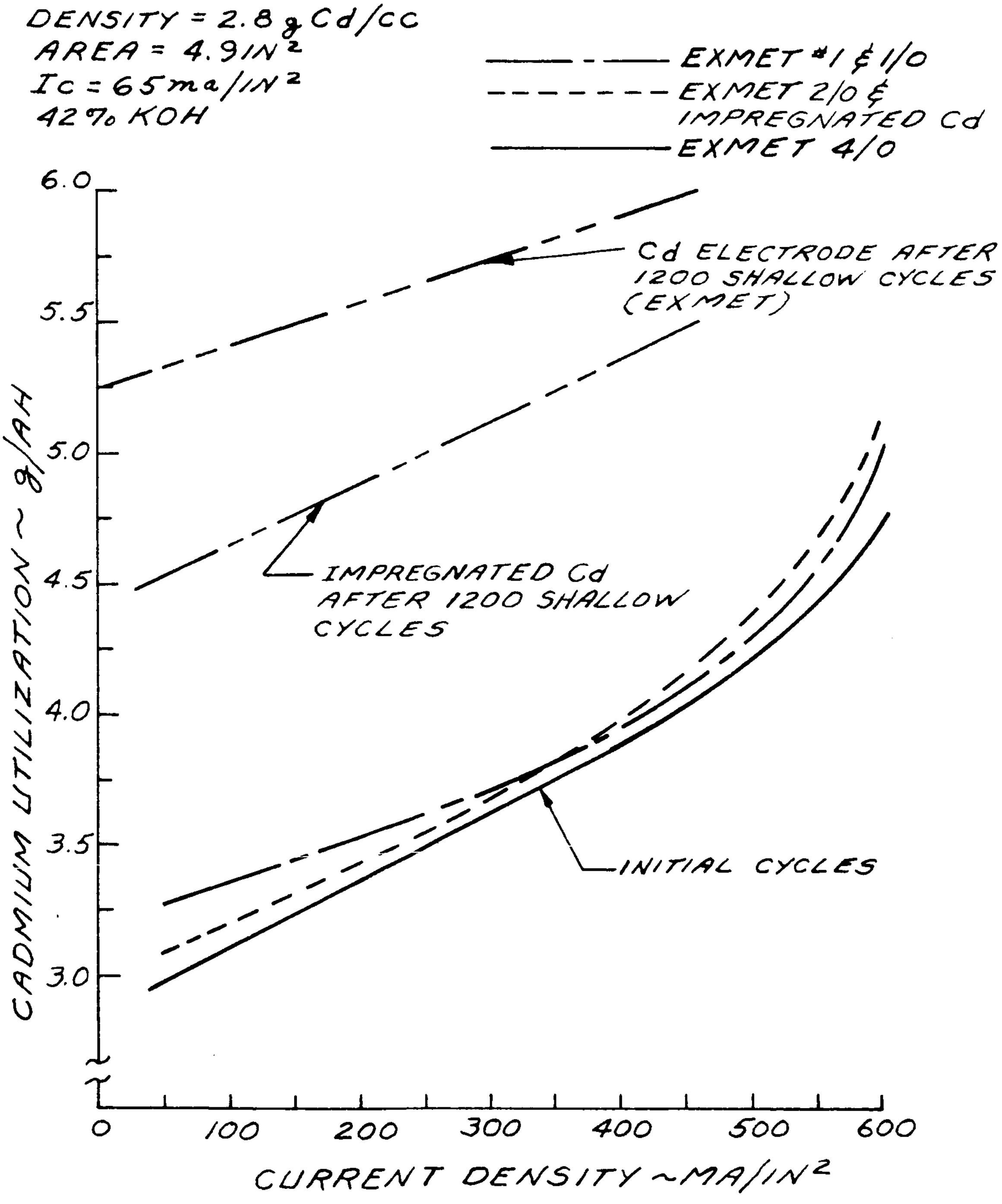


Fig. 10

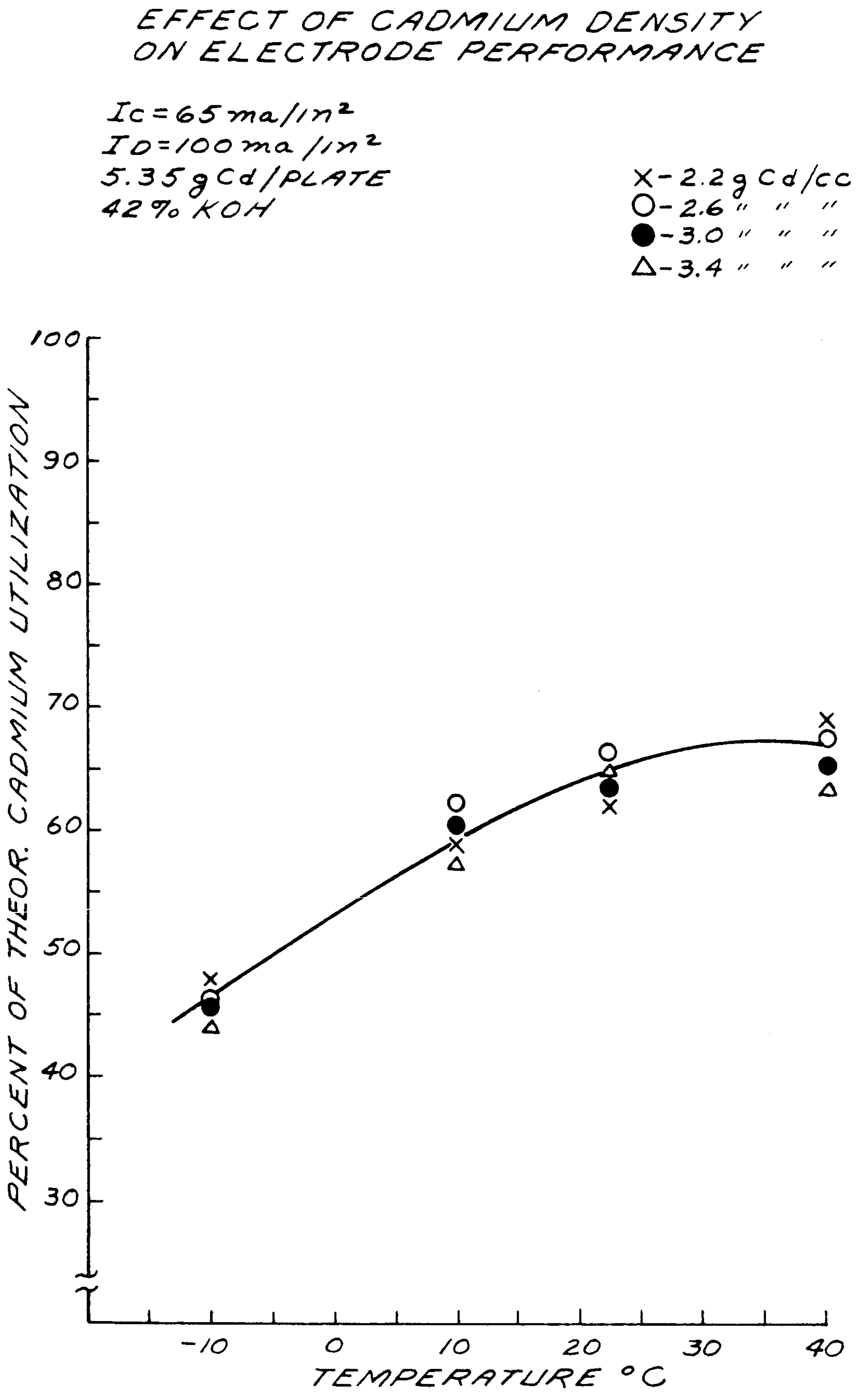

EFFECT OF CADMIUM DENSITY ON ELECTRODE PERFORMANCE
$I_C = 65\ ma/in^2$
$I_D = 100\ ma/in^2$
5.35 g Cd/PLATE
42% KOH
× - 2.2 g Cd/cc
○ - 2.6 " " "
● - 3.0 " " "
△ - 3.4 " " "
PERCENT OF THEOR. CADMIUM UTILIZATION
100
90
80
70
60
50
40
30
-10
0
10
20
30
40
TEMPERATURE °C

Fig. 11

EFFECT OF SURFACE AREA OF CdO POWDER ON MATERIAL UTILIZATION

I_C = 15 ma/in² - CYCLE 2　4.8 in²
I_D = 100 ma/in²　4.5 g Cd/PLT.
Cd. DENSITY = 2.8 g/cc
42% KOH

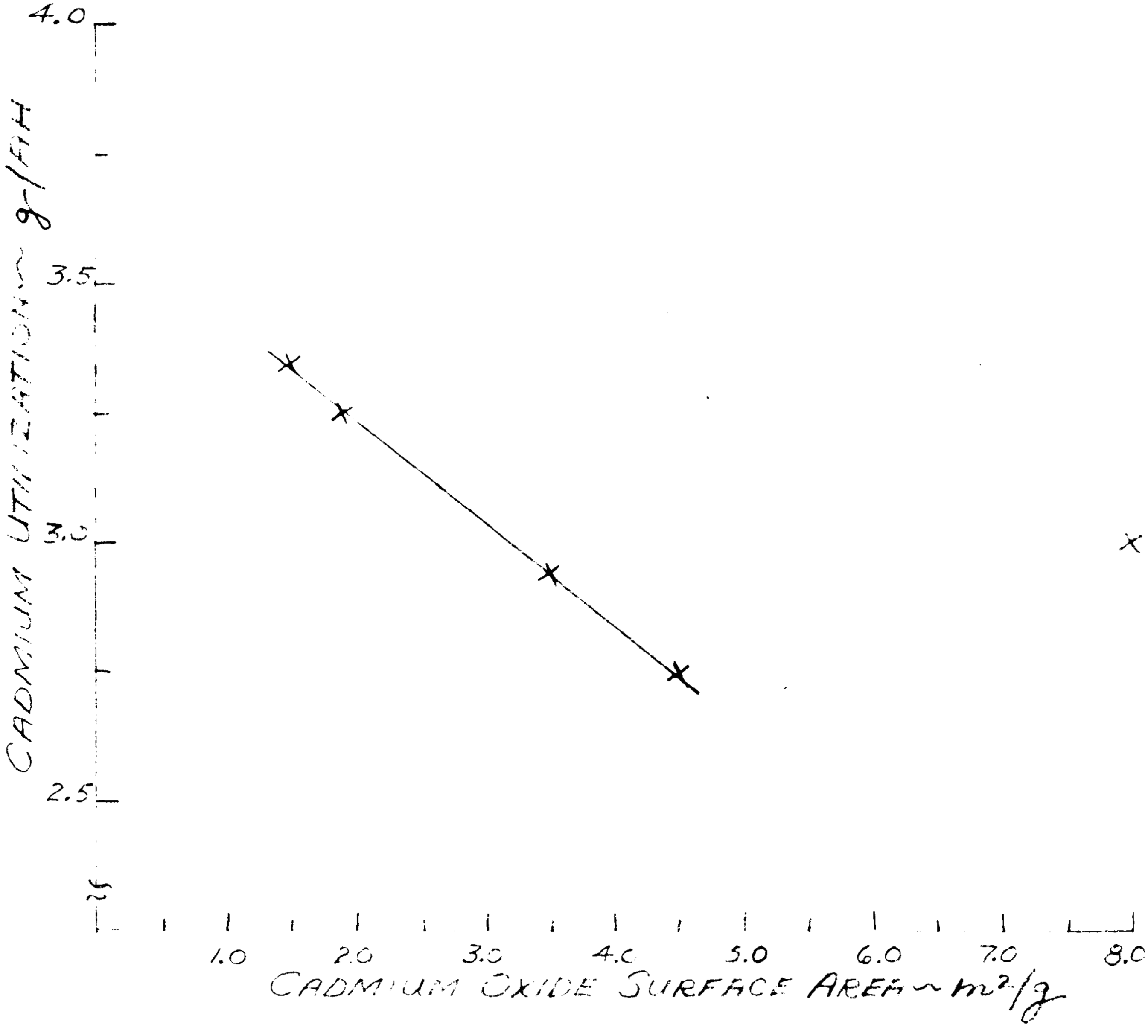
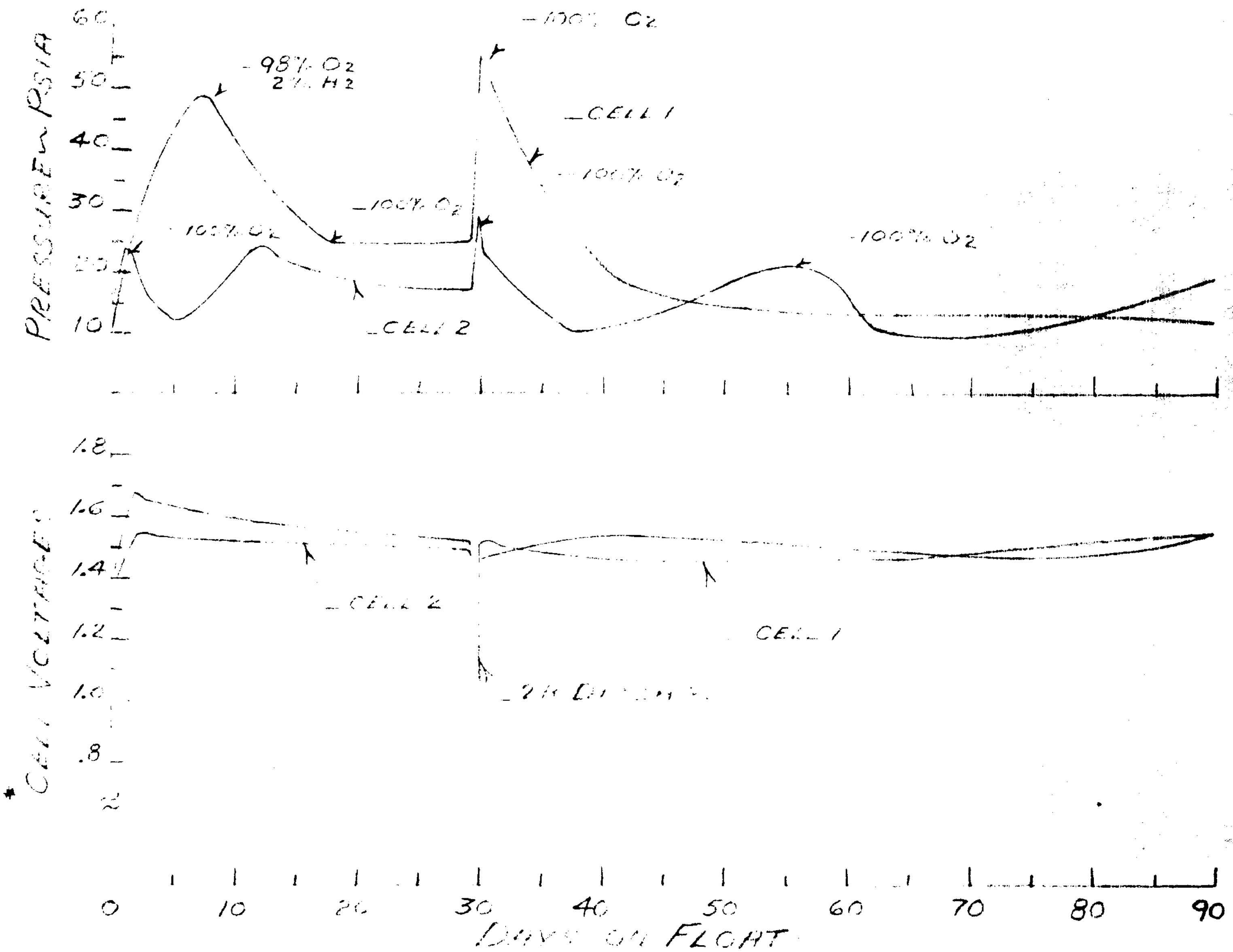


Fig. 6

PROLONGED CONSTANT POTENTIAL CHARGING
CELL CHARACTERISTICS



*NOTE: 5-CELL BATTERY FLOAT VOLTAGE = 7.75V

Fig. 13